Peroxide-Induced Condensation of Olefins and Polychloroethylenes[1]

Louis Schmerling

Universal Oil Products Company, Des Plaines, Illinois 60016

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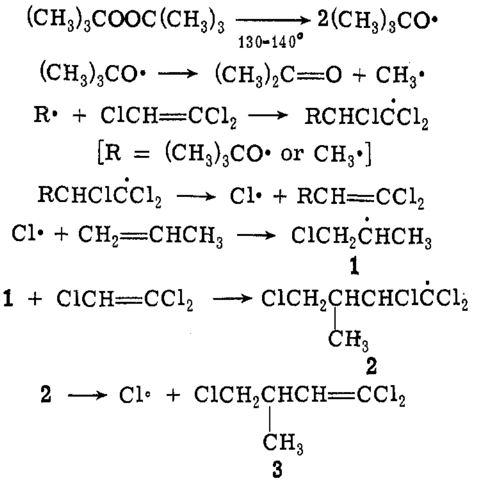
Because a chlorine atom adds to a doubly bonded carbon of an olefin much more readily than it abstracts a hydrogen atom attached to an allylic carbon atom, the peroxide-induced reaction of propene with trichloroethylene yields 1,1,4-trichloro-3-methyl-1-butene (**3**) as the chief primary product rather than 1,1-dichloro-1,4-pentadiene (**6**), the product which would form if the allylic hydrogen atom were involved in a reaction analogous to the formation of (3,3-dichloroallyl)benzene by the peroxide-induced condensation of toluene and trichloroethylene, a reaction which involves chlorine abstraction of a benzylic hydrogen atom. Similarly, the primary products of the condensation of propene with *cis*-dichloroethylene and with tetrachloroethylene are 1,4-dichloro-3-methyl-1-butene (**7**) and 1,1,2,4-tetrachloro-3-methyl-1-butene (**9**), respectively. By-products consist chiefly of the products of the reaction of more than 1 mol of one of the reactants with 1 or more mol of the other. Corresponding products are obtained with other alkenes, for example, 2-pentene or 1-octene, and with cyclohexene. The mechanism of the reaction is discussed.

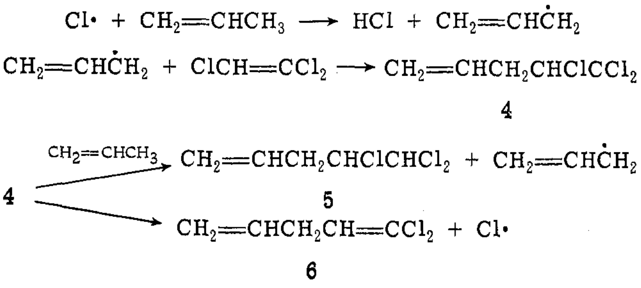
The di-*tert*-butyl peroxide induced reaction of propene with trichloroethylene yields 1,1,4-trichloro-3-methyl-1-butene (**3**) as the chief primary product. Its formation apparently occurs by the following pathway.



$$(CH_3)_3COOC(CH_3)_3 \xrightarrow[130-140°]{} 2(CH_3)_3CO\cdot$$
$$(CH_3)_3CO\cdot \longrightarrow (CH_3)_2C{=}O + CH_3\cdot$$
$$R\cdot + ClCH{=}CCl_2 \longrightarrow RCHCl\dot{C}Cl_2$$
$$[R = (CH_3)_3CO\cdot \text{ or } CH_3\cdot]$$
$$RCHCl\dot{C}Cl_2 \longrightarrow Cl\cdot + RCH{=}CCl_2$$
$$Cl\cdot + CH_2{=}CHCH_3 \longrightarrow \underset{\textbf{1}}{ClCH_2\dot{C}HCH_3}$$
$$\textbf{1} + ClCH{=}CCl_2 \longrightarrow \underset{\textbf{2}}{ClCH_2\underset{CH_3}{\underset{|}{C}}HCHCl\dot{C}Cl_2}$$
$$\textbf{2} \longrightarrow Cl\cdot + \underset{\textbf{3}}{ClCH_2\underset{CH_3}{\underset{|}{C}}HCH{=}CCl_2}$$

The chlorine atom formed in the final step adds to propene to start a new cycle.

