thol).[6] Although no definite product of the reduction could be either isolated or identified, a black and obviously impure material could be extracted from the recovered *m*-dinitrobenzene with 10% aqueous hydrogen chloride, and then precipitated from the extract by the addition of a base.

The solutions of *m*-dinitrobenzene in hydrazine and in ethylenediamine were found to be unstable at room temperature since the colors, which were initially formed, soon faded. The natures of the decompositions were not studied, however, and no electrolyses in these solvents were carried out.

Summary

Contrary to the report of Field, Garner and Smith, the electrolysis of *m*-dinitrobenzene in liquid ammonia gives hydrogen at the cathode and nitrogen at the anode. The nitro compound is also partially reduced. It is therefore probable that such a solution contains an *ammonium* salt. A reasonable structure for the anion is suggested.

CHICAGO 37, ILLINOIS RECEIVED JANUARY 20, 1949

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[6] R. L. Shriner and R. C. Fuson, "The Systematic Identification of Organic Compounds," John Wiley and Sons, New York, N. Y., 2nd edition, 1940, pp. 50f.

[CONTRIBUTION FROM THE RESEARCH AND DEVELOPMENT LABORATORIES, UNIVERSAL OIL PRODUCTS COMPANY]

Peroxide-induced Condensation of Saturated Hydrocarbons with Polychloroethylenes

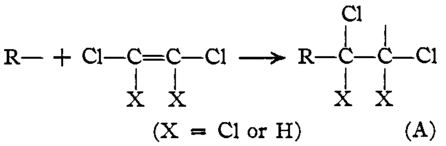
BY LOUIS SCHMERLING AND JAMES P. WEST

Chlorovinylation of saturated hydrocarbons by polychloroölefins occurs when the reactants are heated with a catalytic amount of an organic peroxide at a temperature at least as high as the decomposition temperature of the peroxide. The chain reaction which is involved in this reaction may be indicated as

(1) $\mathrm{R'OOR'} \longrightarrow \mathrm{2R'O—}$ (*e. g.*, $\mathrm{R'} = t\text{-}\mathrm{C_4H_9}$ or $\mathrm{C_6H_5CO}$)

(2) $\mathrm{R'O— + RH \longrightarrow R— + R'OH}$

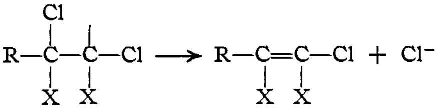
(3)



$$\mathrm{R— + Cl{-}\underset{X}{\underset{|}{C}}{=}\underset{X}{\underset{|}{C}}{-}Cl \longrightarrow R{-}\overset{Cl}{\overset{|}{\underset{X}{\underset{|}{C}}}}{-}\overset{|}{\underset{X}{\underset{|}{C}}}{-}Cl}$$

(X = Cl or H) (A)

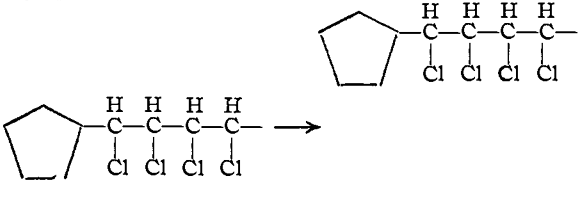
(4)

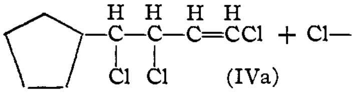


$$\mathrm{R{-}\overset{Cl}{\overset{|}{\underset{X}{\underset{|}{C}}}}{-}\overset{|}{\underset{X}{\underset{|}{C}}}{-}Cl \longrightarrow R{-}\underset{X}{\underset{|}{C}}{=}\underset{X}{\underset{|}{C}}{-}Cl + Cl^-}$$

(5) $\mathrm{Cl— + RH \longrightarrow R— + HCl}$

The alkyl radical formed as in step 5 begins a new cycle as in step 3. The radical (A) may lose a chlorine atom as in step 4 or it may add to a second molecule of the polychloroethylene to yield high-boiling products. Such high-boiling products were actually obtained but were not investigated except in the case of the reaction of cyclopentane with *trans*-dichloroethylene (expt. 6)





(IVa)

Not only isoparaffins but also *n*-paraffins undergo the condensation reaction. Even propane may be employed: 1,1-dichloro-3-methyl-1-butene and 1,1,2-trichloro-3-methyl-1-butene, respectively, may be prepared in quite satisfactory yields by the reaction of this paraffin with tri- and tetrachloroethylene. The products seem to contain more or less of the products involving the intermediate formation of the *n*-propyl radical.

