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Corresponding Member of the Academy of Sciences of the USSR A. D. PETROV, G. I. NIKISHIN, and G. V. SOMOV

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Abstract

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HIGH-TEMPERATURE CONDENSATION OF TETRACHLOROETHYLENE WITH AROMATIC HYDROCARBONS AND OLEFINS

Shmerling and West (1 2) showed that di- and trichlorovinyl groups can be introduced into molecules of paraffins, isoparaffins, and alkylbenzenes by condensation of tri- or tetrachloroethylene with the above hydrocarbons, with initiation of the reaction by tert-butyl peroxide under nitrogen pressure of 50 atm. The main products of the reaction of tri- and tetrachloroethylene with propane are, respectively, 1,1-dichloro-3-methylbutene-1 and 1,1,2-trichloro-3-methylbutene-1, whose content in the reaction products amounts to 75–80%. In addition to these chloroolefins, 1,1-dichloropentene-1 and 1,1,2-trichloropentene-1 evidently are formed. The reaction with isobutane proceeds similarly; in this case, replacement of hydrogen by chlorovinyl groups occurs predominantly at the tertiary carbon atom. In the reaction of toluene with tri- and tetrachloroethylene, only 2,3,3-trichloroallylbenzene and 3,3-dichloroallylbenzene are formed; in the reaction of trichloroethylene with ethylbenzene, 3,3-dichloro-1-methylallylbenzene is formed, i.e., replacement of hydrogen by a di- or trichlorovinyl group occurs at the α-carbon atom of the side chain (2). These authors, however, did not succeed in introducing the trichlorovinyl group into the aromatic nucleus. When tetrachloroethylene was treated with benzene under the conditions described above, only a small amount of hexachlorobutadiene was formed. The yields of chlorovinylation products were 1.3–2.5 moles per mole of peroxide (18–45%) (2).

In the present work, a description is given of a new method for synthesizing chlorohydrocarbons containing the trichlorovinyl group. This method consists in the interaction of hydrocarbons with tetrachloroethylene in an empty quartz tube (flow system) at 550-590°. The reaction proceeds according to the following probable scheme:

$$\mathrm{Cl_2C{=}CCl_2} \rightarrow \mathrm{Cl_2C{=}CCl}\cdot + \mathrm{Cl}\cdot,$$

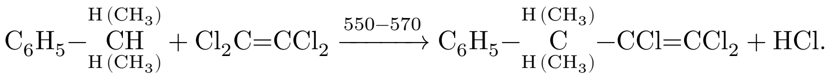
$$\mathrm{Cl}\cdot + \mathrm{RH} \rightarrow \mathrm{HCl} + \mathrm{R}\cdot,$$

$$\mathrm{Cl_2C{=}CCl}\cdot + \mathrm{R}\cdot \rightarrow \mathrm{R{-}CCl{=}CCl_2}.$$

It had previously been established that, in the interaction of tetrachloroethylene with methyl alcohol at 570°, trichloroallyl alcohol is formed (^{3}). It turned out that this reaction has a more general character. By passing a mixture of benzene and tetrachloroethylene through a tube, we succeeded in obtaining trichlorovinylbenzene in a yield of 14.4% calculated on the starting materials and 55% calculated on the benzene consumed. Part of the benzene was thereby converted into diphenyl:

$$C_6H_6 + Cl_2C{=}CCl_2 \rightarrow C_6H_5CCl{=}CCl_2 + C_6H_5{-}C_6H_5 + HCl.$$

The reaction of benzene with trichloroethylene proceeds analogously, as a result of which dichlorovinylbenzene is formed. In the interaction of tetrachloroethylene with alkylbenzenes—toluene, ethylbenzene, isopropylbenzene, and *p*-xylene —the trichlorovinyl group enters only the alkyl radical; replacement of a hydrogen atom of the benzene nucleus does not occur in these cases:



$$C_6H_5{-}\underset{H\,(CH_3)}{\overset{H\,(CH_3)}{CH}} + Cl_2C{=}CCl_2 \xrightarrow{550-570} C_6H_5{-}\underset{H\,(CH_3)}{\overset{H\,(CH_3)}{C}}{-}CCl{=}CCl_2 + HCl.$$

For the reaction product of tetrachloroethylene with toluene, an IR spectrum was obtained. The position of the overtones of out-of-plane C—H vibrations in the region of 5-6 μ corresponds to that usually observed for monosubstituted benzenes (4).