It may be concluded that the chain reaction is propagated by a chlorine atom which adds to the double bonds of the olefins and which is eliminated from the product of the condensation of the resulting radical with the trichloroethylene. In the related reaction of toluene with trichloroethylene, the reaction chain is propagated by hydrogen abstraction of a benzylic hydrogen atom from the toluene and subsequent addition of the so-formed benzyl radical to the trichloroethylene, followed by the elimination of a chlorine atom, resulting in the formation of (3,3-dichloroallyl)benzene.[2] Abstraction of an allylic hydrogen atom from propene by a chlorine atom does not occur under the reaction conditions because addition of a chlorine to the doubly bonded carbon atoms of an olefin is a more rapid reaction than is abstraction of hydrogen from an allylic carbon atom. Thus, the relative rates[3] of addition of a chlorine atom at −9° to the double bonds of 1-butene, *cis*-2-butene, and *trans*-2-butene are 11.7, 12.0, and 11.4, respectively (compared to 1.0 for abstraction of a cyclohexane hydrogen). On the same basis, the relative rates of abstraction of allylic hydrogen of atoms at −9° from the butenes are 0.76, 0.60, and 0.69, respectively. Hence, the rates of addition are respectively 15.4, 20.0, and 26.5 times the rates of abstraction. Therefore, the mechanism shown above occurs rather than the following.



$$Cl\cdot + CH_2{=}CHCH_3 \longrightarrow HCl + CH_2{=}CH\dot{C}H_2$$
$$CH_2{=}CH\dot{C}H_2 + ClCH{=}CCl_2 \longrightarrow \underset{\textbf{4}}{CH_2{=}CHCH_2CHCl\dot{C}Cl_2}$$
$$\textbf{4} \xrightarrow{CH_2=CHCH_3} \underset{\textbf{5}}{CH_2{=}CHCH_2CHClCHCl_2} + CH_2{=}CH\dot{C}H_2$$
$$\textbf{4} \longrightarrow \underset{\textbf{6}}{CH_2{=}CHCH_2CH{=}CCl_2} + Cl\cdot$$

Abstraction of allylic hydrogen from propene does occur during the high-temperature (above 200°) chlorination of propene to produce allyl chloride as major product.[5]

In the toluene reaction, the chlorine atom abstracts a benzylic hydrogen[2] more readily than it adds to the aromatic double bond with subsequent loss of a hydrogen atom, an addition which would result in nuclear chlorination.

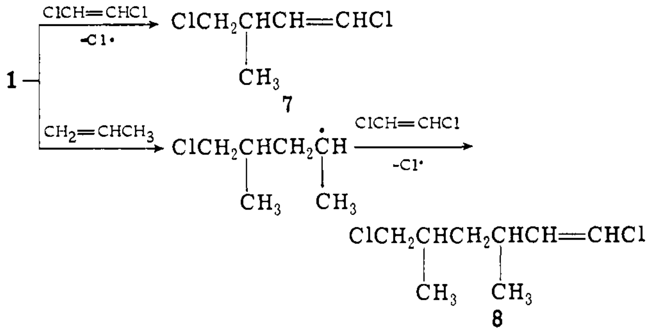
Loss of a chlorine atom from a carbon atom adjacent to the electron-deficient carbon atom of a free radical with resultant formation of a double bond has been observed in many reactions.[4]

That the primary product of the reaction of propene and trichloroethylene was **3** rather than **5** or **6** was suggested by carbon–hydrogen analysis and by the MS, ir, and NMR data. Mass spectrometric analysis of the compound (calcd mol wt 173.5) showed molecular ion peaks at *m/e* 172, 174, 176, and 178 in the correct ratios for three chlorine atoms in the molecule. The major fragmentation was loss of $-CH_2Cl$. The ir spectrum indicated the presence of a methyl group and of a double bond. More definite information was obtained by NMR analysis, utilizing spin decoupling, which was in agreement with the structure **3**.

A complex mixture of higher molecular weight products was also formed by the propene–trichloroethylene reaction; about 35–40% of the reaction product was too high boiling to be distilled by conventional means. It apparently consisted of polycondensation (telomeric) compounds.

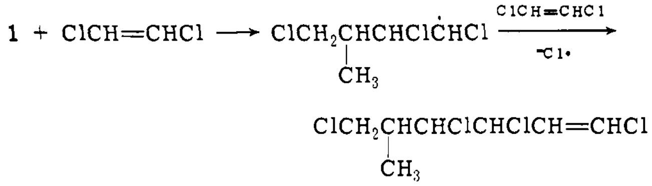
When propene and *cis*-dichloroethylene were heated with di-*tert*-butyl peroxide at 130–140°, the major product was **8**, the product of the reaction of two molecules of the alkene with one of the dichloroethylene; the primary, 1:1, reaction product **7** was formed in minor amount.

Mass spectrographic analysis of material separated from a higher boiling fraction (a complex mixture) suggested that the product of the reaction of two molecular proportions of *cis*-dichloroethylene with one of propene was also formed.



