SYNTHESIS OF ALKYLAROMATIC CHLOROHYDROCARBONS, CONTAINING THE TRICHLOROVINYL GROUP

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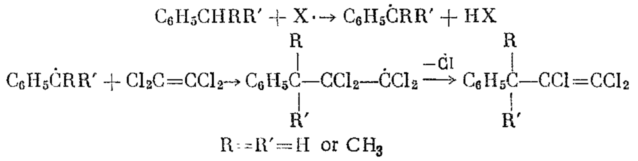
Alkylaromatic chlorohydrocarbons, containing the trichlorovinyl group, can be produced by various methods. There are reports in the literature on the synthesis of these compounds by the splitting out of chlorine or hydrogen chloride from the corresponding saturated polychlorohydrocarbons [1, 2]. They have also been synthesized by the condensation of aliphatic unsaturated chlorohydrocarbons with aromatic hydrocarbons according to the Friedel-Crafts reaction [3]. An original method of introducing the trichlorovinyl group into the alkylbenzene molecule is based upon the reaction of free radical addition of hydrocarbons to tetrachloroethylene according to the scheme [4]



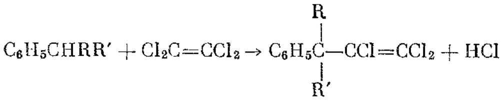
$$C_6H_5CHRR' + X\cdot \rightarrow C_6H_5\dot{C}RR' + HX$$

$$C_6H_5\dot{C}RR' + Cl_2C{=}CCl_2 \rightarrow C_6H_5\underset{R'}{\overset{R}{C}}-CCl_2-\dot{C}Cl_2 \xrightarrow{-\dot{Cl}} C_6H_5\underset{R'}{\overset{R}{C}}-CCl{=}CCl_2$$

$$R{=}R'{=}H \text{ or } CH_3$$

In this way, 1,1,2-trichloro-3-phenylpropene-1 was produced from toluene and tetrachloroethylene in amounts of 2.5 moles per mole of tert-butyl peroxide, which was used as the initiator.

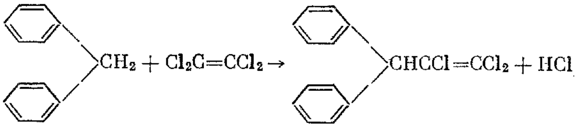
In one of our previous communications, it was shown that chlorohydrocarbons with a trichlorovinyl group are readily formed in the reaction of alkylbenzene with tetrachloroethylene in the gas phase at the temperature 550-570° [5].



$$C_6H_5CHRR' + Cl_2C{=}CCl_2 \rightarrow C_6H_5\underset{R'}{\overset{R}{C}}-CCl{=}CCl_2 + HCl$$

The reaction of tetrachloroethylene with aliphatic alcohols proceeds analogously [6]. Chlorohydrocarbons and their numerous derivatives are widely used as pesticides. This circumstance stimulated further investigations on the high-temperature condensation of tetrachloroethylene with alkylaromatic hydrocarbons and chlorohydrocarbons. We also synthesized a number of substances, using other methods for this purpose.

It was established that tetrachloroethylene reacts rather readily with mesitylene: a condensation product can be obtained in 17% yield calculated on the basis of the starting materials at 435-445° (time of stay of the substances in the reaction zone ~ 40 sec). The similar reaction with toluene is virtually unfeasible at temperatures below 500° [5]. The condensation of tetrachloroethylene with diphenylmethane:



proceeds less readily than that with mesitylene. To obtain 1,1,2-trichloro-3,3-diphenylpropene-1, it was necessary to raise the temperature to ~ 530°, and this in turn gave rise to thermal decomposition of part of the initial hydrocarbon and products formed.

Para-chlorotoluene and ortho-chlorotoluene, produced by diazotization of the corresponding toluidines, form condensation products at 550-580° in yields of 10-20% calculated on the basis of the starting materials and 60-70% calculated on the basis of the substances reacted:

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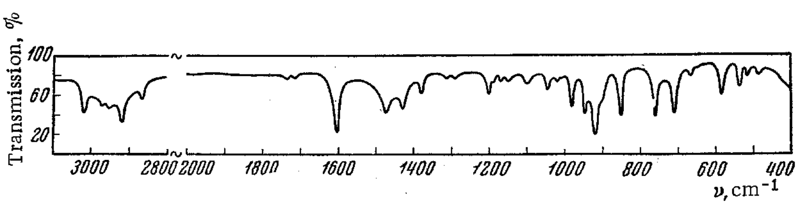


Fig. 1. IR spectrum of 1,1,2-trichloro-3-(3',5'-dimethylphenyl)-propene-1.