Cycloparaffins behave similarly. Those which were investigated include cyclopentane, cyclohexane and methylcyclohexane.

Data for the various experiments are summarized in Table I. The best yields of chloroölefin based on the peroxide were about 5 or 6 moles per mole of peroxide charged. Since each mole of peroxide theoretically furnished 2 moles of initiating radicals, it may be concluded that the longest reaction chains involved about three cycles. Longer chains could probably have been obtained by more efficient utilization of the peroxide, for example, by adding it to the reaction mixture gradually. This is indicated by the fact that the reaction of methylcyclohexane with trichloroethylene in the presence of 0.005, 0.015 and 0.046 mole, respectively, of *t*-butyl perbenzoate at 115° resulted in the formation of 6.2, 4.7 and 1.8 moles of (dichlorovinyl)-methylcyclohexane per mole of peroxide; on the other hand, the actual yields of product based on the trichloroethylene were, respectively, 10, 23 and 28%. The decrease in chain length with increase in the concentration of peroxide seems to indicate that one of the chain-terminating reactions involved is hydrogen (or chlorine) transfer between the condensation intermediates (A) to yield a saturated and an unsaturated compound. "Dimerization" of these radicals may also occur.

TABLE I

CONDENSATION OF SATURATED HYDROCARBONS WITH CHLOROETHYLENES

Expt.	Reactants					Temp., °C.	Chief product				Higher boiling prod., g.
	Hydrocarbon		Chloro-olefin, moles	Peroxide				Yield		Moles Mole R_2O_2	
	Kind	Moles		Kind[a]	Moles		Compd.	Moles	%		
				Hydrocarbon plus 1,2-Dichloroethylene							
1	C_3H_8	2.5	0.67[b]	Bu_2O_2	0.055	130–135	I	0.07	10	1.3	2
2	*i*-C_4H_{10}	2.9	.62[c]	Bu_2O_2	.055	130–134	II	.22	35	4.0	8
3	*i*-C_4H_{10}	2.6	.52[d]	Bu_2O_2	.055	130–140	II	.20	38	3.6	11
4	*i*-C_4H_{10}	1.3	.62[d]	BzO_2Bu	.026	114–116	II	.13	21	5.0	18
5	*n*-C_5H_{12}	1.5	.69[b]	Bu_2O_2	.027	130–137	III	.05	7	1.9	..
6	*c*-C_5H_{10}	1.4	1.03[d]	Bu_2O_2	.172	130–140	IV	.17	17	1.0	
							IVa	.05	10	0.3	22
7	*c*-C_6H_{12}	1.0	0.52[b]	Bu_2O_2	.055	130–140	V	.10	19	1.8	13
8	None	0.0	.31[b]	Bu_2O_2	.027	130–140	XIV	.05	32	1.9	6
				Hydrocarbon plus Trichloroethylene							
9	C_3H_8	2.6	.46	Bu_2O_2	.055	133–137	VI	0.14	31	2.5	13
10	*i*-C_4H_{10}	1.9	.46	Bu_2O_2	.055	130–134	VII	.21	46	3.8	15
11	C_6H_{14}[e]	0.5	.50	Bu_2O_2	.027	135–138	VIII	.03	6	1.1	12
12	C_6H_{14}[f]	1.0	1.00	Bu_2O_2	.110	130–140	IX	.13	13	1.2	23
13	*c*-C_6H_{12}	0.5	0.49	Bu_2O_2	.055	130–140	X	.11	23	2.0	19
14	*c*-C_7H_{14}[g]	.5	.30	BzO_2Bu	.005	112–116	XI	.031	10	6.2	3
15	*c*-C_7H_{14}[g]	.5	.31	BzO_2Bu	.015	112–114	XI	.071	23	4.7	12
16	*c*-C_7H_{14}[g]	.5	.30	BzO_2Bu	.046	112–115	XI	.083	28	1.8	13
17	*c*-C_7H_{14}[g]	.5	.30	BzO_2Bu	.015	160–160	XI	.052	17	3.5	5
18	*c*-C_7H_{14}[g]	.5	.30[h]	BzO_2Bu	.015	110–114	XI	.096	32	6.4	14
19	None	.0	.38	Bu_2O_2	.027	133–137	XV	.091	49	3.4	4
				Hydrocarbon plus Tetrachloroethylene							
20	C_3H_8	2.3	.31	Bu_2O_2	.027	130–136	XII	.085	27	3.1	4
21	*i*-C_4H_{10}	2.7	.45	Bu_2O_2	.055	132–138	XIII	.032	7	0.6	1
22	None	0.0	.24	Bu_2O_2	.027	130–135	..	Little reaction			

