MONTREAL PROTOCOL

ON SUBSTANCES THAT DEPLETE

THE OZONE LAYER

UNEP

REPORT OF THE
TECHNOLOGY AND ECONOMIC ASSESSMENT PANEL

SEPTEMBER 2018

VOLUME 4

RESPONSE TO DECISION XXVI/5(2) ON LABORATORY AND ANALYTICAL USES

REVISION – OCTOBER 2019[1]

[1] Revised due to a correction in data for laboratory and analytical uses and adjustments made to some of the reported production data for those uses, consistent with the reported Article 7 data. Reported data for 2017 are also included. Associated changes have been made only to Chapter 2 and relevant parts of the Executive Summary;

these changes do not alter the overall conclusions of the September 2018 report.

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Montreal Protocol
On Substances that Deplete the Ozone Layer

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RESPONSE TO DECISION XXVI/5(2) ON LABORATORY AND ANALYTICAL USES, REVISION – OCTOBER 2019

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Co-ordination:	**Technology and Economic Assessment Panel**
Composition of the report:	Helen Tope, Jianjun Zhang
Layout and formatting:	Marta Pizano, Helen Tope (UNEP TEAP)
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Foreword

September 2018 TEAP Report

The September 2018 TEAP Report consists of five volumes:

Volume 1*: Decision XXIX/4 TEAP Task Force Report on destruction technologies for controlled substances (Addendum to the May 2018 Supplemental Report)*

Volume 2*: Decision XXIX/8 on the future availability of halons and their alternatives*

Volume 3: *MBTOC CUN assessment report (final report)*

Volume 4: *Response to Decision XXVI/5(2) on laboratory and analytical uses, Revision - October 2019* [2]

Volume 5: *Decision XXIX/10 Task Force Report on issues related to energy efficiency while phasing down hydrofluorocarbons (updated final report)*

The UNEP Technology and Economic Assessment Panel (TEAP):

Bella Maranion, co-chair	US	Roberto Peixoto	BRA
Marta Pizano, co-chair	COL	Fabio Polonara	IT
Ashley Woodcock, co-chair	UK	Ian Porter	AUS
Paulo Altoe	BRA	Rajendra Shende	IN
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Adam Chattaway	UK	Dan Verdonik	US
Marco Gonzalez	CR	Helen Walter-Terrinoni	US
Sergey Kopylov	RF	Shiqiu Zhang	PRC
Kei-ichi Ohnishi	J	Jianjun Zhang	PRC

[2] Revised due to a correction in data for laboratory and analytical uses and adjustments made to some of the reported production data for those uses, consistent with the reported Article 7 data. Reported data for 2017 are also included. Associated changes have been made only to Chapter 2 and relevant parts of the Executive Summary; these changes do not alter the overall conclusions of the September 2018 report.

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RESPONSE TO DECISION XXVI/5(2) ON LABORATORY AND ANALYTICAL USES REVISION– OCTOBER 2019

TABLE OF CONTENTS

Executive Summary

Laboratory and analytical uses of controlled substances have included: equipment calibration; extraction solvents, diluents, or carriers for specific chemical analyses; inducing chemical-specific health effects for biochemical research; as a carrier for laboratory chemicals; and for other critical purposes in research and development where substitutes are not readily available or where standards set by national and international agencies require specific use of the controlled substances.

Decision IV/25 establishes criteria and procedures that permit the production and consumption of controlled substances beyond their production phase-out, in relation to the control measures under Article 2. Under decision VI/9, parties authorised an essential use exemption for laboratory and analytical uses for the first time, according to conditions established at the 6th meeting of the parties. These conditions authorise essential use production for laboratory and analytical purposes only if the controlled substances are manufactured to high purity and supplied in re-closable containers and in small quantities: this became known as the global essential use exemption.

Paragraph 2 of decision XXVI/5 requests the Technology and Economic Assessment Panel (TEAP) to report on the development and availability of laboratory and analytical uses that can be performed without using controlled substances (within the context of extending the global essential use exemption until the end of 2021). This report forms TEAP's response to decision XXVI/5.

The global essential use exemption applies to controlled substances in Annex A, B, C Groups II and III, and Annex E, as relevant to the Article 2 control measures for Article 5 and non-Article 5 parties. This report limits its focus primarily on controlled substances already included under the global essential use exemption for laboratory and analytical uses. It provides some information on the known laboratory and analytical uses of Annex C Group I. Annex F controlled substances are not included in this report.

The global quantity of ozone-depleting substances produced (for use within the same party) for laboratory and analytical uses is relatively small (151 tonnes in 2016, 162 tonnes in 2017). Carbon tetrachloride is the main controlled substance produced for these uses (more than 98 per cent); the production of other controlled substances is relatively very small. Reported production (for use within the same party) for laboratory and analytical uses in non-Article 5 parties was 21 tonnes in 2016 (about 14 per cent of the reported global total), and 12 tonnes in 2017. Article 5 parties began reporting production data for LAUs in 2009, with an overall decrease in reported production (for use within the same party) from a peak of 257 tonnes in 2010 to 130 tonnes (about 86 per cent) in 2016, and 150 tonnes in 2017.

TEAP reported in detail in 2008, 2009, 2010 and 2011 on the availability of alternatives for laboratory and analytical uses of ozone-depleting substances. This report considers available alternatives, and potential barriers to their adoption, in Article 5 and non-Article 5 parties.

A review of standards for analytical procedures has been undertaken; the major standards related bodies were considered in this review. Difficulties and/or complexities in adopting the alternatives may be creating greater barriers for Article 5 parties.

Recommendations have been made based on currently available information and building on the previous reviews (see Chapter 4).

Parties may wish to consider removing the procedures listed in the table below from the global exemption for laboratory and analytical uses of ODS, at a date to be determined by parties.

Table ES.1 Recommendation of laboratory and analytical procedures to be removed

ODS Type	**Procedures**
Methyl bromide	Laboratory uses as a methylating agent
Carbon tetrachloride (CTC)	Reaction solvents
CTC	A solvent for IR, Raman and NMR spectroscopy
CTC	Grease removal and washing of NMR tubes
CTC	Iodine partition and equilibrium experiments
CTC	Determination of hydrocarbons in water, air, soil or sediment
CTC	Determination of moisture and water
1,1,1-trichloroethane (TCA)	Determination of bromine index
CTC	Determination of iodine index

In addition, parties may wish to consider recalling that any decision taken to exclude a use from the global exemption would not prevent a party from nominating a specific use for an exemption under the essential uses procedure, as set out in decision IV/25.

Parties may wish to consider establishing cooperation with standards organisations, to facilitate and accelerate the development or revision of standards for the replacement of ODS in analytical uses.

Parties may also wish to consider providing:

- more comprehensive data (e.g. on consumption);
- sharing information on alternatives and on the revision of standards that use ODS;
- possible support for the development and/or revision of standards, and/or training, where needed.

Many standards still require the use of small quantities ODS. There may come a point when the continued exclusion of specific laboratory and analytical uses on a case by case basis from the global exemption creates potential confusion for practitioners and regulators. Monitoring of, and adherence to, specific authorised uses of ODS in laboratory and analytical applications may become increasingly challenging as the exclusion list expands.

1 Introduction

1.1 Decision XXVI/5(2): Global laboratory and analytical-use exemption

The 26th Meeting of the Parties determined in decision XXVI/5:

"Recalling *decisions VII/11 and XXI/6, in which the Meeting of the Parties requested all parties to urge their national standards-setting organizations to identify and review their standards for laboratory and analytical procedures that mandate the use of Montreal Protocol controlled substances with a view to adopting, where possible, laboratory and analytical products and processes that do not use controlled substances,*

Recalling *also decisions VII/11, XI/15, XVIII/15 and XIX/18, by which the Meeting of the Parties eliminated specific uses from the global exemption for laboratory and analytical uses,*

1. *To extend the global laboratory and analytical-use exemption until 31 December 2021, under the conditions set out in Annex II to the report of the Sixth Meeting of the Parties and decisions XV/8, XVI/16 and XVIII/15, for the controlled substances under the Montreal Protocol in all annexes and groups except Annex C, group 1;*

2. *To request the Technology and Economic Assessment Panel to report no later than 2018 on the development and availability of laboratory and analytical procedures that can be performed without using controlled substances under the Montreal Protocol;*

3. *To encourage parties to continue to investigate domestically the possibility of replacing ozone-depleting substances in laboratory and analytical uses and to share the resulting information.*"

This report forms the Technology and Economic Assessment Panel's response to paragraph 2 of this decision.

1.2 Background

Laboratory and analytical uses of controlled substances have included: equipment calibration; extraction solvents, diluents, or carriers for specific chemical analyses; inducing chemical-specific health effects for biochemical research; as a carrier for laboratory chemicals; and for other critical purposes in research and development where substitutes are not readily available or where standards set by national and international agencies require specific use of the controlled substances.

Decision IV/25 establishes criteria and procedures that permit the production and consumption of controlled substances beyond their production phase-out, in relation to the control measures under Article 2. A controlled substance qualifies as essential only if:

i) it is necessary for the health, safety or is critical for the functioning of society (encompassing cultural and intellectual aspects); and

ii) there are no available technically and economically feasible alternatives or substitutes that are acceptable from the standpoint of environment and health;

Production and consumption are permitted only if:

i) all economically feasible steps have been taken to minimize the essential use and any associated emission of the controlled substance; and

ii) the controlled substance is not available in sufficient quantity and quality from existing stocks of banked or recycled controlled substances, also bearing in mind the developing countries' need for controlled substances;

At the 6th Meeting, parties authorised an essential use exemption for laboratory and analytical uses for the first time in decision VI/9, according to conditions set out in Annex II of the report for that meeting (see Appendix 1). Annex II authorises essential use production for laboratory and analytical purposes only if the controlled substances are manufactured to high purity and supplied in re-closable containers and in small quantities[3]: this became known as the global essential use exemption. Other than these quality specifications, Annex II also required that parties shall annually report for each controlled substance produced: the purity; the quantity; the application, specific test standard, or procedure requiring its uses; and the status of efforts to eliminate its use in each application. The Annex also required that parties shall also submit copies of published instructions, standards, specifications, and regulations requiring the use of the controlled substance.

"Parties shall annually report on each controlled substance produced: the purity; the quantity; the application, specific test standard, or procedure requiring its uses; and the status of efforts to eliminate its use in each application. Parties shall also submit copies of published instructions, standard specifications, and regulations requiring the use of the controlled substance."

"... used or surplus substances should be collected and recycled, if practical. The material should be destroyed if recycling is not practical."

In order to elaborate on laboratory uses and to assist the collection of data, parties adopted at their 7th Meeting (Decision VII/11), a non-exhaustive illustrative list of categories and examples of laboratory uses, as specified in Annex IV of the meeting report. This decision also excluded specific uses from the global exemption that were not exclusive to laboratory and analytical uses and/or where alternatives were available (see Appendix 1).

Various decisions have subsequently extended the global laboratory and analytical use exemption under these specified conditions, excluded additional specific uses from the global exemption, and/or requested the Technology and Economic Assessment Panel (TEAP) to report on developments in alternatives to the use of controlled substances. Decision XXI/6 extended the applicability of the global essential use exemption to countries operating under Article 5 for controlled substances subject to relevant Article 2 control measures.

Where alternatives are available for laboratory and analytical uses of controlled substances, decisions have been made to exclude those uses from the exemption because they were no longer considered essential. Decisions VII/11, XI/15, XVIII/15 and XIX/18 have eliminated

[3] The purity standards and other requirements placed on laboratory and analytical uses are given in Annex II of the report of the Sixth Meeting of the Parties, and include the following: (i) purity requirements; (ii) criteria that controlled substances for laboratory and analytical uses shall be supplied only in re-closable containers or high pressure cylinders smaller than three litres or in 10 millilitres or smaller glass ampoules; and (iii) advice concerning preparation of mixtures containing the controlled substances, labelling, recovery and reuse, and annual reporting of activities.

the following laboratory and analytical uses from the global exemption for laboratory and analytical uses:

a) Refrigeration and air conditioning equipment used in laboratories, including refrigerated laboratory equipment such as ultra-centrifuges;

b) Cleaning, reworking, repair, or rebuilding of electronic components or assemblies;

c) Preservation of publications and archives;

d) Sterilization of materials in a laboratory;

e) Testing of oil, grease and total petroleum hydrocarbons in water;

f) Testing of tar in road-paving materials;

g) Forensic finger-printing;

h) All laboratory and analytical uses of methyl bromide except:

    i) As a reference or standard:

        - To calibrate equipment which uses methyl bromide;

        - To monitor methyl bromide emission levels;

        - To determine methyl bromide residue levels in goods, plants and commodities;

    ii) In laboratory toxicological studies;

    iii) To compare the efficacy of methyl bromide and its alternatives inside a laboratory;

    iv) As a laboratory agent which is destroyed in a chemical reaction in the manner of feedstock;

i) Testing of organic matter in coal.

Decision XVIII/15 authorizes the production and consumption of methyl bromide subject to the conditions applied to the global essential use exemption for laboratory and analytical uses contained in Annex II to the report of the 6th Meeting of the parties, and adopts a category of laboratory and analytical uses of methyl bromide allowable under the global exemption:

a) As a reference or standard:

    i) To calibrate equipment which uses methyl bromide;

    ii) To monitor methyl bromide emission levels;

    iii) To determine methyl bromide residue levels in goods, plants and commodities;

b) In laboratory toxicological studies;

c) To compare the efficacy of methyl bromide and its alternatives inside a laboratory;

d) As a laboratory agent which is destroyed in a chemical reaction in the manner of feedstock.

Decision IX/17 added that data for consumption and production should be reported annually under a global essential use exemption framework to the Secretariat so that the success of reduction strategies may be monitored. Decision X/19 further clarified that any decision taken to remove the global exemption should not prevent a party from nominating a specific use for an exemption under the essential uses procedure, as set out in decision IV/25.

1.3 Scope and limitations

Paragraph 2 of decision XXVI/5 requests TEAP to report on the development and availability of laboratory and analytical uses that can be performed without using controlled substances (within the context of extending the global essential use exemption until the end of 2021, for controlled substances except Annex C group 1). This report forms TEAP's response to this decision.

The former Chemicals Technical Options Committee (CTOC) reported in detail in 2008[4], 2009[5], 2010[6] and 2011[7] on the availability of alternatives for laboratory and analytical uses of ODS in response to decisions by parties. TEAP recommended a range of additional laboratory and analytical uses for their removal from the global essential use exemption. This report builds on the previous work and considers available alternatives to laboratory and analytical uses of ODS, and potential barriers to their adoption, in Article 5 and non-Article 5 parties.

International and/or national standards for laboratory and analytical uses are often adopted across a number of countries. A country without its own national standards-setting organisation can adopt international standards or national standards published by another country. As such, there is some technical uniformity in the suite of standards for laboratory and analytical methods, which are adopted across Article 5 and non-Article 5 parties. The scientific community also adopts laboratory methods based on the body of international publications, scientific theory and knowledge. As such, there is also reasonable technical uniformity in the suite of laboratory methods adopted across Article 5 and non-Article 5 parties. However, technical and economic barriers to the adoption of alternatives can differ depending on individual circumstances (e.g. availability of specialized scientific equipment or laboratory and analytical reagents). A main barrier to change is often the adoption of new standards and the associated resource-intensive process.

This report's review of standard analytical procedures was challenging for the following reasons:

- There is a considerable body of documented international and national standard analytical methods, and the adopted standards can vary from country to country and cover a wide range of different applications;

[4] UNEP May 2008 Report of the TEAP, Volume 1, Progress Report, pg. 54.

