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

The Peroxide-induced Condensation of Polychloroethylenes with Aromatic Hydrocarbons[1]

BY LOUIS SCHMERLING AND JAMES P. WEST

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The peroxide-induced condensation of a polychloroethylene with an aromatic hydrocarbon containing a side-chain in the presence of an organic peroxide at its decomposition temperature results in the chlorovinylation of the side-chain, the product containing one chlorine atom less than the chloroethylene. Thus, the reaction of toluene with *trans*-dichloroethylene, trichloroethylene and tetrachloroethylene yields, as principal isomer in each case, (3-chloroallyl)-benzene, (3,3-dichloroallyl)-benzene and (2,3,3-trichloroallyl)-benzene, respectively. No chlorovinylation occurred when benzene was treated with trichloroethylene in the presence of di-*t*-butyl peroxide at 130–140°. The only product which was isolated was the dimer of trichloroethylene, indicating that hydrogen attached to an alkyl side chain is essential. There was little reaction when 1,2-dibromoethylene was substituted for the chloro analog.

Chlorovinylation of the side chain occurs when alkylbenzenes are treated with polychloroethylenes in the presence of a catalytic amount of an organic peroxide at a temperature at least as high as the decomposition temperature of the peroxide. The peroxide-induced condensation of toluene with *trans*-dichloroethylene, for example, in the presence of di-*t*-butyl peroxide at 130–140° results in the formation of (3-chloroallyl)-benzene (see Table I). The mechanism of the reaction may be formulated as

TABLE I

CONDENSATION OF AROMATIC HYDROCARBONS WITH CHLOROETHYLENES

	Reactants					Chief product				
Expt.	ArH, moles	Chloroölefin[a] Kind	Chloroölefin[a] Moles	R_2O_2,[b] Moles	Temp., °C.	Compd.	Yield G.	Yield %	Moles/mole R_2O_2	Higher boiling prod., g.
				Toluene plus chloroethylenes						
1	1.0	Cl_2	0.50	0.055	130–140	I	14	18	1.7	9
2	1.0	Cl_3	.50	.055	130–140	II	22	23	2.1	16
3	1.1	Cl_4	.30	.055	130–140	III	30	45	2.5	6
4	1.1	Cl_4	.32	.041[c]	110–115	III	18	25	2.0	5
				Ethylbenzene plus chloroethylenes						
5	0.48	Cl_2	0.48	0.055	130–140	IV	12	18	1.3	9
6	.67	Cl_3	.40	.075[d]	130–140	V	24	30	1.6	15[e]
				Indan plus chloroethylenes						
7	0.77	Cl_2	0.52	0.055	130–140	VI	17	18	1.7	13
8	.80	Cl_3	.38	.055	130–140	VII	27	13	2.5	15
				Benzene plus trichloroethylene						
9	1.0	Cl_3	0.50	0.055	130–140	VIII	19	14	1.3	10
				Toluene plus 1,2-dibromoethylene						
10	0.27	Br_2	0.20	0.028	130–140	..	3[f]	..	...	..

[a] Cl_2 = *trans*-dichloroethylene; Cl_3 = trichloroethylene; Cl_4 = tetrachloroethylene; Br_2 = 1,2-dibromoethylene. [b] Di-*t*-butyl peroxide, unless otherwise footnoted. [c] *t*-Butyl perbenzoate. [d] Also 10 g. of anhydrous potassium carbonate. [e] Includes 9-g. fraction boiling at 100–150° at 4 mm. which became partially crystalline on standing; m.p. of 0.7 g. obtained by filtration, 124–125° (2,3-diphenylbutane). [f] High-boiling tar.

TABLE II

PROPERTIES OF THE CONDENSATION PRODUCTS

		B.p.,				Analyses,[c] %					
						Calcd.			Found		
Compd.	Formula[a]	°C.	Mm.	B.p. at 760 mm., °C.[b]	$n^{20}D$	C	H	Cl	C	H	Cl
I	$PhCH_2CH{=}CHCl$[d]	53–53	2.0	208–208	1.5385						
II	$PhCH_2CH{=}CCl_2$	87–88	3.5	242–244	1.5491	57.78	4.31	37.91	56.01	4.47	39.40[e]
III	$PhCH_2CCl{=}CCl_2$	89–91	1.8	262–265	1.5635	48.79	3.19	48.02	48.91	3.28	47.91
IV	$PhCHMeCH{=}CHCl$	73–74	3.0	226–229	1.5329	72.07	6.65	21.28	71.12	6.65	22.72
V	$PhCHMeCH{=}CCl_2$	95–96	4.0	249–250	1.5392	59.73	5.01	35.26	59.75	5.68	35.01
VI	$C_9H_9CH{=}CHCl$	87–88	1.7	260–262	1.5532	73.94	6.21	19.85	73.94	6.28	20.00
VII	$C_9H_9CH{=}CCl_2$	101–103	1.5	285–287	1.5685	61.99	4.73	33.28	62.24	4.93	33.08
VIII	$(CHCl{=}CCl_2)_2$[f]	75–76	2.2	239–240	1.5432[g]	18.28	0.77	80.95			