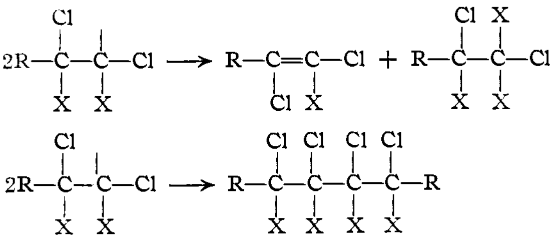
[a] Bu_2O_2 = di-*t*-butyl peroxide; BzO_2Bu = *t*-butyl perbenzoate. [b] Mixture of *cis*- and *trans*-dichloroethylene. [c] *cis*-Dichloroethylene. [d] *trans*-Dichloroethylene. [e] 2,2-Dimethylbutane. [f] 2,3-Dimethylbutane. [g] Methylcyclohexane. [h] Also 100 g. water.

TABLE II

PROPERTIES OF THE CONDENSATION PRODUCTS

Compd.	Formula[a]	B. p.		B. p. at 760 mm., °C.[b]	n^{20}_D	Analyses,[c] %					
						Calcd.			Found		
		°C.	Mm.			C	H	Cl	C	H	Cl
I	$C_3H_7CH{=}CHCl$[d]	86–88	726	.....	1.4229						
II	$(CH_3)_3CCH{=}CHCl$[e]	104–107	750	.....	1.4280						
III	$C_5H_{11}CH{=}CHCl$	60–62	61	133–135	1.4333	63.37	9.88	26.75	62.27	9.79	28.53
IV	*c*-$C_5H_9CH{=}CHCl$	63–64	29	154–155	1.4740[f]	64.35	8.49	27.16	63.75	8.48	28.14
IVa	*c*-$C_5H_9CHClCHClCH{=}CHCl$	53–55	2	205–208	1.4912[g]	47.50	5.76	46.74	46.55	6.50	46.84
V	*c*-$C_6H_{11}CH{=}CHCl$	69–71	21	174–176	1.4778	66.41	9.08	24.51	65.55	9.15	25.33
VI	$(CH_3)_2CHCH{=}CCl_2$[h]	58–58	96	119–119	1.4452	43.19	5.80	51.01	43.12	5.97	50.53
VII	$(CH_3)_3CCH{=}CCl_2$[h]	134–135	726	.....	1.4550						
VIII	$C_6H_{13}CH{=}CCl_2$	29–31	2	184–186	1.4650						
IX	$C_6H_{13}CH{=}CCl_2$	26–27	1	187–189	1.4688	53.03	7.79	39.18	53.19	7.70	39.40
X	*c*-$C_6H_{11}CH{=}CCl_2$[h]	37–38	1.5	200–201	1.4970	53.63	6.76	39.61	53.74	6.44	40.03
XI	*c*-$C_6H_{10}(CH_3)CH{=}CCl_2$	74–75	3	223–224	1.4928	55.95	7.31	36.74	56.04	7.05	36.60
XII	$(CH_3)_2CHCCl{=}CCl_2$	149–151	756	.....	1.4783						
XIII	$(CH_3)_3CCCl{=}CCl_2$	47–48	4	183–184	1.4878	38.41	4.84	56.15	38.38	4.62	56.76
XIV	$(ClCH{=}CHCl)_2$	31–33	1	189–192	1.5162	24.78	2.08	73.15	25.25	2.36	69.12
XV	$(ClCH{=}CCl_2)_2$	94–96	5	235–238	1.5440	18.28	0.77	80.95	18.58	1.09	74.14