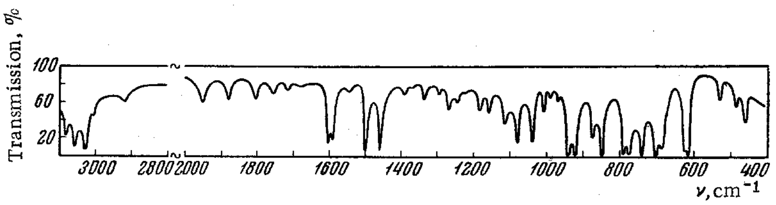
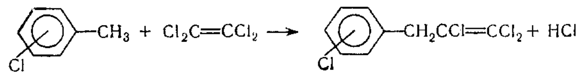
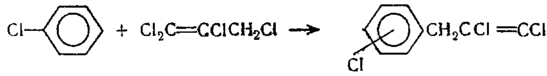


Fig. 2. IR spectrum of 1,1,2-trichloro-3,3-diphenylpropene-1.

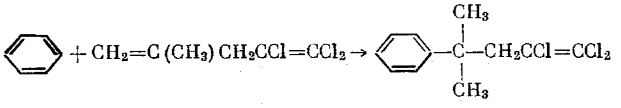


The reaction of tetrachloroethylene with dichlorotoluene, which was synthesized by chlorination of toluene, proceeds analogously. Para-bromotoluene, in contrast to para-chlorotoluene, is relatively stable, under the experimental conditions at temperatures below 525°. However, at this temperature practically none of its condensation product with tetrachloroethylene can be obtained: the yield of $p\text{-}BrC_6H_5CH_2CCl=CCl_2$ is only ~2%; moreover, substantial amounts of higher boiling substances are formed.

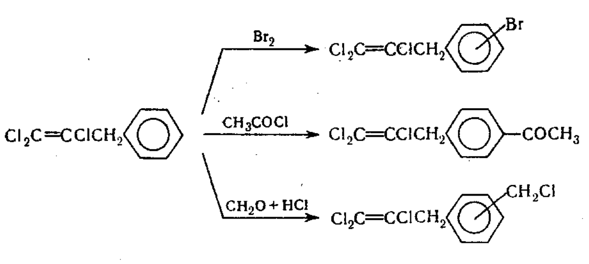
For the introduction of the trichlorovinyl group into the molecules of aromatic compounds (benzene, chlorobenzene, mesitylene), we also used their condensation with 1,1,2,3-tetrachloropropene-1



With mesitylene the yield of the product was ~98%, with benzene 72%, and with chlorobenzene 60%. A similar reaction can also be carried out with the participation of the C =C bond of the aliphatic component



A series of derivatives was obtained from 1,1,2-trichloro-3-phenylpropene-1 for a study of their herbicidal action



For some of the synthesized substances, we recorded the IR spectra on the UR-10 spectrograph in the region of 400-3100 cm^{-1}. The liquid samples were photographed in a layer 0.02-0.03 mm thick, the solid samples pressed in KBr.

TABLE 1

Components of reaction, moles		A : B	Temperature, °C	Rate of delivery, g/h	Yield of $C_9H_6Cl_4$, %
tetrachloroethylene (A)	chlorotoluene (B)				
0.5	0.5	1 : 1	540-545	32.5	11
1	0.5	2 : 1	540-545	51	20
0.5	1	1 : 2	540-545	56	12
2.5	0.5	5 : 1	525-530	95	18

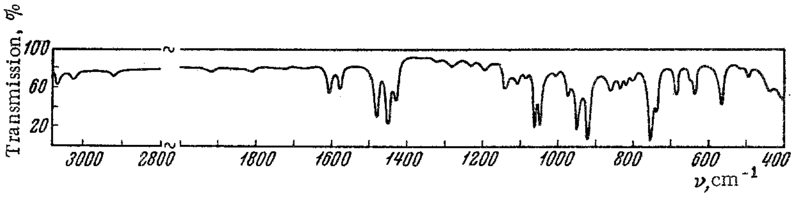


Fig. 3. IR spectrum of 1,1,2-trichloro-3-(2'-chlorophenyl)propene-1.

EXPERIMENTAL

Reactions of High-Temperature Condensation. The experiments were conducted according to the procedure described in [5, 6] in an empty quartz tube with a diameter of 23 mm, placed in a tubular electric furnace 600 mm long. The mixture of reagents was delivered to the tube uniformly by drops. The vapors emerging from the tube were condensed in a vapor condenser. The starting materials and products formed were distilled off from the condensate.