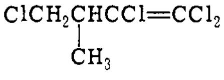
$$1 \xrightarrow[-Cl\cdot]{ClCH=CHCl} \underset{\substack{CH_3\\ 7}}{ClCH_2CHCH=CHCl}$$

$$1 \xrightarrow{CH_2=CHCH_3} \underset{CH_3\quad CH_3}{ClCH_2CHCH_2\dot{C}H} \xrightarrow[-Cl\cdot]{ClCH=CHCl} \underset{\substack{CH_3\quad CH_3\\ 8}}{ClCH_2CHCH_2CHCH=CHCl}$$



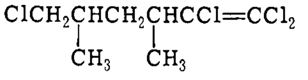
$$1 + ClCH=CHCl \longrightarrow \underset{CH_3}{ClCH_2CHCHCl\dot{C}HCl} \xrightarrow[-Cl\cdot]{ClCH=CHCl} \underset{CH_3}{ClCH_2CHCHClCHClCH=CHCl}$$

The reaction of propene with tetrachloroethylene in the presence of decomposing di-*tert*-butyl peroxide similarly yielded 1,1,2,4-tetrachloro-3-methyl-1-butene (**9**) and 1,1,2,6-tetrachloro-3,5-dimethyl-1-hexene (**10**), the now-to-be-expected products of the condensation of tetrachloroethylene with one and two molar proportions of propene, respectively. A high-boiling fraction was shown by MS analysis to consist chiefly of $C_{11}H_{18}Cl_4$, the product of the condensation of 3 mol of propene with 1 mol of tetrachloroethylene.



$$\underset{CH_3}{ClCH_2CHCCl=CCl_2}$$

9



$$\underset{CH_3\quad CH_3}{ClCH_2CHCH_2CHCCl=CCl_2}$$

10

The thermal reaction of propene with tetrachloroethylene at 590° [6] involved allylic hydrogen abstraction and resulted in the formation of 1,1,2-trichloro-1,4-pentadiene (**11**), formed, it was believed, by the following mechanism.[6]

$$Cl_2C=CCl_2 \longrightarrow Cl_2C=\dot{C}Cl + Cl\cdot$$

$$Cl\cdot + CH_2=CHCH_3 \longrightarrow HCl + CH_2=CH\dot{C}H_2$$

$$CH_2=CH\dot{C}H_2 + Cl_2C=\dot{C}Cl \longrightarrow \underset{11}{CH_2=CHCH_2CCl=CCl_2}$$

The following chain reaction is probably a more plausible mechanism for the formation of **11**.

$$Cl\cdot + CH_2=CHCH_3 \longrightarrow HCl + CH_2=CH\dot{C}H_2$$

$$CH_2=CH\dot{C}H_2 + Cl_2C=CCl_2 \longrightarrow CH_2=CHCH_2CCl_2\dot{C}Cl_2 \longrightarrow 11 + Cl\cdot$$

Other olefins reacted in analogous manner with the polychloroethylenes. Thus, the reaction of trichloroethylene with ethylene in the presence of decomposing di-*tert*-butyl peroxide resulted in the formation of 1,1,4-trichloro-1-butene (**12**) and 1,1,6-trichloro-1-hexene (**13**) together with very much of the higher molecular weight telomers.

The peroxide-induced condensation of ethylene with tetrachloroethylene was reported previously.[7] The investigators state, "Chloroolefins which cannot polymerize can take part in a telomerization reaction with olefins. In this process the chloroolefins function as carrier of the chain reaction and supply end groups to the molecules of the telomers. Among reactions of this type, the telomerization of ethylene with tetrachloroethylene is of considerable interest as a method of synthesizing reactive tetrachloroalkenes containing an even number of carbon atoms in the molecule.

$$CCl_2=CCl_2 + nCH_2=CH_2 \xrightarrow[(e.g., t\text{-}Bu_2O_2)]{initiator} Cl(CH_2CH_2)_nCCl=CCl_2"$$

It was also stated that tetrachloroethylene is a less reactive carrier of the reaction chain than carbon tetrachloride.

It was obviously believed that, of the polychloroethylenes, only tetrachloroethylene could undergo telomeric condensation with ethylene because the others (unlike tetrachloroethylene) readily polymerizes when treated with decomposing peroxide.[8] It was suggested that the reaction chain involved a sequence analogous to that involved in the peroxide-induced reaction of carbon tetrachloride or chloroform with ethylene.

$$Cl_2C=\dot{C}Cl + CH_2=CH_2 \longrightarrow Cl_2C=CClCH_2\dot{C}H_2$$

$$Cl_2C=CCl_2 + Cl_2C=CClCH_2\dot{C}H_2 \longrightarrow Cl_2C=\dot{C}Cl + Cl_2C=CClCH_2CH_2Cl$$

In view of the facts that such a mechanism involves abstraction of chlorine attached to a vinylic carbon atom and that the other polychloroethylenes and other olefins also undergo condensation with each other, it may be concluded that the reaction chain suggested in this paper is more plausible.

