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Abstract

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REACTION OF DI-, TRI-, AND TETRACHLOROMETHANES WITH METALLIC LITHIUM—A NEW METHOD FOR PREPARING CHLOROCARBENES

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One of the widely used methods for preparing halocarbenes is the reaction of di- and polyhalomethanes with lithium alkyls (^{1}) or lithium aryls (^{2}).

However, the presence of organolithium compounds in the reaction mixture leads—especially when the nucleophilicity of the carbene acceptors is low—to an undesirable interaction, in most cases, of the carbenes formed with the starting RLi ($^{1-3}$). This lowers the yields of carbene adducts with the acceptors employed and complicates the overall picture of the reaction.

In view of the foregoing, the reaction of the same di- and polyhalomethanes directly with alkali metals is of considerable interest. However, earlier attempts (^{4},^{5}) to carry out the interaction of CH_2Cl_2, $CHCl_3$, and other polyhalomethanes with potassium, sodium, and even lithium in the absence of polar solvents led, as a rule, to explosions.*

Having undertaken a broad study of the interaction of various di- and polyhalides of Group IVB elements with alkali metals in polar solvents, we have shown the possibility of directly preparing, by this route, various carbenes (^{6}) and carbenoids (^{7}). In the present work we have investigated in detail the reaction of a series of di- and polychloromethanes with metallic lithium (sodium) in simple ethers. The most suitable solvent for this reaction proved to be tetrahydrofuran (THF), in which CH_2Cl_2, $CHCl_3$, CCl_4, and $CBrCl_3$ reacted with lithium (temperature from −20 to 40°) very readily and smoothly, without any induction period, even when it was diluted with a considerable amount of olefin or another carbene acceptor. Replacement of THF by diethyl ether or another dialkyl ether practically completely suppressed the indicated interaction. Such a sharp difference between diethyl ether and THF is apparently connected chiefly with the greater polarization of the C—H and C—Hal bonds of the starting di-(poly)-chloromethanes in the more basic and polar THF (μ1.70 D as compared with 1.15 D for $(C_2H_5)_2O$), which, when metallic lithium is used instead of its compounds, evidently has decisive significance. In a similar way, as is known (^{8}), the role of THF is also explained in the formation of organometallic compounds from vinyl halides and other halides with immobile halogens.

The chlorocarbenes formed as a result of the interaction of di-(poly)-chloromethanes with lithium were identified in the form of adducts with cyclohexene or other olefins (1-methylcyclohexene, tetramethylethylene), as well as with piperidine and tri-*n*-butylphosphine. In this case, here as in experiments with RLi ([1],[2]), from $CHCl_3$, $CBrCl_3$, and CCl_4 exclusively dichlorocarbene was formed, and from CH_2Cl_2 —monochlorocarbene (possibly together with methylene):

$$H_2CCl_2 \xrightarrow[\text{THF}]{\text{Li}} LiCHCl_2 \xrightarrow{-\text{LiCl}} :CHCl \xrightarrow{>C=C<} \text{chloronorcarane},$$

$$XCCl_3 \xrightarrow[\text{THF}]{\text{Li}} LiCCl_3 \xrightarrow{-\text{LiCl}} :CCl_2 \xrightarrow{>C=C<} \text{dichloronorcarane},$$

where X is H, Br, or Cl.

The yields of the chlorocyclopropanes (chloronorcaranes) obtained under these conditions varied, depending on the properties of the starting reagents and on the experimental temperature, from 10 to 40% of theory (Table 1).

Table 1

Starting di-(poly)halomethane	Reaction temperature, °C	Reaction products: name	Yield, % (based on starting polyhalomethane)
CH_2Cl_2	10-15	7-Chloronorcarane	11.5
Same	3-5	Same	12
$CHCl_3$	10-15	7,7-Dichloronorcarane	36
Same	10	Same	27.5
Same	−10	Same	28.5
$CBrCl_3$	15	Same	28
Same	0	Same	29.5
CCl_4	35-40	Same	13

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* The gaseous reaction products of $CHCl_3$ with sodium or potassium in the presence of oxygen consisted of 50-60% phosgene ([5]), which indicates the possibility of dichlorocarbene formation under these conditions:

$$HCCl_3 \xrightarrow{\text{Na(K)}} :CCl_2 \xrightarrow{O_2} COCl_2.$$

Starting di-(poly)halomethane	Reaction temperature, °C	Reaction products: name	Yield, % (based on starting polyhalomethane)
Same	10	Same	27
Same	0	Same	19

Note. In all experiments, 0.2 mole of di-(poly)halomethane, 1 mole of cyclohexene, 0.65 g-atom of lithium, and 100 ml of THF were taken.