Reaction of Tetrachloroethylene with Mesitylene. A mixture of 83 g tetrachloroethylene and 120 g mesitylene was passed through the tube for 4 h at 435-445°. From the condensate obtained (175 g) we isolated 21.6 g (17% yield) 1,1,2-trichloro-3-(3',5'-dimethylphenyl)propene-1 with b.p. 120-121° (2 mm); n_D^{20} 1.5545; d_4^{20} 1.2434. Found %: C 52.86; H 4.58; MR 64.38. $C_{11}H_{11}Cl_3$. Calculated %: C 52.94; H 4.44; MR 63.72. The IR spectrum is cited in Fig. 1. We obtained 12 g of a high boiling residue.

Reaction of Tetrachloroethylene with Diphenylmethane. A mixture consisting of 83 g tetrachloroethylene and 84 g diphenylmethane was passed through a tube for 5 h at 525-535°. We obtained 158 g of the condensate, from which 21.6 g (14.5% yield) 1,1,2-trichloro-3,3-diphenylpropene-1 with b.p. 146-148° (0.5 mm); n_D^{20} 1.6073; d_4^{20} 1.2950. Found %: Cl 35.72, 35.69; MR 79.40. $C_{15}H_{11}Cl_3$. Calculated %: Cl 35.74; MR 78.82. The IR spectrum is cited in Fig. 2. High boiling residue 9.5 g.

Reaction of Tetrachloroethylene with Para-chlorotoluene. A mixture of 83 g tetrachloroethylene and 63.3 g para-chlorotoluene was passed through a tube at 540-545 g for 4.5 h. From 130 g of the condensation obtained, 14 g of 1,1,2-trichloro-3-(4'-chlorophenyl)propene-1 with b.p. 102-103° (1 mm), n_D^{20} 1.5760; d_4^{20} 1.4260. Found %: C 42.60, 42.64; H 2.55, 2.72; Cl 54.79, 54.98; MR 59.40. $C_9H_6Cl_4$. Calculated %: C 42.23; H 2.36; Cl 55.41; MR 59.26. High boiling residue 9 g.

Table 1 contains the results of four experiments. In the last three experiments, the second component is chlorotoluene, produced by chlorination of toluene in the presence of iron powder. According to gas-liquid chromatography, it represents chiefly the para-isomer.

Reaction of Tetrachloroethylene with Ortho-chlorotoluene. A mixture of 166 g tetrachloroethylene and 63.3 g ortho-chlorotoluene was passed through a tube at 575-580° for 8 h. From the condensate obtained we isolated 12.6 g (10%) 1,1,2-trichloro-3-(2'-chlorophenyl)propene-1 with b.p. 105-106° (1 mm); n_D^{20} 1.5775; d_4^{20} 1.4281. Found %: Cl 55.66, 55.56; MR 59.44. $C_9H_6Cl_4$. Calculated %: Cl 55.41; MR 59.26. The IR spectrum is given in Fig. 3.

Reaction of Tetrachloroethylene with Dichlorotoluene. Dichlorotoluene was produced in two steps: by the chlorination of toluene to monochlorotoluene, followed by the chlorination of

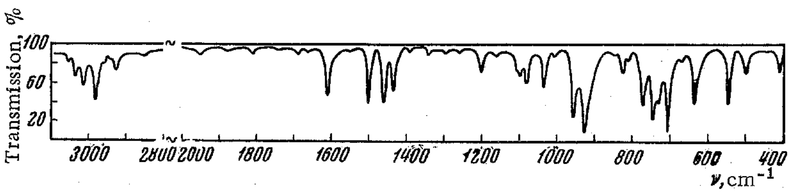


Fig. 4. IR spectrum of 1,1,2-trichloro-3-phenylpropene-1.

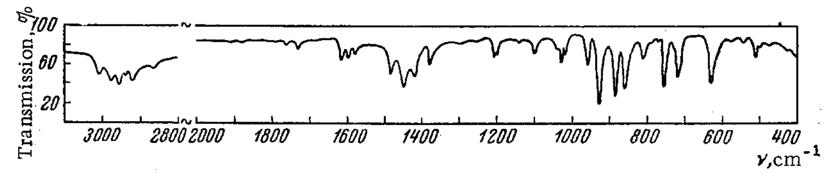


Fig. 5. IR spectrum of 1,1,2-trichloro-3-(2',4',6'-trimethylphenyl)-propene-1.