[a] Of principal isomer. [b] Calculated from boiling point under reduced pressure using Dippencott nomograph, *Ind. Eng. Chem.*, **38**, 320 (1946). [c] Microanalyses by Mr. C. W. Beazley, Micro-Tech Laboratories, Skokie, Illinois. [d] Henry, *Ber.*, **8**, 414 (1875). [e] Schmerling, THIS JOURNAL, **70**, 381 (1948). [f] d^{20}_4, 0.9944; MR_D (calcd.), 36.76; MR_D (obs.) 36.81 [g] d^{20}_4 1.1806; MR_D (calcd.), 55.87; MR_D (obs.), 55.86. [h] Schmerling, THIS JOURNAL, **71**, 701 (1949).



$$2R-\underset{X}{\overset{Cl}{C}}-\underset{X}{C}-Cl \longrightarrow R-\underset{Cl}{C}=\underset{X}{C}-Cl + R-\underset{X}{\overset{Cl}{C}}-\underset{X}{\overset{X}{C}}-Cl$$

$$2R-\underset{X}{\overset{Cl}{C}}-\underset{X}{C}-Cl \longrightarrow R-\underset{X}{\overset{Cl}{C}}-\underset{X}{\overset{Cl}{C}}-\underset{X}{\overset{Cl}{C}}-\underset{X}{\overset{Cl}{C}}-R$$

The effect of changes in other reaction conditions was also investigated with methylcyclohexane and trichloroethylene as reactants and *t*-butyl perbenzoate as the peroxide. When the reaction temperature was 160° (expt. 17) instead of 115° (the decomposition temperature of the peroxide), the yield of primary product was decreased (17% instead of 23%). Carrying out the reaction in the presence of water (expt. 18) resulted in an increased yield, 32%. This yield was even higher than that obtained using three times as much peroxide in the absence of water; at the same time, the efficiency was higher as is shown by the fact that the mole ratio of primary product to peroxide was even slightly higher than when one-third as as much peroxide was used.

There was little difference in behavior between *cis*- and *trans*-dichloroethylene. For example, the same yield of chlorohexene was obtained by the reaction of either isomer with isobutane in the presence of decomposing di-*t*-butyl peroxide (expts. 2 and 3). This is in marked contrast with the aluminum chloride-catalyzed condensations of *cis*- and *trans*-dichloroethylene with isobutane[1] or with *t*-butyl chloride.[2] In the isobutane reaction, 1,1,2-trichloro-3,3-dimethylbutane was obtained in 35% yield when the *cis* isomer was used, and in less than 5% yield when the *trans* compound was used. Similarly, in the *t*-butyl chloride condensation, this trichlorodimethylbutane was produced in 75 and 2% yields, respectively, with *cis*- and *trans*-dichloroethylene. These results seem to point to a significant difference between the ease of addition of *t*-butyl radicals and of *t*-butyl carbonium ions to hindered double bonds.

Experimental

Condensation of Hydrocarbons with Chloroethylenes.—The hydrocarbons, the chloroethylene, and the peroxide were weighed into a glass liner (cooled in a bath at −78° when the gaseous hydrocarbons, propane and isobutane, were employed). The liner was sealed into an Ipatieff-type rotating autoclave of 850 cc. capacity, nitrogen was charged to a pressure of 50 atm., and the autoclave was then heated, the temperature being raised gradually during four hours from 110 to 115° when the peroxide was *t*-butyl perbenzoate[3] and from 130 to 140° when it was di-*t*-butyl peroxide.[3] The autoclave was permitted to stand overnight, after which the gas was discharged to the atmosphere, and the liquid product (usually a dark amber liquid containing dissolved hydrogen chloride) was washed with dilute alkali and with water, dried over potassium carbonate, and distilled through a 14-inch total reflux fractionation column.[4]

Polymerization of Chloroethylenes.—In order to determine the physical properties of the products obtained in the absence of the hydrocarbons, the chloroethylenes were heated with di-*t*-butyl peroxide at 130–140° (expts. 8, 19 and 22). Dichloroethylene and trichloroethylene were dimerized whereas tetrachloroethylene underwent little reaction.