In accordance with the expected ease of metalation of the indicated polychloromethanes, $CBrCl_3$ and $CHCl_3$ generated dichlorocarbene under milder conditions (optimal temperatures, respectively, −15-0° and from −10 to 10°) than CCl_4 (10-15°). Data from experiments on the competing interaction of an equimolar mixture of $CHCl_3$ and CCl_4 with lithium in THF in the presence of an excess of cyclohexene at 0-10° showed that chloroform in this reaction is indeed 1.6-1.7 times more active than carbon tetrachloride.

Dichlorocarbene generated by the action of lithium from tri- and tetrachloromethanes forms the corresponding adducts also with other carbene acceptors. Thus, when this reaction was carried out in the presence of piperidine, there occurred, as was to be expected(9), insertion of dichlorocarbene into the N—H bond, followed after hydrolysis by formation of N-formylpiperidine (yields 5-10%):

$$CH_2(CH_2)_3NH + {:}CCl_2 \longrightarrow CH_2(CH_2)_3NCCl_2H \xrightarrow{H_2O} CH_2(CH_2)_3NC(=O)H.$$

The chlorine-containing adducts formed as a result of the addition of chlorocarbenes, as a rule, underwent under the experimental conditions (Li + THF) a number of further transformations, which led to the known decrease in the yields of these adducts. In particular, it was shown by special experiments that 7,7-dichloronorcarane (I) reacts rather readily with lithium in THF over the temperature range from −10 to 10°, leading to formation of alkylidenecarbene (II) and, further, products of its isomerization and addition, for example to the solvent:

$$(I) \xrightarrow[THF]{Li} \text{lithiochloro derivative} \xrightarrow{-LiCl} (II) \xrightarrow{THF} (III) + \text{mixture of hydrocarbons } C_7H_{10} + \text{resin}.$$

Similarly, Moore and co-workers(10) earlier observed addition of carbene II, formed by the action of lithium alkyls on I, to the α-C—H bond of diethyl ether (solvent). In contrast to II, the less reactive dichlorocarbene obtained from tri- and tetrachloromethanes and lithium, or from $CHCl_3$ and potassium tert-butoxide, at temperatures from −20 to 30° practically did not add to THF.

In order to confirm the intermediate formation of carbenes in the reactions of di- and polychloromethanes with metallic lithium, we carried out competitive dichloromethylenation of an equimolar mixture of cyclohexene and 1-methylcyclohexene, and also of cyclohexene and tetramethylethylene, by the action of lithium on tri- or tetrachloromethane. In this case, in full agreement with the electrophilic addition mechanism accepted for singlet carbenes, the ratio between 7,7-dichloronorcarane (I) and 1-methyl-7,7-dichloronorcarane in the first experiment was $\sim 1 : 7$, and between I and tetramethylgem-dichlorocyclopropane in the second was $\sim 1 : 50$. These values correspond exactly to the comparative reactivity of the indicated olefins (Ka/Kb) toward $:CCl_2$ (from $HCCl_3$ and tert. C_4H_9OK), determined earlier by us (^{11}) and by Doering (^{12}).

Experimental Part

All substances, before being introduced into the reaction, were distilled on a column; the olefins were first purified by prolonged boiling over sodium wire. The purity of the starting reagents was monitored chromatographically. Chromatographic determinations were carried out on a gas–liquid chromatograph with a thermal-conductivity detector, constructed by the Special Design Bureau of the Institute of Organic Chemistry, Academy of Sciences of the USSR. All experiments with alkali metals were carried out in an atmosphere of dry purified nitrogen.

Reaction of di-(poly)chloromethanes with lithium in the presence of olefins. a) To a mixture of 4.5 g (0.65 g-atom) of small pieces of lithium, 82 g (1 mole) of dry cyclohexene, and 100 ml of abs. THF, 0.2 mole of di- or polychloromethane was added dropwise over 1 h with vigorous stirring by a steel turbine stirrer. The mixture was then stirred for another 0.5–1 h, separated from unchanged lithium, washed with water, dried, distilled, and analyzed by gas–liquid chromatography (columns 0.4 × 200 cm with 10% Apiezon "L" or polysiloxane "Siss" on Chromosorb "W"; carrier gas He; temperature 100–130°). The results of these experiments are given in Table 1.

Replacement of lithium by sodium or of THF by diethyl ether practically excluded the indicated reaction.

The reference 7-chloronorcarane (a mixture of two stereoisomers) and 7,7-dichloronorcarane required for identification were obtained by us according to (^{1}) and (^{11}), and their properties fully coincided with the properties of the corresponding chloronorcaranes isolated from the experiments presented in Table 1.

b) Analogously to the experiments with cyclohexene, the reaction of CCl_4 with lithium was carried out in the presence of 1-methylcyclohexene at 10–12°. The yield of 1-methyl-7,7-dichloronorcarane, identical with that described earlier (^{11}), was 33.5% of theoretical.

