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Trichloroethylene in organic synthesis

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Abstract. The literature data on the chemistry of trichloroethylene are surveyed. Reactions involving the addition of inorganic and organic reagents to trichloroethylene are examined and cycloaddition reactions with participation of trichloroethylene are classified. A systematic account is given of the reactions of trichloroethylene with various nucleophiles occurring with the substitution of 1 – 3 chlorine atoms by nucleophilic residues. The elimination and oxidation reactions of trichloro-ethylene as well as aspects of the practical application of its derivatives are considered. The analysis demonstrates the extensive possibilities for the synthesis of polyfunctional organic compounds of various classes from trichloroethylene. The bibliography includes 310 references.

I. Introduction

Trichloroethylene (TCE) is nowadays one of the main products of organochlorine synthesis, the annual production of which is more than 1 million tonnes.[1] Its practical applications are exceptionally extensive and are being continually expanded. It is one of the most important technical solvents and is used in various branches of industry and for domestic purposes. It is employed as an inhalation agent for narcosis and anaesthesia in medicine. Industrial methods of synthesis from trichloroethylene of a number of important products, including chloroacetic acid, pentachloroethane, and dichloroacetyl chloride, have been developed.

The synthetic possibilities of TCE as a polyfunctional compound containing three chlorine atoms and a carbon – carbon double bond are very great. It enters into chemical reactions of various types (substitution, elimination, addition, oxidation, etc.), which makes it a valuable and in certain cases an irreplaceable intermediate in organic synthesis.

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The publication of a large number of studies on TCE chemistry, which have revealed various new aspects of its synthetic and practical use, required a systematic survey. The very first data on TCE chemistry were briefly described in two communications.[2,3] The state of research in TCE chemistry towards the beginning of the 1980s was given in greater detail in a monograph.[4] Extensive information about the reactions of TCE, published during the last 10 – 15 years, have still not been surveyed and analysed critically. Only reactions involving the addition to TCE of compounds containing N – Cl bonds and the thiylation of TCE have been considered in recently published reviews.[5-7]

Experimental data on the chemical reactions of TCE collected and dealt with systematically in the present review include communications and patent data up to 1993.

II. Addition reactions

Addition to TCE has been used to synthesise a wide variety of polyfunctional organochlorine compounds. This reaction of TCE is one to have been most thoroughly investigated.

1. Halogenation

Initial studies of the reaction of halogens (chlorine, bromine, and fluorine) with TCE showed that it leads mainly to the formation of the corresponding adducts — 1,2,2-trichloro-1,2-dihaloethanes.[2-4] Iodine does not react with TCE; positive results were not obtained even when the reaction was initiated by γ-radiation.[8]

Pentachloroethane **1** can be synthesised by the addition of chlorine to TCE in both gas and liquid phases.[9] The chlorination of TCE in the dark proceeds only slightly, but the rate of reaction increases sharply in the presence of ethylene.[10] When TCE is chlorinated with a solution of chlorine in carbon tetrachloride (under illumination from an incandescent filament lamp), pentachloroethane is formed in a quantitative yield.[11] The role of radical addition increases significantly in the presence of complex-forming solvents (benzene, carbon disulfide).

The interaction of TCE with chlorine in liquid hydrogen fluoride proceeds by an electrophilic mechanism via the formation of ion pairs and leads to compound **1** and the coupled chlorofluorination products — 1,1,2,2-tetrachloro-1-fluoroethane. The overall yield of pentachloroethane and tetachlorofluoroethane relative to the TCE which has reacted is 82% and their ratio is 85 : 15.[12]

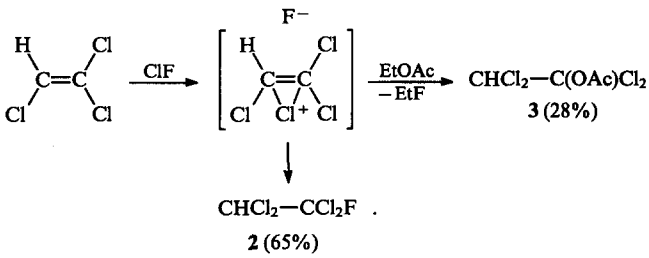
Under pressure and in the presence of free radical initiators, chlorination of TCE is more far reaching, leading ultimately to the formation of CCl_4 and C_2Cl_6.[13]

Other chlorinating agents have no advantages over chlorine. Thus the chlorination of TCE with a solution of trichloroamine in methylene chloride (molar ratio NCl_3 : TCE = 0.04 : 0.09) in the presence of small amounts of added benzoyl peroxide (BP) affords pentachloroethane in 41% yield.[14] In the interaction of perchloryl fluoride with TCE in the presence of aluminium halides, addition of two halogen atoms from the aluminium halide is observed. When $AlCl_3$ is used, pentachloroethane is produced.[15] The oxychlorination reaction of TCE in the presence of hydrogen chloride, oxygen, and the Deacon catalyst involves additive chlorination with formation of compound **1**, which is subsequently dehydrochlorinated to tetrachloroethylene.[16] When epoxyethane or epoxycyclohexane reacts with TCE and liquid chlorine, coupled chlorination of TCE accompanied by telomerisation is observed.[17]

Bromine adds readily to TCE both in the presence and absence of catalysts, affording a 1,2-adduct — 1,2-dibromo-1,1,2-trichloroethane.[2,18]

The interaction of TCE with fluorine proceeds less selectively than with chlorine and bromine, a mixture of chlorofluoroalkanes being formed; the main product is 1,1,2-trichloro-1,2-difluoroethane.[2] The formation of side products is appreciably reduced when the reaction is carried out at 70–85 °C.[19,20] Data on the gas-phase fluorination of TCE in the presence of chromium catalysts have been published.[21,22]

The reactions of TCE with mixed halogens have been investigated for the reaction with chlorine monofluoride, which added readily to TCE.[23] It is suggested that, owing to the appreciable polarity of the Cl–F bond and the high electrophilicity of the chlorine atom in the ClF molecule, the addition is electrophilic. In order to establish the mechanism of this reaction, the chlorofluorination was carried out in the presence of an external nucleophile (ethyl acetate).[24] The reaction gave a mixture of products **2** and **3**, the formation of which may be represented by the following scheme:



The results demonstrate that the mode of addition of both the internal (F^-) and the external (EtOAc) nucleophiles to TCE is virtually the same.

The reaction of TCE with the SbF_5–HF–Cl_2 system has been investigated[25] and it has been shown that this system is a source of stoichiometric equivalents of chlorine monofluoride. The reaction afforded the coupled halofluorination product $CHCl_2CCl_2F$ in a quantitative yield. When the SbF_5–HF–Br_2 system was used, the product was 2-bromo-1,1,2-trichloro-1-fluoroethane.

2. Hydrohalogenation

On reaction with excess gaseous dry hydrogen chloride in the presence of small amounts of $FeCl_3$ at room temperature, TCE gives 1,1,1,2-tetrachloroethane **4** in 49% yield. When $FeCl_3$ is replaced by $AlCl_3$ (5%–10%), the yield of the adduct **4** increases to 86%–88% (reaction temperature 30–40 °C). At a higher temperature (50 °C and above), the yield of compound **4** falls and the formation of 1,1,2,2-tetrachloroethane, 1,1,2,4,4- and 1,1,2,3,4-pentachlorobutadienes, and hexachlorobenzene is observed.[2] A method has been proposed recently for the synthesis of tetrachloroethane **4** by hydrochlorination of TCE in the presence of $FeCl_3$ or $AlBr_3$ at a pressure exceeding 500 kPa and at a temperature in the range 10–160 °C. Thus, when gaseous HCl was introduced into a mixture of 2 moles of TCE and 1% of $FeCl_3$ (relative to the weight of TCE) up to a pressure of 3.46 MPa and the mixture was heated for 3 h at 70–80 °C, the target product was obtained in 96.4% yield.[26]

Hydrogen bromide adds to TCE only in the presence of catalysts. Ionic addition (small amounts of added $FeCl_3$ and $AlCl_3$) follows the Markovnikov rule and leads to the formation of 1-bromo-1,1,2-trichloroethane (80%). In the presence of peroxides, anti-Markovnikov addition of hydrogen bromide to TCE occurs (the Kharasch 'peroxide effect') with the exclusive formation of 2-bromo-1,1,2-trichloroethane (yield 91%).[27]

The interaction of hydrogen fluoride with TCE under the influence of various catalysts has been described in the patent literature.[28–36] These reactions proceed in a complex manner and lead to a mixture of chlorofluoro-compounds, among which derivatives containing 3–4 fluorine atoms predominate. Thus, when a gaseous stream of TCE and HF (1 : 3.5) is passed over γ-Al_2O_3 on a metallic support at 230 °C, mainly 2-chloro-1,1,1-trifluoroethane **5** is formed (yield 91.5%).[28] Reaction of TCE with hydrogen fluoride proceeds similarly in the presence of chromium(III) halides on activated charcoal.[29] When HF is brought into contact with TCE over a chromium catalyst [1%–10% chromium(III) oxide] deposited on β- and/or α-AlF_3 and treated with 1,2-dichloro-1,1,2,2-tetrafluoroethane, 1,1,1-trifluoroethane is formed at 350 °C in 95% yield.[30] When the 6% CrO_3 + 3% $TiCl_3/Al_2O_3$ catalyst treated beforehand with hydrogen fluoride is used, the products of the reaction of TCE with HF at 500 °C are compound **5** (50%) and 1,1,1,2-tetrafluoroethane (20%).[31] According to other data,[32,33] the halides TaF_5, NbF_5, $MoCl_5$, and $TiCl_4$ are also catalysts of the reaction of HF with halogenated alkenes, including TCE.

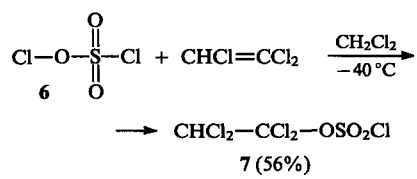
The reaction of TCE with anhydrous HF under pressure in an autoclave takes place at 115–130 °C. In the presence of fluorination catalysts (arsenic and antimony compounds to which transition metal derivatives have been added[34–36]), the yield of the main reaction product — 2-chloro-1,1,1-trifluoroethane **5** — reaches 87%–92%.

Methods for the synthesis of monofluoro- and difluoro-derivatives from TCE have been proposed in recently published patents.[37,38] It has been shown[37] that, in the presence of an aluminium oxide–magnesium oxide catalyst (Al_2O_3 : MgO = 3 : 1) subjected to a preliminary treatment with HF, the main products of the interaction of TCE with HF were 1,1,2-trichloro-1-fluoroethane (53%) and 1,2-dichloro-1,1-difluoroethane (41.5%). The formation of compound **5** was observed in this process, but its yield did not exceed 1.1%. 1,1,2-Trichloro-1-fluoroethane — the product of the Markovnikov addition of hydrogen fluoride to TCE — was obtained in 80% yield in the presence of WF_6 at 50–150 °C and at a pressure of 137 kPa.[38]

Hydrogen iodide does not add to TCE. After prolonged illumination of a mixture of TCE with hydrogen iodide, only partial reduction of TCE to 1,1,2-trichloroethane was observed.[2]

3. Addition of certain other reagents

Chlorine chlorosulfonate **6**, which has become available recently, readily undergoes Markovnikov addition to TCE to form 1,1,2,2-tetrachloroethyl chlorosulfonate **7**.[39,40]



Chlorine and fluorine fluorosulfonates react similarly with TCE, affording respectively 1,1,2,2-tetrachloroethyl fluorosulfonate (yield 80.7%) and 1,1,2-trichloro-2-fluoroethyl fluorosulfonate (yield 70%).[41,42] After brief heating of a mixture of TCE and sulfur dichloride (2:1) in the presence of Bu_3PO_4 at 110 °C, 1,1,2,2-tetrachloroethanesulfenyl chloride is formed.[43] Under radical conditions this reaction gives a similar product only after prolonged irradiation of the mixture, in the presence of small amounts of added phosphorus trichloride, by light from a mercury lamp.[44]

UV irradiation of equimolar amounts of thiocyanogen chloride and TCE in acetic acid gave two α-chloro-β-thiocyanato-derivatives with preferential formation of the anti-Markovnikov isomer: $CHCl_2C(SCN)Cl_2$ (yield 52%) and $CHCl(SCN)CCl_3$ (yield 6%).[45] It is noteworthy that TCE does not react with thiocyanogen chloride heterolytically.[46]

In the presence of SbF_3, the reaction of trifluoromethyl hypochlorite with TCE gives a high yield of 1,1,2,2-tetrachlorotrifluoromethoxyethane.[47]

4. Addition reactions leading to the formation of new C–C bonds

Reactions involving the condensation of various organic compounds with TCE have opened a pathway to the synthesis of compounds with dichloro- and trichloro-vinyl groups which are difficult to synthesise. Such reactions proceed both in the presence of radical initiators and under the influence of the Friedel–Crafts catalysts.

a. Radical condensation

The chlorovinylation of saturated hydrocarbons with the aid of TCE, which proceeds on treatment with organic peroxides, was first achieved by Schmerling[48] in 1949. He later investigated the condensation of TCE with alkenes,[49–51] alicyclic compounds,[52] and benzene derivatives.[53] The products of these reactions — compounds with β,β-dichlorovinyl groups — have found applications in the synthesis of alkenynes,[49] chlorinated alkenylbenzenes,[50] and cycloalkenes containing a triple bond in a side chain.[52]

A series of patents have been devoted to the development of methods of synthesis of the practically important 1,1-dichloro-4-methylpenta-1,3-diene, which is based on the condensation of TCE with isobutene (or a *tert*-butyl halide).[54–58]

This reaction can be achieved both in the liquid and gas phases (125–550 °C) in the presence of 0.05–5 mol% of radical initiators. However, it is noteworthy that a high yield of the target product is attained only when a twofold to threefold excess of TCE is employed. On the other hand, in the presence of an excess of isobutene, preferential formation of 2,5-dimethylhexa-1,5-diene is observed.

The photochemical addition of bromotrichloromethane to TCE leads to the formation of a complex mixture of products, among which the following have been found: $CHClBr-CBrCl_2$ (2%), $CCl_3-CHCl-CBrCl_2$ (< 1%), CCl_3-CCl_3 (30%), $CBrCl=CHCl$ + $CHBr=CCl_2$ (26.5%), $CCl_3-CCl=CHCl$ (0.9%), $CCl_3-CH=CCl_2$ (29.1%), and $CHCl_2-CBrCl_2$ (11.9%).[59] The kinetics and mechanism of this reaction have been investigated.[60]

The interaction of TCE with hexane in the presence of *tert*-butyl peroxide (TBP) has been studied in detail.[61] It has been established that the reactivities of the hydrogen atoms of the first, second and third carbon atoms in hexane are respectively 0.04, 1.68, and 1.0. The chlorovinylation of hexane occurred mainly in the 2-position and to a lesser extent in the 3-position. The formation of the main products of this reaction can be represented schematically as follows:

$$ROOR \longrightarrow 2\,RO^{\cdot}$$

$$RO^{\cdot} + C_6H_{14} \longrightarrow ROH + {}^{\cdot}C_6H_{13}$$

$${}^{\cdot}C_6H_{13} + CHCl{=}CCl_2 \longrightarrow C_6H_{13}{-}CHCl{-}{}^{\cdot}CCl_2$$

$$C_6H_{13}{-}CHCl{-}{}^{\cdot}CCl_2 + C_6H_{14} \longrightarrow$$

$$\longrightarrow C_6H_{13}{-}CH{=}CCl_2 + HCl + {}^{\cdot}C_6H_{13}$$

R = Bu^t; ${}^{\cdot}C_6H_{13}$ = $MeC^{\cdot}HBu^n$ or $EtC^{\cdot}HPr^n$.

When hexane is treated with a mixture of TCE and carbon tetrachloride, the main reaction product is 2-chlorohexane and dichlorovinyl derivatives are not then formed.

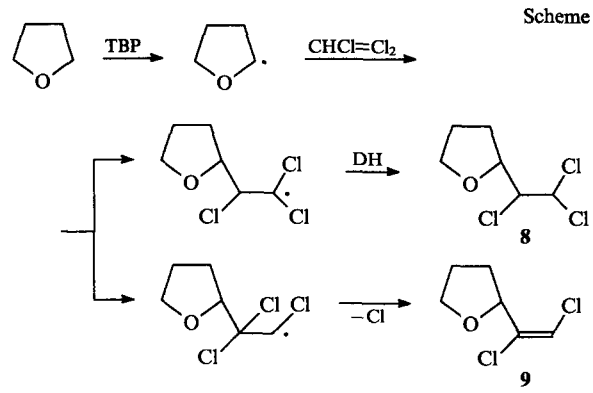
The high-temperature condensation of TCE with naphthalene at 535 °C leads to a complex mixture of isomeric products — *cis*-RCCl=CHCl, *trans*-RCCl=CHCl, $RCH=CCl_2$, *cis*-R'CCl=CHCl, *trans*-R'CCl=CHCl, and $R'CH=CCl_2$ (R = β-$C_{10}H_7$, R' = α-$C_{10}H_7$).[62] The isomer $RCH=CCl_2$ predominates, but it could only be isolated in 10.6% yield in a pure form, which undoubtedly lowers the preparative value of this reaction.

Reaction of TCE with 1- and 2-methylnaphthalenes proceeds via the side chain to form a mixture of the corresponding dichloropropenylnaphthalenes.[63] Under these conditions, the main products contained the α,α-dichloropropenyl fragment (yield ~90%), which makes this reaction preparatively promising.