Characterization of Products

1-Chloro-3,3-dimethyl-1-butene (II).—The infrared spectrum[5] of this product was compared (Fig. 1) with those of the 1-chloro-3,3-dimethyl-1-butene prepared[2] by the action of zinc on 1,1,2-trichloro-3,3-dimethylbutane and by the dehydrochlorination of 1,1-dichloro-3,3-dimethylbutane over calcium chloride at 450°. The spectra were all quite similar, II containing 80 to 90% of the previously prepared material (which was probably a mixture of *cis*- and *trans*-isomers).

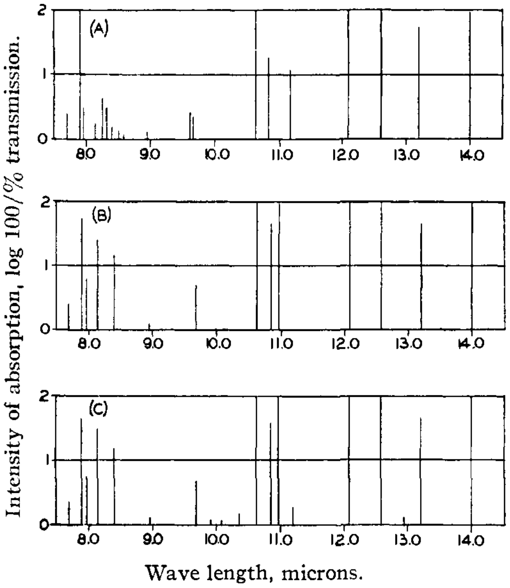


Fig. 1.—Infrared absorption spectra of 1-chloro-3,3-dimethyl-1-butene products: (A) i-C_4H_{10} + ClCH=CHCl + t-Bu_2O_2 (expt. 3); (B) $(CH_3)CCHClCHCl_2$ + Zn (ref. 1); (C) $(CH_3)_3CCH_2CHCl_2$ + $CaCl_2$ (ref. 1).

1,1-Dichloro-3-methyl-1-butene (VI).—Quite pure samples of 1,1-dichloro-3-methyl-1-butene were prepared previously[6] by two methods: the reaction of isopropyl chloride with vinylidene chloride and the action of alcoholic potash on 1,1,2-trichloro-3-methylbutane. Comparison of the infrared spectrum of VI with the spectra of these products indicated that VI contained approximately 75% of 1,1-dichloro-3-methyl-1-butene (Fig. 2). The remainder of the material may have been 1,1-dichloro-1-pentene, formed via the reaction of a *n*-propyl radical with trichloroethylene or 1,2-dichloro-3-methyl-1-butene formed via the "reverse" condensation of an isopropyl radical with the trichloroethylene (*i. e.*, the isopropyl radical added to the carbon atom which holds two chlorine atoms).

1,1-Dichloro-3,3-dimethyl-1-butene (VII).—Infrared analysis (Fig. 3) of this material showed that it contained

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[1] L. Schmerling, THIS JOURNAL, **70**, 379 (1948).

[2] L. Schmerling, *ibid.*, **68**, 1655 (1946).

[3] Purchased from Union Bay State Company, Cambridge, Mass.

[4] C. L. Thomas, H. S. Bloch and J. Hoekstra, *Ind. Eng. Chem., Anal. Ed.*, **10**, 153 (1938).

[5] The authors are indebted to Dr. W. S. Gallaway and Mr. Edmond Baclawski, Physics Division, Universal Oil Products Company, for the infrared absorption analyses.

[6] L. Schmerling, THIS JOURNAL, **71**, 701 (1949).