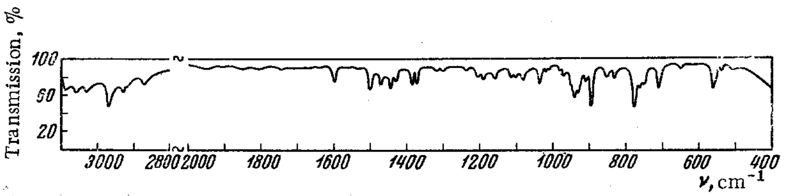


Fig. 6. IR spectrum of 1,1,2-trichloro-4-methyl-4-phenylpentene-1.

monochlorotoluene to dichlorotoluene [7]. The product boiled at 200-208°; n_D^{20} 1.5480; according to the available data it consists of 58% 2,4-dichlorotoluene and 42% 3,4-dichlorotoluene [7].

A mixture of 166 g tetrachloroethylene and 80.5 g dichlorotoluene was passed through a tube in a period of 7 h at 575-585°. From 208 g of the condensate obtained we isolated 21.5 g (15%) 1,1,2-trichloro-3-(dichlorophenyl)propene-1 with b.p. 107-108° (0.5 mm); n_D^{20} 1.5894; d_4^{20} 1.5133. Found %: Cl 61.07, 61.34; MR 64.71. $C_9H_5Cl_5$. Calculated %: Cl 61.07; MR 64.09. High boiling residue 7 g.

Reaction of 1,1,2,3-Tetrachloropropene-1 with Benzene. To a suspension of 0.5 g $AlCl_3$ in 19.5 g of benzene, 9 g of 1,1,2,3-tetrachloropropene-1 was added with mixing over a period of 45 min. The reaction mass was mixed at room temperature for another 5 h and then treated with a 3% solution of HCl. A total of 8 g (72%) 1,1,2-trichloro-3-phenylpropene-1 with b.p 70-71° (1 mm); n_D^{20} 1.5625; d_4^{20} 1.3173. Found %: Cl 48.09, 47.97; MR 54.58. $C_9H_7Cl_3$. Calculated %: Cl 48.02; MR 54.42. According to the data of [5]: b.p. 80-82° (2 mm); n_D^{20} 1.5636; d_4^{20} 1.3196 [5]. The IR spectrum is cited in Fig. 4.

Reaction of 1,1,2,3-Tetrachloropropene-1 with Mesitylene. To 84 g mesitylene we added 2 g of $AlCl_3$ and then slowly 18 g of 1,1,2,3-tetrachloropropene-1. After the reaction mass was allowed to stand overnight and then subjected to the usual treatment, 26 g (98%) 1,1,2-trichloro-3-(2',4',6'-trimethylphenyl)propene-1 with m.p. 87.5-88.5° (methanol) was isolated. Found %: Cl 40.80, 40.85. $C_{12}H_{14}Cl_3$. Calculated %: Cl 40.35. The IR spectrum is given in Fig. 5.

Reaction of 1,1,2,3-Tetrachloropropene-1 with Chlorobenzene. To 33.8 g chlorobenzene we added 2.7 g $AlCl_3$, then over a period of 2 h, 18 g of 1,1,2,3-tetrachloropropene-1. The reaction mass was mixed for 2 h at 40°, for 4 h at room temperature, and allowed to stand overnight. We obtained 15 g (59%) 1,1,2-trichloro-3-(chlorophenyl)propene-1 with b.p. 97-98° (0.5 mm); n_D^{20} 1.5753; d_4^{20} 1.4269. Found %: C 42.16, 41.86; H 2.53, 2.39; Cl 55.30, 55.12; MR 59.81. $C_9H_6Cl_4$. Calculated %: C 42.23; H 2.36; Cl 55.41; MR 59.26.

Reaction of 1,1,2-Trichloro-4-methylpentadiene-1,4 with Benzene. To a suspension consisting of 1.8 g $AlCl_3$ and 117 g benzene, we added 35.8 g 1,1,2-trichloro-4-methylpenta-

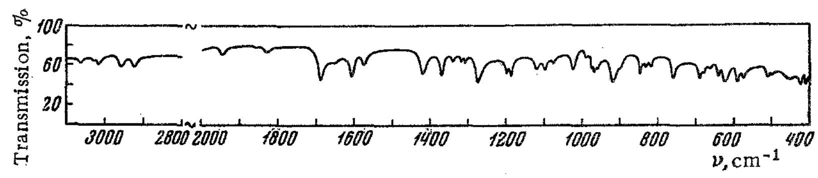


Fig. 7. IR spectrum of 1,1,2-trichloro-3-(4′-acetophenyl)propene-1.