The addition to TCE of *m*-carbaboran-9-yl radicals, formed on photolysis of bis(*m*-carbaboran-9-yl)mercury, has been achieved recently.[64] The radical-adduct obtained is stabilised by elimination of a chlorine atom, affording 9-(2,2-dichlorovinyl)-*m*-carbaborane in 50% yield; 9-chloro-*m*-carbaborane (8%) and *m*-carbaborane (10%) were also isolated.

In the presence of TBP, tetrahydrofuran reacts with TCE to form 1,2,2-trichloro-1-(tetrahydro-2-furyl)ethane **8** (main product), 1,2-dichloro-1-(tetrahydro-2-furyl)-ethylene **9**, and 1,2-dichlorohex-1-en-3-one.[65] The presence of 1,2-dichlorohex-1-en-3-one among the reaction products confirms that hydro-2-furyl radicals arising on treatment with the peroxide are consumed in both addition and isomerisation reactions. The formation of the first two products is presented in Scheme 1.

Scheme 1



DH = hydrogen donor.

It has been shown that the phenyl radicals obtained on decomposition of 2-phenylazopropan-2-ol add to the less-substituted carbon atom of TCE. The $PhCHCl-{}^{\cdot}CCl_2$ radicals are formed and stabilised in this case by hydrogen atom abstraction, and not by chlorine atom loss, affording trichlorophenylethane in 48% yield. The interaction of TCE with 1-cyclohexenyl radicals, formed on decomposition of 1-(1-azacyclohexenyl)cyclohexanol, gives a product with a similar group in the side chain — cyclo-$C_6H_9CHClCHCl_2$ (23%).[66]

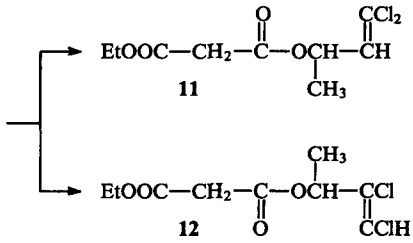
Syntheses based on the reaction of TCE with alcohols, acids, ethers, and amines have opened a pathway to the preparation of a whole series of polyfunctional compounds which were previously difficult to obtain. Thus the reaction of TCE with methanol (525–540 °C), initiated by CCl_4 and $CHCl_3$ in a quartz flow reactor, leads to $CCl_2=CHCH_2OH$ in 22% yield.[67] A method has been developed for the synthesis of chlorinated alcohols of the type $CHCl_2CCl_2CRR'OH$ and $CCl_2=CClCRR'OH$ on the basis of the reaction of alcohols RR'CHOH (where R and R' = Alk or H) with TCE in the presence of organic peroxides.[68,69]

2-Alkyl-3,4-4-trichlorobutyric acids have been synthesised in preparative yields from TCE and carboxylic acids, having an α-hydrogen atom, in the presence of peroxide initiators at 40–200 °C.[70]

Esters react with TCE under similar conditions, mainly the α-carbon atom of the alcohol component of the ester molecule participating under these conditions in the formation of a new carbon–carbon bond in the adducts.[71,72] The reaction of diethyl malonate **10** with TCE proceeds via two pathways with formation of compounds **11** and **12**.

$$CH_2(COOEt)_2 + CHCl=CCl_2 \longrightarrow$$

10



11 **12**

Dichlorovinyl-substituted amines $C_7H_{15}CH(CH=CCl_2)NH_2$ and *cyclo*-$C_6H_{10}(CH=CCl_2)NH_2$ have been obtained by the reaction of TCE with the corresponding amines in the presence of TBP.[73]

b. Heterolytic addition

The synthesis of the practically important nonachloro-pentene is based on the reaction of hexachloropropene with TCE on heating in the presence of catalysts [$AlCl_3$ and metallic aluminium in proportions of (2–6):1].[74]

Aromatic compounds interact with TCE to form condensation products. However, one should note that the reactions of benzene and ethylbenzene with TCE are accompanied by appreciable tar formation and are of no practical value.[75,76] Benzene derivatives **13**, containing between 2 and 4 substituents, react with TCE, affording substituted α,β-dichloro-styrenes **14** in preparative yields.[77]

$$\underset{\mathbf{13}}{R_nC_6H_{6-n}} + CHCl=CCl_2 \xrightarrow{AlCl_3} \underset{\mathbf{14}}{R_nC_6H_{5-n}CCl=CHCl}$$

R = Alk, Hal, Alk_{Hal}; n = 2–4.

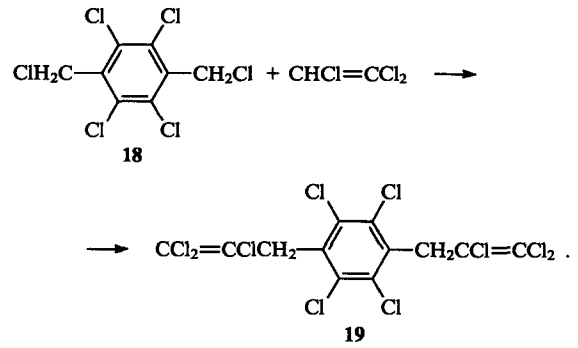
Polychlorotoluenes **15** react with TCE to form the chlorinated propenylbenzenes **16** and **17**.[78,79]

$$\underset{\mathbf{15}}{RCl} + CHCl=CCl_2 \longrightarrow \underset{\mathbf{16,17}}{RCCl=CCl_2} + HCl$$

R = $C_6Cl_5CH_2$ (**16**), $C_6Cl_5CCl_2$ (**17**).

It is noteworthy that, apart from compound **17**, *cis*- and *trans*-$C_6Cl_5-CCl=CCl-CCl_3$, $C_6Cl_5C=CCl(CCl_2)_2CCl_2$ and *trans*-$C_6Cl_5-CCl=CClCCl_2CHClCCl_3$ are also formed in the reaction of TCE with perchlorotoluene.

2,3,5,6-Tetrachloro-1,4-bis(2,3,3-trichloroprop-2-enyl)-benzene **19** is a product of the interaction of 2,3,5,6-tetrachloro-1,4-bis(chloromethyl)benzene **18** with TCE. Its formation may be represented by the following scheme:[80]



18 **19**

Substituted chlorodiphenylethylenes $(p\text{-}ROC_6H_4)_2C=CHCl$ (R = H, Me) are obtained by the reaction of PhOR with TCE in the presence of trifluoromethanesulfonic acid.[81]

In the presence of sulfuric acid, trichloroethylene and formaldehyde condense, (the Prins reaction), with formation of α-chloro-β-hydroxypropionic acid **20**, which is dehydrated under the reaction conditions, giving α-chloroacrylic acid **21**. In the presence of alcohol, the reaction product is methyl α-chloro-acrylate **22**.[82]

$$CH_2O + CHCl=CCl_2 \xrightarrow{80\%\ H_2SO_4} HOCH_2-CHCl-COOH \longrightarrow$$

20

$$\xrightarrow{H^+,\ T} \underset{\mathbf{21}}{CH_2=CCl-COOH}$$

$$\xrightarrow{H^+/EtOH} \underset{\mathbf{22}}{CH_2=CCl-COOEt}$$

The condensation of TCE with bis(chloromethyl)ether in methylene chloride or carbon disulfide in the presence of aluminium chloride proceeds readily. The reaction product is bis-(2,3,3,3-tetrachloropropyl) ether **23** (yield 87.5%).[83,84] The ether **23** can be obtained using 1,3,5-trioxane instead of bis(chloromethyl) ether, which is a powerful lachrymator. When dry hydrogen chloride was passed through a mixture of TCE, 1,3,5-trioxane, and aluminium chloride, the yield of the ether **23** was 92%.



$$+ CHCl=CCl_2 \xrightarrow{HCl,\ AlCl_3} \underset{\mathbf{23}}{(CCl_3CHClCH_2)_2O}$$

On treatment with zinc, perfluoroalkyl iodides and TCE condense with formation of β,β-dichlorovinylperfluoroalkanes $R_FCH=CCl_2$, which are the starting compounds in the synthesis of valuable perfluoroalkanoic acids.[85]

5. Addition reactions leading to the formation of a carbon–heteroatom bond

a. Radical thiylation

The reaction of aromatic thiols **24** with TCE in the presence of benzoyl peroxide (BP) leads to aryl β,β-dichlorovinyl sulfides **25**.[86–89]

$$\underset{\mathbf{24}}{XC_6H_4SH} + CHCl=CCl_2 \xrightarrow[-HCl]{BP} \underset{\mathbf{25}}{XC_6H_4S-CH=CCl_2}$$

X = 4-MeO, 4-Me, 3-Me, H, 4-Cl, 4-NO_2.

Diaryl disulfides are side products in this reaction, while in the interaction of TCE with *p*-nitrothiophenol oxidation products of β,β-dichlorovinyl *p*-nitrophenyl sulfide—the corresponding sulfone and sulfoxide—were detected.

Thiylation of TCE by aliphatic thiols, which leads also in this case to the formation of the corresponding β,β-dichlorovinyl sulfides, can be more conveniently carried out with irradiation by UV light and heating of the reaction mixture (the TCE : thiol ratio varies from 3 : 1 to 4 : 1).[88,89] The free-radical chlorovinylation of diaryl disulfides **26** by TCE leads to the formation of a complex mixture of products.[90,91]

$$ArSSAr + CHCl{=}CCl_2 \xrightarrow{h\nu} ArS{-}CH{=}CCl_2 + ArS{-}CCl{=}CHCl + ArS{-}CCl{=}CCl_2 + ArS{-}CHCl{-}CCl_3 + Cl_2C{=}CH{-}CCl_2{-}CHCl_2$$

26 **25** **27** **28** **29** **30**

Ar = *p*-MeC_6H_4, Ph, *p*-ClC_6H_4.

Earlier studies on the free-radical thiylation of TCE and other polychloroalkenes and diaryl sulfides have been surveyed by Voronkov et al.[7]

b. Synthesis of compounds with C–N and C=N bonds

Voronkov and coworkers[92,93] investigated the addition of compounds containing a N–Hal bond to TCE and demonstrated its extensive synthetic possibilities. Thus, the reaction of *N,N*-dichloroarenesulfonamides **31** with TCE leads to pentachloroethane and (trichloroethylidene)arenesulfonamides **32**.[92,93]

$$RNCl_2 + CHCl{=}CCl_2 \longrightarrow RN{=}CHCCl_3 + CHCl_2{-}CCl_3$$

31a–c **32a–c** **1**

R = $PhSO_2$ (**a**), *p*-$MeC_6H_4SO_2$ (**b**), *p*-$ClC_6H_4SO_2$ (**c**).

The reactions of TCE with *N,N*-dibromobenzenesulfonamide,[94] *N,N*-dibromourethane,[95] and *N,N*-dichloroethylphosphoramide[96] proceed similarly. They afforded respectively *N*-(2-bromo-2,2-dichloroethylidene)benzenesulfonamide, *N*-(2-bromo-2,2-dichloroethyl)ethoxycarbonylimine, and 1,1,1-trichloro-2,2-bis(diethylphosphoramido)ethane. The interaction of *N,N*-dichlorourethane with TCE leads to chloral *N*-ethoxycarbonylimine.[97] When water is introduced into the reaction mixture, chloral reacts with it and the urethane formed as a side product, giving 2,2,2-trichloro-1,1-bis(*N*-ethoxycarbonylamino)ethane (50%) and 2,2,2-trichloro-1-(*N*-ethoxycarbonylamino)-1-hydroxyethane (20%).[98] The free-radical mechanism of the reactions involving the addition of *N,N*-dichlorobenzenesulfonamide and *N,N*-dichlorourethane to TCE was subsequently confirmed.[99]

It has been shown[100] that the reactions of *N,N*-dichloroacetamide **33a** and *N,N*-dichlorobenzamide **33b** with TCE under an inert atmosphere give reaction products of the corresponding chloral acylimines **34a** and **34b**—1,1-diacetamido-2,2,2-trichloroethane **35a**, 1,1-dibenz-amido-2,2,2-trichloroethane **35b**, *N*-(2,2,2-trichloro-1-hydroxy-ethyl)acetamide **36a**, *N*-(2,2,2-trichloro-1-hydroxyethyl)benzamide **36b**, and pentachloroethane:

$$RCONCl_2 + CHCl{=}CCl_2 \longrightarrow RCON{=}CHCCl_3 + CHCl_2{-}CCl_3$$

33a,b **34a,b** **1**

$$RCON{=}CHCCl_3 \xrightarrow{RCONH_2 \mid H_2O} (RCONH)_2CHCCl_3 \;\; RCONHCH(OH)CCl_3$$

35a,b **36a,b**

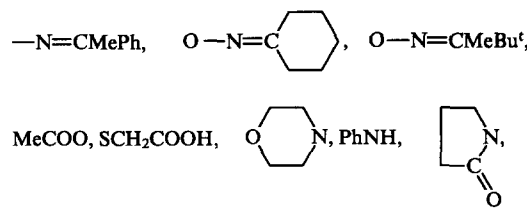
R = Me (**a**), Ph (**b**).

The high electrophilicity of the acylimines obtained from trichloroethylidenearenesulfonamides and TCE made it possible to introduce them into reactions with nucleophiles, without preliminary isolation, and to develop ways of obtaining different polyfunctional compounds having the general formula

$CCl_3CHR'(NHSO_2R)$ (Refs 101–104)

R = Ph, 4-MeC_6H_4;

R′ = OH, OMe, OEt, OPh, $PhSO_2NH$, 4-$MeC_6H_4SO_2NH$, PhC(O)NH, MeC(O)NH, OBu^n, OCH_2CH_2Cl, O

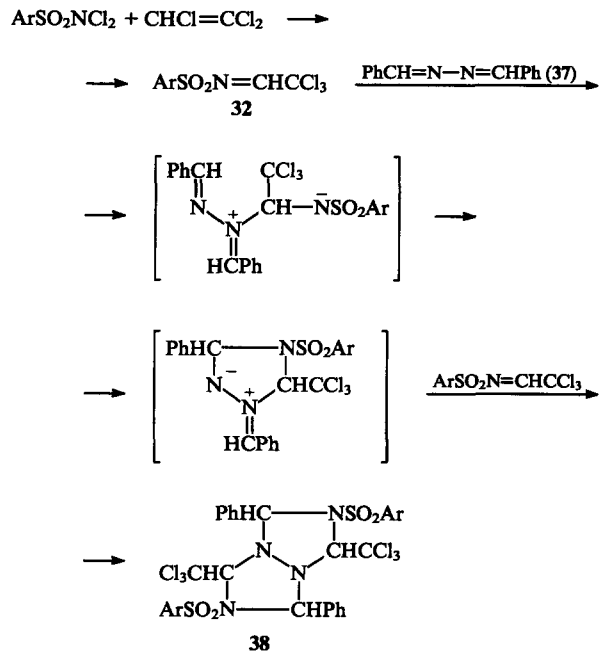


PhNHNH, PhNHC(O)NH, MeNH, Bu^tNH.

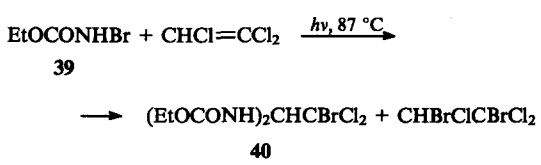
The reaction of *N*-(2,2,2-trichloroethylidene)arenesulfonamides, obtained from *N,N*-dichloroarenesulfonamides and TCE, with bifunctional nucleophiles such as mercaptoethanol and monoethanolamine proceeds via the mercapto- and hydroxy-groups respectively, giving the corresponding adducts—*N*-[2,2,2-trichloro-1-(2-hydroxyethylthio)ethyl]- and *N*-[1-(2-aminoethoxy)-2,2,2-trichloroethyl]-arenesulfonamides; in reactions with ethylene glycol, the products of both mono- and bis-*o*-amidoalkylation of the latter were obtained: *N*-[2,2,2-trichloro-1-(2-hydroxyethoxy)ethyl]arenesulfonamides and 1,2-(1-arenesulfonamido-2,2,2-trichloroethoxy)ethanes. The products of the reactions of *N*-(2,2,2-trichloroethylidene)arenesulfonamides with mercaptoethanol—*N*-[2,2,2-trichloro-1-(2-hydroxyethylthio)ethyl]arenesulfonamides—give rise to 3-arenesulfonyl-2-trichloromethyl-1,3-thiazolidines on successive treatment with thionyl chloride and then alkali.[105]

In the reactions of chloral arenesulfonylimines **32** with benzylideneazine **37**, the latter behaves as a 1,3-dipolar reagent, which combines with 2 moles of the imine to form 1,3,5,7-tetraazabicyclo[3.3.0]octanes **38**.[106]

It has been shown recently[107] that the product of the interaction of *N*-bromourethane **39** with TCE is 2-bromo-2,2-dichloro-1,1-di(ethoxycarbonylamino)ethane **40**. The reaction mechanism includes a series of processes—disproportionation of *N*-bromourethane to *N,N*-dibromourethane and urethane, the reaction of *N,N*-dibromourethane with TCE to form *N*-(2-boromo-2,2-dichloroethylidene)ethoxycarbonylamine, and the addition of urethane to the latter—which lead to the final product **40**.

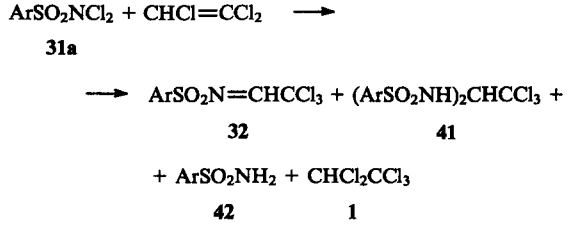


Ar = Ph, 4-MeC_6H_4, 4-ClC_6H_4.



The reactions of *N*-haloamides with TCE have been considered in greater detail in two reviews,[5,6] covering studies up to and including 1987.