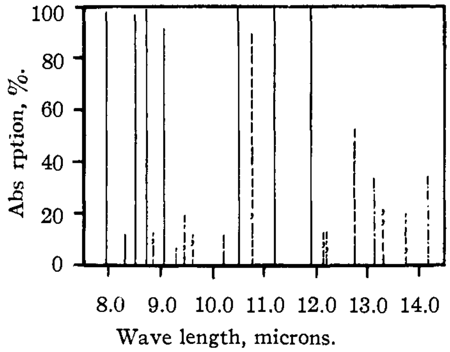

Fig. 2.—Infrared absorption spectra of 1,1-dichloro-3-methyl-1-butene products: (A) C_3H_8 + $ClCH{=}CCl_2$ + t-Bu_2O_2 (expt. 9); (B) i-C_3H_7Cl + $CH_2{=}CCl_2$ + $AlCl_3$ (ref. 6) or $(CH_3)_2CHCH_2CCl_3$ + KOH (ref. 6). Absorptions present in both products —; absorptions present in product A only - - - - -; absorptions present in product B only ·-·-·-·-·-.

about 80% of 1,1-dichloro-3,3-dimethyl-1-butene which had been obtained previously[6] by the reaction of t-butyl chloride with vinylidene chloride and the action of alcoholic potash on 1,1,2-trichloro-3,3-dimethylbutane. The remaining 20% may have been 1,1-dichloro-4-methyl-1-pentene or 1,2-dichloro-3,3-dimethyl-1-butene.

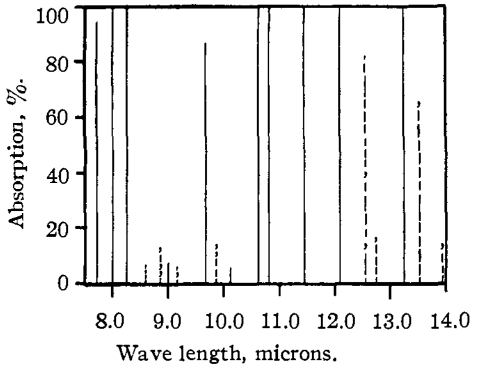

Fig. 3.—Infrared absorption spectra of 1,1-dichloro-3,3-dimethyl-1-butene products: (A) i-C_4H_{10} + $ClCH{=}CCl_2$ + t-Bu_2O_2 (expt. 10); (B) t-C_4H_9Cl + $CH_2{=}CCl_2$ + $AlCl_3$ (ref. 6) or $(CH_3)_3CCH_2CCl_3$ + KOH (ref. 6). Absorptions present in both products —; absorptions present in product A only - - - - -.

1,1-Dichloro-2-cyclohexylethylene (X).—Comparison of the infrared spectrum of this product with that of the 1,1-dichloro-2-cyclohexylethylene obtained[6] by the condensation of cyclohexyl chloride with vinylidene chloride in the presence of aluminum chloride indicated that the product contained about 80 to 90% of the dichlorocyclohexylethylene (Fig. 4).

χ-(2,2-Dichlorovinyl)-1-methylcyclohexane (XI).—A sealed tube containing 10 g. of the chloride and 100 g. of water was heated at 275° for five hours. The product was made alkaline, and then extracted with ether to remove unreacted material. Acidification of the alkaline solution yielded an oil which was taken up in ether, dried and distilled. The major portion of the product (5 cc.) boiled at 108–109° at 2 mm. pressure, n^{20}_{D} 1.4360. It was χ-methylcyclohexaneacetic acid, probably 1-methylcyclohexaneacetic acid.