[5] UNEP May 2009 Report of the TEAP, Volume 1, Progress Report, pg. 51.

[6] UNEP May 2010 Report of the TEAP, Volume 2, Progress Report, pg. 53.

[7] UNEP May 2011 Report of the TEAP, Volume 1, Progress Report, pg. 51.

- It is difficult to identify and access a complete range of relevant published standards set by organisations, such as the International Organization for Standardization (ISO), ASTM International (ASTM), the European Committee for Standardization (CEN).

With the limited resources available to it, and in the absence of recent input from parties, TEAP has been limited in its capacity to undertake a comprehensive review of the circumstances of individual countries. Nevertheless, a review of standards for analytical procedures has been undertaken, within the limitations, and recommendations have been made based on currently available information and building on the previous reviews by CTOC.

The global essential use exemption applies to controlled substances in Annex A, B, C Groups II and III, and Annex E, as relevant to the Article 2 control measures for Article 5 and non-Article 5 parties. This report limits its focus primarily on controlled substances already included in the global essential use exemption for laboratory and analytical uses. At the time of writing the September 2018 report, Annex C, Group I (HCFCs) were not yet included under the global essential use exemption. Decision XXX/8 now includes Annex C, group I, substances in the global laboratory and analytical use exemption under the same conditions and on the same timeline as in paragraph 1 of decision XXVI/5. This report provides some information on the known laboratory and analytical uses of Annex C Group I. Annex F controlled substances are not included in this report.

1.4 This Report

TEAP and its MCTOC worked entirely by email and other electronic means in completing its report. TEAP and its MCTOC conducted online and literature research, reviewed other publicly available information, and consulted with experts. Standards organisations, such as the International Organization for Standardization (ISO), ASTM International (ASTM), the European Committee for Standardization (CEN), the Standardization Administration of the People's Republic of China (SAC) and US EPA, were referenced. Data reported by parties, on controlled substances used for laboratory and analytical purposes, was provided by the Ozone Secretariat to the TEAP and its MCTOC.

A summary of recommendations is presented in Chapter 4.

2 Production and import data reported for laboratory and analytical uses

This chapter provides an analysis of reported production and import data for laboratory and analytical uses (LAUs), which may provide a focus for the remaining priorities in this application.

2.1 Reported data

Parties have reported the production and import of controlled substances used for laboratory and analytical purposes to the Ozone Secretariat from 1996 onwards. The Ozone Secretariat provided data to the MCTOC on production and import from 1996 to 2016. 40 Parties have reported their import data to Ozone Secretariat, covering more than 46 different ozone-depleting substances (ODS), with their data varying greatly from tonnes to grams. Only seven parties operating under non-Article 5, and one party operating under Article 5, have reported production data.

Table 2.1 List of parties that reported production/consumption data for LAUs to the Ozone Secretariat during the period 1996-2016

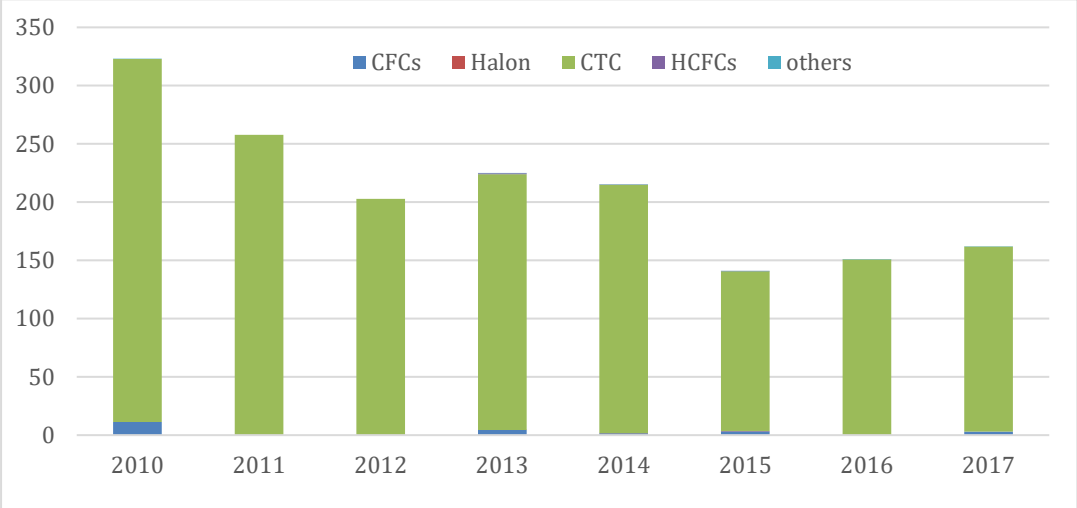
	Non-Article 5	Article 5
1	Australia	Argentina
2	Belarus	Bahrain
3	Canada	Bhutan
4	Croatia	Bolivia
5	Czech Republic	Bosnia and Herzegovina
6	EU	Brazil
7	Israel	Chile
8	Italy	China
9	Japan	Colombia
10	Korea	Cuba
11	Liechtenstein	Ecuador
12	Netherlands	El Salvador
13	New Zealand	Guyana
15	Norway	Haiti
16	Poland	Indonesia
17	Romania	Mauritius
18	Russian Federation	Mexico
19	San Marino	Nepal
20	Serbia	Oman
21	Singapore	South Africa
22	Slovakia	Sri Lanka
23	Slovenia	
24	Switzerland	
25	North Macedonia	
26	Turkey	
27	Turkmenistan	
28	USA	

2.2 Global production and import data for LAUs

Figure 2.1 and Figure 2.2 show the total global quantities of ODS produced (for use within the same party)[8] and imported as reported by parties for LAUs in recent years. While this data does not provide a complete picture of global production and consumption, as defined by the Protocol, of ODS for LAUs, an overall decrease in the reported quantities produced and imported can be seen from 2010 to 2017, with the last three years showing an almost stable level of production (for use within the same party).

In 2016, the global quantity of ODS produced (for use within the same party) for LAUs was 151 tonnes (162.0 tonnes in 2017), with CTC as the main ODS produced. In 2016, the total global quantity of imported ODS for LAUs was 4.828 tonnes (0.8 tonnes in 2017), with CTC and CFC-113 as the main ODS.

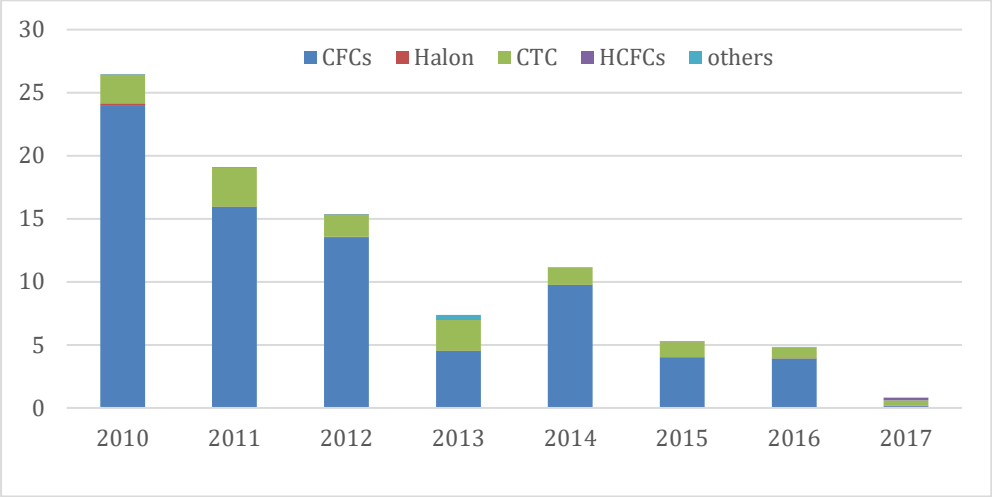
Figure 2.1 Reported global ODS production (for use within the same party) for LAUs (tonnes), 2010-2017



Others includes Annex B, Group III 1,1,1-trichloroethane (TCA) and Annex E, Group I methyl bromide (CH_3Br)

[8] Production data available is the reported quantity of production for laboratory and analytical usage only within the producing party. This production data does not include any quantities produced that were exported.

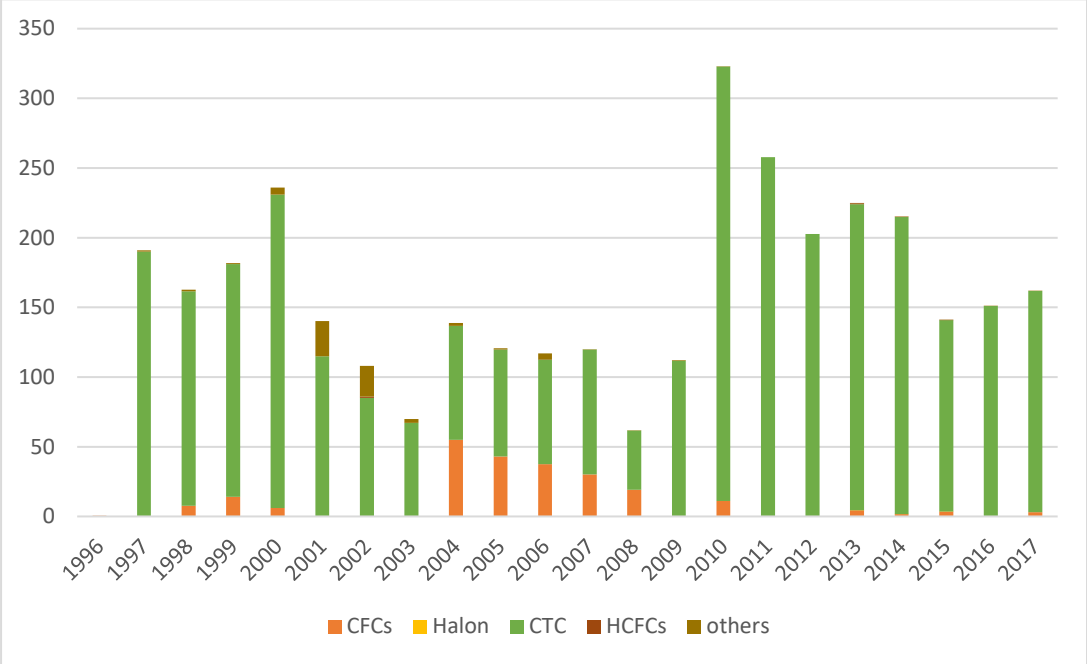
Figure 2.2 Reported global ODS imports for LAUs (tonnes), 2010-2017



Others includes Annex B, Group III 1,1,1-trichloroethane (TCA) and Annex E, Group I methyl bromide (CH_3Br)

The global production (for use within the same party) has been categorized by ODS type in Figure 2.3. There are 25 ODS that have been reported for production for laboratory and analytical use. CTC is the dominant ODS of total global production for LAUs, followed by CFC-113 and 1,1,1-trichloroethane (TCA) in tonnes of annual production. In 2016, the total reported production of CTC was 150.9 tonnes, which represents 99.96% of the total global production of ODS for LAUs (158.9 tonnes, 98% of the total, in 2017). The production of other ODS is relatively very small.

Figure 2.3 Reported global production (for use within the same party) for LAUs by ODS type (tonnes), 1996-2017

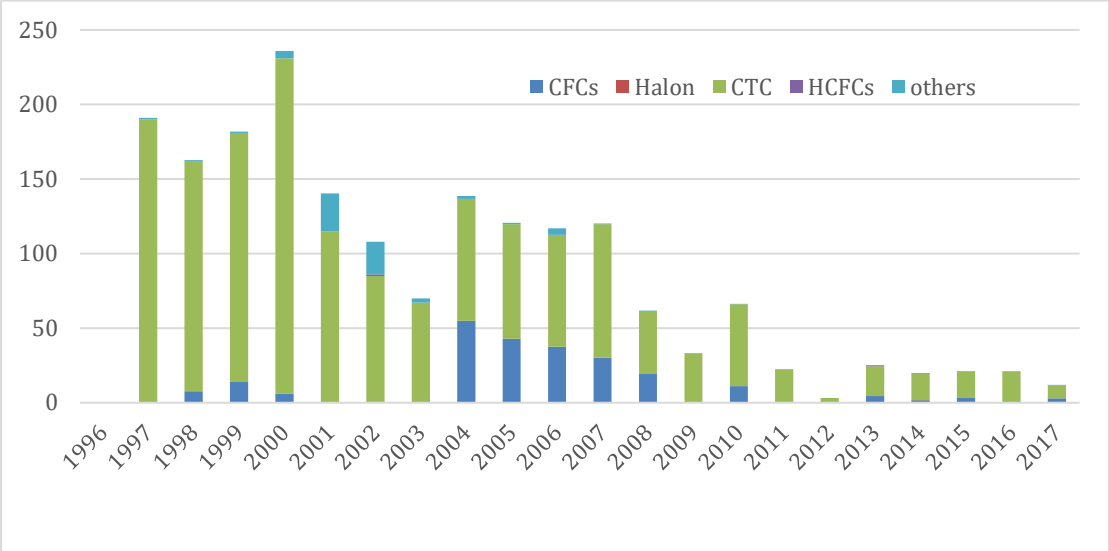


Others includes Annex B, Group III 1,1,1-trichloroethane (TCA) and Annex E, Group I methyl bromide (CH_3Br)

2.3 Production of ODS in non-Article 5 and Article 5 parties for LAUs

The reported production (for use within the same party) of ODS for LAUs in non-Article 5 parties is presented in Figure 2.4. Production in all non-Article 5 parties was 191 tonnes in 1997, reached a peak of 225 tonnes in 2000, and then has gradually dropped to 20.9 tonnes in 2016 (12.0 tonnes in 2017). CTC is the predominant ODS being produced for LAUs in recent years, followed by CFC-113, which is produced in some years.

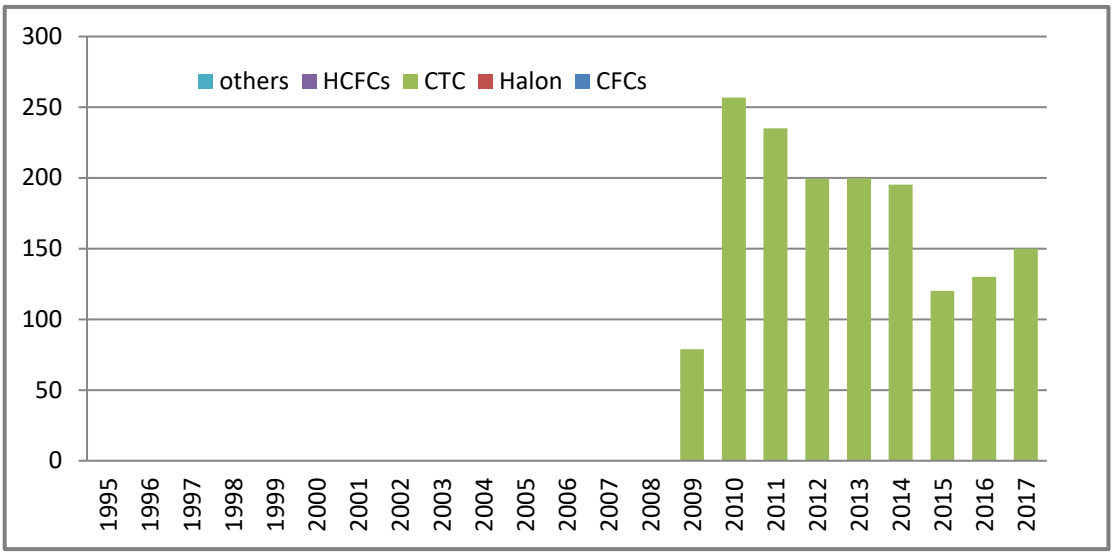
Figure 2.4 Total production for LAUs reported by non-Article 5 parties, 1996-2017 (tonnes)



Others includes Annex B, Group III 1,1,1-trichloroethane (TCA) and Annex E, Group I methyl bromide (CH_3Br)

Article 5 parties began reporting production data for LAUs in 2009, as shown in Figure 2.5. CTC is the only ODS reported by Article 5 parties. An overall decrease in reported production (for use within the same party) can be seen during the period, from a peak of 256.9 tonnes in 2010 to 130.0 tonnes in 2016 (150.0 tonnes in 2017).