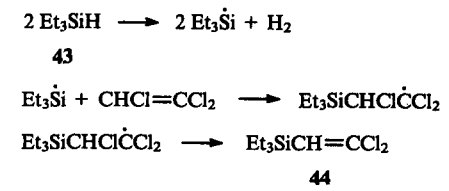
The ionic addition of *N*-haloamides to unsaturated compounds, including TCE, has been studied inadequately compared with the radical addition. It is known only that the interaction of *N*,*N*-dichloroarenesulfonamide **31a** with TCE in the presence of Lewis acids gives a complex mixture of compounds **1**, **32**, **41**, and **42**.[108,109]



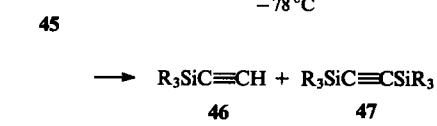
The reaction of TCE with the amide **31a** on heating and subsequent addition of acetamide to the reaction mixture leads to $PhSO_2NHCH(NHCOMe)CCl_3$. When acetoxime was used instead of acetamide, the product $PhSO_2NHCH.(ON=CMe_2)CCl_3$ was obtained.[108] It has been shown that *N*-(2,2,2-trichloro-ethylidene)arenesulfonamides can be used, without isolating them from the reaction mixture, as arenesulfonamidoalkylating agents. The *C*-alkylation of thiophene[110] and aromatic compounds[111] has been achieved with their aid.

c. Synthesis of compounds with a C–Si bond

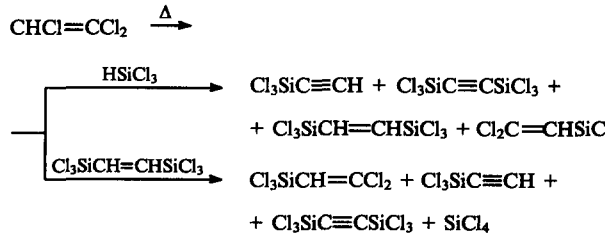
The dichlorovinylation of triethylsilane **43** has been carried out with the use of TCE (the reaction is initiated by γ-radiation). The formation of dichlorovinyltriethylsilane **44** can be represented as a free-radical addition–elimination mechanism.[112]



The interaction of trialkylchlorosilanes **45** with TCE in the presence of lithium gives the trialkylethynylsilanes **46** in 44%–54% yield. The side products of this reaction are bis(trialkylsilyl)alkynes **47**.[113]



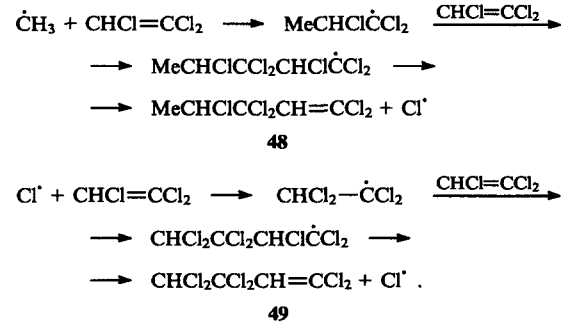
The gas-phase thermal reactions of TCE with trichlorosilane[114] and 1,2-bis(trichlorosilyl)ethylene[115] are more complicated.



Other organosilicon compounds with ethynyl groups—diorganoethynylchlorosilanes and diorganoethynylalkoxysilanes—have been obtained by the reaction of TCE with diorganodichlorosilanes and diorganoalkoxychlorosilanes respectively in $PO(NMe_2)_3$ in the presence of zinc dust.[116]

6. Dimerisation of trichloroethylene

On treatment with various initiators, TCE can dimerise to form $C_4H_2Cl_6$ or products of its dehydrochlorination having the composition C_4HCl_5.[117–121] Despite the fact that numerous studies were devoted to these processes, in particular the reactions occurring in the presence of free-radical initiators, the available information about the structure of the dimer formed remained contradictory for a long time.[117] It has been shown recently that the products of the reaction of acetyl peroxide with TCE are 1,1,3,3,4-pentachloropent-1-ene **48** and 1,1,3,3,4,4-hexachlorobut-1-ene **49** (in yields of 0.6 and 4.0 mole per mole of the peroxide respectively). The formation of these substances can be explained in terms of the following scheme:[122]



Hexachlorobutene **49** is a readily available and extremely valuable organic intermediate. The synthetic possibilities of compound **49** and of its derivatives have been reflected in a large series of studies by the authors of the present review.[123–133]

The dimerisation of TCE under the influence of fluorosulfonic acid proceeds differently: two hexachlorobutenes containing the CCl_3, $CHCl=CClCHClCCl_3$, and $CCl_3CH=CClCHCl_2$ groups are formed in an overall yield of 37%.[134] At high temperatures (460–530 °C) trichloroethylene dehydrodimerises, giving principally hexachlorobutadiene (30%) and hexachlorobenzene (24%).[135,136]

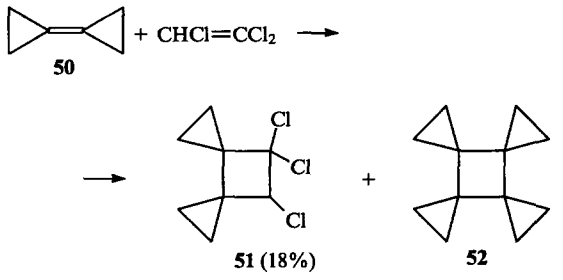
The results of early studies of the interaction of TCE with aluminium chloride are contradictory.[137–139] Detailed investigation of this reaction showed that 2*H*-pentachlorobuta-1,3-diene predominates among the three isomers of C_4HCl_5 formed.[140]

7. Cycloaddition reactions

Cycloaddition reactions with participation of TCE opened a synthetic pathway to chlorine-containing cyclic compounds which were previously difficult to obtain. Methods for cyclobutane ring construction have been most thoroughly developed in this series.

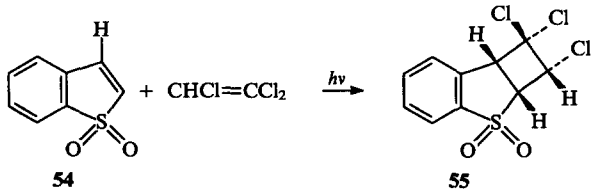
a. [2+2]-cycloaddition reactions

When a mixture of bicyclopropylidene **50** and TCE was heated (at 180 °C) for 96 h, 7,7,8-trichlorodispiro[2.0.2.2]octane **51** and the cyclopropylidene cyclic dimer **52** were obtained.[141,142]

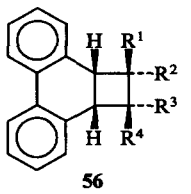


The cycloaddition reaction of dehydrobenzene, generated in situ from benzenediazonium-2-carboxylate, with TCE gives 1,1,2-trichlorobenzocyclobutene **53** in 18% yield. The use of dehydrobenzene, generated in 1,2-dichloroethane and containing a 15-fold excess of TCE, increased the yield of the target trichloro-derivative **53** to 42%, but it was contaminated by 2% of biphenyl.[143]

On irradiation of a mixture of benzo[*b*]thiophene 1,1-dioxide **54** and TCE with light at a wavelength of 300 nm and above, the adduct **55** was obtained in 52% yield.[144]

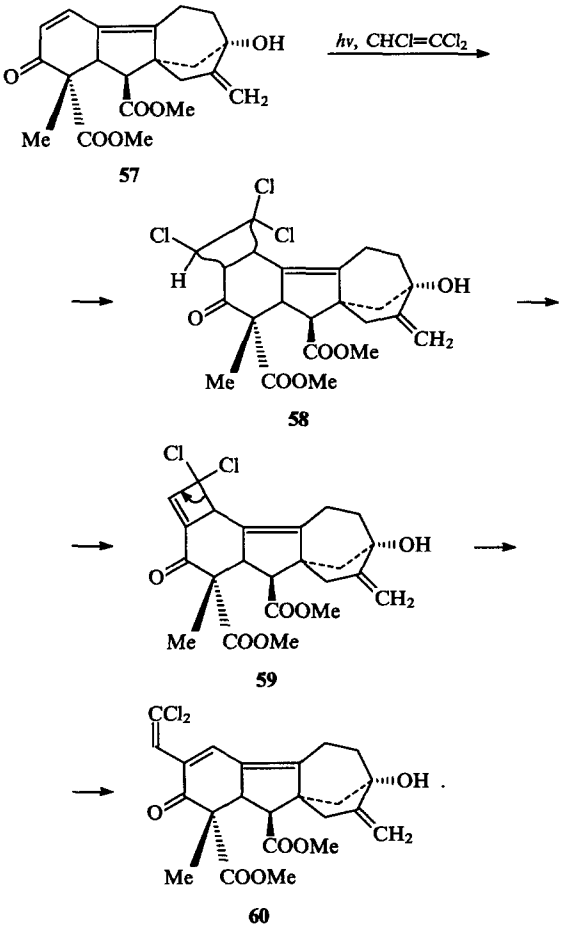


The photochemical reaction between phenanthrene and TCE leads to two cyclic adducts—the *anti*- and *syn*-isomers of 1,1,2-trichloro-1,2,2a,10b-tetrahydrocyclobuta[*e*]phenanthrene **56**—in an overall yield of 55%. Each adduct has *cis*-stereochemistry at the 2a- and 10b-positions and the *anti*-isomer ($R^1 = R^2 = R^4 = Cl$, $R^3 = H$) and the *syn*-isomer ($R^1 = R^2 = R^3 = Cl$, $R^4 = H$) were isolated in 48% and 7% yields respectively.[145]



1,4,5,8-Tetraazaphenanthrene also undergoes the cycloaddition reaction. When its mixture with TCE was irradiated with UV light, a cyclic adduct was obtained in 32% yield.[146]

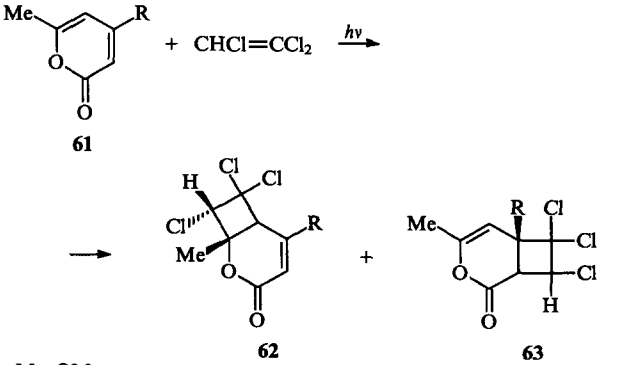
Photolysis of the dimethyl ester of 3-dehydrogibberellenic acid **57** in the presence of an excess of TCE in methylene chloride leads to two dimers (50%) and the photoadduct **58**.[147] Apparently owing to the presence of a chlorine atom in the β-position relative to the CO group, the latter is unstable and, after elimination of HCl and isomerisation of the highly strained cyclobutene derivative **59**, is converted into the stable final product **60** in 43% yield in accordance with the following scheme:



It is noteworthy that the photocycloaddition of the dienone **57** to TCE is distinguished by a high stereospecificity and leads to only one adduct.

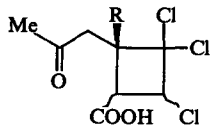
The photochemical syntheses of a series of new heterocyclic systems from 2-pyrones and 2-pyridones have been achieved. These reactions proceed in the presence of various sensitisers.

2-Pyrones **61** afford two types of cyclic adducts—**62** and **63**.[148]

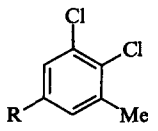


R = Me, OMe.

Hydrolysis of the cyclic adducts formed as a result of TCE addition to the C(3)=C(4) double bond of 2-pyrones yielded compounds **64** and **65**.



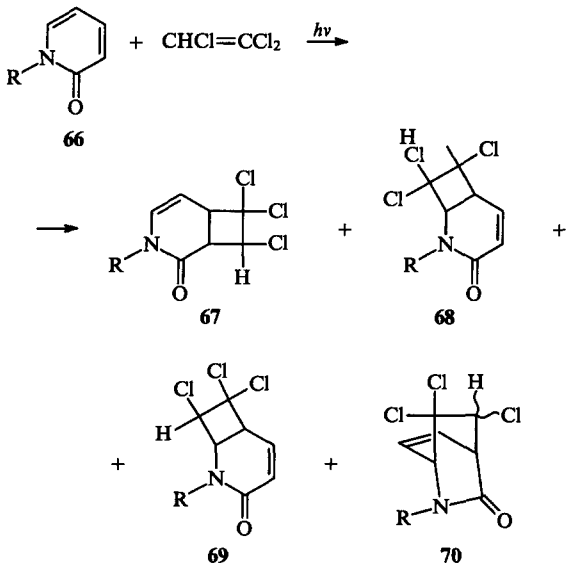
64



65

The reactions of 2-pyridones **66** with TCE gave a complex mixture of cyclic adducts **67**–**70**, among which the 5,6-adducts **68** and **69** predominate.[149]

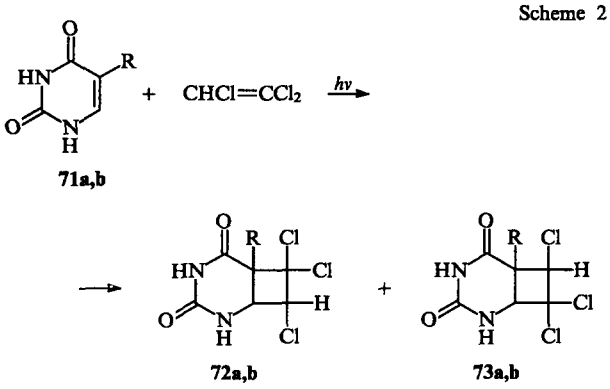
7,7,8-Trichloro-2-R-2-azabicyclo[2.2.2]oct-5-en-3-one **70**, formed as a result of the Diels–Alder reaction, is a [4+2]-adduct.



66 **67** **68** **69** **70**

The photochemical reactions of TCE with thymine **71a** and 5-fluorouracil **71b** opened a pathway to the synthesis of the corresponding cyclobutapyrimidinediones **72** and **73** (Scheme 2).[150]

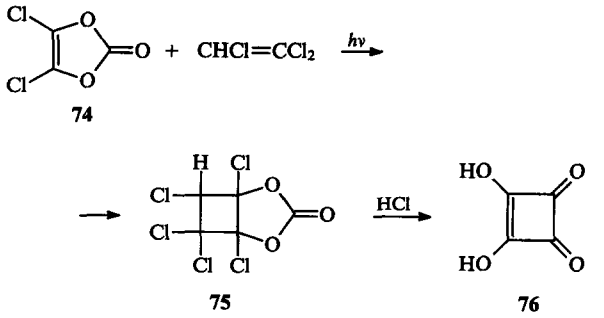
Scheme 2



71a,b **72a,b** **73a,b**

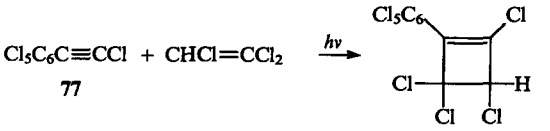
R = Me (a); R = F (b).

Quadratic acid **76**, which is of practical value, has been synthesised by the reaction of TCE with dichlorovinyl carbonate **74** and subsequent hydrolysis of the cyclic adduct — 1,2-carbonyldioxy-1,2,3,3,4-pentachlorocyclobutane **75**.[151]



74 **75** **76**

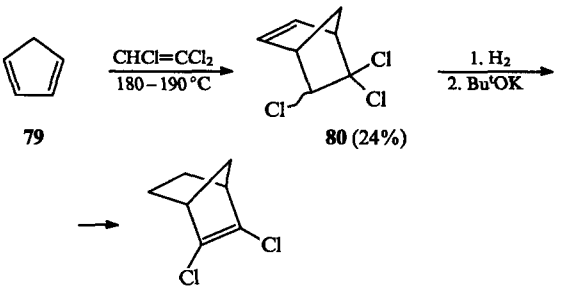
TCE has been used to achieve the direct synthesis of cyclobutene derivatives in the reaction of perchlorophenylacetylene **77** with TCE. When a mixture of the alkyne **77** with TCE, present in large excess in a sealed Pyrex tube, was irradiated with UV light, 3*H*-nonachloro-1-phenylcyclobutene **78** was obtained.[152]



77 **78** (58%)

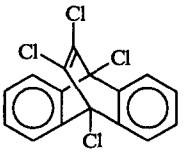
b. The Diels–Alder reaction

The [4+2]-cycloaddition reaction of TCE has been investigated only for certain cyclic dienes. Thus cyclopenta-1,3-diene **79** reacts with TCE to form 5,5,6-trichloronorbornene **80**.[153] Successive hydrogenation of the adduct **80** and dehydrochlorination of the saturated compound obtained yielded 2,3-dichloro-2-norbornene **81**.[154,155]



79 **80** (24%) **81** (17%)

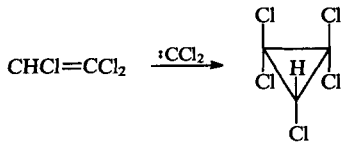
When 9,10-dichloroanthracene is treated with TCE (autoclave, 230 °C, 48 h), a mixture of Diels–Alder adducts is formed, the main one being 1,4,7,8-tetrachlorodibenzobicyclo[2.2.2]octatriene **82**.[156]



82 (10%)

c. Cyclopropane formation reactions

The formation of cyclopropane rings by reaction with dihalocarbenes is known to be one of the best methods for this purpose. Since both TCE and dihalocarbenes have pronounced electrophilic properties, it might have been expected that reaction between them would proceed with difficulty. Indeed pentachlorocyclopropane **83** has been obtained only after prolonged refluxing (~$2^1/_2$–5 days) of a mixture of TCE and sodium trichloroacetate in 1,2-dimethoxyethane.[157]



83 (22.4%)

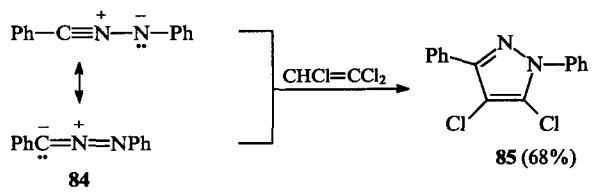
By varying the conditions in the cyclopropane formation reaction, it was later possible to raise the yield of the adduct **83** to 45%.[158,159] By generating dichlorocarbene from organomercury compounds, it is possible to carry out the cyclopropane formation reaction at room temperature. Thus, cyclopropane **83** has been obtained in 22% yield by the reaction of bromodichloromethyl-(cyclohexyl)mercury with TCE.[160]

The simpler method for the generation of $:CCl_2$ from sodium trichloroacetate in the presence of phase transfer catalysts makes it possible to carry out the cyclopropane formation reaction in an aqueous medium, but the adduct **83** is formed in a low yield (~9%).[161]

Methods for the synthesis of halocyclopropenes and halocyclopropanes,[158,162] which were previously scarce, and a convenient method for the synthesis of 7,7-difluorocyclopropabenzene[163] and other compounds have been developed which involve the use of pentachlorocyclopropane **83**.

e. Other cycloaddition reactions

It has been found[164] that, on interaction with TCE, diphenylnitrile imine **84** behaves as a 1,3-dipolar reagent. This reaction is completed by the formation of 4,5-dichloro-1,3-diphenylpyrazole **85** and is an example of the [3+2]-cycloaddition reaction.