Some peroxide-induced reactions, for example the addition of carbon tetrachloride to olefins, occur much more readily with 1-alkenes than with alkenes which have internal double bonds. In the present reaction, trichloroethylene underwent condensation with 2-pentene under the standard conditions to give a 12 mol % yield of 1,1,4-trichloro-3-ethyl-1-pentene and 1,1,4-trichloro-3-methyl-1-hexene (**14**, see Table I), produced via addition of chlorine atoms to 2-pentene to yield two isomeric radicals which reacted to form the isomeric trichloroheptenes, the structures of which were suggested by the MS and NMR spectra.

The reaction of 1-octene with trichloroethylene under the same conditions resulted in a 10 mol % yield of the 1:1 condensation product believed to be 1,1-dichloro-3-(chloromethyl)-1-nonene (**15**), on the basis of the probable mechanism of formation. Compounds formed by condensation of 2 and 3 mol of octene per mole of trichloroethylene were also formed.

1-Octene is sufficiently high boiling to permit carrying out its condensation with trichloroethylene under atmospheric pressure. Heating the reactants with benzoyl peroxide (Table II, expt 8) under reflux (93–100°) for 1.5 hr gave a liquid product shown by GC to contain **15** in about 8 mol % yield. Further heating with two intermittent additions of benzoyl peroxide resulted in increase of the yield to 20 mol % and finally to 32 mol %.

Condensation of cyclohexene with trichloroethylene in the presence of di-*tert*-butyl peroxide at 130–140° yielded 17 mol % of 1-(2,2-dichlorovinyl)-2-chlorocyclohexene (**16**)

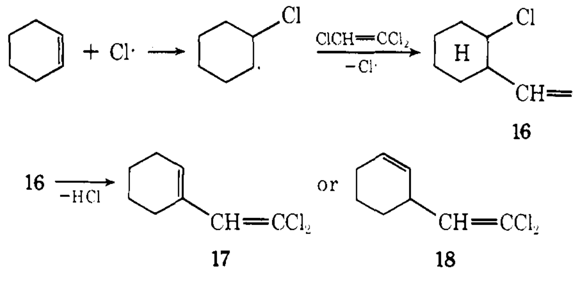


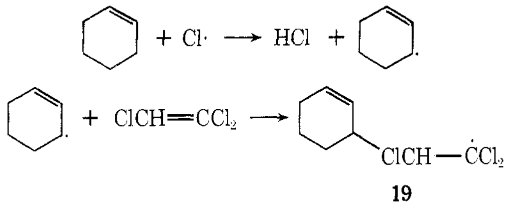
Table I
Properties of the Polychloroalkenes

Compd	Formula	Bp, °C	mm	Bp at 760 mm, °C[a]	Anal., %[b]			
					Calcd		Found	
					C	H	C	H
3	$ClCH_2CHMeCH{=\!=}CCl_2$	59	9.4	178	34.62	4.07	35.01	4.03
7	$ClCH_2CHMeCH{=\!=}CHCl$[c]	37–91	41	110–180	43.20	5.80	45.47	6.34
8	$ClCH_2CHMeCH_2CHMeCH{=\!=}CHCl$	110–111	41	201–202	53.06	7.79	52.74	7.52
9	$ClCH_2CHMeCCl{=\!=}CCl_2$	79	9.8	202	28.88	2.91	29.52	3.06
10	$ClCH_2CHMeCH_2CHMeCCl{=\!=}CCl_2$	66	0.5	244	38.43	4.84	38.85	4.85
12	$ClCH_2CH_2CH{=\!=}CCl_2$	60–68	14.0	170–179	30.13	3.16	30.80	3.30
13	$ClCH_2(CH_2)_3CH{=\!=}CCl_2$	89–116	12.5	207–238	38.43	4.84	38.26	4.66
14	$CH_3CHClCHEtCH{=\!=}CCl_2$[d]	81	9.8	207	42.70	5.66	41.71	5.50
15	$ClCH_2CHHexCH{=\!=}CCl_2$	77	0.4	263	49.30	6.98	49.87	7.00
16	$ClC_6H_{10}CH{=\!=}CCl_2$	103	9.3	232	45.00	5.19	46.23	5.20
17 + 18	$C_6H_9CH{=\!=}CCl_2$	76	9.8	199	54.26	5.69	54.27	5.78

[a] Calculated from boiling point under reduced pressure using nomograph prepared for hydrocarbon boiling point conversions: S. B. Lippincott and M. M. Lyman, *Ind. Eng. Chem.*, 38, 320 (1946). [b] The analysis of several of the compounds does not agree with the calculated values because the compounds (as shown by GC) are contaminated with impurities which could not readily be separated. [c] Structure of small sample isolated by preparative GLC from fraction shown was determined by MS, NMR, and/or ir. [d] Mixed with $CH_3CH_2CHClCHMeCH{=\!=}CCl_2$.

and its dehydrochlorination product, a mixture of 1-(2,2-dichlorovinyl)cyclohexene (**17**) and 3-(2,2-dichlorovinyl)cyclohexene (**18**).