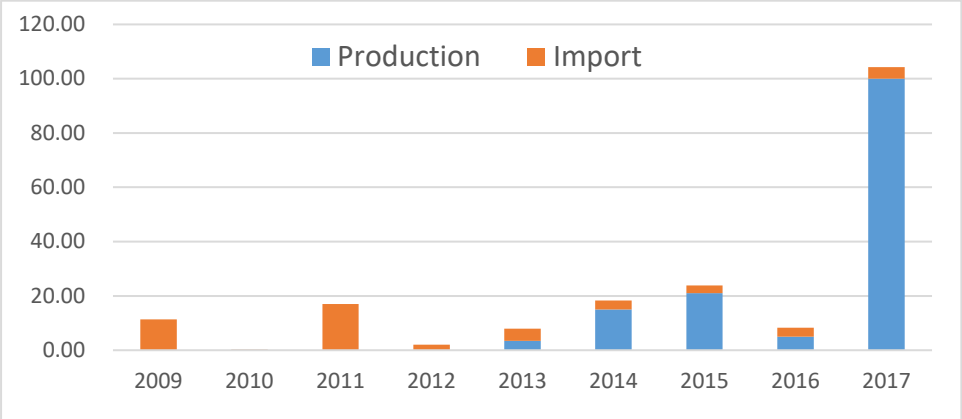
Figure 2.5 Total production for LAUs reported by Article 5 parties, 1996-2017 (tonnes)



2.4 Production and import of methyl bromide for LAUs

The reported global production (for use within the same party) and import of methyl bromide for LAUs has remained low in the last decade. The sum of the reported production and imports of methyl bromide varies from 604 kilograms in 2006, 11 kilograms in 2009, 3 kilograms in 2016 (104 kilograms in 2017). These reported quantities account for a very minor part of the total annual reported ODS production (for use within the same party) and imports in laboratory and analytical uses.

Figure 2.6 Reported global production (for use within the same party) and import of methyl bromide for LAUs, 2009-2017 (kilograms)



When compared with the reported quantity of methyl bromide consumed in QPS (8,370 tonnes[9]), in critical uses (554 tonnes[10]), and produced for feedstock uses (4,200 tonnes) in 2016, the sum of the reported quantities of methyl bromide produced (for use within the same party) and imported for laboratory and analytical uses is very minor (8 kilograms).

2.5 Production and import of HCFCs for LAUs

At the time of writing the September 2018 report, Annex C Group I (HCFCs) were not yet included under the global essential use exemption. Decision XXX/8 now includes Annex C, group I, substances in the global laboratory and analytical use exemption under the same conditions and on the same timeline as in paragraph 1 of decision XXVI/5. This section provides some information on the known laboratory and analytical uses of Annex C Group I. For 2016, while no production (for use within the same party) was reported, the quantity of imported HCFCs reported by parties for laboratory and analytical uses was 30 kg (HCFC-21, -22, -123, -141b, -233, -242, -252, HBFC-21B2, -22B1).

[9] UNEP May 2018 Report of the TEAP, Volume 3, Progress Report, pg. 18.

[10] UNEP May 2018 Report of the TEAP, Volume 3, Progress Report, pg.17.

3 Laboratory and analytical uses and their alternatives

3.1 Background

Following reviews by the Chemicals Technical Options Committee (CTOC) in 2008[11], 2009[12], 2010[13] and 2011[14], alternatives to the use of controlled substances were identified for a range of laboratory and analytical uses. As a result, TEAP recommended a list of laboratory and analytical uses for possible removal from the global essential use exemption. These were not adopted through a decision of parties.

An overview review of these and other laboratory and analytical uses has been undertaken by MCTOC, and recommendations have been made based on currently available information and building on the previous reviews by CTOC. This chapter provides details of this review. Recommendations can be found in Chapter 4.

3.2 Laboratory solvent and reagent uses

Many laboratory uses of controlled substances have been phased out through the use of alternative chemicals and/or procedures. Laboratory uses of ODS, e.g. as a common solvent or cleaning agent, have largely been phased out in developed countries and are disappearing from laboratories in developing countries, by using alternatives with similar chemical properties (e.g. polarity and solvent properties).

CTC is a useful laboratory chemical for one or more of the following reasons: reasonably good solvency; does not attack common materials including many elastomers used in reaction vessels; non-flammable, and not easily degraded under conditions of use; easily removed by evaporation or distillation without excessive energy consumption; readily available at affordable prices.

For these reasons, CTC has been widely used as a solvent in synthetic organic chemistry for reactions in which two or more components are dissolved in the solvent to react under heating to form new substances. The products of these reactions are recovered by cooling, followed by appropriate 'work up' that often involves evaporation (and potential recovery) of the CTC. Many of the industrial uses of CTC stem from patented procedures that were developed in laboratories. Where such laboratory work is destined to become an industrial process, consideration needs to be given to finding an alternative solvent at the outset.

TEAP has reported in its progress reports the details of CTC uses in laboratory and analysis procedures and has identified alternative procedures for which CTC can be replaced. As part of investigations made by the Chemicals Technical Options Committee (CTOC) in 2008[11], 2009[12], 2010[13] and 2011[14], TEAP recommended a list of procedures that could be removed from the global exemption for laboratory and analytical uses of CTC. For this report, MCTOC has reviewed the use of CTC as a solvent in reactions involving *N*-bromosuccinimide.

[11] UNEP May 2008 Report of the TEAP, Volume 1, Progress Report, pg. 54.

[12] UNEP May 2009 Report of the TEAP, Volume 1, Progress Report, pg. 51.

[13] UNEP May 2010 Report of the TEAP, Volume 2, Progress Report, pg. 53.

[14] UNEP May 2011 Report of the TEAP, Volume 1, Progress Report, pg. 51.

It has been difficult to find alternatives to some laboratory uses of ODS where portions of the ODS molecules are incorporated into the products of the chemical reactions, e.g. methyl bromide used as a methylating agent. Since the ODS can be destroyed, through conversion to non-ODS products, and/or the laboratory procedures are conducted on a much smaller scale (e.g. than those in industry), the emissions from such uses are likely to be miniscule. Following its 2017 findings, in this report MCTOC makes recommendations regarding methyl bromide used as a methylating agent.

3.2.1 CTC used as a solvent in reactions involving N-bromosuccinimide

There has been one laboratory solvent use of CTC that has proven difficult to replace with suitable alternatives: bromination reactions using *N*-bromosuccinimide (NBS).

TEAP reported in the past decade that CTC was the only solvent suitable for use in certain reactions of organic chemicals, notably bromination reactions involving NBS. In its progress report in 2015, TEAP identified that α,α,α-trifluorotoluene could be a suitable alternatives for CTC in NBS reactions.

In this report, MCTOC has made a comprehensive literature search and found that many studies have been done in recent years on alternative procedures for NBS related bromination reactions. Detailed information is provided in Appendix 2: Alternatives for Use of Carbon Tetrachloride (CTC) as a Solvent for Bromination Reactions involving NBS.

Tables 3.1 summarises the reaction procedures and the relative alternatives to CTC (see also Appendix 2). It is found that for different reaction procedures there are different options available for alternatives to the use of CTC, under similar reaction conditions and with comparable reaction results.

These findings allow TEAP and its MCTOC to recommend that CTC used as a reaction solvent (including in reactions involving NBS) can be excluded from the global essential use exemption for laboratory and analytical uses.

Table 3.1 Alternatives, or alternative procedures, for CTC in reactions involving NBS

Reaction Procedure	Alternatives to CTC
Wohl–Ziegler bromination	Chlorinated solvents (chloroform, 1,2-dichloroethane, dichloromethane) Non-chlorinated solvents ((trifluoromethyl)benzene, acetonitrile, ionic-liquid etc.)
Electrophilic substitution reaction	DMF**,** THF, acetic acid-chloroform
Electrophilic addition reaction	DME, THF, or t-butanol, dichloromethane
Oxidation reaction	Cyclodextrin-water, aqueous THF-H_2SO_4

DMF: *N*,*N*-Dimethylformamide; THF: Tetrahydrofuran, H_2SO_4: sulfuric acid.

3.2.2 Methyl bromide used as a methylating agent

One of main laboratory uses of methyl bromide is as a methylating agent in chemical reactions to deliver a methyl group to a chemical substrate. Literature research shows that there are many alternatives to using methyl bromide as a methylating agent (see Appendix 3). These alternatives are nearly always used in preference to methyl bromide. Methyl bromide is a toxic gas, which limits greatly its practicality in this application. Cost and availability are not barriers to uptake of the alternatives, although long-term users of methyl bromide in these

applications may need to experiment so as to adapt their practice to the alternative methylating agents.

These findings allow TEAP and its MCTOC to recommend that methyl bromide used as a methylating agent in laboratories can be excluded from the global essential use exemption for laboratory and analytical uses.

3.3 Standards related to laboratory and analytical use of ODS and their alternatives

Standards play an important role in leading and facilitating the replacement of ODS in laboratory and analytical uses. Standard methods are adopted and followed because they allow comparisons over time and between different laboratories. The use of a standard method is often required by a customer as a form of quality assurance for a product, or by a regulatory authority. Considerations, such as the ease and reliability of the assay, workplace health and safety, or the availability of substances under inter-governmental agreements, such as the Montreal Protocol, can cause new standards to be written. Standards development or revision has to undergo a rigorous procedure, which usually takes time and is accompanied by a cost, and often lags behind the identification of the need for change. In addition, users can be slow to adopt new standards for a number of reasons, including cost, familiarity with techniques, availability of equipment, and validation of the new method including comparability of results measured using previous and new methods.

In its previous progress reports, the former CTOC provided some information on the development of standards that do not use ODS, especially in relation to standards that previously used CTC. It shows that international bodies, such as ASTM International and ISO, have been continuing to work on the development of new standard methods to replace ODS in laboratory and analytical uses. The European Commission published a laboratory ODS Registry Manual in January 2017, to guide laboratories and suppliers of ODS for laboratory and analytical uses in the registration process allowing continued use of ODS. The manual also provides a list of standard methods for which alternatives exist for ODS in LAUs[15].

In this report, MCTOC has reviewed the current status of standards; the major standards related bodies, such as ISO, ASTM International, the European Committee for Standardisation (CEN), the Standardization Administration of the People's Republic of China (SAC) and US EPA, were considered in this review. Since it is difficult to acquire the full paper of all of the standards, instead abstracts of the standards containing key words were relied upon for information on alternatives or alternative procedures that do not use ODS. Some bodies seemed to have eliminated the use of some ODS for their standards; for example, a search for CTC on the CEN database discovered no results. A list of standards identified in the review that do not use ODS is provided in Appendix 4. A summary sample of a few standards for which alternatives are available follows.

For the test on the **determination of hydrocarbons** (oil, grease etc.) in water or soil, CTC is the common solvent used in this standard procedure, CFC-113, which is also an ODS, was previously selected as an alternative for CTC, in some cases due to the toxicity concern of CTC. A wide range of alternatives are now available for both CTC and CFC-113, including hydrocarbons, such as hexane, and chlorinated solvents, such as methylene chloride.

[15] https://ec.europa.eu/clima/policies/ozone/ods_en,

For the test on the **determination of iodine index or bromine index**, in which CTC and 1,1,1-trichloroethane were used as solvent, a mixture of glacial acetic acid with other solvents, such as cyclohexane, methanol and chloroform, could be adopted.

For the test on the **determination of moisture and water** in animal and vegetable fats and oils, or petroleum products and bituminous materials, alternatives such as xylene, methanol, aromatic solvents, and paraffinic solvents could be selected for different analytical procedures.

For the test on the **determination of phenol in water**, chloroform is recognized as alternative for CTC by organisations, such as ISO, ASTM and US EPA. However, ISO still allows the use of ODS for the standard, "Water quality — Determination of phenol index — 4-Aminoantipyrine spectrometric methods after distillation" (see Appendix 5).

ASTM also developed a new procedure that uses methyl isobutyl ketone as a solvent for the replacement of CTC in the **determination of lead in gasoline**, which will be helpful in the development of new analytical methods for the determination of the content of other metals in water or soil. There are many standards to determine the content of metals in water or soil, and more time will be needed before the use of ODS can be eliminated for this category.

However, even though the international standard bodies and non-Article 5 parties have made great progress on standards development or revision to replace ODS in analytical use, there are standards that still allow the use of ODS, as listed in Appendix 5. For some standards, the alternative or alternative procedures may exist, but the ODS method still remains as an active standard for these standard bodies, implying some barrier in adopting the alternatives or alternative procedures in standards development or revision.

Difficulties and/or complexities in adopting the alternatives may be creating greater barriers for Article 5 parties. China, for example, investigated CTC in laboratory and analytical uses in China[16] and listed more than 30 standards using CTC that require revision. Recent information indicates that little progress has been made for most of these standards, except for some standards for the determination oil and grease in water, some of which are still under development.

As previously outlined in 2011 TEAP Progress Report, the reasons that non-ODS methods are not adopted in Article 5 parties are adherence to standard methods that use ODS, and the cost of implementing new methods including training. In the first instance, where purely national standards are involved, skilled practitioners within those countries have the capability to adopt the alternative procedures. Only in the few cases, where an international standard exists and there is no non-ODS alternative, should it be necessary to persist with the use of ODS. In the second instance, the cost of transition should be sustainable, although the cost of alternative substances or procedures may be higher than those of the ODS methods they replace. It takes time and skilled resources to implement new methods; however, in many cases, non-ODS alternatives are available and may have been adopted already by international standards bodies or in non-Article 5 parties.

Parties may wish to consider establishing cooperation with standards organisations, to facilitate and accelerate the development or revision of standards for the replacement of ODS in analytical uses.

[16] http://odslab.chinareagent.com.cn/, accessed September 2018 (in Chinese).

3.4 Methyl bromide used as a reference or standard, or in laboratory studies

Decision XVIII/15 authorizes the production and consumption of methyl bromide for laboratory and analytical uses subject to the conditions applied to the global exemption, and adopts a category of laboratory and analytical uses of methyl bromide that is allowable:

(a) As a reference or standard:

(i) To calibrate equipment which uses methyl bromide;

(ii) To monitor methyl bromide emission levels;

(iii) To determine methyl bromide residue levels in goods, plants and commodities;

(b) In laboratory toxicological studies;

(c) To compare the efficacy of methyl bromide and its alternatives inside a laboratory;

(d) As a laboratory agent which is destroyed in a chemical reaction in the manner of feedstock;

TEAP believes that the current usage of methyl bromide as a reference or standard, in laboratory toxicological studies, and for comparison of methyl bromide and its alternatives inside a laboratory, is likely to be minor, possibly in the kilograms range globally. The likelihood of significant amounts (or any amounts) used this way has diminished as there are very few trials done on methyl bromide, with fewer on insect mortality studies and laboratory emission studies with barrier films. There is a possibility that these amounts, especially for insect mortality studies, could increase slightly if QPS uses were controlled further under the Montreal Protocol although the global quantities would remain very small. Nevertheless, methyl bromide used as a reference or standard, or in laboratory studies, will likely continue for as long as methyl bromide is used in applications (e.g. QPS or horticultural uses).