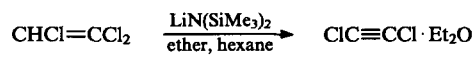
84

85 (68%)

III. Elimination reactions

Among elimination reactions, the dehydrochlorination of TCE and to a lesser extent its dechlorination have been investigated in the greatest detail. The elimination of a hydrogen chloride molecule from TCE proceeds on treatment with alkalies and leads to the formation of dichloroethyne **86**, which is an extremely explosive product.[165] When the dehydrochlorination of TCE is carried out in diethyl ether, dichloroethyne is isolated in the form of the stable complex $ClC{\equiv}CCl \cdot Et_2O$ **87**. Various modifications of this method have been described.[166-169]

Under laboratory conditions, small amounts of compound **86** can be obtained by treating a TCE–ether mixture with lithium hexamethyldisilazide in hexane, but this procedure requires the use of an expensive base and careful drying of the reactants.[170]



87

Two improved methods for the synthesis of dichloroethyne have been proposed recently. One of them is based on the phase transfer catalytic method. Makosza and coworkers[171] showed earlier that, in the presence of ammonium catalysts, TCE gives rise to the trichlorovinyl anion, which decomposes above 40 °C to form dichloroethyne.[172] Treatment of a mixture of TCE and ether with a 50% aqueous solution of NaOH in the presence of triethylbenzylammonium chloride (TEBA) at 70 °C led to the formation of complex **87** in a high yield.

Another rapid method for the synthesis of pure dichloroethyne, also in a high yield, is based on the reaction of TCE with potassium hydride in tetrahydrofuran (THF) in the presence of catalytic amounts of methanol.[173] When TCE is exposed to laser radiation, the dehydrochlorination reaction predominates and dechlorination is a side process.[174-179] When low pressures are employed, the yield of dichloroethyne **86** diminishes, whereas that of chloroethyne **88** increases. On exposure to an electric discharge at a reduced pressure, TCE gives rise to chloroethyne **88**.[180-182]

The reaction of TCE with naphthalenesodium in pentane or THF leads to the complete dechlorination of TCE with formation of ethyne and ethene (overall yield 97%).[183]

IV. Substitution reactions

1. Interaction of trichloroethylene with nucleophiles

Nucleophilic substitution at a vinyl carbon atom is known to be difficult. In some studies, one can encounter the claim even nowadays that TCE does not enter into nucleophilic substitution reactions. Indeed, under the usual conditions, TCE is not hydrolysed by aqueous solutions of alkalies, which makes it possible to employ them for the purification of TCE. However, under certain conditions TCE does react with nucleophiles of different nature, which can be accounted for by the presence in its molecule of the C=C electrophilic bond. The synthesis of a wide variety of products has been achieved by using nucleophilic substitution reactions of TCE.

The reactions of nucleophiles with chloroethenes can proceed via at least two pathways: (1) via the addition–elimination mechanism;[184] (2) via the elimination–addition mechanism.[185] TCE apparently reacts with nucleophiles via the second mechanism. Dichloroethyne is formed initially and the nucleophile then adds to it. The nucleophilic addition stage proceeds stereoselectively and constitutes an anti-process, which leads in most cases to final products with the (*E*)-configuration.

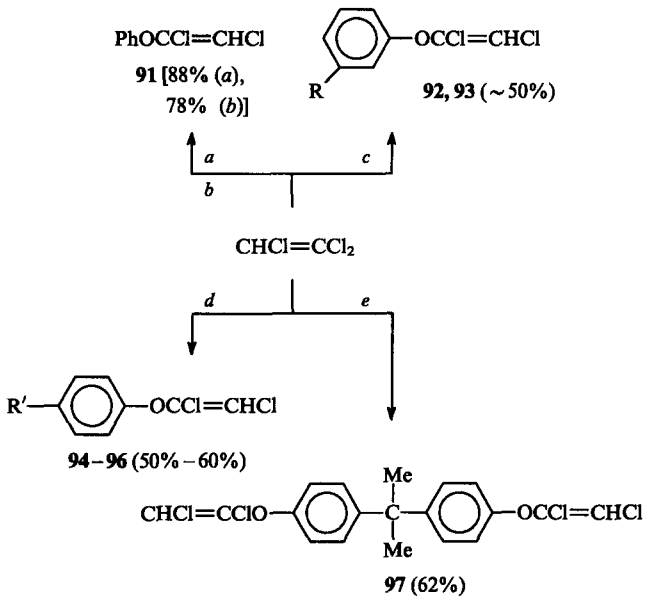
a. Interaction with O-nucleophiles

The reaction of O-nucleophiles with TCE was first investigated in its reaction with sodium ethoxide: the product was 1,2-dichlorovinyl ethyl ether **89**.[2]

The interaction of sodium alkoxides with TCE has been studied recently in very great detail in connection with the use of alkyl dichlorovinyl ethers **90** for the synthesis of various derivatives of alkoxyalkynes.[186] It was found that alkoxides of primary and secondary alcohols react with TCE on refluxing to form the ethers **90** in moderate yields (34%–54%).

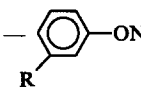
According to a patent,[187] ether **89** is obtained by treating TCE with an alcoholic solution of alkali and is used subsequently in the synthesis of 2-bromo-2-chloro-1,1,1-trifluoroethane. The reactions of sodium phenoxide and its derivatives with TCE proceed readily in aprotic solvents.[188-190] It has been shown recently that TCE interacts with various phenols also under phase-transfer catalytic conditions in the presence of Makosza's catalysts.[191] The products of these reactions are the 1,2-dichlorovinyl ethers **91–97** having the (*E*)-configuration. The simplest and most convenient method for the synthesis of the ethers is under the conditions of phase-transfer catalysis.

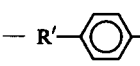
When two chlorine atoms in the TCE molecule are replaced by nucleophilic residues, chloroketene acetals are formed. It was found that potassium *tert*-butoxide interacts extremely vigorously with TCE, affording the acetal **98**,[186] whereas the acetal **99**—the product of the reaction of sodium β-methoxyethoxide and TCE—takes place under fairly severe conditions.[192]

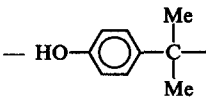


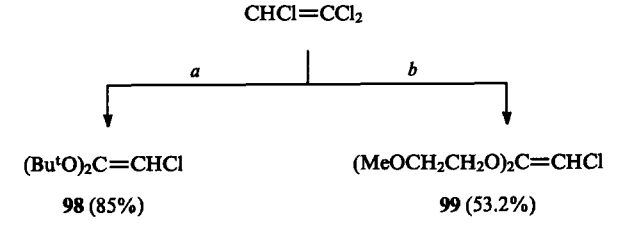
a — PhOH; Na + MeOH, DMFA;[188]

b — PhONa; DMSO;[189]

c —  (R = NO_2, Me); DMFA;[190]

d —  (R' = Me, Et, NO_2); H_2O, NaOH, $C_6H_5CH_2\overset{+}{N}(Pr^n)_3Cl^-$;[191]

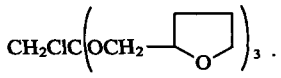
e — ; H_2O, NaOH.[191]



a — Bu^tOK, THF, −60 °C;[186]

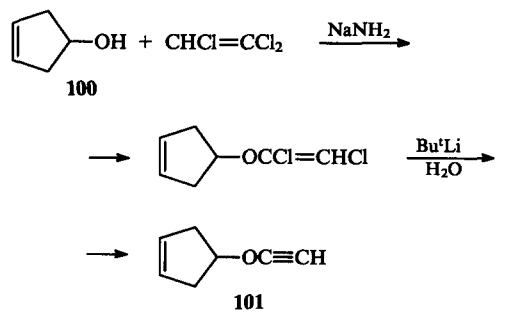
b — $MeOCH_2CH_2ONa$, xylene, 100–130 °C.[192]

The product of the interaction of TCE with tetrahydrofurfuryl alcohol and sodium under a nitrogen atmosphere is the orthoester

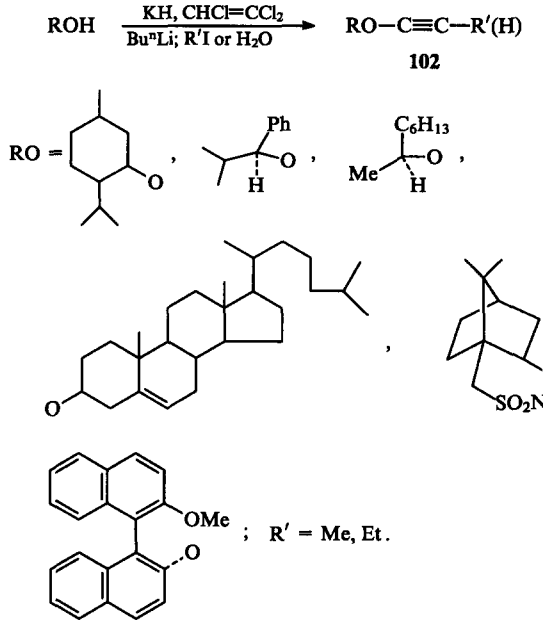


which indicates the possibility of the addition of a molecule of the nucleophile to the intermediate chloroketene.[193]

Convenient methods for the synthesis of acetylenic esters from TCE have been proposed recently.[194,195] The possibility of the synthesis of the alkyne **101** has been demonstrated in the reaction of cyclopentenol **100** with TCE.[194]



A simple and general method of synthesis of acetylenic ethers **102** has been developed on the basis of secondary alcohols and TCE.[195]

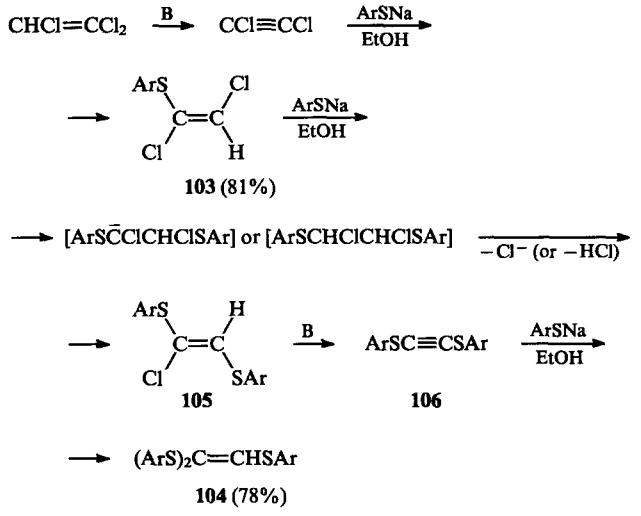


; R' = Me, Et.

A new and effective two-stage synthesis of propargyl ethers $ROCH_2C{\equiv}CH$ [R = cyclohexyl, (−)-menthyl, (−)-bornyl, or 1-adamantyl] has been achieved by isomerising 1-propynyl ethers $ROC{\equiv}CMe$, obtained from the corresponding secondary alcohols and TCE, on treatment with potassium 3-aminopropylamide.[196] According to a patent,[197] TCE and other alkenyl polyhalides are used in the esterification of resin acids and their derivatives.

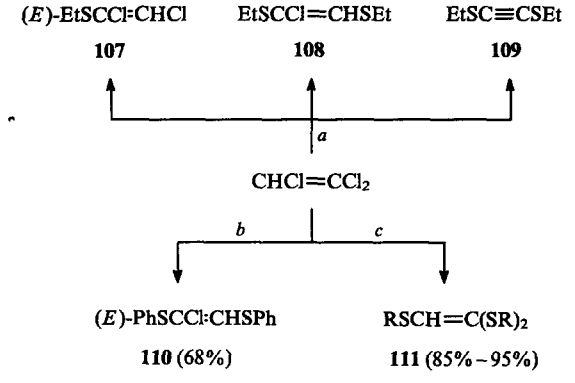
b. Interaction with S-nucleophiles

When TCE interacts with S-nucleophiles, products containing one or several thiolate residues are formed depending on the reaction conditions. A detailed study has been made of the reaction of sodium *p*-methylthiophenoxide with TCE, which proceeds only in the presence of sodium ethoxide.[198] For a 1 : 1 reactant ratio and after brief heating of the mixture, the main reaction product is 1,2-dichloro-1-(*p*-tolylthio)ethylene **103**. In the presence of a four-fold excess of the thiolate and after prolonged heating of the reactant mixture, 1,1,2-tris(*p*-tolylthio)ethylene **104** was obtained. By varying the reaction conditions, it was also possible to isolate the intermediates in this reaction: 1-chloro-1,2-di(*p*-tolylthio)-ethylene **105** and di(*p*-tolylthio)ethylene **106**. The results show that the reaction of TCE with sodium toluene *p*-thiolate proceeds via elimination–addition and addition–elimination mechanisms:



B = base, Ar = *p*-MeC_6H_4.

The reaction of other thiolates with TCE in aprotic solvents also leads to the initial formation of (*E*)-1,2-dichlorovinylation products, for example compound **107**, which can be involved in further reactions, giving compounds with two and three thiolate groups, for example, compounds **108–111**.

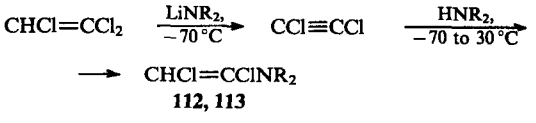


a — EtSNa, DMF;[188]
b — PhSNa, PhSNa : TCE = 3 : 1, DMF;[199]
c — Pr^{i}SNa or MeSNa, DMF.[199]

c. Interaction with N-nucleophiles

TCE reacts with amines only in the presence of strong bases, which shows that the reaction proceeds via the elimination–addition mechanism. The 1,2-dichlorovinylation of certain amines has been achieved with TCE, and convenient methods have also been developed for the formation of chloroketene aminals, diaminoalkynes, and glycine and its derivatives.

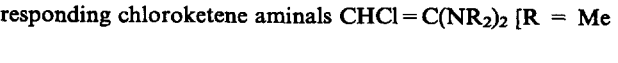
The dichlorovinylation of aliphatic amines has been investigated in relation to dimethyl- and diethyl-amines. 1,2-Dichloro-1-(*N*,*N*-dialkylamino)ethylenes **112** and **113** have been obtained by treating TCE initially with lithium dialkylamide in ether and then with the amine.[200]



R = Me (**112**, yield 75%); R = Et (**113**, yield 85%).

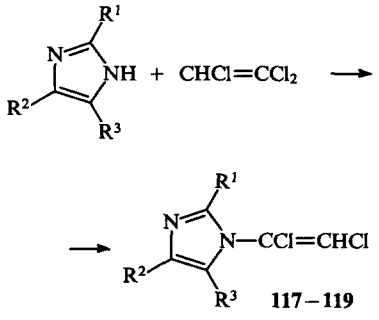
On heating (60–70 °C) with an excess of dimethyl- and diethyl-amine, the enamines **112** and **113** are converted into the corresponding chloroketene aminals $CHCl=C(NR_2)_2$ [R = Me (compound **114**), R = Et (compound **115**)].[200] The mono- and di-substituted products **112–115** have found applications in the synthesis of diaminoalkynes of the type $R_2N-C\equiv C-NR_2$,[200,201] which are important synthons.[202]

The direct synthesis of these compounds has been developed only for bis(dimethylamino)ethyne **116**, which is obtained via the reaction[203]



116 (60%)

The interaction of TCE with heterocyclic amines has been more widely investigated. Thus treatment of TCE with a mixture of potassium hydride and imidazole in THF in the presence of catalytic amounts of methanol leads to the formation of *N*-(1,2-dichlorovinyl)imidazole in 80% yield.[173] Another method has been proposed[204] for the alkenylation of imidazole and its derivatives, which involves treatment of the reaction mixture with an aqueous solution of NaOH in the presence of dimethyl sulfoxide (DMSO). The reaction proceeds stereoselectively with formation of the corresponding (*E*)-derivatives of imidazole **117–119** in 60%–62% yield.