The dichlorovinylcyclohexene mixture consisted (according to NMR analysis) of about 15% of **17** and 85% of **18**. It might have been expected that it would contain more **17** than **18**, since the hydrogen atom attached to the tertiary allylic carbon atom in **16** would be expected to be more readily eliminated to form hydrogen chloride than would a hydrogen attached to a secondary carbon atom. Formation of more **18** than **17** indicates that abstraction of an allylic hydrogen by a chlorine atom competed with the above chlorine-addition reaction.



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$$\mathbf{19} \longrightarrow \mathbf{18} + Cl\cdot$$

Such allylic hydrogen abstraction occurs with cyclohexene (but not with alkenes) because the relative rate (at 77.8°) for abstraction of an allylic hydrogen by a trichloromethyl radical as compared to addition of the radical to a doubly bonded carbon is 0.83 for cyclohexene and only 0.029 for *cis*-2-butene.[9]

As with the 1-octene, heating cyclohexene and trichloroethylene under reflux with benzoyl peroxide added in small batches resulted in a continuously increasing yield of **16** to about 19 mol % after five additions of the peroxide and 13 hr of reflux.

While 1,2-dichloroethylene reacts with toluene in the presence of decomposing peroxides to yield (3-chloroallyl)benzene,[2] the analogous reaction with 1,2-dibromoethylene does not occur, apparently because the intermediate bromine atoms (or bromine-containing intermediate radicals) do not abstract hydrogen from the toluene side chain to maintain the reaction chain. In the present reaction the intermediate chlorine atoms add to double bonds, and it therefore seemed possible that bromine atoms formed during the reaction of polybromoethylenes might maintain the chain and yield brominated condensation compounds. However, very little reaction occurred when either 1,2-dibromoethylene or tribromoethylene was heated with propene and di-*tert*-butyl peroxide at 130–140°. Most of each of the polybromoethylenes was recovered unchanged. It seems necessary to conclude that steric factors are involved which prevent the addition of bromoalkyl radicals to the polybromoethylenes.

Experimental Section

The di-*tert*-butyl peroxide experiments were carried out in glass liners in an Ipatieff-type rotating autoclave of 850 ml capacity. The normally liquid olefin, the polychloroethylene, and the peroxide (amounts shown in Table II) were weighed into the glass liner which was then sealed into the autoclave and nitrogen was added to a pressure of 30 atm. Condensible gaseous olefins were added by volume from a calibrated Jerguson gage before adding the nitrogen. The autoclave was rotated and heated at 130–140° for 4 hr. It was allowed to cool to room temperature overnight, the pressure was released, and the autoclave was opened. The product was worked up by distillation and characterized by preparative gas chromatography (GC) as discussed below. While it was often not possible to isolate pure products for ultimate (C and H) analysis by distillation, pure samples for characterization were obtained by preparative GC.

When benzoyl peroxide was used, the reactants were heated under reflux in a mercury-sealed stirred glass flask, the peroxide being added intermittently (with intermediate cooling to permit GC analysis of the product) as indicated in Table II.

While the identity of one of the products (**15** formed from 1-octene and trichloroethylene) was suggested on the basis of the mechanism, the structures of the remainder were confirmed by ir (Beckman IR-9), NMR (Varian A-60), and/or MS (CEC, Model 103C) analysis of material separated by preparative GC (Varian Aerograph Autoprep).[10] The specimen was passed through 5- or 10-ft columns containing 20% Carbowax 20M on Chromosorb A; the initial temperature was 70° and was programmed to 220° at 10°/min, using a helium flow rate of 75 ml/min. In many cases quite pure samples for characterization were isolated by fractional distillation (see below).

Trichloroethylene and Propene. Product boiling at 59° (4.4 mm) was examined by ir, MS, and NMR. Ir showed the presence of a methyl group and of a double bond. MS showed molecular ion peaks at *m/e* 172, 174, 176, and 178 in the correct ratios for three chlorine atoms in the molecule; the major fragmentation included *m/e* 123, 125, and 127 due to loss of CH_2Cl, and *m/e* 85 and 87 due to loss of CH_2Cl and HCl. The presence of traces of a higher homolog (M + 42) was apparent. More conclusive information was obtained by NMR analysis utilizing spin decoupling. It was found that the doublets at δ 3.49 and 1.13, even though they exhibited the same coupling constant, were not interacting with each other. The spin-decoupling experiments revealed that the doublets at δ