3.5 Laboratory and analytical uses of HCFCs

Non-Article 5 parties are likely to require HCFCs for laboratory and analytical uses, for example to be used as analytical standards for the measurement of atmospheric levels of HCFCs, and for the research into and development of new substances. The following laboratory and analytical uses for HCFCs have been reported and may continue to require HCFCs post-2020 due to slow progress in moving to alternatives.

- Reference chemical (in analytical methods and for enforcement) e.g. HCFC-21, HCFC-22, HCFC-31, HCFC-122, HCFC-123, HCFC-124, HCFC-133a, HCFC-141b, HCFC-142b, HCFC-151a, HCFC-233;
- Feedstock (reagent in laboratory chemical synthesis) e.g. HCFC-22, HCFC-242, HCFC -252;
- Solvent (inert solvent in laboratory chemical synthesis) e.g. HCFC-31;
- Reference chemical (in toxicological studies) e.g. HCFC-21;
- ODS as a component in samples to be tested.

Laboratory and analytical use of HCFCs as a reference chemical will continue for as long as HCFCs are used in applications.

4 Recommendations for laboratory and analytical uses that can be performed without using controlled substances

Following investigations made by the Chemicals Technical Options Committee (CTOC) in 2008[17], 2009[18], 2010[19] and 2011[20], TEAP identified a number of laboratory and analytical procedures, for which alternatives to the use of ODS were available, and it recommended their removal from the global essential use exemption. In the preambular text of Decision XXI/6 in 2009, parties noted these identified procedures (see Appendix 1, Decision XXI/6).

Case studies presented in the 2009 TEAP Progress Report showed that most laboratory and analytical uses of ODS in non-Article 5 Parties had ceased. Alternatives were identified by CTOC for almost all uses (see Appendix 6), and the list of methods for which alternatives were available included in the preambular text of decision XXI/6.

In that decision, among other things, parties were concerned to understand the potential impact on Article 5 parties of making changes to the global exemption to exclude additional laboratory and analytical uses. At the time, in 2009, Article 5 parties were soon to be subject to the 2010 control measures under Article 2, and then the global exemption for laboratory and analytical uses and its related exclusions would apply.

As mentioned in Chapter 3, this current review has shown that the adoption of alternatives to ODS laboratory and analytical uses is still underway in Article 5 parties, with barriers such as adherence to standards using ODS, cost and time. In addition, in some cases, ISO and ASTM International still list standards requiring the use of ODS.

Based on the previous recommendations by TEAP and from this investigation, parties may wish to consider removing the procedures listed in Table 4.1 from the global exemption for laboratory and analytical uses of ODS, at a date to be determined by parties. This list is shorter than the previous list that was recommended by TEAP (as reflected in the preambular text of Decision XXI/6) to allow more time for the revision of old standards or the development of new standards and for the adoption of those standards in Article 5 parties.

[17] UNEP May 2008 Report of the TEAP, Volume 1, Progress Report, pg. 54.

[18] UNEP May 2009 Report of the TEAP, Volume 1, Progress Report, pg. 51.

[19] UNEP May 2010 Report of the TEAP, Volume 2, Progress Report, pg. 53.

[20] UNEP May 2011 Report of the TEAP, Volume 1, Progress Report, pg. 51.

Table 4.1 Recommendation of laboratory and analytical procedures to be removed

ODS Type	Procedures
Methyl bromide	Laboratory uses as a methylating agent
Carbon tetrachloride (CTC)	Reaction solvents
CTC	A solvent for IR, Raman and NMR spectroscopy
CTC	Grease removal and washing of NMR tubes
CTC	Iodine partition and equilibrium experiments
CTC	Determination of hydrocarbons in water, air, soil or sediment
CTC	Determination of moisture and water
1,1,1-trichloroethane (TCA)	Determination of bromine index
CTC	Determination of iodine index

In addition, parties may wish to consider recalling that any decision taken to exclude a use from the global exemption would not prevent a party from nominating a specific use for an exemption under the essential uses procedure, as set out in decision IV/25.

Parties may wish to consider establishing cooperation with standards organisations, to facilitate and accelerate the development or revision of standards for the replacement of ODS in analytical uses.

Parties may also wish to consider providing:

- more comprehensive data (e.g. on consumption);
- sharing information on alternatives and on the revision of standards that use ODS;
- possible support for the development and/or revision of standards, and/or training, where needed.

Many standards still require the use of small quantities of ODS. There may come a point when the continued exclusion of specific laboratory and analytical uses on a case by case basis from the global exemption creates potential confusion for practitioners and regulators. Monitoring of, and adherence to, specific authorised uses of ODS in laboratory and analytical applications may become increasingly challenging as the exclusion list expands.

Appendix 1: Relevant decisions for laboratory and analytical uses

This collation of relevant decisions, or parts thereof, is not exhaustive.

Decision VI/9: Essential-use nominations for controlled substances other than halons for 1996 and beyond

3. That for 1996 and 1997, for Parties not operating under paragraph 1 of Article 5 of the Protocol, production or consumption necessary to satisfy essential uses of ozone-depleting substances for laboratory and analytical uses are authorized as specified in Annex II to the report of the Sixth Meeting of the Parties;

Annex II of the report of the 6th Meeting of the Parties in relation to Decision VI/9

Conditions applied to exemption for laboratory and analytical uses

1. Laboratory purposes are identified at this time to include equipment calibration; use as extraction solvents, diluents, or carriers for chemical analysis; biochemical research; inert solvents for chemical reactions, as a carrier or laboratory chemical and other critical analytical and laboratory purposes. Production for laboratory and analytical purposes is authorized provided that these laboratory and analytical chemicals shall contain only controlled substances manufactured to the following purities:

	%
CTC (reagent grade)	99.5
1,1,1-trichloroethane	99.0
CFC-11	99.5
CFC-13	99.5
CFC-12	99.5
CFC-113	99.5
CFC-114	99.5
Other w/Boiling P>20º C	99.5
Other w/Boiling P<20º C	99.0

2. These pure controlled substances can be subsequently mixed by manufacturers, agents, or distributors with other chemicals controlled or not controlled by the Montreal Protocol as is customary for laboratory and analytical uses.

3. These high purity substances and mixtures containing controlled substances shall be supplied only in re-closable containers or high pressure cylinders smaller than three litres or in 10 millilitre or smaller glass ampoules, marked clearly as substances that deplete the ozone layer, restricted to laboratory use and analytical purposes and specifying that used or surplus substances should be collected and recycled, if practical. The material should be destroyed if recycling is not practical.

4. Parties shall annually report for each controlled substance produced: the purity; the quantity; the application, specific test standard, or procedure requiring its uses; and the status of efforts to eliminate its use in each application. Parties shall also submit copies of published instructions, standards, specifications, and regulations requiring the use of the controlled substance.

Decision VII/11: Laboratory and analytical uses

5. To adopt an illustrative list of laboratory uses as specified in Annex IV of the report of the Seventh Meeting of the Parties to facilitate reporting as required by decision VI/9 of the Sixth Meeting of the Parties;

6. To exclude the following uses from the global essential-use exemption, as they are not exclusive to laboratory and analytical uses and/or alternatives are available:

    - Refrigeration and air-conditioning equipment used in laboratories, including refrigerated laboratory equipment such as ultra-centrifuges;

    - Cleaning, reworking, repair, or rebuilding of electronic components or assemblies;

    - Preservation of publications and archives; and

    - Sterilization of materials in a laboratory;

Annex IV of the Report of the Seventh Meeting of the Parties

Categories and examples of laboratory uses

(This list is not exhaustive)

1. Research and development (e.g. pharmaceutical, pesticide, CFC and HCFC substitutes)

    1.1 Reaction solvent or reaction feedstock (e.g. Diels-Alder and Friedel-Craft Reactions, RuO_3 oxidation, allelic side bromination, etc.)

2. Analytical uses and regulated applications (including quality control)

    2.1 Reference

        - Chemical (ODS monitoring, volatile organic compound (VOC) Detection, Equipment Calibration)

        - Toxicant

        - Product (adhesive bond strength, breathing filter test)

    2.2 Extraction

        - Pesticide and heavy metal detection (e.g. in food)

        - Oil mist analysis

        - Colour and food additive detection

        - Oil detection in water and soil

    2.3 Diluent

        - Zinc, copper, cadmium detection in plants and food

- Micro-chemical methods to determine molecular weight or oxygen
- Measuring drug purity and residual determination
- Sterilization of lab equipment

2.4 Carrier (Inert)

- Forensic methods (e.g. fingerprinting)
- Titration (cholesterol in eggs, drug chemical characteristics, "Iodine value", e.g. in oils and chemical products)
- Analytical equipment (Spectroscopy (Infra-red, Ultra-violet, Nuclear Magnetic Resonance, fluorescence), chromatography (High-pressure liquid chromatography, gas chromatography, thin-layer chromatography)

2.5 Tracer

- Sanitary engineering

2.6 Miscellaneous (including testing)

- Ingredient in material for testing (e.g. asphalt, metal fatigue and fracturing)
- Separation media (separation of extraneous materials such as filth and insect excreta from stored food products)

3. Miscellaneous (including biochemical)

3.1 Laboratory method development

3.2 Sample preparation using solvent

3.3 Heat transfer medium

Decision IX/17: Essential-use exemption for laboratory and analytical uses of ozone-depleting substances

2. That data for consumption and production should be reported annually under a global essential-use exemption framework to the Secretariat so that the success of reduction strategies may be monitored;

Decision X/19: Exemption for laboratory and analytical uses

1. To extend the global laboratory and analytical essential-use exemption until 31 December 2005 under the conditions set out in annex II of the report of the Sixth Meeting of the Parties;

2. To request the Technology and Economic Assessment Panel to report annually on the development and availability of laboratory and analytical procedures that can be performed without using the controlled substances in Annexes A and B of the Protocol;

3. That the Meeting of the Parties shall each year, on the basis of information reported by the Technology and Economic Assessment Panel in accordance with paragraph 2 above, decide on any uses of controlled substances which should no longer be eligible under the exemption for laboratory and analytical uses and the date from which any such restriction should apply;

4. That the Secretariat should make available to the Parties each year a consolidated list of laboratory and analytical uses that the Parties have agreed should no longer be eligible for production and consumption of controlled ozone-depleting substances under the global exemption;

5. That any decision taken to remove the global exemption should not prevent a Party from nominating a specific use for an exemption under the essential uses procedure set out in decision IV/25.

Decision XI/15: Global exemption for laboratory and analytical uses

The *Eleventh Meeting of the Parties* decided in Dec. XI/15 to eliminate the following uses from the global exemption for laboratory and analytical uses for controlled substances, approved in decision X/19, from the year 2002:

(a) Testing of oil, grease and total petroleum hydrocarbons in water;

(b) Testing of tar in road-paving materials; and

(c) Forensic finger-printing.

Decision XV/8: Laboratory and analytical uses

1. To extend the global laboratory and analytical use exemption under the conditions set out in annex II of the report of the Sixth Meeting of the Parties until 31 December 2007;

2. To request the Technology and Economic Assessment Panel to report annually on the development and availability of laboratory and analytical procedures that can be performed without using the controlled substances in Annexes A, B and C (group II and group III substances) of the Protocol;

Decision XVI/16: Laboratory and analytical uses

The *Sixteenth Meeting of the Parties* decided in Dec. XVI/16:

Recalling decision IX/17 on essential-use exemptions for laboratory and analytical uses of ozone-depleting substances,

Noting the report of the Implementation Committee requesting guidance from the Parties on the use of bromochloromethane for laboratory and analytical uses,

Considering that decision XV/8 requests the Technology and Economic Assessment Panel to report annually on the development and availability of laboratory and analytical procedures that can be performed without using controlled substances in Annexes A, B and C, groups II and III, of the Protocol,

1. To include in the global laboratory and analytical use exemption under the conditions set out in annex II of the report of the Sixth Meeting of the Parties substances in Annex C, groups II and III, of the Protocol,

2. To apply the conditions set out in paragraphs 3, 4 and 5 of decision X/19 to paragraph 1 of the present decision.

Decision XVII/10: Laboratory and analytical critical uses of methyl bromide

The *Seventeenth Meeting of the Parties* decided in Dec. XVII/10:

1. To authorize, for Parties not operating under paragraph 1 of Article 5 of the Protocol, production and consumption of the controlled substance in Annex E of the Protocol, necessary to satisfy laboratory and analytical critical uses;

2. To agree, subject to paragraph 3 of the present decision, that the relevant illustrative uses listed in annex IV to the report of the Seventh Meeting of the Parties are laboratory and analytical critical uses until 31 December 2006, subject to the conditions applied to exemption for laboratory and analytical uses contained in annex II to the report of the Sixth Meeting of the Parties;

3. That the uses listed in subparagraphs (a) and (c) of paragraph 6 of decision VII/11 and decision XI/15 are excluded from the uses agreed in paragraph 2 of the present decision;

4. To request the Technology and Economic Assessment Panel to consider the uses and criteria referred to in paragraph 2 of the present decision in terms of the relevance of their application to laboratory and analytical critical uses of methyl bromide;

5. To further request the Technology and Economic Assessment Panel to consider other possible laboratory and analytical uses for methyl bromide for which information is available;

6. That the Technology and Economic Assessment Panel report to the Open-ended Working Group at its twenty-sixth meeting on the outcomes of paragraphs 4 and 5 of the present decision;

7. To adopt an illustrative list of analytical and laboratory critical uses for methyl bromide at its Eighteenth Meeting of the Parties;

8. To request the Technology and Economic Assessment Panel to report in 2007 and every other year thereafter on the development and availability of laboratory and analytical procedures that can be performed without using the controlled substance in Annex E of the Protocol;

9. That the Meeting of the Parties shall, on the basis of information reported by the Technology and Economic Assessment Panel in accordance with paragraph 8 of the present decision, decide on any uses which should no longer be agreed as laboratory and analytical critical uses and the date from which any such restriction should apply;

10. That the Secretariat should establish and maintain for the Parties a current and consolidated list of laboratory and analytical critical uses that the Parties have agreed are no longer laboratory and analytical critical uses;

11. That any decision taken pursuant to paragraph 9 of the present decision should not prevent a Party from nominating a specific use under the critical use procedure set out in decision IX/6.

Decision XVIII/15: Laboratory and analytical critical uses of methyl bromide

The *Eighteenth Meeting of the Parties* decided in Dec. XVIII/15:

Noting with appreciation the work undertaken by the Chemicals Technical Options Committee and the Methyl Bromide Technical Options Committee in considering, in accordance with decision XVII/10, the relevance to laboratory and analytical critical uses of methyl bromide of the categories of uses listed in annex IV to the report of the Seventh Meeting of the Parties,

Acknowledging that in decision VII/11, adopted in 1995, Parties were encouraged to identify and review the use of ozone-depleting substances in order to adopt where possible ozone-depleting substance-free technologies,

Noting that the aforementioned committees have reported that alternatives to methyl bromide are available for many laboratory and analytical critical uses, including methylating agent uses,

Noting that the aforementioned committees were not in favour of classifying field trials using methyl bromide as laboratory and analytical critical uses because of the impracticality and cost of using a large number of small containers of 99 per cent pure methyl bromide and that Parties wishing to carry out such field trials could submit critical-use nominations for that purpose,

Recognizing that some laboratory and analytical critical uses listed in the committees' report are applicable to both quarantine and pre-shipment and to feedstock uses, which are not controlled under the Montreal Protocol,

1. To authorize, for Parties not operating under paragraph 1 of Article 5, the production and consumption of the controlled substance in Annex E of the Protocol necessary to satisfy laboratory and analytical critical uses and subject to the conditions established in paragraph 2 of the present decision;

2. Subject to the conditions applied to the exemption for laboratory and analytical uses contained in annex II to the report of the Sixth Meeting of the Parties, to adopt a category of laboratory and analytical critical use to allow methyl bromide to be used:

    (a) As a reference or standard:

        (i) To calibrate equipment which uses methyl bromide;

        (ii) To monitor methyl bromide emission levels;

        (iii) To determine methyl bromide residue levels in goods, plants and commodities;

    (b) In laboratory toxicological studies;

    (c) To compare the efficacy of methyl bromide and its alternatives inside a laboratory;

(d) As a laboratory agent which is destroyed in a chemical reaction in the manner of feedstock;

3. That any decision taken pursuant to the present decision does not preclude a Party from nominating a specific use under the critical use procedure described in decision IX/6.