[a] Of principal isomer. [b] Calculated from boiling point under reduced pressure using Lippincott nomograph, *Ind. Eng. Chem.*, **38**, 320 (1946). [c] Microanalyses by Mr. C. W. Beazley, Micro-Tech Laboratories, Skokie, Illinois. [d] *Cf.* P. Bert, *Bull. soc. chim.*, [4] **37**, 880 (1925). [e] Contamination with about 4% VIII is indicated. [f] *Cf.* L. Schmerling and J. P. West, THIS JOURNAL, **71**, 2016 (1949). [g] Density at room temperature, 1.58.

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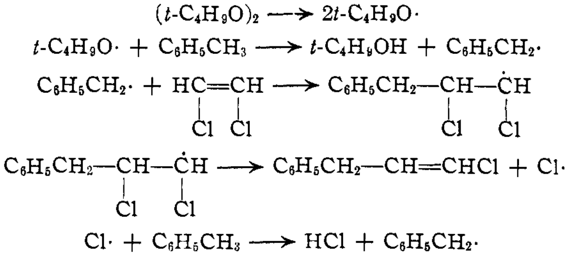
[1] Presented before the Division of Organic Chemistry during the 123rd meeting of the American Chemical Society at Los Angeles, March, 1953.

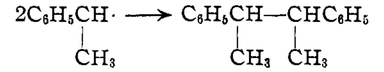


$$(t\text{-}C_4H_9O)_2 \longrightarrow 2t\text{-}C_4H_9O\cdot$$
$$t\text{-}C_4H_9O\cdot + C_6H_5CH_3 \longrightarrow t\text{-}C_4H_9OH + C_6H_5CH_2\cdot$$
$$C_6H_5CH_2\cdot + \underset{Cl}{HC}{=}\underset{Cl}{CH} \longrightarrow C_6H_5CH_2{-}\underset{Cl}{CH}{-}\underset{Cl}{\dot{C}H}$$
$$C_6H_5CH_2{-}\underset{Cl}{CH}{-}\underset{Cl}{\dot{C}H} \longrightarrow C_6H_5CH_2{-}CH{=}CHCl + Cl\cdot$$
$$Cl\cdot + C_6H_5CH_3 \longrightarrow HCl + C_6H_5CH_2\cdot$$

The (3-chloroallyl)-benzene was characterized by comparing its infrared spectrum with that of the product prepared by the reaction of benzene with 1,3-dichloropropene in the presence of aluminum chloride dissolved in nitromethane.

The reaction of toluene with trichloroethylene in the presence of di-*t*-butyl peroxide at 130–140° yielded a product believed to be (3,3-dichloroallyl)-benzene. The condensation with tetrachloroethylene under the same conditions produced what was apparently chiefly (2,3,3-trichloroallyl)-benzene; a lower yield was obtained when *t*-butyl perbenzoate was used as peroxide at 110–115°.

Chlorophenylbutenes were similarly formed from ethylbenzene and *trans*-dichloroethylene or trichloroethylene. 2,3-Diphenylbutane was isolated from the latter reaction product; its formation involved self-condensation of the intermediate methylbenzyl radical.[2]



$$2\underset{CH_3}{C_6H_5CH}\cdot \longrightarrow C_6H_5\underset{CH_3}{CH}{-}\underset{CH_3}{CHC_6H_5}$$

When an attempt was made to condense benzene with trichloroethylene in the presence of di-*t*-butyl peroxide, the only reaction product which was isolated was the dimer of trichloroethylene, obtained in about 14% yield. This result indicates that hydrogen attached to an alkyl side chain is necessary for the chlorovinylation.