Table II
Condensation of Polychloroethylenes with Olefins

	Reactants					Chief Products			
Expt	Chloroethylene	Mol	Olefin	Mol	*t*-Bu_2O_2, mol	Kind	g	Mol	%
1	$C_2H_2Cl_2$[b]	0.97	C_3H_6	1.2	0.05	**7**	2[a]	0.01	1
						8	8	0.04	7
						Higher bp	10		
2	C_2HCl_3	1.17	C_3H_6	1.2	0.06	**3**	32	0.18	16
						Higher bp	75		
3	C_2Cl_4	0.90	C_3H_6	1.2	0.06	**9**	12	0.058	6
						10	18	0.072	12
						Higher bp	16		
4	C_2HCl_3	1.15	C_2H_4	1.5	0.06	**12**	6	0.04	4
						13	4	0.02	3
						Higher bp	30		
5	C_2HCl_3	0.71	2-C_5H_{12}	0.82	0.06	**14**	17	0.085	12
						Higher bp	16		
6	C_2HCl_3	0.68	1-C_8H_{16}	0.88	0.10	**15**	17	0.070	10
						Higher bp	48[c]		
7	C_2HCl_3	0.38	1-C_8H_{16}	0.22	0.03[d]	**15**	17[a]	0.070	32
8	C_2HCl_3	1.03	c-C_6H_{10}	0.77	0.04	**17** + **18**	12	0.068	9
						16	14	0.060	8
						Higher bp	10		
9	C_2HCl_3	0.49	c-C_6H_{10}	0.37	0.05[e]	**16**	16[a]	0.07	19

[a] Estimated by GLC; separated and characterized by preparative GLC plus MS, NMR, and/or ir. [b] *cis*-Dichloroethylene. [c] Includes fractions boiling at 139–141° (1.1 mm) [326–327° (760 mm)] and 147–151° (1.2 mm) (333–337°), elemental analysis of which suggested that they consisted of $C_{18}H_{33}Cl_3$ and $C_{26}H_{49}Cl_3$, respectively, mixed with minor amounts of other compounds. [d] Benzoyl peroxide added in three portions: 1 g at beginning of experiment; 2 g more after 1.5 hr refluxing; 3 g more after 2.5 hr more refluxing; reflux continued for 3 hr. [e] Benzoyl peroxide added in five portions: 2 g at beginning; 2 g after 12 hr; 2 g after 2 hr; 3 g after 4 hr; and 3 g after 2 hr followed by an additional 3 hr heating.

5.80, 3.49, and 1.13 were all coupling with a multiplet centered between δ 2.99 and 2.93. The nature of the multiplet was difficult to determine from the spectrum, but knowing the number of protons of each type which were coupling and the coupling constants from first-order rules, it was concluded that the multiplet was a sextet of doublets. The number of protons found were one attached to a doubly bonded carbon atom, two attached to a carbon atom holding a chlorine atom, one attached to a saturated tertiary carbon atom, and three constituting a methyl group. It was concluded that **3** was 1,1,4-trichloro-3-methyl-1-butene.

***cis*-Dichloroethylene and Propene.** A fraction boiling at 108–110° (41 mm) showed a major GC peak and two minor peaks. The MS of the major peak had molecular ions at *m/e* 180 and 182. Major fragmentation was M − Cl (*m/e* 145), M − CH_3 (*m/e* 165), and M − 2Cl (*m/e* 109). These data agree with the structure, 1,6-dichloro-3,5-dimethyl-1-hexene, proposed for **8**.

One of the minor GC peaks had molecular ion peaks at *m/e* 138 and 140 in the ratio for two chlorine atoms per molecule. Major fragments were M − Cl (*m/e* 103, 105), M − CH_3 (*m/e* 123, 125), M − HCl (*m/e* 102, 104), and M − CH_3Cl (*m/e* 89, 91). A possible structure is 1,4-dichloro-3-methyl-1-butene (**7**).

The other minor peak (*m/e* 256) contained oxygen but no chlorine. It was not identified.

Tetrachloroethylene and Propene. The MS of a fraction boiling at 79° (9.8 mm) had molecular ion peaks at *m/e* 206, 208, 210, 212, and 214 in the proper ratio for four chlorine atoms per molecule. Major fragment ions were at *m/e* 157, 159, 161, and 163 (M − CH_2Cl) in the ratio for three chlorine atoms per molecule at *m/e* 191, 193, 195, 197, 199 (M − CH_3) and at *m/e* 171, 173, 175, 177 (M − Cl). These data suggest that **9** is 1,1,2,4-tetrachloro-3-methyl-1-butene.