Decision XIX/18: Laboratory and analytical-use exemption

1. To extend until 31 December 2011 the global laboratory and analytical-use exemption, under the conditions set out in annex II of the report of the Sixth Meeting of the Parties and decisions XV/8, XVI/16, and XVIII/15, for the controlled substances in all annexes and groups of the Montreal Protocol except Annex C, group 1;

Decision XXI/6: Global laboratory use exemption

The *Twenty-First Meeting of the Parties* decided in Dec. XXI/6:

Noting the reports of the Technology and Economic Assessment Panel (TEAP) provided under Decision XVII/10 and under Decision XIX/18 on laboratory and analytical uses of ozone depleting substances (ODS).

Noting that TEAP has identified in its report a number of procedures for which alternatives to the use of ODS are available, as summarised below:

a) Analyses in which the ODS is used as a solvent for spectroscopic measurements:

   i) of hydrocarbons (oil and grease) in water or soil

   ii) of simethicone (polydimethylsiloxane)

   iii) when recording infrared and nuclear magnetic resonance (NMR) spectra, including hydroxyl index

b) Analyses in which the ODS is used as a solvent for electrochemical methods of analysis of:

   i) cyanocobalamin

   ii) bromine index

c) Analyses involving selective solubility in the ODS of:

   i) cascarosides

   ii) thyroid extracts

   iii) polymers

d) Analyses in which the ODS is used to preconcentrate the analyte, for:

   i) liquid chromatography (HPLC) of drugs and pesticides

   ii) gas chromatography of organic chemicals such as steroids

iii) adsorption chromatography of organic chemicals

e) Titration of iodine with thiosulfate (iodometric analyses) for determination of:

i) iodine

ii) copper

iii) arsenic

iv) sulphur

f) Iodine and bromine index measurements (titrations)

g) Miscellaneous analyses, namely

i) stiffness of leather[21]

ii) jellification point

iii) specific weight of cement

iv) gas mask cartridge breakthrough

h) Use of ODS as a solvent in organic chemical reactions

i) O- and N-difluoromethylation

i) General use as laboratory solvent, namely

i) washing of NMR tubes

ii) removal of greases from glassware

Recalling Decisions VII/11, XI/15, XVIII/15 and XIX/18 that already eliminated the following uses from the global exemption for laboratory and analytical uses:

(a) Refrigeration and air conditioning equipment used in laboratories, including refrigerated laboratory equipment such as ultra-centrifuges;

(b) Cleaning, reworking, repair, or rebuilding of electronic components or assemblies;

(c) Preservation of publications and archives;

(d) Sterilization of materials in a laboratory;

(e) Testing of oil, grease and total petroleum hydrocarbons in water;

[21] TEAP/CTOC noted in the 2010 TEAP Progress Report, pg. 56, that information provided about the use of CTC in determining stiffness of leather had been in error, and therefore the procedure mentioned (ASTM D2821) was not relevant or of concern to the global exemption.

(f) Testing of tar in road-paving materials;

(g) Forensic finger-printing;

(h) All laboratory and analytical uses of methyl bromide except:

(i) As a reference or standard:

– To calibrate equipment which uses methyl bromide;

– To monitor methyl bromide emission levels;

– To determine methyl bromide residue levels in goods, plants and commodities;

(ii) In laboratory toxicological studies;

(iii) To compare the efficacy of methyl bromide and its alternatives inside a laboratory;

(iv) As a laboratory agent which is destroyed in a chemical reaction in the manner of feedstock;

(i) Testing of organic matter in coal

Recalling the conditions applied to the exemption for laboratory and analytical uses contained in Annex II of the report of the Sixth Meeting of the Parties.

1. to extend the applicability of the global laboratory and analytical use exemption also to countries operating under Article 5(1) from 1 January 2010 until 31 December 2010 for all ODS except those in Annex B Group III, Annex C Group I and Annex E.

2. to extend the global laboratory and analytical use exemption beyond 31 December 2010 until 31 December 2014:

(a) for Parties operating under Article 5(1) for all ODS except those in Annex B Group III, Annex C Group I and Annex E, and

(b) for Parties not operating under Article 5(1) for all ODS except those in Annex C Group

3. to request all Parties to urge their national standards-setting organisations to identify and review those standards which mandate the use of ODS in laboratory and analytical procedures with a view to adopting, where possible, ODS-free laboratory and analytical products and processes;

4. to request the Ozone Secretariat to enter into discussion with the International Organization for Standardization (ISO), ASTM International (ASTM), the European Committee for Standardization (CEN) as well as with other relevant multinational standardisation organisations encouraging them to identify methods based on ODS and to expedite the inclusion of non-ODS alternative methods, techniques and substances in their standard methods;

5. to request the TEAP and its Chemicals Technical Options Committee to complete the report as requested under Decision XIX/18 and to provide for the 30th Open-ended Working Group meeting

   (a) a list of laboratory and analytical uses of ODS, including those uses where no alternatives exist.

   (b) to identify the international and national standards that require the use of ODS and to indicate the corresponding alternative standard methods not mandating the use of ODS.

   (c) to consider the technical and economical availability of those alternatives in Article-5 and non- Article-5 parties as well as to ensure that the alternative methods show similar or better statistical properties (for example accuracy or detection limits).

6. to request TEAP while continuing its work as described in paragraph 5, to evaluate the availability of alternatives for those uses already banned under the global exemption in Parties operating under Article 5(1), considering technical and economical aspects. By the 30th meeting of the Open-ended Working Group TEAP should present its findings and recommendations whether exemptions would be required for parties operating under paragraph 1 of Article 5 for any of the uses already banned.

7. to allow Parties operating under paragraph 1 of Article 5 until 31 December 2010 to deviate from the existing laboratory and analytical use bans in individual cases, where a Party considers that this is justified, and to ask Parties to revisit this issue at the 22nd Meeting of the Parties.

8. to request the Ozone Secretariat to update the list of laboratory and analytical uses that the Parties have agreed should no longer be eligible under the global exemption, as required by Decision X/19 and to write to Parties reporting laboratory and analytical uses of ozone depleting substances encouraging them to transition to non-ozone depleting alternatives, where allowed by their national standards.

9. to request Parties to continue to investigate domestically the possibility of replacing ODS in those laboratory and analytical uses listed in the report by the TEAP and to make this information available to the Ozone Secretariat by 30 April 2010.

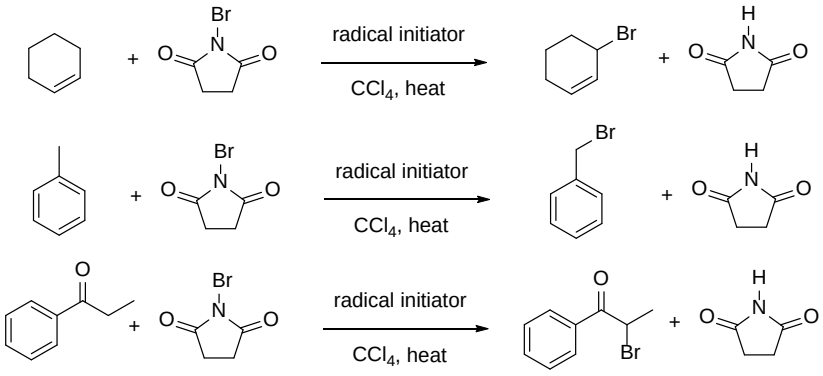
10. to encourage UNEP to invite representatives of the Chemicals Technical Options Committee to regional network meetings to raise awareness of ODS alternatives for laboratory and analytical uses where problems have been specifically identified by members of that network. Where considered necessary other representatives from competent authorities of Parties could be invited to participate in the meeting.

Appendix 2: Alternatives for use of carbon tetrachloride (CTC) as a solvent for bromination reactions involving *N*-bromosuccinimide (NBS)

N-Bromosuccinimide (NBS) is a relatively safe and user-friendly brominating agent that is used as a source for bromine, both in radical reactions and various electrophilic reactions. NBS is also an oxidizing agent. For example, bromination of substrates such as alcohols and amines with NBS, followed by elimination of HBr in the presence of a base, leads to the products of net oxidation, in which no bromine has been incorporated. In these reactions, CTC has long been used as a solvent, owing to its good solvency, non-flammability and chemically stability, and readily availability at affordable prices. However, it is both toxic and carcinogenic and, because it exhibits ozone-layer damaging properties, efforts have been made in the past few years to develop greener bromination procedures, mainly focusing on the substitution of hazardous CCl_4 by more benign solvents. Below is a brief review of the studies on alternatives for CTC as a solvent in these processes.

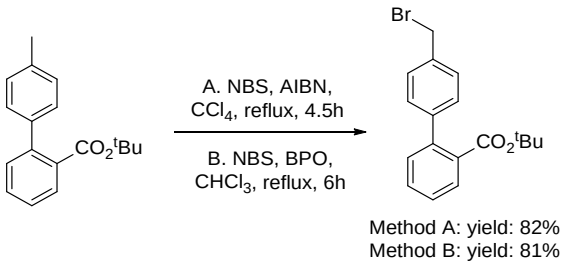
1. Radical substitution reactions (Wohl–Ziegler bromination)

The classical Wohl–Ziegler bromination is a radical reaction that involves the allylic, benzylic or α-carbonylic bromination of hydrocarbons using NBS in refluxing CCl_4 in the presence of a radical initiator such as UV, benzoyl peroxide (BPO) or 2,2-azobis(isobutyronitrile) (AIBN) and nowadays is still often the method of choice for this type of substitutions. The traditional choice of solvent has been CCl_4 which combines optimum properties of solubility, reaction temperature, and ease of product isolation.



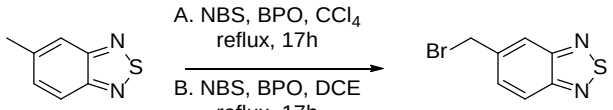
Several bromination protocols using chlorinated solvents (chloroform, 1,2-dichloroethane, dichloromethane, etc.) or non-chlorinated solvents (benzene, petroleum ether, heptane, CS_2, trifluoromethylbenzene, acetonitrile, methyl formate, methyl acetate, ethyl acetate and pivalate, methanol (MeOH), ethanol (EtOH), water, ionic liquids, even solvent-free, etc.) have been developed[1].

Generally, chlorinated solvents such as chloroform, 1,2-dichloroethane, dichloromethane are the most common alternatives for this type of radical substitution. Sometimes, chloroform gives similar or better results particularly in large-scale runs, since succinimide is soluble in hot chloroform, thus yielding a homogeneous solution. Tert-butyl 4'-(bromomethyl)-biphenyl-2-carboxylate could be obtained in the same yield both in CCl_4 and chloroform[2].



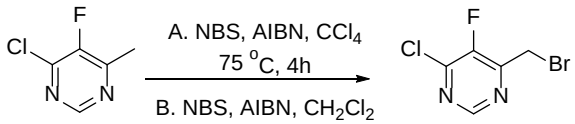
Method A: yield: 82%
Method B: yield: 81%

CCl_4 also could be replaced by 1, 2-dichloroethane for the bromination of 5-methyl-2, 1, 3-benzothiadiazole[3].



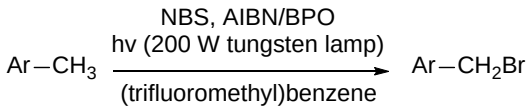
Method A: yield: 75%
Method B: yield: 75%

Dichloromethane is less toxic than CCl_4. However, the bromination with NBS needs longer reaction time due to its low boiling point[4].

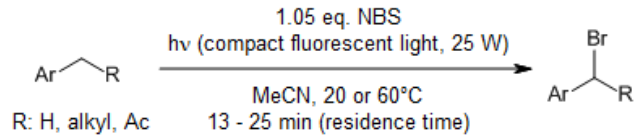


Method A: yield: 94%
Method B: yield: 95%

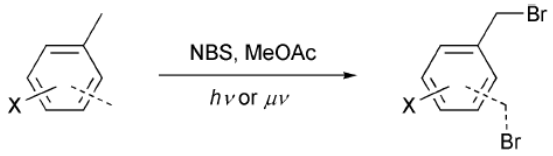
A variety of benzylic brominations were performed by using *N*-bromosuccinimide in (trifluoromethyl)benzene with photochemical activation. This system provides clean, rapid, and high-yielding reactions with replacement of conventional solvents, such as CCl_4, by less-toxic (trifluoromethyl)benzene[5].



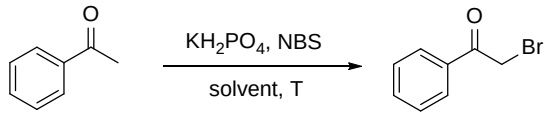
The radical reactions were activated with a readily available household compact fluorescent lamp (CFL) using a simple flow reactor design based on transparent fluorinated ethylene polymer tubing. All of the reactions were carried out using acetonitrile as the solvent, thus avoiding hazardous chlorinated solvents such as CCl_4[6].



Instead of the commonly used CCl_4 or other chlorinated solvents, methyl acetate (MeOAc) was used as an environmentally more benign solvent for these bromination reactions. Benzylic bromides became accessible in short reaction times via direct a-bromination of the corresponding arenes in MeOAc under microwave conditions[7].

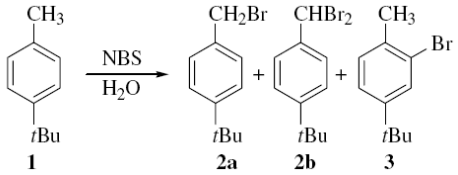


Ketones are regioselectively mono-brominated using NBS in EtOH in presence of 10% KH_2PO_4 as catalyst, with good to excellent isolated yields of the desired products within a short period of time (10-20 min). This approach increased the selectivity of monobromination vs. dibromination[8].



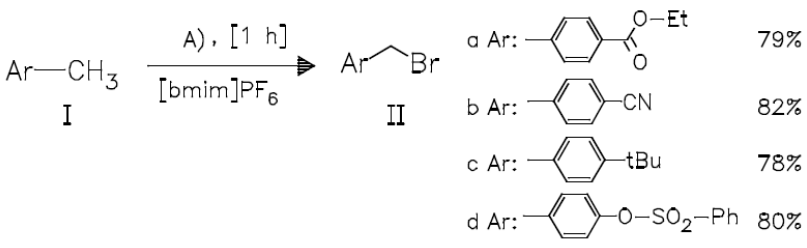
Entry	Solvent	Temp (°C)	Time	Yield[b] (%)
1	Et_2O	25-30	2 h	24
		Reflux	30 min	32
2	THF	25-30	4 h	18
		Reflux	20 min	35
3	MeOH	25-30	5 h	61
		Reflux	25 min	82
4	EtOH	25-30	7 h	52
		Reflux	10 min	96

This report showed that water is a very good medium for a 'greener' protocol for the Wohl–Ziegler bromination and moreover the initiator and heat are substituted by visible light activation of the radical chain reaction. A further advantage of this reaction system is the simple isolation protocol, as the only reaction residue is succinimide which is soluble in water[9].