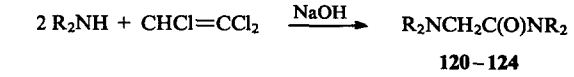


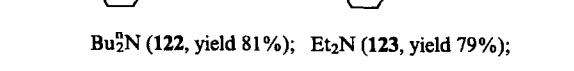
$R^1 = R^2 = R^3 = H$ (**117**); R^1 = Ph, $R^2 = R^3 = H$ (**118**);
$R^1 = H$, $R^2 = R^3$ = Ph (**119**).

N-[(*E*)-1,2-dichlorovinyl]benzimidazole is formed in 60% yield from benzimidazole and TCE under similar conditions.

The interaction of carbazole and its derivatives with TCE under phase-transfer catalytic conditions has been investigated recently.[205] On treatment with aqueous NaOH and catalytic amounts of triethylbenzylammonium chloride, this reaction proceeds stereoselectively via the intermediate formation of dichloroacetylene **86**, affording high yields (~80%) of 9-[(*E*)-1,2-dichlorovinyl]carbazole derivatives.

A new general method of synthesis of symmetrically substituted, *N*,*N*,*N*′,*N*′-tetraalkylglycine amides **120–124** has been developed based on the reaction of TCE with more nucleophilic secondary amines under phase-transfer catalytic conditions.[172,206]

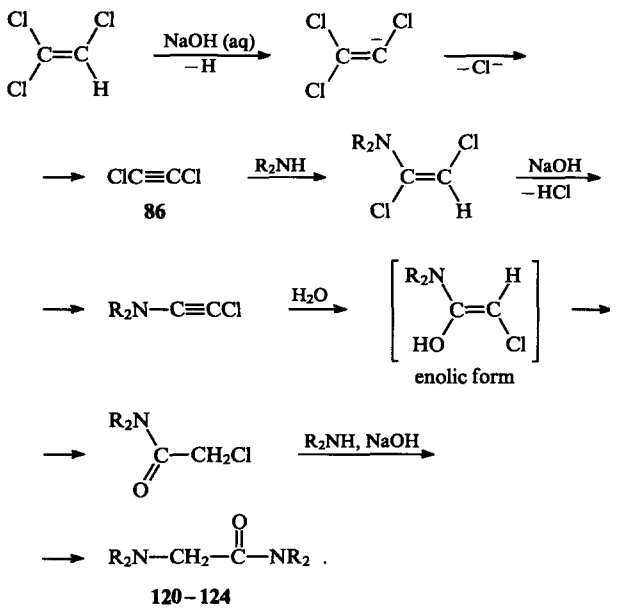




Bu^n_2N (**122**, yield 81%); Et_2N (**123**, yield 79%);
Me_2N (**124**, yield 51%).

The less nucleophilic aromatic amines do not react with TCE under these conditions.

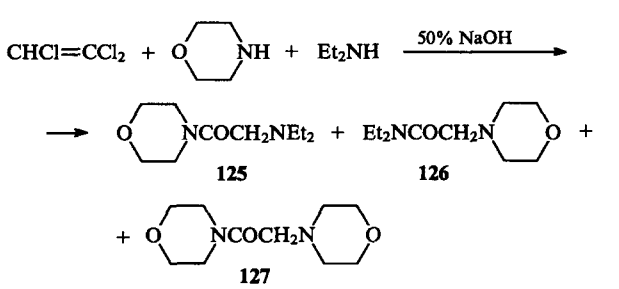
It has been suggested that the reaction takes place via the intermediate trichlorovinyl anion,[171] which is converted into the alkyne **86** and the latter reacts with the amine in accordance with the mechanism



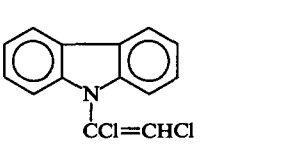
120–124

In order to confirm the postulated mechanism, an attempt was made to isolate the intermediates, but R_2NCOCH_2Cl was isolated only in the reaction of TCE with morpholine.

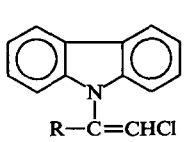
The reactions of TCE with a mixture of two unequally nucleophilic amines in the presence of phase-transfer catalysts is of definite synthetic interest. Thus, when a mixture of morpholine and diethylamine was used, the glycine amide derivatives **125–127** were obtained, the main product being compound **125**.[207]



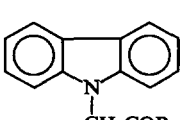
Treatment of TCE with carbazole and a secondary aliphatic amine leads to the formation of the products **128–130**, the yields of which depend on the nature of the aliphatic amine and the ratios of all the reactants.[208]



128



129

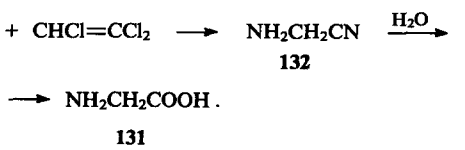


130

R = Et_2N, Pr_2N, .

The synthesis of glycine, **131**, based on the reaction of TCE with an aqueous ammonia solution is important.[209,210] The reaction takes place in an autoclave on treatment with various alkaline catalysts, among which the most effective is $NaHCO_3$. Under optimum conditions (14% aqueous ammonia, pressure 294 kPa, temperature 180 °C, 4 h), the yield of glycine is 71.6%.

It has been suggested that the reaction proceeds via the initial formation of aminoacetonitrile **132** in accordance with the mechanism



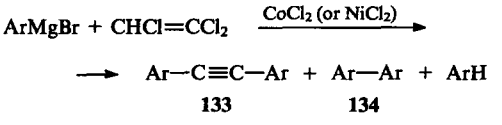
131

Indeed, when anhydrous ammonia and lower temperatures (70–80 °C) are used, the main reaction product is the nitrile **132** (yield 70%).[211]

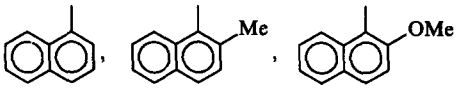
d. Reactions with C-nucleophiles

Study of the reactions of TCE with C-nucleophiles is of undoubted interest because the problem of new C–C bond formation is extremely pressing.

The reaction of TCE with organomagnesium compounds leads to the formation of a complex mixture of substances.[189] Grignard reagents are known to be fairly strong bases and moderate nucleophiles, so that the occurrence of competing elimination and substitution reactions is possible. In the presence of catalysts, TCE reacts with Grignard reagents more selectively and the nature of the catalyst influences the mode of the reaction more significantly. Thus aromatic Grignard reagents and TCE afford diarylalkynes **133** and biaryls **134** (by reduction of the Grignard reagent) on treatment with cobalt(II) or nickel(II) salts.[212]

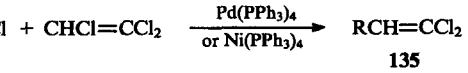


Ar = Ph, *p*-MeC_6H_4, 1,3,5-$Me_3C_6H_2$,



The yields of the alkynes **133** depend on the structure of the reagent employed. For example, in the reaction of TCE with 1,3,5-$Me_3C_6H_2MgBr$ the yield of the corresponding alkyne is 48%, whereas when phenylmagnesium bromide was used the target product was obtained in a yield of only 5%.

The interaction of TCE with organomagnesium compounds proceeds differently in the presence of phosphinepalladium-(nickel) catalysts. A simple method of synthesis of substituted 1,1-dichloroalkenes **135** has been developed which employs the reaction of a Grignard reagent with TCE catalysed by tetrakis-(triphenylphosphine)palladium (or nickel).[213] It has been suggested that the reaction proceeds via the initial formation of intermediates involving the oxidative addition of the catalyst in a monosubstituted position in TCE. The intermediate then reacts with the Grignard reagent and is converted into the corresponding alkene after reductive elimination.

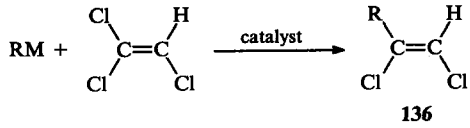


135

R = n-C_8H_{17} (65%–75%), n-C_6H_{13} (60%–72%), Bu^i (55%), Pr^i (52%), cyclo-C_6H_{11} (81%).

The reaction proceeds under mild conditions (room temperature, solvent—mixture of ether with benzene), but we may note that phenylmagnesium bromide gives a mixture of three products in 40% yield under these conditions.

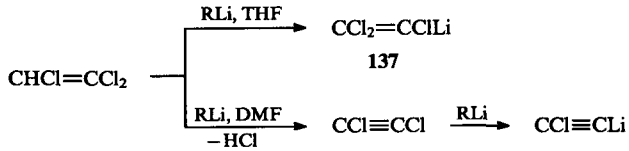
The regio- and stereo-selective monoalkylation and monoarylation of TCE by Grignard reagents or organozinc reagents was achieved for the first time in the presence of the phosphinepalladium catalyst $\{PdCl_2[Ph_2P(CH_2)_4PPh_2]\}$.[214] In this case, the reaction involves the CCl_2 group of TCE and is completed by the formation of monosubstituted (*Z*)-1,2-dichloroethylenes **136** in good or high yields.



136

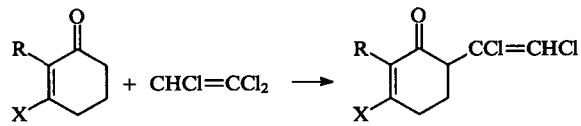
R = Ph, 4-ClC_6H_4,  M = MgBr or ZnCl.

When TCE was treated with organolithium compounds, metallation products of both TCE (trichlorovinyllithium **137**)[215] and dichloroethyne (chloroethynyllithium **138**) were obtained.[189]



The carboxylation of vinyllithium **137** leads to the formation of trichloroacrylic acid in 81% yield.[179]

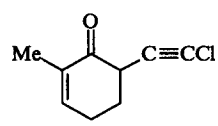
It has been shown in a number of studies[216–218] that TCE is an effective agent for the alkenylation of tertiary conjugated enolates. Although the latter are in fact ambident nucleophiles, only their tertiary carbon atoms are subjected to electrophilic attack. Thus lithium enolates, obtained from the substituted cyclohexenones **139** and **140** (lithium dialkylamide, THF, −78 °C), react with TCE under mild conditions, giving the 1,2-dichlorovinylation products—the dichlorovinyl ketones **141** and **142**.[216]



139, 140 **141, 142**

X = OEt, R = H (**139, 141**); X = H, R = Me (**140, 142**).

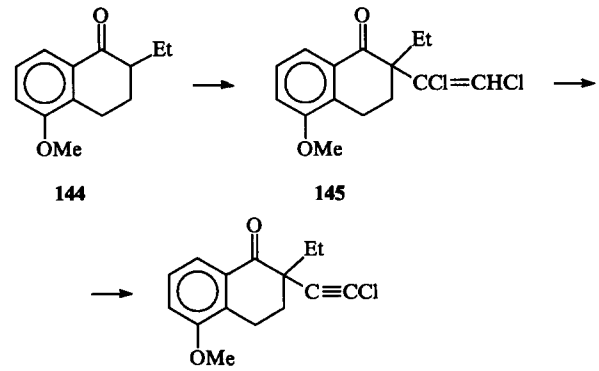
When the enolate **140** is used, the chloroalkyne **143** is formed as well.



143

It has been shown with the aid of X-ray diffraction that the ketone **142** has the (*E*)-configuration.

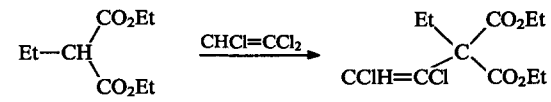
Two products are formed in the reaction of the lithium enolate of the substituted tetralinone **144** with TCE: the dichloroalkyne **145** and the chloroalkyne **146**. The complete conversion of compound **144** into the chloroalkyne derivative **146** (yield 44%) is achieved by repeated treatment of the mixture of products with lithium dialkylamide (THF, −78 to 20 °C).



144 **145**

146

Diethyl ethylmalonate **147** condenses with TCE under more severe conditions (NaH, THF, HMPA, refluxing), forming compound **148**.

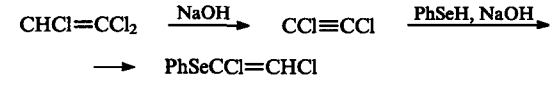


147 **148**

The dichlorovinylation of ethyl 2-acetylpropionate proceeds similarly. The reactions with participation of deuteriated TCE have shown that the dichlorovinylation of the tertiary enolates investigated takes place by the elimination–addition mechanism via dichloroethyne as an intermediate.[217] The condensation of enolates with TCE can be formally regarded as a reaction involving substitution of a chlorine atom in the dichloromethylene group of TCE. The attempt to extend this reaction to other types of enolates was unsuccessful.[218]

e. Reactions with other nucleophiles

It has been shown[219,220] that selenophenol reacts with TCE in concentrated NaOH solution to form 1,2-dichlorovinyl phenyl selenide **149** in a high yield. The reaction is catalysed by ammonium salts and leads to the (*Z*)-isomer for an equimolar ratio of the catalyst and the selenol. In the presence of a tenfold excess of the selenol, a mixture of the (*Z*)- and (*E*)-isomers is formed. It has been suggested that the interaction of the selenol with TCE takes place by the elimination–addition mechanism and subsequent isomerisation of the (*Z*)-selenide, formed initially, to the thermodynamically more stable (*E*)-isomer.



(*Z*, *E*)-**149**

Diethyl ether is used to bind the dichloroethyne formed *in situ*. The nucleophilic substitution of chlorine in TCE by the PhSe-ion in ethanol and DMF also leads to a mixture of the (*Z*)- and (*E*)-selenides, but the product yields are appreciably lower than in a two-phase system.

The interaction of TCE with diphenyl and dimethyl diselenides **150** in the presence of tributylbenzylammonium chloride as the phase-transfer catalyst proceeds, on the whole, similarly to the reaction with the selenol. However, under these conditions, an appreciable amount of trichlorovinyl selenides **151** and 1,2-dichloro-1,2-bis(organoseleno)ethylenes **152** is formed together with the expected (*Z*)-1,2-dichlorovinyl selenides and the products of their isomerisation [the (*E*)-isomers].[221]

$$CHCl{=}CCl_2 + \underset{\mathbf{150}}{RSeSeR} \xrightarrow{(10\%-15\%)\ NaOH-Et_2O} \underset{\mathbf{152}}{RSeCCl{=}CClSeR} + \underset{\mathbf{151}}{RSeCCl{=}CCl_2} + Z(E)\text{-}RSeCCl{=}CHCl$$

R = Ph, Me.

The data obtained can be accounted for by the formation, in the course of the reaction, of selenolate ions RSe^- by heterolytic cleavage of the selenides in an alkaline medium, the ions adding to the $CCl{\equiv}CCl$ generated in situ from TCE.

TCE is phosphonylated by the sodium salts of dialkyl phosphites. Depending on the structure of the phosphites employed and the reaction conditions, the esters of tri- and/or tetra-phosphonic acids are produced.[222]

f. Hydrolysis

When TCE vapour is passed through concentrated sulfuric acid heated to 180 °C, a technically valuable product is formed — monochloroacetic acid **153**.[1] In order to increase the yield of the acid **153** and to reduce the process temperature, it is recommended that the hydrolysis be carried out at a reduced temperature.[1,223]

A method has been proposed for the synthesis of monochloroacetyl chloride through hydrolysis of TCE in the liquid phase in the presence of partly suspended iron(II) chloride with continuous passage of hydrogen chloride under pressure. The acid **153** is in this case a side product of the reaction.[224,225] Alkaline hydrolysis of TCE (steel reactor, sodium methoxide, 60–65 °C) leads to the formation of methyl monochloroacetate.[226]

2. Interaction with electrophiles

The reactions examined above confirm that TCE has pronounced electrophilic properties. One can therefore postulate that its interaction with electrophiles is difficult and is possible only with electrophiles stronger than TCE itself.

According to patent data,[227,228] TCE reacts with nitric acid. Thus, when TCE is refluxed with 30%–80% aqueous HNO_3 and also on slow addition of 90%–100% HNO_3 to TCE at 65–75 °C, trichloronitroethylene is formed in a preparative yield. However, together with the nitration of TCE, the molecules of the latter are degraded, which results in the formation of dichlorodinitromethane.

Trichloroethylenesulfonyl chloride has been obtained in high yield by the reaction of TCE with chlorosulfonic acid.[229] The reaction is carried out at the boiling point of TCE (87 °C), the hydrogen chloride formed being removed by passing dry nitrogen through the reaction mixture.

V. Oxidation reactions

1. The effect of oxygen

The oxidation of TCE by oxygen, the study of which was begun as early as 1911,[220] is nowadays being investigated in fair detail commercially. Its main products are dichloroacetyl chloride **154** and trichloroepoxyethane **155**, the yields of which depend to a considerable extent on the oxidation reaction conditions.