c) The experiments on "competitive" addition were carried out by the slow addition of 0.2 mole of $CHCl_3$ to a mixture of 0.5 mole of cyclohexene, 0.5 mole of 1-methylcyclohexene, 0.5 g-atom of lithium, and 100 ml of THF at 7-12°, or of 0.12 mole of CCl_4 to a mixture of 0.3 mole of cyclohexene, 0.3 mole of tetramethylethylene, 0.3 g-atom of lithium, and 100 ml of THF at 0-10°. The products formed were treated and analyzed in the usual manner. In the first experiment, 6.5 mmoles (3.2%) of 7,7-dichloronorcarane and 45 mmoles (22.5%) of 1-methyl-7,7-dichloronorcarane were obtained; in the second, 0.8 mmole (0.7%) of 7,7-dichloronorcarane and 42.5 mmoles (35.5%) of 1,1,2,2-tetramethyl-3,3-dichlorocyclopropane, b.p. 48° (10 mm), m.p. 48-49° (from alcohol).

Found, %: C 50.40, 50.40; H 7.40, 7.35; Cl 42.01, 42.12
$C_7H_{12}Cl_2$. Calculated, %: C 50.32; H 7.23; Cl 42.44

According to (^{12}), m.p. 49.8-50.5°.

Reaction of tetrachloromethane with lithium in the presence of piperidine. To 4.2 g (0.6 g-atom) of lithium, 85 g (1 mole) of piperidine, and 100 ml of THF was added 46 g (0.3 mole) of CCl_4 (15-30°, 40 min). The mixture was stirred for another 30 min and filtered. The fil—

The trate was treated with water, dried over K_2CO_3, and distilled. The reaction products were chromatographed on a 0.4 × 200 cm column with 2% Apiezon "M" on Chromosorb "W" at 190° (carrier gas He, 100 ml/min). The yield of N-formylpiperidine was 9% of theory. An authentic sample of this compound was prepared by boiling equimolar amounts of HCOOH and piperidine for 7 h (^{9}), b.p. 95-96° (10 mm), n_D^{20} 1.4787.

From the higher-boiling reaction products, N,N′-dipiperidyl ketone was isolated, yield 8.5% of theory, b.p. 102-103° (1.5 mm), m.p. 46-47° (from *n*-hexane).

Found, %: C 67.40, 67.44; H 10.33, 10.20; N 14.32, 14.34
$C_{11}H_{20}N_2O$. Calculated, %: C 67.30; H 10.27; N 14.27

In the IR spectrum of the latter, recorded in a KBr pellet, there is an intense band at 1650 cm^{-1}, characteristic of a carbonyl group. In the literature (^{13}), for this ketone the b.p. is given as 296-298°, m.p. 42-43°.

In a similar experiment carried out at 0-10°, 5% N-formylpiperidine and 7.5% N,N′-dipiperidyl ketone were obtained.

Reaction of 7,7-dichloronorcarane with lithium. To a stirred mixture of 4.5 g (0.65 g-atom) of lithium and 100 ml of THF was added, over 20 min, 33 g (0.2 mole) of 7,7-dichloronorcarane (I) at 0-10°. After the usual work-up, the charge with 2 g of resin of b.p. > 220° (1.5 mm) was separated by distillation into 5 g of a fraction with b.p. 108-114° (765 mm), n_D^{20} 1.4837; 4.5 g (13.5%) of unchanged I; and 10 g (30% based on the initial I) of 7-tetrahydrofuryl norcarane, which, by analogy with (^{10}), probably has structure III, b.p. 96-96.5° (10 mm), n_D^{20} 1.4840, d_4^{20} 1.0041.

Found, %: C 79.05, 79.02; H 10.79, 10.83
$C_{11}H_{18}O$. Calculated, %: C 79.46; H 10.91

Raman spectrum ($\Delta\nu$, cm^{-1}): 152 (2), 287 (2), 445 (1), 634 (0), 773 (0), 788 (1), 928 (8 sh), 969 (0 sh), 1026 (5 sh), 1083 (2 sh), 1177 (1 sh), 1219 (1 sh), 1277 (2 sh), 1447 (6 sh), 2861 (9 sh), 2905 (1), 2939 (6 sh), 2996 (1 sh), 3025 (0).

The fraction with b.p. 108-114° (765 mm) was a mixture of unsaturated and saturated alicyclic hydrocarbons of composition C_7H_{10} (^{10}) with an admixture of oxygen-containing compounds. In the IR spectrum, frequencies were found at 1690 cm^{-1} (carbonyl group), 1640 and 3080 cm^{-1} (terminal double bond), 1600, 2995, and 3015 cm^{-1} (nonterminal double bond).

In a similar experiment carried out at $-6°$ in the presence of 1 mole of cyclohexene, 47% unchanged I, 12.5% III, 2% hydrocarbons C_7H_{10}, and 3 g of resin with b.p. $> 170°$ (2 mm) were obtained.

When the reaction of I with lithium was carried out in diethyl ether, only 3 g of resin with b.p. $> 200°$ (4 mm) was obtained.

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