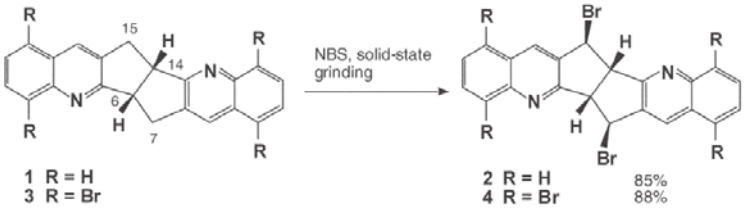
40 W bulb, 27 °C, 22 h 86% 6%

Environmentally-friendly Wohl–Ziegler bromination of benzylic methyl groups was successfully carried out in ionic-liquid systems[10].



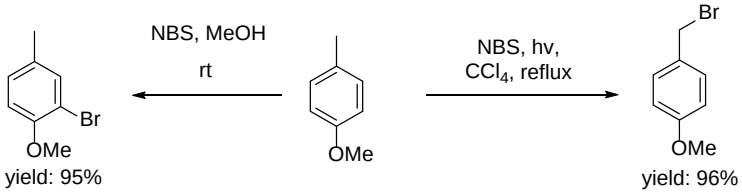
A): 1.2 equiv. NBS, 0.1 equiv. AIBN (cat.), 60–65°C

Bromination also can takes place in the solid state in the absence of toxic and ozone-depleting CCl_4 solvent. Most importantly, the regio- and stereo-selectivity encountered in the solution phase reactions is retained when solvent is omitted[11].

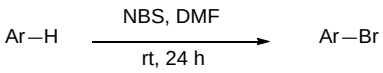


2. Electrophilic substitution reactions

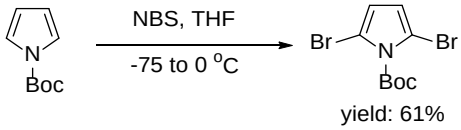
NBS is an available and popular reagent employed mostly in free radical substitutions but also for the electrophilic substitution of aromatic rings. Under some conditions, aromatic compounds can be brominated using NBS as electrophile. It is shown that the electrophilic substitution of benzene ring is favoured in more polar solvents. Otherwise, the free radical reaction in the α-site was favourable[12].



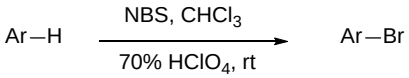
Phenols, anilines, and other electron-rich aromatic compounds can be mono-brominated using NBS in DMF with higher yields and higher levels of para selectivity than with Br_2[13].



N-Substituted pyrroles are brominated with NBS in THF to afford 2-bromopyrroles (1 equivalent) or 2,5-dibromopyrroles (2 equivalents) with high selectivity, whereas bromination with Br_2 affords the thermodynamically more stable 3-bromopyrroles[14].



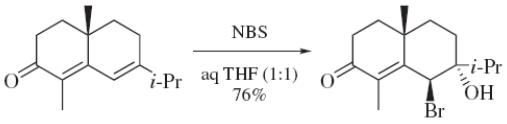
Thiophenes are also selectively brominated in the 2-position using NBS in acetic acid–chloroform[15].



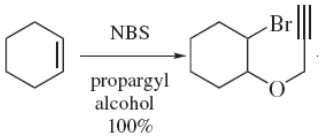
3. Electrophilic addition reactions

NBS also can be used for electrophilic additions to C=C such as bromohydration, bromolactonization, and other additions. The conditions for the bromohydration of alkenes involve the portion-wise addition of NBS to a solution of the alkene in 50–75% aqueous DME, THF, or t-butanol at 0°C. High selectivity for Markovnikov addition and

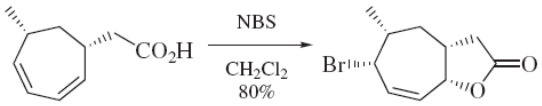
anti stereochemistry results from attack of the bromonium ion intermediate by water. In the bromohydration of polyalkenic compounds, high selectivity is regularly achieved for attack of the most electron-rich double bond[16].



Bromoetherification of alkenes can be achieved using NBS in the desired alcohol as the solvent. Using propargyl alcohol the reaction has been extended to an annulation method for the synthesis of α-methylene-γ-butyrolactones[17].

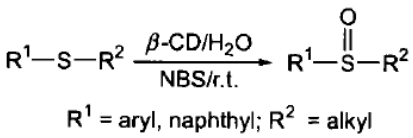


NBS is also an effective reagent for bromolactonization of unsaturated acids and acid derivatives with the same high stereo and Markovnikov selectivity. Dienes, such as the cycloheptadiene derivative shown, may react exclusively via syn-1,4-addition[18].

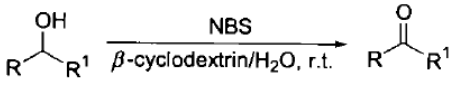


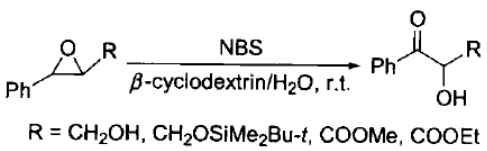
4. Oxidation reactions

The selective oxidation of sulfides to sulfoxides could be performed with NBS catalyzed by cyclodextrin in water. Moreover, the reaction proceeds under neutral and mild conditions and can be carried out easily at room temperature with recycling of cyclodextrin[19].

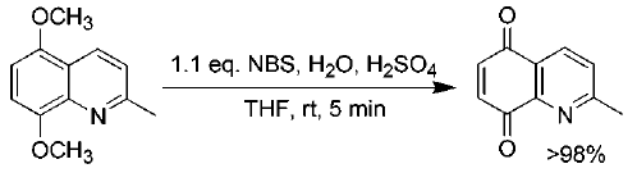


The biomimetic oxidation of various alcohols and epoxides with NBS catalyzed by cyclodextrin in water has also been developed[20].

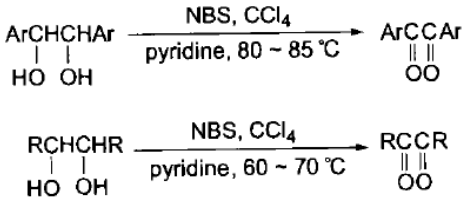




Fused 1,4-dimethoxybenzenes could be oxidized to benzoquinones by oxidation. The oxidative demethylation of 5,8-dimethoxy-2-methylquinoline using 1.1 equivalents of NBS in aqueous THF and a catalytic amount of H_2SO_4 at 20°C for 5 min gave 2-methylquinoline-5,8-dione in 98% yield without bromination[21].



The synthesis of benzils and aliphatic 1,2-diketones of cyclic and open chain compounds from corresponding hydrobenzoins and 1,2-diols by refluxing with NBS in CCl_4 in presence or absence of pyridine was also reported[22].



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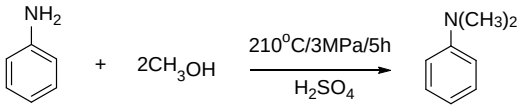
Appendix 3: Methylating agent alternatives to methyl bromide

Methyl bromide can be used in a laboratory as a methylating agent in chemical reactions to deliver a methyl group to a chemical substrate. This application is believed to be very minor. There are many alternatives to using methyl bromide as a methylating agent. A summary of alternative methylating agents is presented below. These alternatives are nearly always used in preference to methyl bromide.

1. Methylating agent used under acidic conditions (methanol, dimethyl ether, dimethylaniline)

Methanol, dimethyl ether and dimethylaniline are very weak methylating agents. In the case of acidic conditions (Brønsted or Lewis acid), they methylate active amines and carboxylic acids as nucleophiles. Many of these reactions require the use of special catalyst or an autoclave.[2]



2. Methylating agent used under basic conditions

2.1 Methyl halide

2.1.1 Methyl Iodide (MeI)

Methyl iodide is an excellent substrate for SN_2 substitution reactions. It is sterically open for attack by nucleophiles, and iodide is a good leaving group. It is used for alkylating carbon, oxygen, sulfur, nitrogen, and phosphorus nucleophiles.[3] The iodide leaving group in MeI may cause side reactions, as it is a powerful nucleophile. Being highly reactive, MeI is more toxic and carcinogenic than other methyl halides.

2.1.2 Methyl Chloride (MeCl)

Chloromethane is employed as a methylating agent attacking C-, O-, N-, P-, S-, Se-, and Te-based nucleophiles; organometallic derivatives provide source of $Me^{\delta-}$ in reactions with >C=O, M–X, halogen, etc., and also as a base towards C–H; radical substitution of Me by C•, halogen, etc. The reactivity of methylation is lower than methyl iodide and methyl bromide.[4]

2.2 Methyl ester

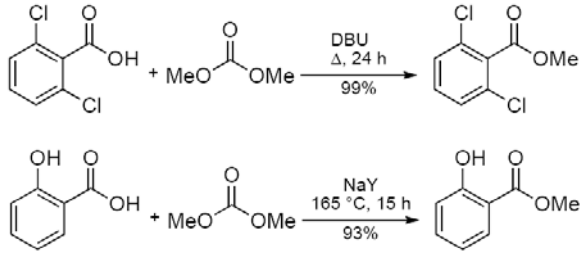
2.2.1 Dimethyl sulfate (DMS)

Dimethyl sulfate is best known as a powerful reagent for the methylation of phenols, amines, and thiols. Typically, one methyl group is transferred more quickly than the second. Methyl transfer is typically assumed to occur via an SN_2 reaction.[5] Compared to other methylating agents, dimethyl sulfate is preferred by the industry because of its low cost and high reactivity.

2.2.2 Dimethyl carbonate (DMC)

Dimethyl carbonate methylates anilines, phenols and carboxylic acids. It has been shown to be a safe and environmentally friendly replacement for DMS and methyl halides. But it is a

relatively weak methylating agent compared to those traditional reagents.[6] In the presence of K_2CO_3 or DBU it is more reactive. The reagent also methylates phenols but can be chemoselective for acids in the presence of NaY Faujasite.



2.2.3 Methyl trifluoromethansulfonate (MTFS)

Methyl trifluoromethansulfonate is a powerful methylating reagent (about four orders of magnitude more reactive than methyl iodide and Me_2SO_4). It alkylates faster and with wider range of substrates than traditional methylating agents. One ranking of alkylating agents is $(CH_3)_3O^+$> MTFS ≈ MFS > $(CH_3)_2SO_4$> CH_3I. It will alkylate many functional groups that are only weakly basic such as aldehydes, amides, and nitriles. It does not methylate benzene or the bulky 2,6-di-tert-butylpyridine.[7]

2.2.4 Methyl fluorosulfonate (MFS)

Methyl fluorosulfonate is closely related to methyl trifluoromethansulfonate.[7]

2.2.5 Methyl methanesulfonate (MMS)

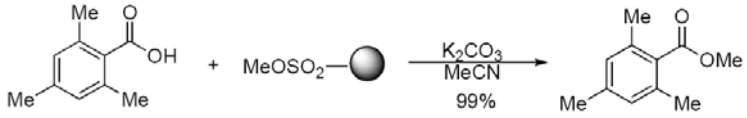
Methyl methanesulfonate is an exogenous alkylating agent and a carcinogen in biological research. It is also a suspected reproductive toxicant and may also be a skin/sense organ toxicant. It is used in cancer treatment.[8]

2.2.6 Trimethyl phosphate (TMP)

Trimethyl phosphate is a mild methylating agent for the preparation of methyl esters of hindered carboxylic acids and serves as an alternative to toxic dimethyl sulfate. It can also affect the *O*-methylation of unprotected amino acids, dimethylation of anilines and related heterocyclic compounds (purine, pyrimidine, imidazole et al.).[9]

2.2.7 Polymer-bound methyl sulfonate

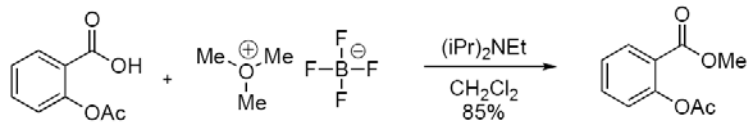
Instead of the sulfonate esters, modern alternative is to use polymer-bound methyl sulfonate, which is easily handled, allows simple work-up and is recyclable.[10]



2.3 Oxonium salts ($Me_3O•BF_4$)

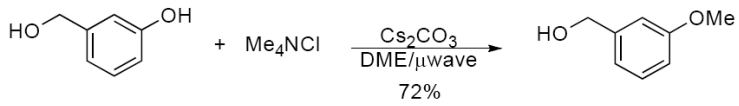
In aqueous conditions, it is possible to use Meerwein methylation, using the corresponding oxonium salts ($Me_3O•BF_4$) with $NaHCO_3$. However, these salts are rapidly hydrolyzed in water. A better procedure with these reagents is to use dichloromethane as solvent and a bulky

amine as base. Under these conditions, even sterically hindered or sensitive acids can be alkylated.[11]



2.4 Tetramethylammonium salts

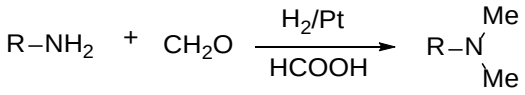
Tetramethylammonium salts are other replacement alkylating agents which are non-volatile and non-carcinogenic. However, due to their lower reactivity, high temperatures (such as the injection port during a gas chromatographic analysis) are required. For the alkylation of phenols, microwave conditions have been used with success. The reaction is chemoselective for the phenolic hydroxyl group over the alcohol.[12]



3. Methylating agent used under neutral conditions

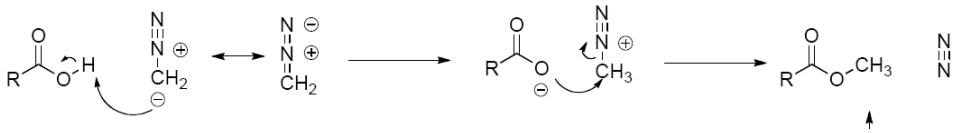
3.1 Formaldehyde aqueous solution

Formaldehyde aqueous solution can be used in methylation of primary or secondary amine (Eschweiler–Clarke reaction). Formic acid or H_2/Ptis is also needed as the source of hydride. This reaction will not produce quaternary ammonium salts, but instead will stop at the tertiary amine stage.[13]



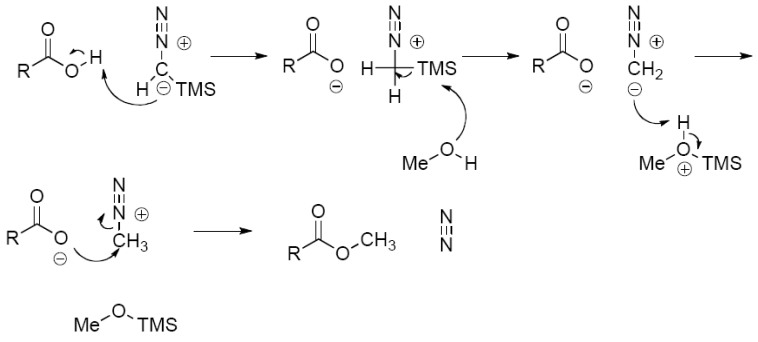
3.2 Diazomethane

The methylation of carboxylic acids and other acidic functional groups is often carried out in neutral conditions using diazomethane (CH_2N_2).[14] However, due to its toxicity and the explosive nature of diazomethane (as well as the danger in the preparation and the carcinogenicity of the commercially available precursors), several alternative reagents recently have been developed.