In the reaction of tetrachloroethylene with ethylbenzene and isopropylbenzene, the trichlorovinyl radical replaces hydrogen, evidently, not only at the α-, but also at the β-carbon atom of the side chain. Table 1 gives the conditions

Table 1

No. of experiments	Hydrocarbon	Amounts of hydrocarbon : tetrachloroethylene taken into the reaction, g-mol	Temp., °C	Feed rate, g/h	Feed rate, l/l · min	Residence time in the reaction zone, sec	Yield, %
1	C_6H_6	1.9 : 1.9	590	28.5	1.41	42.5	14.4

No. of experiments	Hydrocarbon	Amounts of hydrocarbon : tetrachloroethylene taken into the reaction, g-mol	Temp., °C	Feed rate, g/h	Feed rate, l/l · min	Residence time in the reaction zone, sec	Yield, %
2	$C_6H_5CH_3$	0.56 : 0.56	570	46.5	3.08	19.5	5.7
3	$C_6H_5CH_3$	0.48 : 0.48	570	29.2	1.94	30.8	7.7
4	$C_6H_5CH_3$	0.49 : 0.49	570	17.9	1.19	50.2	18
5	$C_6H_5CH_3$	1 : 1	550	33.6	1.48	40.7	10
6	$C_6H_5CH_3$	0.5 : 1	550	39.7	1.6	37.5	19.4
7	*p*-$CH_3C_6H_4CH_3$	0.75 : 0.75	570	26.2	1.67	36	12.5
8	$C_6H_5CH_2CH_3$	0.5 : 0.5	550	28.6	1.77	34	21.2
9	$C_6H_5CH_2CH_3$	1 : 2	550	24.0	1.38	43.5	26.7
10	$C_6H_5CH(CH_3)_2$	1.5 : 1.5	560	30.8	0.52	115	11.3
11	$C_6H_5CH(CH_3)_2$	1 : 1	570	26	1.56	38.5	14.6
12	$CH_3-CH{=}CH_2$	1 : 1	550	26.7	0.63	96.6	11.1
13	$CH_3-CH{=}CH_2$	2.5 : 0.5	590	32.6	1.28	47	24.5
14	$(CH_3)_2C{=}CH_2$	1.3 : 1	580	30.9	0.72	83.3	16.2
15	$(CH_3)_2C{=}CH_2$	1.4 : 0.7	580	22	0.58	103.4	22.8
16	C_2H_4 *	2 : 1	570	26	1.56	38.4	11.5
17	$C_6H_5CH_3$ *	0.5 : 0.5	550	26.3	0.95	63.1	11.9

* The second component is trichloroethylene.

of the experiments and the yields of the products of condensation of tetrachloroethylene and trichloroethylene with benzene, alkylbenzenes, propylene, and isobutylene. The yields were calculated on the amount of components taken into the reaction. Calculated on the consumed substances, the yield of trichlorovinylbenzene was 50%, dichlorovinylbenzene 20-50%, trichloroallylbenzene 50-80%, the product of condensation of tetrachloroethylene with ethylbenzene 40-75%, and with isopropylbenzene 20-45%. In the reaction of tetrachloroethylene with toluene at 570° and an equimolecular ratio of the components, the best results were obtained in experiment No. 4, where the rate of passage of the substances through the tube was 1.19 min^{-1}. An increase in the rate entails a decrease in the yield of the reaction product. The yield of trichloroallylbenzene increases noticeably if, in the initial mixture of the reaction components, the amount of tetrachloroethylene is twice the amount of toluene (experiment No. 6). An analogous picture is observed in the experiments on the condensation of tetrachloroethylene with ethylbenzene. In the interaction of tetrachloroethylene with propylene and isobutylene, the reaction proceeds at the methyl group, as a result of which dienes with the positions of the multiple bonds 1,4 are formed

$$\mathrm{Cl_2C = CCl_2 + CH_3{—}CH = CH_2 \rightarrow Cl_2C = CCl{—}CH_2{—}CH = CH_2 + HCl.}$$

The terminal position of the double bond in the hydrocarbon part of the molecule of 1,1,2-trichloropentadiene-1,4 was confirmed by an IR spectrum, in which frequencies of 1640 and 3085 cm^{-1} were detected. The yields of $\mathrm{Cl_2C = CCl{—}CH_2{—}CH = CH_2}$, calculated on tetrachloroethylene consumed in the reaction, were 45-60%; of $\mathrm{Cl_2C = CCl{—}CH_2{—}C(CH_3) = CH_2}$, 55-65%. An attempt to obtain $\mathrm{Cl_2C = CCl{—}CH = CH_2}$ under analogous conditions by the reaction of $\mathrm{Cl_2C = CCl_2}$ with ethylene was not successful. In all experiments, coke and soot formation were observed in the reaction tube. After the starting substances and the condensation product have been isolated from the reaction mass, a solid or resinous residue remains. At an equimolecular ratio of the reagents, when the amount of each corresponds to 1 g-mol, the largest

the residue was observed in the reaction of tetrachloroethylene with isopropylbenzene, 20-30 g; with ethylbenzene, 6-15 g; toluene, 3-6 g; propylene, 4-5 g; isobutylene, 4-5 g. The properties of the condensation products are presented in Table 2.