The studies on the oxidation of TCE published up to 1970 have been examined in a monograph.[4] The oxidation of TCE under the influence of ionising radiation has been described in a recent monograph.[231]

The patents, published during the last 10–15 years and devoted to this problem, are concerned primarily with improvement of the synthesis of compound **154**.[232–241] It has been shown[233] that the photochemical oxidation of TCE at 70–80 °C in the presence of catalytic amounts of a chloride in DMF makes it possible to obtain compound **154** in 90% yield with ~90% conversion of TCE. Compound **154** has been obtained in a high yield also by oxidising TCE in the presence of azobisisobutyronitrile (AIBN) or benzoyl peroxide and trialkylamines,[234] pyridines,[235,236] quinoline, and isoquinoline.[237] The rate of oxidation increases appreciably when TCE containing small amounts of added compound **154** is irradiated by short-wavelength light.[238] The target product **154** was obtained with 99.47% purity and 99.9% conversion by varying the power of the UV irradiation.[239]

There are data showing that haloalkenes are oxidised on heating under pressure without a catalyst.[240] In industry, dichloroacetal chloride is obtained by the continuous oxidation of TCE with air or an oxygen–air mixture at 170 °C under a pressure of 491 kPa in the presence of benzoyl peroxide and amide catalysts.[241]

Trichloroepoxyethane **155** — the second main product formed on oxidation of TCE — is extremely reactive and is used in the synthesis of a wide variety of substances. It is obtained by McKinney's method[242] involving the autoxidation of TCE in methanol in the presence of RCOOOH under irradiation with light from an Hg lamp[243] or as a result of radiation-chemical oxidation.[244]

Study of the low-temperature photoinitiated oxidation of TCE showed that selectivity in epoxide formation increases after the addition of aromatic ketones and on irradiation with light at $\lambda = 300$ nm for low (15%–20%) conversions of TCE. An increase in the yield of the epoxide is also promoted by carrying out the process at low temperatures.[245] The radiation-chemical method of synthesis of the epoxide **155** is promising because in this case the oxidation reaction proceeds at low temperatures.[246]

The characteristic features of the oxidation of haloalkenes, including TCE, have been examined in communications[247–250] and monographs.[231,251–253]

Results of kinetic studies on the oxidation of TCE in both liquid and gas phases indicate a radical-chain oxidation mechanism. However, the mechanism of the oxidation of TCE has not hitherto been fully elucidated.

Certain quantitative characteristics of the liquid-phase AIBN-initiated oxidation of TCE have been established recently.[254,255] It has been shown that, in the presence of the above initiator, TCE is oxidised via a radical-chain mechanism, compounds with long chains ($n \gg 10$) without degenerate branching being obtained. The epoxide **155** and dichloroacetyl chloride **154** are formed simultaneously, their ratio remaining constant at ~3, i.e. the selectivity with respect to the epoxide is ~75%–80%.

Taking into account the literature data on the oxidation kinetics of alkenes[252,253] and haloalkenes,[250,251] Kucher et al.[255] proposed on the basis of the results obtained a mechanism for TCE oxidation in which, together with the radical pathway, a molecular pathway leading to the formation of the epoxide **155** is described. In the gas-phase oxidation of TCE, the main reaction product is also dichloroacetyl chloride.[256] Various modifications of the gas-phase oxidation reactions of TCE have been examined.[257]

Interesting data have been obtained for the joint oxidation of certain organic compounds with TCE. It was concluded[258] that the co-oxidation of cyclohexane with TCE, which gives rise to very reactive peroxyl radicals, can serve as an effective method for the regulation of both the rate and selectivity of the oxidation of cyclohexane to alcohol, a ketone, and adipic acid. The co-oxidation of cyclohexane with TCE at 75 °C has been investigated[259] and it has been shown that cyclohexanol and cyclohexanone are formed simultaneously in the chain termination reaction. It was established that, when the TCE concentration is varied from zero to 50 vol.% in a mixture with cyclohexane, the cyclohexanol : cyclohexanone ratio can be varied in the range from 1.75 to 3.3.

It has been established[260] that the presence of two chlorine atoms in the terminal $-CCl_2OO^{\cdot}$ fragment of the peroxyl radicals

leads to an appreciable increase in their electrophilicity and reactivity in the dehydrogenation of organic compounds. It has been shown that the reactivity of secondary C–H bonds in n-alkanes is independent of the length of the carbon skeleton of the molecule.

The co-oxidation of TCE with aromatic alkyl compounds [261] and oxygen-containing aliphatic compounds [262] has been recently investigated and it has also been shown that the reactions involved in hydrocarbon processing, which proceed via a radical mechanism, can be facilitated by their co-oxidation with TCE, which generates highly reactive peroxyl radicals.

The main product of the reaction of TCE with PCl_3 in the presence of oxygen is acetyl chloride **154** (yield 45%), while the phosphorus-containing compounds **156** and **157**, formed as a result of the rupture of the C = C bond of TCE, were found among the side products. [263]

$$CHCl{=}CCl_2 \xrightarrow{PCl_3 + O_2} CHCl_2COCl\ (\mathbf{154}) + Cl_2P(O)CHCl_2\ (\mathbf{156}) + Cl_2P(O)OCHCl_2\ (\mathbf{157})$$

2. The effect of ozone

On treatment with ozone, TCE undergoes oxidative cleavage. The main products of this reaction are phosgene, hydrogen chloride, and carbon oxides. [247,264,265] The kinetics of the ozonisation reaction in various media have been investigated. [266,267] Peroxyformic acid has been detected among the products of the gas-phase reaction of ozone with TCE. [268]

3. The effect of peroxide reagents

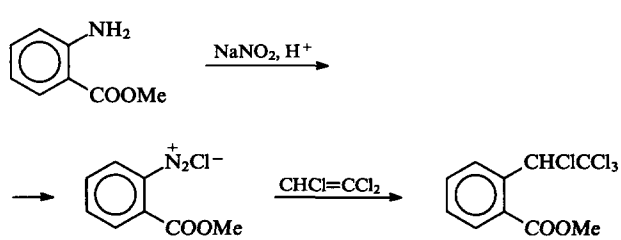
The main products of the reaction of TCE with peracetic acid are dichloroacetic acid and pentachloroethane. The optimum conditions for this reaction have been investigated and possible pathways leading to the formation of the main and side products have been proposed. [269]

The interaction of TCE with benzoyl peroxide leads to the formation of trichloroepoxyethane **155**, which readily isomerises to $CHCl_2COCl$ in the presence of catalysts (for example, Et_4NBr). [270]

VI. Other reactions

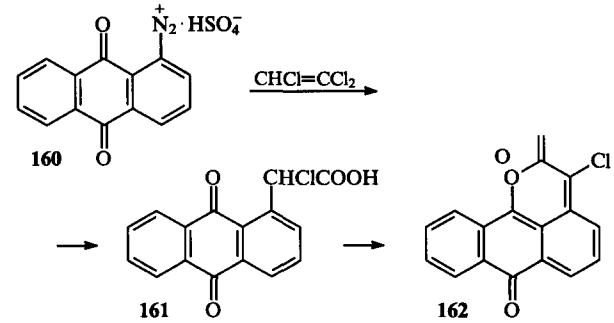
1. Reaction with diazonium compounds

The diazonium derivative of methyl anthranilate **158** reacts with TCE to form methyl *o*-(α,β,β,β-tetrachloroethyl)benzoate **159**. [271]



158 **159**

The reaction of anthraquinonediazonium sulfate **160** with TCE in acetic acid leads to the highly reactive 3-chloro-2*H*,7*H*-dibenzo[*de*,*h*]chromene-2,7-dione **162**, possibly as a result of cyclisation and dehydration of the anthraquinone-1-chloroacetic acid **161** formed initially. [272]



160 **161** **162**

2. The Bott reaction

Bott [273–275] showed that compounds of the adamantane and norbornane series, which form stable carbonium ions in sulfuric acid, react with TCE, affording substituted chloroacetic acids **163**.

$$R^+ + CHCl{=}CCl_2 \xrightarrow{H_2SO_4} RCHCl{-}C^+(Cl)Cl \xrightarrow{\text{solvolysis}} RCHClCOOH\ (\mathbf{163})$$

The syntheses of numerous adamantylchloroacetic acids in preparative yields have been achieved in this way. When the acids formed contain a hydrogen atom at the bridgehead carbon atom of the bridged system, new carbonium ions arise, which results in the appearance of dibasic adamantane-1,3-bis(chloroacetic) acids among the reaction products.

The reaction of norbornene with TCE leads to 2-*exo*-norbornylchloroacetic acid in 66% yield. [273] Numerous substituted benzyl alcohols and their ethers **164**, which give rise to stable benzyl cations in sulfuric acid at temperatures above 80 °C, react with TCE, affording derivatives of α-chlorohydrocinnamic acids **165** in 30%–85% yield. [274,275]

$$RC_6H_4CH_2OR'\ (\mathbf{164}) + CHCl{=}CCl_2 \xrightarrow{H_2SO_4,\ 85-95\ ^\circ C} RC_6H_4CH_2CHClCOOH\ (\mathbf{165})$$

R = *p*-O_2N, *m*-O_2N, *p*-HOOC, *m*-HOOC, *p*-$MeSO_2$, *p*-$PhSO_2$, *p*-Bz; R′ = H or Ac.

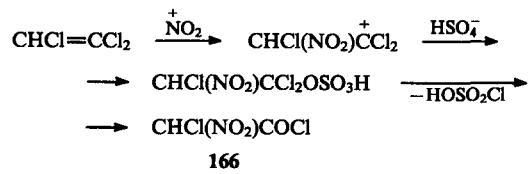
The substituted 1,1,2-trichloroalkenes $RC_6H_4CH_2CCl{=}CCl_2$ are side products in this reaction.

The Bott reaction has undergone further development recently. Thus the interaction of hydroxyadamantanes with TCE in concentrated H_2SO_4 leads to a mixture of the corresponding diadamantylchloroacetic and diadamantanebis(chloroacetic) acids. [276] A method has been proposed for the synthesis of various derivatives of diamantane-4,9-bis(chloroacetic) acid. [277]

We may note, however, that, in the interaction of diamantane-3-spiro-3′-diazirine with TCE under the conditions of the Bott reaction, the corresponding acids are formed in only trace amounts, while the principal products are diamantane, diamantanone, 3-chlorodiamantane, and 1-chlorodiamantane. [278]

3. Reaction with nitric acid and its oxides

The interaction of nitric acid and its oxides with TCE proceeds in a complex manner. The main product of the reaction of TCE with the $HNO_3 + H_2SO_4$ nitrating mixture is the chloride of chloronitroacetic acid **166**, obtained in 80%–85% yield. [279] The acid chloride **166** is apparently formed as a result of the initial addition of the nitronium cation to the double bond of TCE and the subsequent reactions of the carbonium ion. [280]



166

Dichloroacetyl chloride, pentachloroethane, and nitryl chloride were found among the side products of this reaction. The influence of the composition and amount of the nitrating mixture on the nitration process has been investigated.[281]

The interaction of TCE with nitrogen monoxide involves nitration, nitrosation, oxidative degradation, and chlorination reactions, which lead to the formation of 1,1,1,2-tetrachloro-2-nitroethane **167**, dichloroacetic acid **168**, pentachloroethane **1**, 1,1,3,3,4-pentachloro-4-nitrobut-1-ene, and also carbon dioxide and monoxide. The same set of products has been obtained also in the reaction of N_2O_3 with TCE.

In the dark and at a temperature above 100 °C, nitrosyl chloride behaves only as a chlorinating agent. In the reaction of TCE with nitrosyl chloride in sunlight at room temperature, pentachloroethane **1**, 1,1,1,2-tetrachloro-2-nitrosoethane, the nitroalkane **167**, the acid **168**, and a pentachloronitrobutene, whose structure has not been established, were obtained. Consequently, under conditions promoting the formation of free radicals, nitrosyl chloride exhibits nitrosating, nitrating, and oxidising activities.[283]

VII. The practical use of trichloroethylene and its derivatives

By virtue of its high reactivity, incombustibility, and inappreciable toxicity, TCE is an excellent solvent and is used widely in the national economy.[1] In addition, it is used in medicine as a powerful narcotic.[284,285] According to patent data,[286,287] the addition of TCE improves the properties of insecticidal preparations. One of the ways of eliminating hexachloroethane from hexachlorobutadiene is based on the fractional distillation of the mixture in the presence of TCE.[288] The use of this compound as a solvent in the pentafluorobenzylation of organic acids appreciably increases the yield of benzyl esters.[289] In the synthesis of *m*-chloroperbenzoic acid, TCE has also been recognised as the best inert solvent.[290] A new reaction involving the thermal heterocyclisation of arylchlorosilanes in the gas phase, which proceeds in the presence of TCE (and certain other halo-derivatives), has been discovered.[291] Thus the pyrolysis of dichlorodiphenylsilane in a mixture with TCE (1 : 1 ratio) leads to 9,9-dichloro-9-silafluorene (yield 35%).[292,293]

The chemical properties and in particular the poly-functionality of TCE have led to extensive possibilities for its employment in organic synthesis (see the present review) and in chemical engineering[294] as a most valuable intermediate. Industrial methods of synthesis of monochloroacetic acid, which is an intermediate in the synthesis of dyes and pesticidal and medicinal preparations, have been developed on the basis of TCE.[295] The chloride of dichloroacetic acid, formed in the oxidation of TCE, is the main intermediate in the synthesis of the antibiotic levomycetin.[295]

Further examples of the practical use of other TCE derivatives have now been discovered. Thus it has been suggested that 1,2-dibromo-1,1,2-trichloroethane be used as an anaesthetic.[18] The product of the interaction of TCE with HF—1,1,1,2-tetra-fluoroethane—is a potential blood substitute.[31] According to patent data,[296,297] the steroids synthesised with participation of TCE, containing the chloroethynyl group in the C(17) position, possess a broad spectrum of physiological activity. Other TCE derivatives are physiologically active as well, such as—chlorine-containing amines,[73] 2-bromo-2-chloro-1,1,1-trifluoro-ethane,[298] and substituted vinylthioacetamidooxacephalo-sporins.[299]

Many of the compounds obtained with participation of TCE have been proposed as pesticides. Derivatives of urea[190,300,301] and chlorine-containing aromatic compounds[77] exhibit a herbicidal activity. 4-(Diphenylacryloyl)morpholines are used as fungicides[302] and 4-chlorobenzyl 2,2-dichlorovinyl sulfide is a nematocide.[303] Insecticidal activity has been discovered in chloronorbornenes. Trichloronitroethylene,[228] bis(dichlorovinyl) sulfide,[304,305] bis(dichlorovinyl) disulfide,[306] and 1,1-dichloro-4-methylpenta-1,3-diene, which is a product of the condensation of TCE with isobutene (it is used in the synthesis of pyrethroids[56–58]), have a broad spectrum of activity.

Fireproofing agents[307] and flame extinguishers[308] as well as regulators of molecular mass in the manufacture of silicone rubbers and oils[116] have been found among TCE derivatives. The polylactones obtained from TCE and paraformaldehyde are used in the manufacture of insulating materials and detergents.[309]

* * *

The claim that TCE is a relatively unreactive compound can still be encountered in the literature. For example, in a recently published monograph[310] it is noted that TCE does not enter into nucleophilic substitution reactions. However, our analysis demonstrated the extensive synthetic possibilities of TCE, including their use in processes involving the formal nucleophilic substitution of chlorine atoms. Convenient methods of synthesis of polyfunctional compounds of different classes have been developed on the basis of TCE, substances with useful properties, which were previously difficult to obtain, have been synthesised, and new nontrivial features of certain chemical processes have been discovered.

References

1. *Promyshlennye Khlororganicheskie Produkty (Spravochnik)* [(Industrial Chlororganic Products) (Handbook)] (Ed. L A Oshin) (Moscow: Khimiya, 1978)
2. E H Huntress *The Preparation, Properties, Chemical Behavior, and Identification of Organic Chlorine Compounds* (New York: Wiley; London: Chapman and Hall, 1948)
3. *Methoden der Organischen Chemie (Houben–Weyl)* Vol. V/3 (Stuttgart: Georg Thieme, 1962)
4. *Metody Elementoorganicheskoi Khimii. Khlor. Alifaticheskie Soedineniya* (Methods of Organoelement Chemistry. Chlorine. Aliphatic Compounds) (Eds A N Nesmeyanov, K A Kocheshkov) (Moscow: Nauka, 1973)
5. A N Mirskova, G N Drozdova, G G Levkovskaya, M G Voronkov *Usp. Khim.* **58** 417 (1989) [*Russ. Chem. Rev.* **58** 250 (1989)]
6. N N Labeish, A A Petrov *Usp. Khim.* **58** 1844 (1989) [*Russ. Chem. Rev.* **58** 1048 (1989)]
7. M G Voronkov, A V Martynov, A N Mirskova *Sulfur Rep.* **6** 77 (1986)
8. T Manek, H K Wankhade, D V Parvate, A N Garg *Radiochem. Radioanal. Lett.* **58** 373 (1983)
9. R Atkinson, S M Aschmann *Int. J. Chem. Kinet.* **19** 1097 (1987)
10. French P. 2 057 604; *Chem. Abstr.* **76** 58 943 (1972)
11. M L Poutsma, R L Hinman *J. Am. Chem. Soc.* **86** 3807 (1964)
12. N B Mel'nikova, E N Krom, V R Kartashov, L A Ternovskii *Izv. Vyssh. Uchebn. Zaved., Khim. Khim. Tekhnol.* **24** 810 (1981)
13. Jpn. Appl. 79-122 206; *Chem. Abstr.* **92** 93 880 (1980)
14. K W Field, P Kovacic *J. Org. Chem.* **36** 3566 (1971)
15. I V Vigalok, A V Ostrovskaya *Zh. Obshch. Khim.* **41** 1410 (1971)
16. V N Paraskevov, I V Pimenov, Yu G Treger, G S Dasaeva *Kinet. Katal.* **24** 1007 (1983)
17. G A Sidakova, A S Kyazimov *Sopryazhennoe Galogenirovanie Olefinov i Ikh Proizvodnykh s Kislorodsoderzhashchimi Soedineniyami* (Coupled Halogenation of Olefins and Their Derivatives with Oxygen-Containing Compounds) (Baku: AzINNEFTEKhIM, 1973)
18. US P. 3 637 874; *Chem. Abstr.* **76** 85 375 (1972)
19. Eur. Appl. 219 823; *Chem. Abstr.* **107** 58 492 (1987)
20. L Conte, G P Gambaretto, M Napoli, C Gervasutti *J. Fluorine Chem.* **38** 319 (1988)