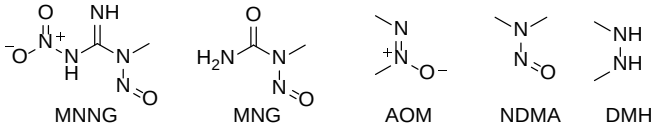


3.3 Trimethylsilyldiazomethane ($TMSCHN_2$)

Trimethylsilyldiazomethane (TMSD) has been touted as a stable and safe alternative to diazomethane, but its use is constrained by its high cost and lower efficiency.[15]



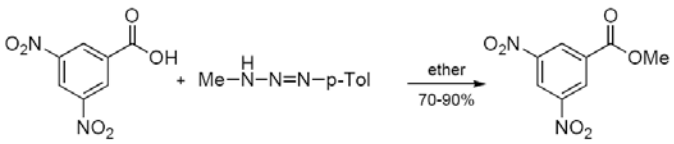
3.4 Methylnitronitrosoguanidine (MNNG), N-methyl-N-nitrosourea (MNU), Azoxymethane (AOM), N-*Nitrosodimethylamine (NDMA), 1,2-dimethylhydrazine (DMH)*



MNNG, NMU, AOM, NDMA, and DMH are reliable carcinogen, mutagen, and teratogen in biological research. They all exhibit the toxicity by transferring methyl group to nucleobases in nucleic acids, which can lead to AT:GC transition mutations. The corresponding mechanisms of methylation are similar to diazomethane.[8]

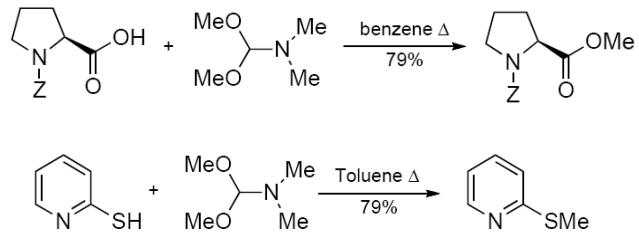
3.5 Aromatic triazenes

The aromatic triazenes, especially of *p*-toluidine, can be used as alkylating agents of carboxylic acids and vinylogous acids. However, these reagents are also carcinogenic and have the risk of being explosive.[16]



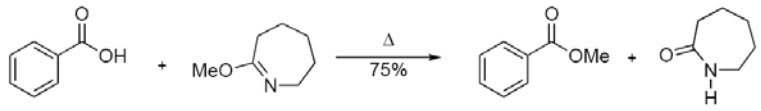
3.6 Dimethyl acetals of N,N-*dimethylformamide (DMF)*

Dimethyl acetals of *N*,*N*-dimethylformamide (DMF) is often useful alkylating agents under neutral conditions. It is most commonly used to form the corresponding esters. Heterocycles with SH, NH and OH can also be methylated with DMF dimethyl acetal.[17]



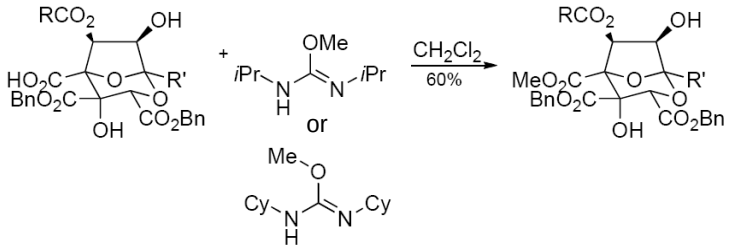
3.7 O-*Methylcaprolactam*

Related to the DMF acetals are the corresponding lactim ethers of cyclic amides. For example, *O*-methylcaprolactam has been shown to alkylate carboxylic acids at high temperatures.[18]



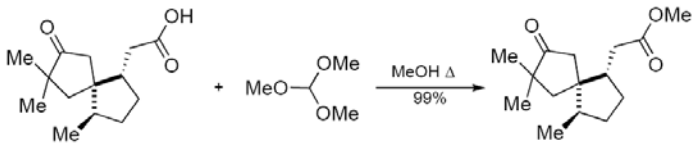
3.8 O-*Methyl isourea*

A variety of esters can be prepared, even in the presence of various functional groups, with *O*-methyl isourea.[19]*O*-Methyl isourea is easily formed from methanol and dicyclohexylcarbodiimide (DCC) or diisopropylcarbodiimide (DIC).



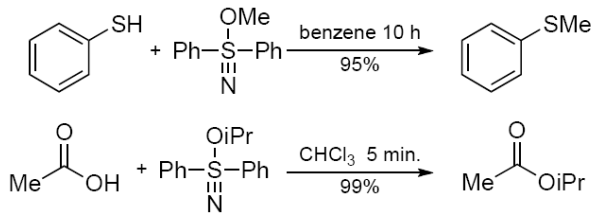
3.9 Trimethyl Orthoformate

Trimethyl orthoformate can be used for the methylation of acids, including amino acids. The reaction is mild enough to chemoselectively form the ester in the presence of other functional groups. The reaction can also be run efficiently in room temperature ionic liquids as solvents.[20]



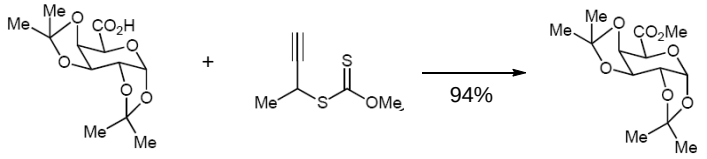
3.10 Alkoxy-λ6-sulfanenitriles (thiazynes)

The surprising chemistry of alkoxy-λ6-sulfanenitriles (thiazynes) has been investigated and these compounds have been found to alkylate carboxylic acids, thiols, phenols and sulfonic acids in essentially quantitative yields at room temperature.[21]



3.11 S-*Propargyl xanthates*

S-propargyl xanthates have been used for the esterification of acids. This method shows high reactivity (even for the synthesis of neopentyl esters, which are notoriously difficult to form) and complete inversion of stereochemistry for secondary alcohols.[22]



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Appendix 4: Non-exhaustive list of standards that do not use ODS

Determination of hydrocarbons (oil, grease, etc.) in water

Standard number	Standard Title	Alternative
ASTM D7066-04(2017)	Standard Test Method for dimer/trimer of chlorotrifluoroethylene (S-316) Recoverable Oil and Grease and Nonpolar Material by Infrared Determination	Dimer/trimer of chlorotrifluoroethylene (S-316)
ASTM D7575-11(2017)	Standard Test Method for Solvent-Free Membrane Recoverable Oil and Grease by Infrared Determination	Membrane
ISO 17993:2002	Water quality-Determination of 15 polycyclic aromatic hydrocarbons (PAH) in water by HPLC with fluorescence detection after liquid-liquid extraction	Hexane, PAHs
ISO 9377-1:2000	Water quality - Determination of hydrocarbon oil index - Part 1: Method using solvent extraction and gravimetry	Petroleum ether
ISO 9377-2:2000	Water quality - Determination of hydrocarbon oil index - Part 2: Method using solvent extraction and gas chromatography	n-Hexane
ISO 15680:2003	Water Quality - Gas-chromatographic Determination of A Number of Monocyclic Aromatic Hydrocarbons, Naphthalene And Several Chlorinated Compounds Using Purge-and-trap And Thermal Desorption	Purge-and-trap
ISO 20595:2018	Water quality — Determination of selected highly volatile organic compounds in water — Method using gas chromatography and mass spectrometry by static headspace technique (HS-GC-MS)	HS-GC-MS
ISO 10301:1997	Water quality — Determination of highly volatile halogenated hydrocarbons — Gas-chromatographic methods	Pentane, hexane, petroleum ether, heptane or xylene
US EPA Method 502.2 Revision 2.1	Volatile Organic Compounds in Water by Purge and Trap Capillary Column Gas Chromatography with Photoionization and Electrolytic Conductivity Detectors in Series	Purge-and-trap

Standard number	Standard Title	Alternative
US EPA Method 524.2 Revision4.1	Measurement of Purgeable Organic Compounds in Water by Capillary Column Gas Chromatography/Mass Spectrometry	GC-MS
US EPA Method 3560	Supercritical Fluid Extraction of Total Recoverable Petroleum Hydrocarbons (TRPHs)	Supercritical CO_2
US EPA Method 1664 Revision A	Extraction of Oil and Grease from Water Samples Using Solid-Phase Extraction (SPE) Cartridge Configuration	Hexane
US EPA 3810	Headspace gas chromatography	Methyl alcohol
US EPA 3820	Hexadecane extraction and screening of purgeable organics	Hexadecane
US EPA 5021B	Volatile organic compound in various sample matrices using equilibrium headspace analysis	Headspace analysis
US EPA 8021B	Aromatic and halogenated volatiles by gas chromatography using photo-ionisation and/or electrolytic conductivity detectors	GC
HJ 893-2017	Water quality–Determination of volatile petroleum hydrocarbons (C6-C9)–Purge and trap / gas chromatography	Purge and trap
HJ 894-2017	Water quality—Determination of extractable petroleum hydrocarbons (C10-C40)—Gas chromatography	Dichloromethane

Determination of hydrocarbons (oil, grease, etc.) in air, soil or sediment

Standard number	Standard Title	Alternative
ISO 16703：2004	Determination of hydrocarbon content (C10 to C40) by gas chromatography after extraction with heptane	Heptane
ISO15009：2016	Gas-chromatographic determination of the content of volatile aromatic hydrocarbons, naphthalene and volatile halogenated hydrocarbons after methanol extraction and purge-and-trap	Methanol
ISO 10694:1995	Soil quality -- Determination of organic and total carbon after dry combustion (elementary analysis)	Elementary analysis
ISO 18287:2006	Soil quality — Determination of polycyclic aromatic hydrocarbons (PAH) — Gas chromatographic method with mass spectrometric detection (GC-MS)	Acetone/petroleum ether
ASTM D5765-16	Solvent extraction of total petroleum hydrocarbons from soil and sediments using closed vessel microwave heating	Acetone/hexane
US EPA 9071B	n-Hexane extractable material (HEM) for sludge, sediment, and solid samples	n-Hexane
US EPA Method 8261A	Volatile organic compounds by vacuum distillation in combination with gas chromatography/mass spectrometry (VD/GC/MS)	VD/GC/MS
US EPA 3550B	Ultrasonic extraction	Acetone/methylene chloride or acetone/hexane
EN 14039:2004	Characterization of waste - Determination of hydrocarbon content in the range of C10 to C40 by gas chromatography	Heptane
EN 14345:2004	Characterization of waste. Determination of hydrocarbon content by gravimetry	Acetone/petroleum

Determination of Iodine value or Bromine value[22]

Standard number	Standard Title	Alternative
ISO 3961:2013	Animal and vegetable fats and oils -- Determination of iodine value	Cyclohexane/glacial acetic acid
ASTM D5768-02(2018)	Standard Test Method for Determination of Iodine Value of Tall Oil Fatty Acids	iso-Octane/cyclohexane
ASTM D1492-13	Bromine index of aromatic hydrocarbons by coulometric titration	Glacial acetic acid/ methanol
ASTM D5554-15	Standard Test Method for Determination of the Iodine Value of Fats and Oils	Glacial acetic acid/cyclohexane
ASTM D5776-14a	Standard Test Method for Bromine Index of Aromatic Hydrocarbons by Electrometric Titration	1-Methyl-2-pyrrolidinone
ASTM D4252-89(2017)	Standard Test Methods for Chemical Analysis of Alcohol Ethoxylates and Alkylphenol Ethoxylates	Chloroform

[22] Value is also referred to as index.

Determination of moisture and water

Standard number	Standard Title	Alternative
ISO 662:2016	Animal and vegetable fats and oils -- Determination of moisture and volatile matter content	Heating method
ISO 934:1980	Animal and vegetable fats and oils. Determination of water content- Entrainment method	Xylene
ISO 8534:2017	Animal and vegetable fats and oils. Determination of water content. Karl Fischer method (pyridine free)	Methanol
ISO 3733:1999	Petroleum products and bituminous materials- Determination of water- Distillation method	Aromatic solvent, petroleum distillate solvent, paraffinic solvents
ISO 6296:2000	Petroleum products. Determination of water. Potentiometric Karl Fischer titration method	Sodium dioctylsulfosuccinate
ISO 12937:2000	Petroleum products. Determination of water. （Coulometric Karl Fischer titration method）	Sodium dioctylsulfosuccinate

Determination of phenol in water

Standard number	Standard Title	Alternative
ASTM D1783-01(2012)e1	Standard test methods for phenolic compounds in water	Chloroform
ISO 6439:1990	Water quality — Determination of phenol index — 4-Aminoantipyrine spectrometric methods after distillation	Chloroform
US EPA Method 4 20.1	Phenolics (Spectrophotometric, Manual 4-AAPWith Distillation)	Chloroform

Determination of metal content

Standard number	Standard Title	Alternative
ASTM D3237-06e1	Standard Test Method for Lead in Gasoline by Atomic Absorption Spectroscopy	Methyl isobutyl ketone

Appendix 5: Non-exhaustive list of standards that still use ODS

	Standard No.	Standard Title
1	ASTM D3467-04(2014)	Standard Test Method for Carbon Tetrachloride Activity of Activated Carbon
2	ASTM D5566-95(2011)	Standard Test Method for Determination of Inorganic Salt Content of Sulfated and Sulfonated Oils
3	ASTM F754 - 08(2015)	Standard Specification for Implantable Polytetrafluoroethylene (PTFE) Sheet, Tube, and Rod Shapes Fabricated from Granular Molding Powders
4	ASTM D3124 - 98(2011)	Standard Test Method for Vinylidene Unsaturation in Polyethylene by Infrared Spectrophotometry
5	ASTM D3703 – 18	Standard Test Method for Hydroperoxide Number of Aviation Turbine Fuels, Gasoline and Diesel Fuels
6	ASTM E1683 - 02(2014)e1	Standard Practice for Testing the Performance of Scanning Raman Spectrometers
7	ASTM D2008 - 12	Standard Test Method for Ultraviolet Absorbance and Absorptivity of Petroleum Products
8	ASTM E169 - 16	Standard Practices for General Techniques of Ultraviolet-Visible Quantitative Analysis
9	ASTM E2036 - 15	Standard Test Method for Nitrogen Trichloride in Liquid Chlorine by High Performance Liquid Chromatography (HPLC)
10	ASTM D1505 - 18	Standard Test Method for Density of Plastics by the Density-Gradient Technique
11	ASTM F218 - 13	Standard Test Method for Measuring Optical Retardation and Analyzing Stress in Glass
12	ASTM E50 - 17	Standard Practices for Apparatus, Reagents, and Safety Considerations for Chemical Analysis of Metals, Ores, and Related Materials
13	ASTM C670 – 15	Standard Practice for Preparing Precision and Bias Statements for Test Methods for Construction Materials
14	ASTM E2106 - 00(2011)	Standard Practice for General Techniques of Liquid Chromatography-Infrared (LC/IR) and Size Exclusion Chromatography-Infrared (SEC/IR) Analyses