The spectrum of the fraction boiling at 66° (0.5 mm) had molecular ion peaks at *m/e* 248, 250, 252, 254, and 256, indicating four chlorine atoms per molecules. Fragment ion peaks were at *m/e* 213, 215, 217, and 219 (M − Cl); they were also seen at M − CH_3, M − CH_2Cl, and M − ClC_4H_8. It may be concluded that **10** is 1,1,2,6-tetrachloro-3,5-dimethyl-1-hexene.

Trichloroethylene and Ethylene. The product was an unusually complex mixture. One GC peak showed molecular ion peaks at *m/e* 158, 160, 162, and 164, the ratio of the peaks indicating three chlorine atoms per molecule. The major fragment ion peaks were *m/e* 109, 111, and 113 (M − CH_2Cl). Other fragment and rearrangement ion peaks were at *m/e* 121, 122, 123, 124 (M − Cl and M − HCl) and at *m/e* 96 and 98 (M − CH_2CH_2Cl). The most probable structure suggested by these data is 1,1,4-trichloro-1-butene (**12**).

Another GC peak had molecular ion peaks at *m/e* 186, 188, 190, and 192 in the proper ratio for three chlorine atoms per molecule. The most intense fragment ion peak was *m/e* 109 (M − CH_2CHCH_2Cl). Rearrangement ion peaks were seen at *m/e* 122, 124 (M − CH_2CH_2Cl) and 96, 98 ($CH_2CH_2CH_2CH_2Cl$) and fragment ion peaks at *m/e* 35 and 36 (Cl and HCl). A compound which fits these data is 1,1,6-trichloro-1-hexene (**13**).

Trichloroethylene and 2-Pentene. The mass spectrum of material boiling at 79–81° (9.8 mm) showed three groups of ion peaks: (1) *m/e* 164, 166, 168; (2) *m/e* 200, 202, 204, 206; and (3) *m/e* 224, 226, 228, 230, 232. Each compound lost chlorine to give M − 35.

The compound of *m/e* 200–206 (**14**) also lost CH_3CH_2. It apparently was 1,1,4-trichloro-3-ethyl-1-pentene mixed with 1,1,4-trichloro-3-methyl-1-hexene. It underwent dehydrochlorination to produce the compounds of *m/e* 164–168, presumably 1,1-dichloro-3-ethyl-1,3-pentadiene and the methylhexadiene isomer; it is possible that the dehydrochlorination occurred during the MS analysis because of the presence of a hydrogen atom attached to an allylic tertiary carbon atom which was adjacent to a secondary carbon atom holding a chlorine atom.

The NMR spectrum of the fraction showed the presence of an internal olefinic proton, two different methine protons, two methyl groups, and a methylene group. These features are common to $CH_3CHClCH(C_2H_5)CH{=}CCl_2$ and to $C_2H_5CHClCH(CH_3)CH{=}CCl_2$, the structures suggested by MS. No evidence for the chloroalkadienes suggested by MS was seen by NMR; they may have been present in low concentration beyond the detection limit of the NMR method, or they may have been formed during the MS analysis.

Trichloroethylene and Cyclohexene. The NMR spectrum of **16** was consistent with the structure of 2-chloro-1-(2,2-dichlorovinyl)cyclohexane. A doublet at δ 5.75 confirmed the presence of vinylic hydrogen ($HC{-}CH{=}CCl_2$) and a multiplet at a chemical shift of δ 3.65 showed a hydrogen atom in HCCl while a multiplet at δ 3.0–1.0 showed nine hydrogen atoms in the cyclohexane ring. The ir spectrum confirmed a cyclohexylalkenyl chloride. Absorptions at 700–950 cm^{-1} indicated a double bond and C–Cl; at 1450 cm^{-1}, a cyclohexane ring; and at 1625 cm^{-1}, a double bond. The absence of a band at 1375 cm^{-1} showed absence of a methyl radical.

The MS of a lower boiling fraction [76° (9.8 mm)] showed molecular tions at *m/e* 176, 178, and 180 in the ratios corresponding to two chlorine atoms. The data correspond to $C_8H_{10}Cl_2$. The ir spectrum showed strong bands at 650–750 cm^{-1} for C–Cl stretch and strong bands at 800–1000 cm^{-1} for C–Cl stretch and olefin. Two bands were observed in the C=C stretch region. No methyl was indicated at 1380 cm^{-1} while CH_2 bonding was observed at 1450 cm^{-1}. On the assumption that the product consisted of two isomers (**17** and **18**), the NMR integrals were consistent with **18** as the major component. NMR spin decoupling revealed that the doublet δ 5.75 was coupling with the proton at δ 3.18. The integral was then found to be consistent with 85% **18** and 15% **17**.