21. L Marangoni, G Rasia, C Gervasutti, L Colombo *Chim. Ind.* **64** 135 (1982)
22. Jpn. Appl. 60-12910; *Chem. Abstr.* **104** 5 561 (1986)
23. G P Gambaretto, M Napoli *J. Fluorine Chem.* **7** 569 (1976)
24. L S Boguslavskaya, N N Chuvatkin, I Yu Panteleeva *Zh. Org. Khim.* **18** 2082 (1982)
25. B V Kunshenko, Nagib Mukhtar Mokhamed, V O Omarov, N N Muratov, L M Yagupol'skii *Zh. Org. Khim.* **28** 672 (1992)
26. Fr. Appl. 2 647 439; *Ref. Zh. Khim.* 18 N 17P (1991)
27. M S Kharasch, J A Norton, F R J Mayo *J. Org. Chem.* **3** 48 (1938)
28. BRD Appl. 2 108 951; *Chem. Abstr.* **77** 139 405 (1972)
29. Jpn. Appl. 73-72105; *Chem. Abstr.* **80** 59 424 (1974)
30. Jpn. Appl. 81-33039; *Chem. Abstr.* **95** 97 010 (1981)
31. Eur. Appl. 295 885; *Chem. Abstr.* **110** 195 124 (1989)
32. A E Feiring *J. Fluorine Chem.* **14** 7 (1979)
33. US P. 4 258 225; *Chem. Abstr.* **95** 6 482 (1981)
34. BRD Appl. 2 719 021; *Chem. Abstr.* **90** 54 453 (1979)
35. BRD Appl. 2 739 621; *Chem. Abstr.* **90** 203 466 (1979)
36. BRD Appl. 2 737 950; *Chem. Abstr.* **90** 168 040 (1979)
37. US P. 4 374 289; *Chem. Abstr.* **98** 197 593 (1983)
38. US P. 4 766 259; *Chem. Abstr.* **110** 97 549 (1989)
39. N S Zefirov, A S Koz'min, V D Sorokin *J. Org. Chem.* **49** 4086 (1984)
40. N S Zefirov, A S Koz'min, V D Sorokin, V V Zhdankin *Zh. Org. Khim.* **22** 898 (1986)
41. A V Fokin, Yu N Studnev, A I Rapkin, I N Krotovich *Izv. Akad. Nauk SSSR, Ser. Khim.* 2374 (1981)
42. L F R Cafferata, J E Sicre *Inorg. Chem.* **13** 242 (1974)
43. Dutch Appl. 76-00091; *Chem. Abstr.* **86** 16 278 (1977)
44. Hungarian Appl. 3 282; *Chem. Abstr.* **76** 112 689 (1972)
45. R G Guy, I Pearson *Bull. Chem. Soc. Jpn.* **50** 541 (1977)
46. R G Guy, I Pearson *Bull. Chem. Soc. Jpn.* **49** 2310 (1976)
47. W A Kamil, F Haspel-Hentrich, J M Shreeve *Inorg. Chem.* **25** 376 (1986)
48. L Schmerling, J P West *J. Am. Chem. Soc.* **71** 2015 (1949)
49. US P. 3 799 997; *Chem. Abstr.* **80** 132 771 (1974)
50. US P. 3 810 947; *Chem. Abstr.* **81** 25 323 (1974)
51. L Schmerling *J. Org. Chem.* **40** 2430 (1975)
52. US P. 4 005 152; *Chem. Abstr.* **87** 39 007 (1977)
53. US P. 3 998 895; *Chem. Abstr.* **86** 106 155 (1977)
54. BRD Appl. 2 629 868; *Chem. Abstr.* **86** 155 188 (1977)
55. Br. P. 1 532 676; *Chem. Abstr.* **90** 186 329 (1979)
56. Br. P. 1 546 804; *Ref. Zh. Khim.* 23 O 433 (1979)
57. Hung. P. 182 860; *Ref. Zh. Khim.* 4 N 9 (1987)
58. W Hewertson, D Holland, D L Milner *J. Chem. Soc., Perkin Trans. 2* 1062 (1978)
59. D P Johari, H W Sidebottom, J M Tedder, J C Walton *J. Chem. Soc., B* 95 (1971)
60. A Horowitz, G Baruch *Int. J. Chem. Kinet.* **12** 883 (1980)
61. F F Rust, Ch S Bell *J. Am. Chem. Soc.* **92** 5530 (1970)
62. R V Kereselidze, V G Tsitsishvili, E D Lubuzh, D B Razmadze *Izv. Akad. Nauk Gruz. SSR, Ser. Khim.* **16** 152 (1990)
63. G I Nikishin, R V Kereselidze, D B Razmadze, E D Lubuzh, A A Dzamukashvili *Soobshch. Akad. Nauk Gruz. SSR* **134** 325 (1989)
64. F K Velichko, V Ts Kampel', V I Dostovalova, V L Antonovich, V I Bregadze *Metalloorg. Khim.* **4** 39 (1991)
65. S V Komarova, D E Kruglov, E V Pastushenko, in *V Vsesoyuz. Nauch. Konf. "Sovremennoe Sostoyanie i Perspektivy Razvitiya Teoreticheskikh Osnov Proizvodstva Khlororganicheskikh Produktov", Baku, 1991 (Tez. Dokl.)* [The Vth All-Union Scientific Conference "The Current State and Prospects for the Development of the Theoretical Principles of the Production of Organochlorine Derivatives, Baku, 1991 (Abstracts of Reports)] p. 122
66. J-M Chang, R Profetto, J Warkentin *J. Am. Chem. Soc.* **103** 7189 (1981)
67. M I Dyusenov, G I Nikishin, B T Dzhetpisov, in *3 Respublikanskaya Nauch.-Tekhn. Konf. po Neftekhimii Akad. Nauk Kaz. SSR, Gur'ev, 1974 (Tez. Dokl.) T. 1* [The Third All Republic Scientific and Technical Conference on Petrochemistry of the Acad. Sci. Kaz. SSR, Gur'ev, 1974 (Abstracts of Reports) Vol. 1] p. 308
68. Jpn. Appl. 53-21111; *Ref. Zh. Khim.* 4 N 28P (1979)
69. USSR P. 694 486; *Byull. Izobret.* **40** 86 (1979)
70. USSR P. 636 222; *Byull. Izobret.* **45** 79 (1978)
71. Jpn. Appl. 58-140 042; *Ref. Zh. Khim.* 4 N 12P (1985)
72. G I Nikishin, Yu N Ogibin, V N Lebedev *Izv. Akad. Nauk SSSR, Ser. Khim.* 1066 (1971)
73. USSR P. 810 670; *Ref. Zh. Khim.* 4 O 336P (1982)
74. USSR P. 515 732; *Ref. Zh. Khim.* 7 O 339P (1977)
75. M M Guseinov, T A Kambarova, Z K Mekhtieva, Z G Yartseva *Dokl. Akad. Nauk Az. SSR* **22**(8) 38 (1966)
76. M M Guseinov, T A Kambarova, Z K Mekhtieva, M T Dzhafarova *Dokl. Akad. Nauk Az. SSR* **25**(8) 37 (1969)
77. US P. 3 957 891; *Chem. Abstr.* **85** 77 845 (1977)
78. BRD Appl. 2 425 991; *Chem. Abstr.* **84** 121 402 (1976)
79. M Ballester, J Castaner *An. R. Soc. Esp. Fis. Quim.* **66** 487 (1970); *Ref. Zh. Khim.* 23 Zh 70 (1972)
80. BRD Appl. 2 333 650; *Chem. Abstr.* **83** 43 004 (1975)
81. US P. 4 139 721; *Chem. Abstr.* **90** 168 275 (1979)
82. D R Adams, S P Bhatnagar *Synthesis* 661 (1977)
83. BRD Appl. 2 057 057; *Chem. Abstr.* **77** 87 853 (1972)
84. Pol. P. 131 012; *Chem. Abstr.* **110** 192 251 (1989)
85. Fr. P. 2 559 479; *Chem. Abstr.* **104** 206 723 (1986)
86. S J Cristol, B B Jarvis *J. Am. Chem. Soc.* **88** 3095 (1966)
87. DDR P. 93 552; *Ref. Zh. Khim.* 13 O 34P (1975)
88. A N Mirskova, A V Martynov, M G Voronkov *Zh. Org. Khim.* **16** 2076 (1980)
89. USSR P. 690 013; *Byull. Izobret.* **37** 89 (1979)
90. A N Mirskova, A V Martynov, M G Voronkov *Zh. Org. Khim.* **18** 1555 (1982)
91. A V Martynov, A N Mirskova, M G Voronkov *Zh. Org. Khim.* **20** 23 (1984)
92. USSR P. 899 543; *Byull. Izobret.* **3** 98 (1989)
93. A N Mirskova, G G Levkovskaya, T I Drozdova, I D Kalikhman, M G Voronkov *Zh. Org. Khim.* **18** 452 (1982)
94. T I Drozdova, A N Mirskova, G G Levkovskaya, I D Kalikhman, M G Voronkov *Zh. Org. Khim.* **24** 1240 (1988)
95. A N Mirskova, I T Gogoberidze, G G Levkovskaya, M G Voronkov *Zh. Org. Khim.* **20** 2235 (1984)
96. A N Mirskova, G G Levkovskaya, M G Voronkov *Zh. Org. Khim.* **23** 1119 (1987)
97. Ya T Bal'on, V E Paranyuk *Zh. Org. Khim.* **19** 1346 (1983)
98. A N Mirskova, G G Levkovskaya, I T Gogoberidze, T I Drozdova, I D Kalikhman, M G Voronkov *Zh. Org. Khim.* **19** 1110 (1983)
99. M B Taraban, V I Mar'yasova, T V Leshina, A N Mirskova, G G Levkovskaya, T I Drozdova, I T Gogoberidze, M G Voronkov *Zh. Org. Khim.* **22** 925 (1986)
100. A N Mirskova, G G Levkovskaya, I T Gogoberidze, I D Kalikhman, M G Voronkov *Zh. Org. Khim.* **21** 269 (1985)
101. USSR P. 803 361; *Byull. Izobret.* **36** 259 (1987)
102. A N Mirskova, T I Drozdova, G G Levkovskaya, S A Guseva, I D Kalikhman, M G Voronkov *Zh. Org. Khim.* **23** 2184 (1987)
103. A N Mirskova, T I Drozdova, G G Levkovskaya, O B Bannikova, I D Kalikhman, M G Voronkov *Zh. Org. Khim.* **18** 1407 (1982)
104. A N Mirskova, G G Levkovskaya, A A Bryuzgin, T I Drozdova, I D Kalikhman, M G Voronkov *Zh. Org. Khim.* **26** 140 (1990)
105. A A Bryuzgin, G G Levkovskaya, A N Mirskova, I D Kalikhman *Zh. Org. Khim.* **26** 1296 (1990)
106. A N Mirskova, G G Levkovskaya, A A Bryuzgin, I D Kalikhman, M G Voronkov *Zh. Org. Khim.* **22** 2173 (1986)
107. T I Drozdova, A N Mirskova, G G Levkovskaya *Zh. Org. Khim.* **26** 1002 (1990)
108. A N Mirskova, T I Drozdova, G G Levkovskaya, E E Kuznetsova, G S Vavil'chenkova, T A Pushechkina, T I Malkova, S K Suslova, M G Voronkov *Khim.-Farm. Zh.* **16** 1479 (1982)
109. A N Mirskova, T I Drozdova, G G Levkovskaya, I D Kalikhman, M G Voronkov *Zh. Org. Khim.* **22** 763 (1986)
110. I T Gogoberidze, G G Levkovskaya, A N Mirskova, M G Voronkov *Zh. Org. Khim.* **20** 1100 (1984)
111. I T Gogoberidze, G G Levkovskaya, A N Mirskova, I D Kalikhman, O B Bannikov, M G Voronkov *Zh. Org. Khim.* **21** 633 (1985)
112. R Aloni, L A Raibenbach, A Horowitz *J. Organomet. Chem.* **171** 155 (1979)
113. R West, L C Quass *J. Organomet. Chem.* **18** 55 (1969)