15	ASTM C799 - 12	Standard Test Methods for Chemical, Mass Spectrometric, Spectrochemical, Nuclear, and Radiochemical Analysis of Nuclear-Grade Uranyl Nitrate Solutions
16	ASTM D3869 - 15	Standard Test Methods for Iodide and Bromide Ions in Brackish Water, Seawater, and Brines
17	ASTM D5160 - 95(2014)	Standard Guide for Gas-Phase Adsorption Testing of Activated Carbon
18	ASTM E1252 - 98(2013)e1	Standard Practice for General Techniques for Obtaining Infrared Spectra for Qualitative Analysis
19	ASTM D4448 - 01(2013)	Standard Guide for Sampling Ground-Water Monitoring Wells
20	ASTM E1982 - 98(2013)	Standard Practice for Open-Path Fourier Transform Infrared (OP/FT-IR) Monitoring of Gases and Vapors in Air
21	ASTM D460 - 91(2014)	Standard Test Methods for Sampling and Chemical Analysis of Soaps and Soap Products
22	ASTM D629 - 15	Standard Test Methods for Quantitative Analysis of Textiles
23	ASTM C761 - 18	Standard Test Methods for Chemical, Mass Spectrometric, Spectrochemical, Nuclear, and Radiochemical Analysis of Uranium Hexafluoride
24	ASTM C169 – 16	Standard Test Methods for Chemical Analysis of Soda-Lime and Borosilicate Glass
25	ASTM D297 - 15	Standard Test Methods for Rubber Products—Chemical Analysis
26	ISO 6439:1990	Water quality — Determination of phenol index — 4-Aminoantipyrine spectrometric methods after distillation
27	ISO 7523:1985	Nickel — Determination of silver, arsenic, bismuth, cadmium, lead, antimony, selenium, tin, tellurium and thallium contents — Electrothermal atomic absorption spectrometric method
28	ISO 7106:1985	Liquefied anhydrous ammonia for industrial use — Determination of oil content — Gravimetric and infra-red spectrometric methods
29	ISO 5796:2000	Rubber compounding ingredients — Natural calcium carbonate — Test methods

30	ISO 1183-1:2012	Plastics — Methods for determining the density of non-cellular plastics — Part 1: Immersion method, liquid pyknometer method and titration method
31	ISO 1183-2:2004	Plastics — Methods for determining the density of non-cellular plastics — Part 2: Density gradient column method
32	ASTM D3326 - 07(2017)	Standard Practice for Preparation of Samples for Identification of Waterborne Oils
33	ASTM D1783 - 01(2012)e1	Standard Test Methods for Phenolic Compounds in Water
34	ASTM D1574 - 04(2013)	Standard Test Method for Extractable Matter in Wool and Other Animal Fibers
35	ASTM D3698-04(2015)	Standard Practice for Solvent Vapor Degreasing Operations
36	ASTM F1147-05(2017)e1	Standard Test Method for Tension Testing of Calcium Phosphate and Metallic Coatings
37	ASTM B322-99(2014)	Standard Guide for Cleaning Metals Prior to Electroplating
38	ISO 15001:2010	Anaesthetic and respiratory equipment — Compatibility with oxygen

Appendix 6: Alternatives to ODS in analytical procedures (CTOC, 2009)

Alternatives to ODS in analytical procedures (CTOC, 2009[23])

ODS	Methodology		Feasible Substitutes	
ODS Type	General use	Methodology	Substance/ Methodology	Methodology
CCl4	Standard method	Analysis of Cyanocobalamin, United States Pharmacopea (USP) Method.	Coulometric electrochemical and ultraviolet detection	Determination of cyanocobalamin, betamethasone, and diclofenac sodium in pharmaceutical formulations, by high performance liquid chromatography. L. González, G. Yuln and M. G. Volonté High-performance liquid chromatography method for the simultaneous determination of thiamine hydrochloride, pyridoxine hydrochloride and cyanocobalamin in pharmaceutical formulations using coulometric electrochemical and ultraviolet detection. Marcin Leszek Marszałł, Anna Lebiedzińska, Wojciech Czarnowski and Piotr Szefer.
CCl4	Standard Method	Analysis of cascarosides	- Dichloromethane, - Chloroform Trichloroethylene	
CCl4	Standard Method	Analysis of simethicone by Infrared spectroscopy / Cleaning of IR cells (Valuation of Simethicone in finished products, using infrared spectroscopy (IR). Method "Simethicone Capsules" of Official Monographs USP XXIV (p. 1519).)	Chloroform Toluene	ICP-AES Determination of Trace Simethicone Levels in Biopharmaceutical Products. J. Qiu, V. Wong, H. Lee, C. Zhou J Pharm Biomed Anal. 2002 Sep 5;30 (2):273-8 12191712. A RP-LC method with evaporative light scattering detection for the assay of simethicone in pharmaceutical formulations. Douglas E Moore, Tina X Liu, William G Miao, Alison Edwards, Russell Elliss. Faculty of Pharmacy, The University of Sydney, Sydney 2006, Australia.
CCl4	Standard Method	Analysis of Trimethoprim. United States Pharmacopea (USP) Method (Also at: S.Z. Qureshi; M.I.H Helaleh; N. Rahman; R.M.A.Q. Jamhour; "Spectrometric determination of trimethoprim by oxidation in drugs formulations; Fresenius J Anal Chem (1997) 357: 1005-1007; Springer-Verlag 1997)	- Acetonitrile and methanol	L. K. Sørensen&, T. H. Elbæk; "Simultaneous Determination of Trimethoprim, Sulfadiazine, Florfenicol and Oxolinic Acid in Surface Water by Liquid Chromatography Tandem Mass Spectrometry"; Chromatographia **2004**, 60, September (No. 5/6); p. 287.
CCl4	General Method	Analysis of conjugated estrogens by gas chromatography		No alternatives found.
CCl4	Standard Method	Analysis of Furazolidone, United States Pharmacopeia (USP) Method	- UV detection	S. M. Hassan / F. A. Ibrahim* / M. S. El-Din / M. M. Hefnawy; "A Stability- Indicating High-Performance Liquid Chromatographic Assay for the Determination of Some Pharmaceutically Important Nitrocompounds"; Chromatographia Vol. 30, No. 3/4, August 1990; p. 176.
CCl4	General method	Analysis of copper gluconate	- Dichloromethane, - Chloroform -Trichloro- ethylene	
CCl4	Standard Method	Gravimetric determination of sulfur, Collaborative International Pesticides Analytical Council CIPAC Method [1]	- Gravimetric method	Gravimetric method using nitric acid. Reflux with ethanol and titration with iodine, according to CIPAC (Collaborative International Pesticides Analytical Council Limited)
CCl4	Standard Method	Determination of specific weight in cement samples (National standard NCh 154 Of. 69 / ASTM C 243-95, Standard test)	- Kerosene Benzene	ASTM C 188-44 (Revised in 1967)

[1] Note: The sulphur is converted by refluxing with sodium sulphite to sodium thiosulphate. The thiosulphate is then titrated with Standard iodine solution. CIPAC Handbook E.

[23] Reproduced without review from 2009 TEAP Report, Table 7.3, pg. 52 onwards.

ODS	Methodology		Feasible Substitutes	
ODS Type	General use	Methodology	Substance/ Methodology	Methodology
CCl4	Standard Method	ASTM D 2821-96[2], Standard Test Method for Measuring the Relative Stiffness of Leather by Means of a Torsional Wire Apparatus	Trichloroethylene	
CCl4	Standard Method	ASTM D 3921-85 (re-approved in 1990), Standard test method for oil and grease and petroleum hydrocarbons in water	Perchloroethylene	ASTM D7066-04
CCl4	Standard Method	Determination of hydrocarbons in water ASTM D3921-96 / D3921-97	Perchloroethylene S-316 (dimer/trimer of chlorotrifluoro-ethylene)	
CCl4	Standard Method	Determination of the jellification point. Method M SAC 10 14 11 (Own method)		No alternatives found
CCl4	Standard Method	Iodine index by volumetry in oil and greases AOCS CD 1-25 "Iodine Value (Wijs)"	- Hexane Cyclohexane and acetic acid Chloroform Iso-octane	Method CD1D-92
CCl4	Standard method	Iodine[3] index by ASTM D1959-97 Standard Test Method for Iodine Value of Drying Oils and Fatty Acids (Withdrawn 2006) ASTM D5554- 95 (2006) Standard Test Method for Determination of the Iodine Value of Fats and Oils.	Cyclohexane and acetic acid and diluted with iodine monobromide solution.	[4] Hanus ISO 3961:1996
CCl4	General Method	Liquid-liquid partitioning method, for iodide and bromide analysis	- Dichloromethane. Chloroform	
CCl4	Standard Method	Extraction of iodine and its derivatives and thyroid extracts from semi-solid pharmaceutical preparation. United States Pharmacopeia (USP) method	- Petroleum ether Hexane Chloroform Dichloromethane Benzene Hexane + ethyl acetate	

[2] Updated by ASTM D2821-00(2005)e1.

[3] The Iodine value expresses the content of compounds with unsaturated carbon-carbon double bonds. It is determined by adding a halogen, e.g. iodine to the simple.

[4] In the determination of the iodine value according to Hanus the sample is dissolved in cyclohexane and acetic acid and diluted with iodine monobromide solution. Potassium iodide and water are added, and the formed iodine is titrated back with sodium thiosulphate solution. The methods according to Wijs and Kauffmann slightly differ from the Hanus method. Information on the accuracy of the methods is given in the test methods. Only in the case of some oils with a high iodine value can the results deviate from one another. Cyclohexane and acetic acid have generally substituted chloroform (trichloromethane, not an ozone depleting substance) and carbon tetrachloride. Also ISO 3961:1996, which is similar to the Wijs method, uses cyclohexane and acetic acid. The modified Hofmann and Green method allows a shorter reaction time, and is recommended for samples containing hydroxy fatty acids because the substitute reactions occurring in this case using the Wijs method do not take place. (Ref. TemaNord 2003:516)

ODS	Methodology		Feasible Substitutes	
TCA	Standard Method	Bromine index ASTM D2710-99 Determination of bromine number ASTM ASTM D1159-07[5]	- Dichloromethane Diethylcarbonate 1-methyl-2-pirrolidone Dichloro- methane	ASTM D 2710[6] ASTM D 1159-07
CCl4	General Method	Determination of copper	- Chloroform Dichloromethane Perchloroethylene Trichloroethylene	Flame Atomic Absorption Spectrometric Methods Research and Development (2) Page 25.
CCl4	General Method	Arsenic extraction	- Chloroform	Atomic Absorption Spectrometry AAE with hydride generation
CCl4	General Method	Analysis of chloride in saline solutions	- Aliphatic hydrocarbon Chloroform Dichloromethane Perchloroethylene In the first cleaning stage: benzene / ether.	
CCl4	Solvent	Washing of NMR (Nuclear Magnetic Resonance) tubes	- Acetone	Washing should be followed by oven- drying of inverted tubes to remove traces of acetone.
CCl4	Solvent	Grease solvent and cleaning of glass materials	- Acetone	A chlorinated solvent such as chloroform, trichloroethylene or dichloromethane may also be used.
CCl4	Solvent	Organic synthesis	- Dichloromethane Chloroform	
CCl4	Carrier (inert); analytical equipmet (Infrared)	Reaction of phenol and aromatics. Oxygen containing functional groups - Noncarbonyl Groups, Example: The determination of hydroxyl values of alcohols, page 34.	- Perchloroethylene	Welcher 6th Edition, p. 1180.[7]
CCl4	Carrier, analytical use.	Solvent in metals analysis by UV- Vis spectrometry, with ditizone (International method). / "Titration of cadmium: Photometric Method with Ditizone", page 44.	- Chloroform Dichloromethane Benzene Toluene Cadmium sulfide can be extracted from solution with iodine	Furman Sixth Edtion pp. 254-256[8]
CCl4	Solvent	Solvent of polymers	- Tetrahydrofurane. Chloroform. Dichloromethane. Dichloroethane	
CCl4	Carrier (inert); analytical equipment - Infrared analysis for spectral range 4000 to 50 cm^{-1}	Spectrophotometry IR (USP XXIII) "Standard practice for general techniques for qualitative infrared analysis E 1252-94", page 26	- Toluene Carbon disulphide	[9]

[5] ASTM D 1159 is generally applicable for gasoline, kerosene and distillates in the gas oil range that fall in specific distillation and bromine number limits. However, the method is not satisfactory for normal alpha-olefins. The method can be used to estimate the percentage of olefins in petroleum distillates boiling up to approximately 315oC by using a calculation method described in the standard. Dichloromethane is temporarily being allowed as an alternative to 1,1,1-trichloroethane (an ozone depleting substance) until a permanent substitute can be identified and adopted by ASTM. A program to identify and evaluate candidate solvents is currently underway in the Subcommittee D02.04. (Ref. TemaNord 2003:516; “Use of ozone depleting substances in laboratories”; © Nordic Council of Ministers, Copenhagen 2003 ISBN 92-893-0884-2).

[6] This method also mentioned dichloromethane as an alternative to TCA.

[7] Research and Development (ICE Consulting, "Consumption of Ozone Depleting Substances (ODS) by Laboratories in the European Community and ODS-Free Methods to Reduce Further ODS Use - Confidential Report Prepared for the European Commission - April 2005".

[8] Research and Development (ICE Consulting, "Consumption of Ozone Depleting Substances (ODS) by Laboratories in the European Community and ODS-Free Methods to Reduce Further ODS Use - Confidential Report Prepared for the European Commission - April 2005".

[9] Research and Development (ICE Consulting, "Consumption of Ozone Depleting Substances (ODS) by Laboratories in the European Community and ODS-Free Methods to Reduce Further ODS Use - Confidential Report Prepared for the European Commission - April 2005".

ODS	Methodology		Feasible Substitutes	
CFC-113	Standard Method	US EPA Office of Water Method 418.1, extraction of total petroleum hydrocarbons from water samples, for analysis by infrared spectroscopy "Petroleum Hydrocarbons, Total Recoverable - Spectrometric, Infrared"	- S-316 (dimer/trimer of chlorotrifluoro-ethylene)	ASTM D 7066-04 "Test Method for dimer/trimer of Chlorotrifluoroethylene S-316 recoverable oil and grease and non-polar material by infrared determination".
CCl4	Carrier (inert), analytical equipment, GC	Adsorption Chromatography (Welcher 6th edition pp 216-219,[10] page 38.	- Petroleum ether Cyclohexane Carbon disulfide Diethyl ether Benzene Esters Chloroform Dichloroethane Alcohols Water Pyridine Organic acid Inorganic acids and bases.	Welcher Sixth Edition pp. 216-219.
CCl4	Vapor producer	Test of breakthrough times of gas mask cartridges and canisters in the National Approval Test of Respirators. Testing of breathing filters (personal safety equipment), 42 CFR part 84	- Cyclohexane	Mitsuya FURUSE1, Seiichiro KANNO, Tsuguo TAKANO and Yoshimi MATSU; "Cyclohexane as an Alternative Vapor of Carbon Tetrachloride for the Assessment of Gas Removing Capacities of Gas Masks"; National Institute of Industrial Health, Kawasaki, Japan; Industrial Health 2001, 39, 1–7.
CCl4	Solvent	*O*- and *N*- difluoromethylations	- Chlorodifluoro-methyl phenyl sulfone	Ji Zhenga, Ya Lia, Laijun Zhanga, Jinbo Hu*.a, Gerrit Joost Meuzelaarb, and Hans-Jürgen; "Chlorodifluoromethyl phenyl sulfone: a novel non-ODS based difluorocarbene reagent for *O*- and *N*- difluoromethylations"; Supplementary Material (ESI) for Chemical Communications. This journal is © The Royal Society of Chemistry 2007.