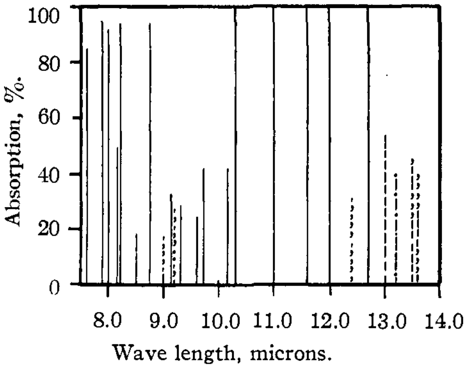

Fig. 4.—Infrared absorption spectra of 1,1-dichloro-2-cyclohexylethylene products: (A) c-C_6H_{12} + $ClCH{=}CCl_2$ + t-Bu_2O_2 (expt. 13); (B) c-$C_6H_{11}Cl$ + $CH_2{=}CCl_2$ + $AlCl_3$ (ref. 6). Absorptions present in both products —; absorptions present in product A only - - - - -; absorptions present in product B only ·-·-·-·-·-.

Anal.[7] Calcd. for $C_9H_{16}O_2$: C, 69.17; H, 10.33. Found: C, 68.97; H, 10.01.

The acid yielded an amide: nacreous flakes, m.p. 135–136°.

Anal.[7] Calcd. for $C_9H_{17}ON$: C, 69.61; H, 11.04; N, 9.0. Found: C, 68.92; H, 10.84; N, 8.32.

1,1,2-Trichloro-3-methyl-1-butene (XII).—The infrared spectrum of this material was compared with that of the trichloromethylbutene obtained by the dehydrochlorination of the product (1,1,1,2-tetrachloro-3-methylbutane containing a minor amount of 1,1,2,2-tetrachloro-3-methylbutane) of the condensation of isopropyl chloride with trichloroethylene in the presence of aluminum chloride.[2] The spectra (Fig. 5) indicated that the two samples had approximately 80% of common component, the "impurities" in each being different. The common component was undoubtedly 1,1,2-trichloro-3-methyl-1-butene while the impurity in XII may have been 1,1,2-trichloro-1-pentene and that in the dehydrochlorination product, 1,1,1-trichloro-3-methyl-2-butene.

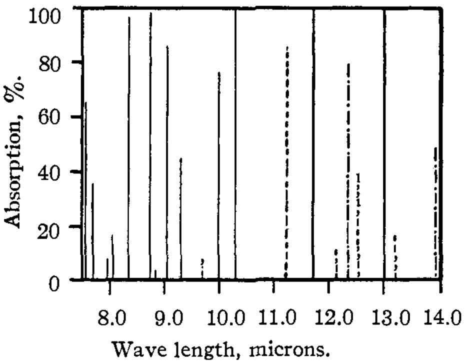

Fig. 5.—Infrared absorption spectra of 1,1,2-trichloro-3-methyl-1-butene products: (A) C_3H_8 + $Cl_2C{=}CCl_2$ + t-Bu_2O_2 (expt. 20); (B) i-C_3H_7Cl + $ClCH{=}CCl_2$ → $C_5H_8Cl_4$ → $(CH_3)_2CHCCl{=}CCl_2$ + HCl (ref. 2). Absorptions present in both products —; absorptions present in product A only - - - - -; absorptions present in product B only ·-·-·-·-·-.

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[7] Microanalysis by Mr. C. W. Beazley, Micro-Tech Laboratories, Skokie, Illinois.

Summary

The peroxide-induced condensation of saturated hydrocarbons (including propane, isobutane, *n*-pentane, cyclopentane, 2,2- and 2,3-dimethylbutane, cyclohexane, and methylcyclohexane) with *cis*- and *trans*-dichloroethylene, trichloroethylene, and tetrachloroethylene is a chain reaction which results in the chlorovinylation of the hydrocarbon, a chloroölefin containing one chlorine atom less than the chloroethylene used being formed. Thus, the reaction of propane with these chlorides yields, as principal isomer in each case, 1-chloro-, 1,1-dichloro- and 1,1,2-trichloro-3-methyl-1-butene, respectively.

The peroxide-induced reaction differs from that catalyzed by aluminum chloride in that both *n*- and isoparaffins give significant yields and the products are unsaturated chlorides instead of saturated chlorides. Furthermore, *cis*- and *trans*-dichloroethylene show little difference in reactivity.

The mechanism of the reaction is discussed.