114. V D Sheludyakov, V I Zhun', V G Lakhtin, V V Shcherbinin, E A Chernyshev *Zh. Obshch. Khim.* **53** 1192 (1983)
115. V D Sheludyakov, V G Lakhtin, V I Zhun', V V Shcherbinin, E E Chernyshev *Zh. Obshch. Khim.* **51** 1829 (1981)
116. Jpn. Appl. 76-19729; *Chem. Abstr.* **85** 108 761 (1976)
117. C Walling *Free Radicals in Solution* (Translated into Russian; Moscow: Izd. Inostr. Lit., 1960)
118. A Roedig, R Kloss *Chem. Ber.* **90** 2902 (1957)
119. W Miller, W H Stafford, W H Taylor, D Laever, A H McQuillan *J. Chem. Soc.* **4485** (1961)
120. E I Babkina *Zh. Obshch. Khim.* **44** 953 (1974)
121. W J Howard, R E Gilbert *J. Org. Chem.* **27** 2685 (1962)
122. Yu A Ol'dekop, R V Kaberdin, E E Buslovskaya *Zh. Org. Khim.* **17** 272 (1981)
123. R V Kaberdin, V I Potkin *Polikhlor-1,3-butadieny* (Polychlorobuta-1,3-dienes) (Minsk: Nauka i Tekhnika, 1991)
124. R V Kaberdin, V I Potkin, Yu A Ol'dekop *Izv. Akad. Nauk B. SSR, Ser. Khim. Nauk* 105 (1985)
125. V I Potkin, R V Kaberdin, E Yu Dubova, Yu A Ol'dekop *Zh. Org. Khim.* **26** 256 (1990)
126. Yu A Ol'dekop, R V Kaberdin *Zh. Org. Khim.* **12** 2039 (1976)
127. Yu A Ol'dekop, R V Kaberdin, E E Buslovskaya, I A Shingel' *Zh. Org. Khim.* **15** 691 (1979)
128. R V Kaberdin, V I Potkin, Yu A Ol'dekop *Zh. Org. Khim.* **26** 1560 (1990)
129. V I Potkin, R V Kaberdin, Yu A Ol'dekop *Zh. Org. Khim.* **27** 56 (1991)
130. R V Kaberdin, V I Potkin, E Yu Dubova, Yu A Ol'dekop *Zh. Org. Khim.* **24** 1618 (1988)
131. V I Potkin, R V Kaberdin, Yu A Ol'dekop *Zh. Org. Khim.* **22** 1389 (1986)
132. V I Potkin, R V Kaberdin *Zh. Org. Khim.* **29** 56 (1993)
133. V I Potkin, R V Kaberdin, Yu A Ol'dekop *Izv. Akad. Nauk B. SSR, Ser. Khim. Nauk* 57 (1992)
134. French Appl. 2 092 817; *Chem. Abstr.*, **77** 113 785 (1972)
135. USSR P. 626 090; *Byull. Izobret.* **36** 101 (1978)
136. V I Perevalova, E N Deryagina, M G Voronkov *Zh. Org. Khim.* **14** 1557 (1978)
137. F Kaufler *Annalen* **433** 48 (1923)
138. A E Kulikova, N M Pinchuk, E N Zil'berman *Zh. Org. Khim.* **3** 1388 (1967)
139. A E Kulikova, N M Pinchuk, A Ya Lazaris *Zh. Org. Khim.* **9** 861 (1973)
140. M Carrega *Bull. Soc. Chim. Fr.* 4163 (1968)
141. W Weber, I Erden, A De Meijere *Angew. Chem.* **92** 387 (1980)
142. A De Meijere, I Erden, W Weber, D Kaufman *J. Org. Chem.* **53** 152 (1988)
143. O Abou-Teim, M C Goodland, J F W McOmie *J. Chem. Soc., Perkin Trans. 1* 2659 (1983)
144. D N Harp, C Heitner *J. Org. Chem.* **38** 4184 (1973)
145. N P Hacker, J F W McOmie *Tetrahedron* **40** 5249 (1984)
146. Park Seung Ki, Shim Sang Chul *Bull. Korean Chem. Soc.* **8** 27 (1987)
147. H K Al-Ekabi, G A W Derwisch, G Adam, K Schreiber *Tetrahedron* **37** 1741 (1981)
148. T Shimo, K Somekawa, Y Wakikawa, H Uemura, O Tsuge, K Imada, K Natabe *Bull. Chem. Soc. Jpn.* **60** 621 (1987)
149. K Somekawa, R Imai, R Furukido, S Kumamoto *Bull. Chem. Soc. Jpn.* **54** 1112 (1981)
150. S Kumamoto, K Somekawa, H Uemura, T Shimo *Kenkyu Hokoku-Asahi Garasa Kogyo Gijutsu Shoreikai* **41** 185 (1982); *Chem. Abstr.* **99** 139 892 (1983)
151. D Bellus, H Fischer, H Greuter, P Martin *Helv. Chim. Acta* **61** 1784 (1978)
152. M Ballester, J Castaner, J Riera, I Tabernoro *J. Org. Chem.* **51** 1413 (1986)
153. G Nagendrappa *Org. Synth.* **53** 173 (1973)
154. Europ. Appl. 283 719; *Chem. Abstr.* **110** 115 542 (1989)
155. E Lewars, S Siddiqi *J. Org. Chem.* **50** 135 (1985)
156. T Miettinen *Acta Chem. Scand., Ser. B* **32** 359 (1978)
157. S W Tobey, R West *J. Am. Chem. Soc.* **88** 2478 (1966)
158. J Sepiol, R L Soulen *J. Org. Chem.* **40** 3791 (1975)
159. W Weber, A Meijere *Chem. Ber.* **118** 2450 (1985)
160. D Seyferth, C K Haas, D Dagani *J. Organomet. Chem.* **104** 9 (1976)
161. E V Dehmlow *Tetrahedron Lett.* **17** 91 (1976)
162. S K Choi, W K Suk *Bull. Korean Chem. Soc.* **2** 83 (1981)
163. C Glueck, V Poignee, H Schwager *Synthesis* 260 (1987)
164. J S Cloves, W Fliege, R Huisgen *Chem. Ber.* **116** 3062 (1983)
165. E Ott *Berichte* **75** 1517 (1942)
166. J H Wotiz, F Huba, R Vendley *J. Org. Chem.* **26** 1626 (1961)
167. R Reimschneider, K Brendel *Liebigs Ann. Chem.* **640** 1 (1961)
168. J Siegel, R A Jones, L Kurlansik *J. Org. Chem.* **35** 3199 (1970)
169. E Kloster-Jensen *Tetrahedron* **27** 33 (1971)
170. A S Kende, P Fludzinski *Synthesis* 455 (1982)
171. A Jonczyk, A Kwast, M Makosza *J. Org. Chem.* **44** 1192 (1979)
172. J Pielichowski, R Popielarz *Synthesis* 433 (1984)
173. J N Denis, A Moyano, A E Greene *J. Org. Chem.* **52** 3461 (1987)
174. A Sudbo, P A Schulz, E R Grant, Y R Shen, Y T Lee *J. Chem. Phys.* **68** 1306 (1978)
175. C Reiser, E M Lussier, C C Jensen, J I Steinfeld *J. Am. Chem. Soc.* **101** 350 (1979)
176. K Walzer, M Tacke *J. Chem. Phys.* **73** 3045 (1980)
177. US P. 4 165 269; *Chem. Abstr.* **91** 147 811 (1979)
178. K Y Choo, T J Kang, Q Won Choi *Chem. Phys. Lett.* **102** 321 (1983)
179. P Kubat, J Pola *Z. Phys. Chem.* **268** 849 (1987)
180. A E Laird, J K Tyler *J. Chem. Soc., Chem. Commun.* 335 (1978)
181. J S Uppal, R H Staley *J. Am. Chem. Soc.* **102** 4144 (1980)
182. J F Caballero, C Wittig *J. Chem. Phys.* **78** 7169 (1983)
183. A Oku, K Kimura *Chem. Express* **5** 181 (1990)
184. W E Truce, M M Boudakian *J. Am. Chem. Soc.* **78** 2748 (1956)
185. W E Truce, M M Boudakian, R F Heine, R J McManimie *J. Am. Chem. Soc.* **78** 2743 (1956)
186. A Loffler, G Himbert *Synthesis* 495 (1992)
187. Polish P. 96 979; *Chem. Abstr.* **90** 86 709 (1979)
188. J Normant *Bull. Soc. Chim. Fr.* 1876 (1963)
189. S Tanimoto, R Taniyasu, T Takahashi, T Miyake, M Okano *Bull. Chem. Soc. Jpn.* **49** 1931 (1976)
190. US P. 3 937 726; *Chem. Abstr.* **85** 192 415 (1976)
191. J Pielichowski, D Bogdal *Pol. J. Chem.* **62** 483 (1988)
192. W C Kurula *J. Org. Chem.* **30** 3926 (1965)
193. W C Kurula, D G Leis *J. Org. Chem.* **29** 2773 (1964)
194. M A Kesselmayer, P S Sheridan *J. Am. Chem. Soc.* **109** 5029 (1987)
195. A Moyano, F Charbonnier, A Greene *J. Org. Chem.* **52** 2919 (1987)
196. C Almansa, A Moyano, M A Pericas, F Serratosa *Synthesis* 707 (1988)
197. US P. 4 405 514; *Chem. Abstr.* **99** 196 905 (1983)
198. W E Truce, R Kassinger *J. Am. Chem. Soc.* **80** 1916 (1958)
199. M Tiecco, L Testaferri, M Tingoli, D Chianelli, M Montanucci *J. Org. Chem.* **48** 4795 (1983)
200. R Van der Heiden, L Brandsma *Synthesis* 76 (1987)
201. S Y Delavarenne, H G Viehe *Chem. Ber.* **103** 1209 (1970)
202. J Ficini *Tetrahedron* **32** 1 (1976)
203. L Rene, Z Janousek, H G Viehe *Synthesis* 645 (1983)
204. J Pielichowski, D Bogdal *Bull. Pol. Acad. Sci., Chem.* **37** 123 (1989)
205. J Pielichowski, D Bogdal *Liebigs Ann. Chem.* 595 (1988)
206. J Pielichowski, R Popielarz *Tetrahedron* **40** 2671 (1984)
207. J Pielichowski, R Popielarz *Stud. Org. Chem. (Amsterdam)* **18** 225 (1984)
208. J Pielichowski, D Bogdal *Bull. Soc. Chim. Belg.* **100** 561 (1991)
209. M Inoue, S Enomoto *Chem. Lett.* 1231 (1978)
210. M Inoue, S Enomoto *Bull. Chem. Soc. Jpn.* **55** 33 (1982)
211. Jpn. Appl. 82-95952; *Chem. Abstr.* **97** 162 405 (1982)
212. A Collet, J Jacques *Synthesis* 38 (1972)
213. V Ratovelomanana, G Linstrumelle, J F Normant *Tetrahedron Lett.* **26** 2575 (1985)
214. A Minato, K Suzuki, K Tamao *J. Am. Chem. Soc.* **109** 1257 (1987)
215. G Kobrich, K Flory *Chem. Ber.* **99** 1773 (1966)
216. A S Kende, M Benechie, D P Curran, P Fludzinski, W Swenson, J Clardy *Tetrahedron Lett.* **20** 4513 (1979)
217. A S Kende, P Fludzinski *Tetrahedron Lett.* **23** 2369 (1982)
218. A S Kende, P Fludzinski, J H Hill, W Swenson, J Clardy *J. Am. Chem. Soc.* **106** 3551 (1984)
219. A V Martynov, N A Mirskova, M G Voronkov *Zh. Org. Khim.* **21** 2467 (1985)
220. A V Martynov, A N Mirskova, I D Kalikhman, M D Voronkov *Zh. Org. Khim.* **24** 509 (1988)
221. A V Martynov, A N Mirskova, M G Voronkov *Zh. Org. Khim.* **25** 1773 (1989)
222. BRD Appl. 3 111 152; *Chem. Abstr.* **98** 126 378 (1983)

223. Rom. P. 58 033; *Chem. Abstr.* **85** 123 353 (1976)
224. Eur. Appl. 4 496; *Chem. Abstr.* **92** 58 239 (1980)
225. Fr. Appl. 2 420 521 (1980); *Izobret. za Rubezhom* **7** 48 (1980)
226. V Sarca, A Magyari, A Buzasiu, V Szebeni, M Paska *Rev. Chim.* **36** 862 (1985)
227. US P. 3 054 828; *Chem. Abstr.* **58** 3 315 (1963)
228. Jpn. P. 14 002; *Ref. Zh. Khim.* 4 N 599P (1967)
229. French P. 2 094 444; *Ref. Zh. Khim.* 8 N 504P (1973)
230. E Erdman *J. Prakt. Chem.* **85** 78 (1911)
231. V V Saraeva *Okislenie Organicheskikh Soedinenii pod Deistviem Ioniziruyushchikh Izluchenii* (Oxidation of Organic Compounds by the Action of Ionising Radiation) (Moscow: Izd. Mosk. Univ., 1991)
232. Pol. P. 106 693; *Chem. Abstr.* **95** 6 527 (1981)
233. BRD Appl. 2 533 181; *Chem. Abstr.* **84** 164 189 (1976)
234. Rom. P. 78 153; *Chem. Abstr.* **99** 121 837 (1983)
235. Rom. P. 75 601; *Chem. Abstr.* **99** 121 832 (1983)
236. Rom. P. 78 095; *Chem. Abstr.* **99** 121 836 (1983)
237. Rom. P. 77 963; *Chem. Abstr.* **99** 121 834 (1983)
238. Jpn. Appl. 59-48435; *Chem. Abstr.* **101** 9 093 (1984)
239. Jpn. Appl. 63-51352; *Chem. Abstr.* **109** 169 876 (1988)
240. US P. 3 959 367; *Chem. Abstr.* **85** 108 280 (1976)
241. Hung. Appl. 31 631; *Chem. Abstr.* **101** 229 996 (1984)
242. L L McKinney, E H Uhing, J L White *Agric. Food Chem.* **3** 413 (1955)
243. S A Kline, B L van Duuren *J. Heterocycl. Chem.* **14** 455 (1977)
244. V A Poluektov, I V Dobrov, A V Chertorizhskii, Yu Ya Mekhryushev *Khim. Promst. (Moscow)* 197 (1976)
245. I P Shevchuk, O I Makogon, T M Tomashevskii, in *6 Vsesoyuzn. Nauch. Konf. po Okisleniyu Organicheskikh Soedinenii v Zhidkoi Faze, L'vov, 1986 (Tez. Dokl.)* [The Sixth All-Union Scientific Conference on the Liquid-Phase Oxidation of Organic Compounds, Lvov, 1986 (Abstracts of Reports)] p. 27
246. V A Poluektov, Yu Ya Mekhryushev *Zh. Fiz. Khim.* **45** 2338 (1971)
247. E Sanhueza, I C Hisatsune, J Heicklen *Chem. Rev.* **76** 801 (1976)
248. A C Razus, A M Glatz, Zs Arvay, F Iordache, F Baded *Rev. Roum. Chim.* **25** 547 (1980)
249. A L Shevchenko, A Yu Ivanov, G M Ostrovskii, V S Levshanov, I V Dobrov *Zh. Prikl. Khim.* **53** 382 (1980)
250. V A Poluektov, A I Chernyavskii *Neftekhimiya* **18** 558 (1978)
251. V A Poluektov, I V Dobrov, Yu Ya Mekhryushev *Teoriya i Praktika Zhidkofaznogo Okisleniya* (Theory and Practice of Liquid-Phase Oxidation) (Moscow: Nauka, 1974)
252. R V Kucher, V I Timokhin, I P Shevchuk, Ya M Vasyutin *Zhidkofaznoe Okislenie Nepredel'nykh Soedinenii v Okisi Olefinov* (Liquid-Phase Oxidation of Unsaturated Compounds to Olefin Oxides) (Kiev: Naukova Dumka, 1986)
253. E A Blyumberg, T V Filippova, V G Dryuk *Kinetika i Kataliz T. 18 (Ser. Itogi Nauki i Tekhniki)* [Kinetics and Catalysis, Vol. 18 (Ser. Advances in Science and Engineering)] (Moscow: Izd. VINITI, 1988)
254. R V Kucher, R I Flyunt, V I Timokhin *Kinet. Katal.* **28** 979 (1987)
255. R V Kucher, R I Flyunt, Yu A Pazderskii, V I Timokhin, I P Shevchuk, O I Makogon, Ar A Berlin *Dokl. Akad. Nauk SSSR* **309** 875 (1989)
256. G Hyubrechts, L Meyers *Trans. Faraday Soc.* **62** 2191 (1966)
257. E Sanhueza, I C Hisatsune, J Heicklen *Adv. Environ. Sci. Technol.* **8** 155 (1977)
258. R V Kucher, V I Timokhin, N A Kravchuk, A P Pokutsa, R I Flyunt, D S Lutsyk *Neftekhimiya* **27** 661 (1987)
259. R V Kucher, V I Timokhin, A P Pokutsa, R I Flyunt *Neftekhimiya* **28** 701 (1988)
260. R V Kucher, V I Timokhin, R I Flyunt *Dokl. Akad. Nauk SSSR* **305** 134 (1989)
261. R I Flyunt, O I Makogon, in *2 Konf. Molodykh Uchenykh-Khimikov, In-t Fiz.-Org. Khimii i Uglekhimii AN USSR, Donetsk, 1990 (Tez. Dokl.)* [The Second Conference of Young Research Chemists, Inst. Phys.-Org. Chem. and Coal-Chem., Acad. Sci. Ukr. SSR, Donetsk, 1990 (Abstracts of Reports)] p. 196
262. O I Makogon, A P Pokutsa, in *Materialy Nauch. Konf. Molodykh Uchenykh Khim. Fakul'teta Uzhgorodskogo Universiteta, Uzhgorod, 1990* (Proceedings of the Scientific Conference of Young Scientists in the Faculty of Chemistry of Uzhgorod University, Uzhgorod, 1990), p. 18
263. C B C Boyce, S B Webb, L Phillips *J. Chem. Soc., Perkin Trans. 1* 1650 (1974)
264. E Mathias, E Sanhueza, I C Hisatsune, J Heicklen *Can. J. Chem.* **52** 3852 (1974)
265. L A Hull, I C Hisatsune, J Heicklen *Can. J. Chem.* **51** 1504 (1973)
266. B I Tarunin, Yu A Aleksandrov, V N Perepletchikova, N V Baklanov *Kinet. Katal.* **18** 1329 (1977)
267. W A Pryor, D Giamalva, D F Church *J. Am. Chem. Soc.* **105** 6858 (1983)
268. H Niki, P D Maker, C M Savage, L P Breitenbach, R I Martinez, J T Herron *J. Phys. Chem.* **86** 1858 (1982)
269. G M Shakhnazaryan *Arm. Khim. Zh.* **27** 111 (1974)
270. Polish P. 122 341; *Chem. Abstr.* **102** 184 732 (1985)
271. L M Yagupol'skii, V B Milevskaya, G I Matyushecheva *Zh. Org. Khim.* **11** 2580 (1975)
272. M V Gorelik, M V Kazankov, M I Bernadskii *Zh. Org. Khim.* **12** 2041 (1976)
273. K Bott *Angew. Chem.* **79** 943 (1967)
274. K Bott *Tetrahedron Lett.* **9** 4979 (1968)
275. K Bott *Chem. Ber.* **103** 3850 (1970)
276. L Vodička, J Burkhard, J Janku *Collect. Czech. Chem. Commun.* **51** 1086 (1986)
277. Czech. P. 240 246; *Chem. Abstr.* **109** 169 923 (1988)
278. L Vodichka, I Burkkhard, P Zakharzh, S D Isaev, S I Saichenko, A G Yurchenko, I Yanku *Zh. Org. Khim.* **21** 2569 (1985)
279. I V Martynov, Yu L Kruglyak, S P Makarov *Zh. Obshch. Khim.* **33** 3382 (1963)
280. Z G Ovsyannikova, M K Baranaev, V K Kurochkin, T A Vasilevskaya, I V Martynov, Yu L Kruglyak *Zh. Org. Khim.* **4** 1209 (1968)
281. V I Anufriev, I V Martynov *Zh. Prikl. Khim.* **63** 1889 (1990)
282. J Tuaillon, R Perrot *Helv. Chim. Acta* **59** 171 (1976)
283. Y Calvez, J Tuaillon, R Perrot *Helv. Chim. Acta* **57** 1433 (1974)
284. M D Mashkovskii *Lekarstvennye Sredstva. T. 1* (Medicines, Vol. 1) (Minsk, Belarus', 1987)
285. D L Hewer *Cah. Anesthesiol* **24** 163 (1976); *Chem. Abstr.* **85** 13 548 (1976)
286. Jpn. Appl. 76-48436; *Chem. Abstr.* **85** 88 539 (1976)
287. Jpn. Appl. 76-48439; *Chem. Abstr.* **85** 138 606 (1976)
288. Jpn. P. 48-42615; *Ref. Zh. Khim.* 16 N 50P (1974)
289. J M Rosenfeld, S Veroushalmi, E Y Osei-Twum *Anal. Chem.* **58** 3044 (1986)
290. Jpn. Appl. 211 565; *Ref. Zh. Khim.* 6 N 92P (1991)
291. E A Chernyshev, N G Komalenkova, L N Shamshin, I A Shashkov *Zh. Org. Khim.* **55** 2317 (1985)
292. USSR P. 571 486; *Byull. Izobret.* **33** 68 (1979)
293. USSR P. 649 720; *Byull. Izobret.* **8** 87 (1979)
294. W C McNeill, in *Kirk–Othmer Encyclopedia of Chemical Technology* Vol. 5 (Eds M Grayson, D Eckroth) (New York: Wiley, 1979) p. 745
295. *Kratkaya Khimicheskaya Entsiklopediya, T. 5* (A Short Chemical Encyclopedia, Vol. 5) (Ed. I L Knunyants) (Moscow: Sov. Entsiklopediya, 1967)
296. US P. 4 447 424; *Chem. Abstr.* **101** 130 975 (1984)
297. Can. P. 1 199 907; *Chem. Abstr.* **105** 79 225 (1986)
298. M-H Yang, H-E Wang, T-Y Ou, H-Ch Wu *K'o Hsuch Fa Chan Yueh K'an* **9** 251 (1981); *Chem. Abstr.* **95** 61 359 (1981)
299. Br. Appl. 2 121 825; *Chem. Abstr.* **101** 151 677 (1984)
300. G Hoerlein, H Schoenowsky, A Studeneer, P Langelueddeke *Z. Naturforsch., C* **28** 653 (1973)
301. US P. 4 013 452; *Chem. Abstr.* **87** 5 675 (1977)
302. Eur. P. 21 975; *Chem. Abstr.* **107** 134 314 (1987)
303. Jpn. P. 73-03368; *Chem. Abstr.* **80** 824 (1974)
304. Belg. P. 627 096; *Chem. Abstr.* **60** 11 899 (1964)
305. US P. 3 790 683; *Chem. Abstr.* **81** 46 373 (1974)
306. US P. 3 109 032; *Chem. Abstr.* **60** 2 769 (1964)
307. BRD Appl. 2 354 001; *Chem. Abstr.* **83** 98 494 (1975)
308. Jpn. P. 74-02108; *Chem. Abstr.* **81** 151 781 (1974)
309. Jpn. Appl. 62-72707; *Chem. Abstr.* **107** 237 573 (1987)
310. N Freemantle *Chemistry in Action, Part 2* (Translated into Russian; Moscow: Mir, 1991)