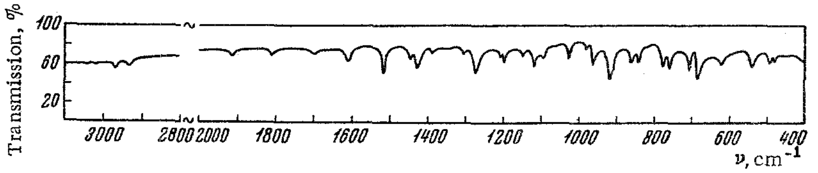


Fig. 8. IR spectrum of 1,1,2-trichloro-3-(chloromethylphenyl)propene-1.

diene-1,4 over a period of 2 h at 15-17°. After mixing at this same temperature for 5 h, the reaction mass was treated in the usual way. We obtained 43 g (85%) 1,1,2-trichloro-4-methyl-4-phenylpentene-1 with b.p. 103-104° (1 mm); n_D^{20} 1.5504; d_4^{20} 1.2346. Found %: Cl 39.76, 39.78; MR 68.06. $C_{12}H_{13}Cl_3$. Calculated %: Cl 40.35; MR 68.36. The IR spectrum is given in Fig. 6.

Reaction of 1,1,2-Trichloro-3-phenylpropene-1 with Bromine. To 65.5 g 1,1,2-trichloro-3-phenylpropene-1 we added 0.65 g of iodine, and then over a period of 4 h at 0°, 18 ml of bromine. After a 24 h exposure at room temperature, the reaction mass was washed with water and with a 10% soda solution. We obtained 38 g (42% on the basis of the 1,1,2-trichloro-3-phenylpropene-1, 60% on the basis of that reacted) of 1,1,2-trichloro-3-(bromophenyl)propene-1 with b.p. 114-115° (1 mm); n_D^{20} 1.5940; d_4^{20} 1.6455. Found %: C 36.29, 36.17; H 2.17, 2.18; Hal 61.88, 61.72; MR 61.95. $C_9H_6BrCl_3$. Calculated %: C 35.98; H 2.01; Hal 62.00; MR 62.14.

Reaction of 1,1,2-Trichloro-3-phenylpropene-1 with Acetyl Chloride. To a suspension prepared from 20 g $AlCl_3$ and 70 ml nitrobenzene, 9.4 g acetyl chloride was added at 0-5°. At the same time, 22.1 g of 1,1,2-trichloro-3-phenylpropene-1 was added to the mixture obtained over a period of 2 h. The reaction mass was mixed for another 2.5 h at 55-65° and then treated in the usual way. We obtained 14 g (53% on the basis of the 1,1,2-trichloro-3-phenylpropene-1 taken, 99% on the basis of that reacted) 1,1,2-trichloro-3-(4′-acetophenyl)propene-1 with b.p. 146-148° (2 mm); m.p. 45.5-46.5° (hexane). Found %: Cl 40.62, 40.59. $C_{11}H_9OCl_3$. Calculated %: Cl 40.36. The IR spectrum is given in Fig. 7.

Chloromethylation of 1,1,2-Trichloro-3-phenylpropene-1. To 85 g nitrobenzene we added 9 g of paraform, 9 g of zinc chloride, then the nitrobenzene was saturated with hydrogen chloride. A stream of hydrogen chloride was passed into the reaction mass for a period of 30 min at 60-65°, and 2 g of zinc chloride and 44.3 g of 1,1,2-trichloro-3-phenylpropene-1 were added. After 2 h, the reaction mass was treated with water and with a 10% soda solution. We obtained 24 g (44.5% of the 1,1,2-trichloro-3-phenylpropene-1 taken, 56% of that reacted) 1,1,2-trichloro-3-(chloromethylphenyl)propene-1 with b.p. 138-141° (2 mm); n_D^{20} 1.5772; d_4^{20} 1.3945. Found %: MR 64.18. $C_{10}H_8Cl_4$. Calculated %: MR 63.94. The IR spectrum is given in Fig. 8. When this liquid was redistilled, a crystalline product was isolated — evidently $p\text{-}ClCH_2C_6H_4CH_2CCl{=}CCl_2$ with m.p. 42.5-44.5° (hexane). Found %: C 44.27, 44.45; H 2.89, 2.83; Cl 52.98, 52.86. $C_{10}H_8Cl_4$. Calculated %: C 44.48; H 2.99; Cl 52.53.

The spectra were obtained by E. D. Lubuzh, for which we should like to express our gratitude.

CONCLUSIONS

1. As a result of the condensation of tetrachloroethylene with alkylaromatic hydrocarbons and chlorohydrocarbons in the gas phase at the temperature 420-570°, unsaturated chlorohydrocarbons with the trichlorovinyl group in the alkyl chain are formed.

2. A series of chlorohydrocarbons, of interest as potential herbicides, was synthesized.

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