Riverside, Illinois Received January 13, 1949

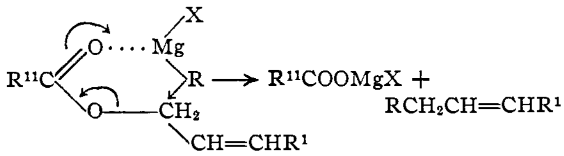
[Contribution from the Department of Chemistry of the University of California at Los Angeles]

Allylic Rearrangements. XXVI. The Reaction of Butenyl Mesitoates and Chlorides with Phenylmagnesium Bromide

By K. W. Wilson, John D. Roberts and William G. Young

In 1941, Arnold, Bank and Liggett[1] suggested that the formation of allylbenzene from the reaction of allyl mesitoate with phenylmagnesium bromide involved the combination of an intermediate allyl carbonium ion with a phenyl carbanion from the Grignard reagent. In a later paper[2] this mechanism was modified since it was found that the reaction of crotyl mesitoate with phenylmagnesium bromide gave only crotylbenzene instead of the mixture of crotyl- and α-methylallylbenzenes expected from an intermediate butenyl carbonium ion. The exclusive formation of crotylbenzene was formulated as being the result of a concerted process involving a cyclic intermediate.

$R^{11}COOCH_2CH{=}CHR^1 + RMgX \longrightarrow$



The reaction of allyl and crotyl mesitoate with phenylmagnesium bromide is analogous to the coupling reactions between allyl halides and Grignard reagents, which with crotyl and α-methylallyl halides[3] and several Grignard reagents give almost exclusively *crotyl* derivatives. For this reason, we have made a comparative study of the reactions of crotyl and α-methylallyl mesitoates and chlorides with phenylmagnesium bromide.

Results and Discussion

The compositions of the butenylbenzene mixtures isolated from the reaction of phenylmagnesium bromide with the butenyl chlorides and mesitoates were determined by fractional distillation and are given in Table I. With crotyl mesitoate only pure crotylbenzene was isolated, while in the other reactions, mixtures of butenylbenzenes were obtained.

Table I

Products from the Reactions of Phenylmagnesium Bromide with Butenyl Mesitoates and Chlorides

Butenyl derivative	Crotylbenzene, %	α-Methylallylbenzene, %
Crotyl mesitoate	100	0
α-Methylallyl mesitoate	83 ± 6	17 ± 3
Crotyl chloride	77 ± 5	23 ± 3
α-Methylallyl chloride	72 ± 5	19 ± 2
Butenyl chloride mixture[a]	81 ± 3	19 ± 2

[a] 41% crotyl chloride, 59% α-methylallyl chloride.

The striking similarity among the product and compositions with α-methylallyl mesitoate, crotyl and α-methylallyl chlorides suggests that the same intermediate, a butenyl carbonium ion, is involved in each of these reactions. Formation of a carbonium ion intermediate is expected to be made possible in these processes by a weakening of the C–X or C–O bond of the chlorides or esters by preliminary coördination with the Grignard reagent. It is not considered that a free carbonium ion is produced but rather that an ion-pair is produced in which the butenyl cation is sufficiently free to effectively lose its identity as either a crotyl or α-methylallyl group. The small difference between the product compositions from the coupling reactions with the isomeric chlorides is typical of many reactions in the butenyl system involving carbonium ions.[4]

The importance of preliminary coördination by the Grignard reagent in producing the butenyl carbonium ion is shown by the fact the sodium derivative of allylbenzene, which is likely to react

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[1] Arnold, Bank and Liggett, This Journal, **63**, 344 (1941).

[2] Arnold and Liggett, *ibid.*, **67**, 337 (1945).

[3] (a) Young, Roberts and Wax, *ibid.*, **67**, 841 (1945); (b) Henne, Chanan and Turk, *ibid.*, **63**, 3474 (1941); (c) Levy and Cope, *ibid.* **66**, 1684 (1944).

[4] (a) Meisenheimer and Link, *Ann.*, **479**, 211 (1930); (b) Young and Lane, This Journal, **59**, 2051 (1939); (c) Roberts, Young and Winstein, *ibid.*, **64**, 2159 (1942); (d) Young and Andrews, *ibid.*, **66**, 421 (1944).