Indan also underwent the condensation reaction. Compounds having the composition corresponding to 1-(2-chlorovinyl)-indan and 1-(2,2-dichlorovinyl)-indan were obtained by the reaction of indan with dichloro- and trichloroethylene, respectively.

Little reaction occurred when toluene was treated with 1,2-dibromoethylene in the presence of di-*t*-butyl peroxide. This apparently is due to the fact that bromine atoms are not good chain-carriers; they abstract hydrogen atoms from the side chains less readily than do chlorine atoms. It was previously shown[3] that the condensation of polybromoethylenes (unlike that of polychloroethylenes) with saturated hydrocarbons similarly occurs in low yield, if at all.

Experimental

Procedure.—A glass liner containing the aromatic hydrocarbon, the chloroethylene and the peroxide was sealed into an Ipatieff-type rotating autoclave of 850-cc. capacity. Nitrogen was pressed in to a pressure of 50 atm. and the autoclave was then heated, the temperature being raised gradually during four hours from 130 to 140° when the peroxide was di-*t*-butyl peroxide and from 110 to 115° when it was *t*-butyl perbenzoate. The autoclave was permitted to stand overnight, the gas was discharged to the atmosphere, and the liquid product was washed with dilute alkali and with water, dried over potassium carbonate and distilled.

(3-Chloroallyl)-benzene.[4]—A solution of 50 g. of 1,3-dichloropropene in 80 g. of benzene was added during one hour to a stirred solution of 5 g. of aluminum chloride and 5 g. of nitromethane in 80 g. of benzene at 0°. The product was stirred for an additional one-half hour, washed with water and alkali, dried and distilled. There was obtained 32 g. of (3-chloroallyl)-benzene (47%); b.p. 50–51° (1.5 mm.), 208–209° (760 mm.), n^{20}_{D} 1.5388.

The physical properties were in good agreement with those of the product obtained by the reaction of toluene with *trans*-dichloroethylene (b.p. 53–53° [2.0 mm.]; 208–208° [760 mm.]; n^{20}_{D} 1.5385). Infrared analysis indicated that the same major component was present in both samples with different and varying concentrations of impurity.[5]

RIVERSIDE, ILLINOIS

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[2] M. S. Kharasch, E. V. Jensen and W. H. Urry, *J. Org. Chem.*, **10**, 401 (1945).

[3] L. Schmerling and J. P. West, THIS JOURNAL, **71**, 2015 (1949).

[4] L. Bert, *Bull. soc. chim.*, [4] **37**, 880 (1925); P. Bert, *Compt. rend.*, **213**, 619 (1941).

[5] Infrared analysis by Mr. Edmond Baclawski, Physics Division, Universal Oil Products Company.

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Condensation of Saturated Halides with Unsaturated Compounds. X. Condensation of *t*-Butyl Halides with Propene, 1-Butene and 2-Butene[1]

BY LOUIS SCHMERLING AND E. E. MEISINGER

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The addition of *t*-butyl chloride to propene in the presence of Friedel–Crafts catalysts yields 2-chloro-4,4-dimethylpentane together with 2- and 3-chloro-2,3-dimethylpentane, the proportion of the various isomers depending on the catalyst used. Pure 2-chloro-4,4-dimethylpentane may be readily obtained by treating the mixture of isomers with water at the reflux temperature to decompose the tertiary halides. The condensation of propene with *t*-butyl bromide and with *t*-butyl iodide takes place in analogous manner. The reaction of *t*-butyl chloride with 1-butene yields 3-chloro-5,5-dimethylhexane as the principal product, while the reaction with 2-butene produces 3-chloro-2,2,3-trimethylpentane and 2-chloro-3,4,4-trimethylpentane together with some chloro-2,3,4-trimethylpentane.

In a previous paper,[2] it was shown that condensation of *t*-butyl chloride or bromide with ethylene in the presence of a Friedel–Crafts metal halide catalyst yields halohexane consisting practically exclusively of 1-halo-3,3-dimethylbutane. It was also indicated[3] that the reaction of *t*-butyl chloride with propene, on the other hand, yields not only the analogous 2-chloro-4,4-dimethylpentane (*i.e.*, the primary product formed by the addition of the alkyl group and the halogen atom to the double bond of the olefin, the halogen adding to the carbon

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[1] Preceding paper in this series, THIS JOURNAL, **74**, 3592 (1952).

[2] L. Schmerling, *ibid.*, **67**, 1152 (1945).

[3] L. Schmerling, *ibid.*, **67**, 1780 (1945).