Table 2

Condensation product	B.p., °C/mm	d_4^{20}	n_D^{20}	MR_D, found	MR_D, calc.	Found, % C	Found, % H	Calculated, % C	Calculated, % H
$C_6H_5CH=CCl_2$	89–90/9	1.2531	1.5852	46.29	44.94	55.29 55.20	3.54 3.54	55.53	3.49
$C_6H_5CCl=CCl_2$	97–98/7	1.3728	1.5832	50.53	49.77				
$C_6H_5CH_2CH=CCl_2$	87–88/5.5	1.2035	1.5500	49.51	49.59				
$C_6H_5CH_2CCl=CCl_2$	80–82/2	1.3196	1.5636	54.55	54.42				
p-$CH_3-C_6H_4-CH_2CCl=CCl_2$*	123–124/7	1.2760	1.5571	59.43	59.06	51.08 50.94	3.95 4.07	51.00	3.85
$C_6H_5CH(CH_3)CCl=CCl_2$*	80–82/2	1.2883	1.5611	59.29	59.07	51.50 51.50	3.88 3.80	51.00	3.85
$C_6H_5-C(CH_3)_2CH=CCl_2$*	84–88/2	1.2798	1.5645	63.48	63.73				
$CH_2=CH-CH_2CCl=CCl_2$*	54–55/20	1.2804	1.4952	38.79	38.84	35.32 35.30	3.09 2.96	35.01	2.94
$CH_2=C(CH_3)-CH_2-CCl=CCl_2$*	167–168	1.2380	1.4957	43.73	43.49	39.08 39.24	3.92 3.99	38.85	3.80

* Obtained for the first time.

Experimental Part

All high-temperature condensation reactions were carried out in an empty quartz tube placed in a catalytic electric furnace. Two furnaces were used—one 600 mm long, with an internal diameter of 40 mm, and one 995 mm long, with an internal diameter of 35 mm. In the short furnace, the experiments were carried out in tubes of diameter 18.5 mm (experiments Nos. 3–5, 7–9, 11, 16, 17) and 22.5 mm (experiments Nos. 1, 2, 6); in the long furnace the tube diameter was 26 mm (experiments Nos. 10, 12–15). The working part of the tubes was taken to be 100 mm shorter than the length of the furnaces. The temperature was measured inside the reaction tube, in its middle part. The space velocity of the reactant vapors was calculated by the formula $V = \frac{nK}{\tau v}$, where n is the number of moles of substances passed through the tube in time τ, v is the volume of the reaction tube (in liters), and K is the volume of vapor of one mole of substance at the temperature of the experiment (assuming that at 530–590° the starting and formed substances obey the gas laws). A prepared mixture of the reaction components was fed into the tube; in the reaction of tetrachloroethylene with propylene and isobutylene, the components were fed into the tube separately. On leaving the furnace, the vapors were condensed in an air condenser and then in a water-cooled condenser. The reaction mixtures were separated into components by distillation on a column. In cases where the starting substances had close boiling points, their ratio in the distilled fractions was determined from a graph of the dependence of the percentage composition of the mixtures on the specific gravity or refractive index. Below we give a detailed description of several experiments.

Trichlorovinylbenzene (experiment No. 1). A mixture consisting of 149 g (1.9 g-mol) of benzene and 315 g (1.9 g-mol) of tetrachloroethylene was passed for 16 h 20 min at 590° through a tube 22.5 mm in diameter. As a result, 416 g of reaction mixture was obtained, from which 110 g (1.41 g-mol) of benzene, 200 g (1.2 g-mol) of tetrachloroethylene, and 57 g of a broad fraction consisting mainly of trichlorovinylbenzene with an admixture of diphenyl were isolated. The residue —38 g—consisted of diphenyl, m.p. 70° (from alcohol). From the broad fraction, whose yield calculated on the starting substances was 14.4%, pure trichlorovinylbenzene was isolated by fractional distillation and chromatography on a column packed with silica gel (100–200 mesh).

2,3,3-Trichloroallylbenzene (experiment No. 4). A mixture consisting of 45 g (0.49 g-mol) of toluene and 81 g (0.49 g-mol) of tetrachloroethylene was passed for 7 h 4 min at a temperature of 570° through a tube with an internal diameter of 18.5 mm. As a result, 117 g of a dark-brown liquid was obtained. On distillation of the reaction mixture, 35.4 g (0.38 g-mol) of toluene, 55 g (0.33 g-mol) of tetrachloroethylene, and 19.5 g of 2,3,3-trichloroallylbenzene were isolated (for properties see Table 2). The yield, calculated on the starting materials, was 18%; on consumed toluene, 80%; on consumed tetrachloroethylene, 55%. High-boiling residue, 3 g.

1,1,2-Trichloropentadiene-1,4 (experiment No. 13). Through a tube 26 mm in diameter at 590°, over 5 h 48 min, 83 g (0.5 g-mol) of tetrachloroethylene and 58 l (2.5 g-mol) of propylene were passed. From 72 g of the resulting reaction mixture, 44 g (0.265 g-mol) of tetrachloroethylene and 21 g of 1,1,2-trichloropentadiene-1,4 were isolated. The yield, calculated on the tetrachloroethylene taken into the reaction, was 24.5%; on that consumed, 52%. Resinous residue, 3 g.

Institute of Organic Chemistry named after N. D. Zelinsky
Academy of Sciences of the USSR

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