Registry No.—**3**, 22118-81-6; **7**, 52890-15-0; **8**, 55681-91-9; **9**, 55681-92-0; **10**, 55681-93-1; **12**, 17219-57-7; **13**, 55681-94-2; **14**, 52026-52-5; **15**, 51951-45-2; **16**, 55681-95-3; **17**, 52026-53-6; **18**, 22024-03-9; *cis*-dichoroethylene, 156-59-2; trichloroethylene, 79-01-6; tetrachloroethylene, 127-18-4; propene, 115-07-1; ethylene, 74-85-1; 2-pentene, 109-68-2; 1-octene, 111-66-0; cyclohexene, 110-83-8.

Supplementary Material Available. Additional ir, MS, and NMR data for compounds **3**, **9**, **10**, **14**, **16**, **17**, and **18** will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036. Remit check or money order for $4.50 for photocopy or $2.50 for microfiche, referring to code number JOC-75-2430.

References and Notes

(1) Presented before the Division of Organic Chemistry at the 162nd National Meeting of the American Chemical Society, Washington, D.C., Sept 1971. The reaction is described in L. Schmerling, U.S. Patent 3,406,210 (Oct 15, 1968). The structures of the products presented in the patent have since been found to be erroneous; the correct structures are presented in this paper.

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(10) See paragraph at end of paper regarding supplementary material.

Photochemistry of Alkenes. IV. Vicinally Unsymmetrical Olefins in Hydroxylic Media[1]

Harold G. Fravel, Jr., and Paul J. Kropp*[2]

Department of Chemistry, University of North Carolina, Chapel Hill, North Carolina 27514

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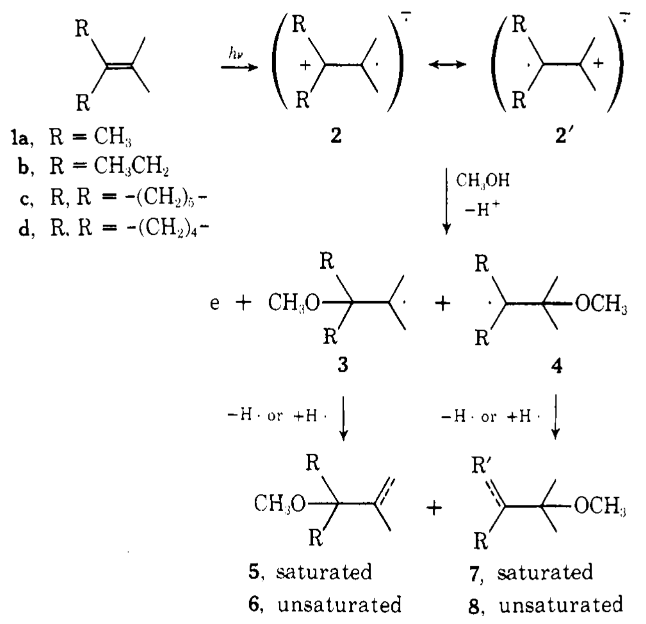
The photochemical behavior of the vicinally unsymmetrical tetrasubstituted olefins **1b–d** in methanol was studied. Each olefin afforded a mixture of saturated and unsaturated ethers **5–8** and hydrocarbons **11–13**. There was no strong dominance in the direction of nucleophilic attack on the excited states from olefins **1b–d**. Isopropylidenenorbornane (**14**) afforded a complex mixture, with the ether **15** and 2-*endo*-isopropylnorbornane (**16**) as the major products. Evidence for the presence of ejected electrons was obtained using sulfur hexafluoride as an electron trap.

In contrast to the triplet manifold of simple alkenes, in which just one excited state (π,π*) is clearly low lying, there are two, and possibly three, excited states in the singlet manifold which are low lying and close in energy. Assignment of two of these as π,π* and π,R(3s) is now widely accepted,[3] and the presence of a π,σ* state of similar energy has also been proposed.[3b] Studies in these laboratories have been directed toward elucidating the *chemical* properties of these excited states and the effects of structure and environment on their reactivities.

Scheme I



It has recently been reported from these laboratories that tri- and, particularly, tetrasubstituted alkenes exhibit novel photochemical behavior which appears to involve the π,R(3s) Rydberg excited state.[1,4] This state arises from promotion of one of the π electrons to a large molecular orbital similar in size and shape to a 3s atomic orbital. As depicted by **2** and **2′**, this process generates radical cation character in the π core of the molecule. In the case of 2,3-dimethyl-2-butene (**1a**) the excited state **2a** is trapped nucleophilically in hydroxylic media to afford a mixture of saturated and unsaturated ethers, as exemplified in Scheme I.[4] This reaction is of mechanistic interest, as it represents one of the first observations of the chemical behavior of the π,R(3s) excited state in solution. Little is known about the π,R(3s) state, including the important question of whether in vicinally unsymmetrical systems there are differences in electron density and, hence, reactivity at the two termini of the radical cation core. The ex-