[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

THE MECHANISM OF THE REACTION BETWEEN LITHIUM *N*-BUTYL AND VARIOUS ORGANIC HALOGEN COMPOUNDS

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The lithium alkyls are reagents that have not been widely used and many of their reactions have not been thoroughly investigated. It is known that they are spontaneously inflammable in air; that they react with almost any type of organic compound containing oxygen;[1] that they react with water to give the hydrocarbon;[2] and that they react with quarternary ammonium halides.[3] It seemed likely that they might be used to advantage in the synthesis of hydrocarbons by allowing them to react with various halogen derivatives of hydrocarbons. The simple reaction that might be expected would be $RX + LiR' \longrightarrow RR' + LiX$.

In investigating the possibilities of this reaction, lithium *n*-butyl was chosen as a typical lithium alkyl because it is comparatively easy to prepare and is quite soluble in petroleum ether. The lithium *n*-butyl solution was prepared in a large reaction flask, measured, analyzed and then transferred to smaller graduated flasks so that a known amount could be used in each reaction. The halogen compound, usually in solution or suspension in purified petroleum ether, was mixed with the lithium *n*-butyl solution in sealed tubes in such a way that no air was admitted.

The reaction between lithium *n*-butyl and the following halogen compounds was studied: *n*-heptyl bromide, trimethylene bromide, methylene iodide, carbon tetrachloride, *β*-bromostyrene, tetrachloro-ethylene, *o*-, *m*- and *p*-bromotoluenes, *o*-dichlorobenzene, hexabromobenzene, *α*-chloropyridine and triphenylchloromethane. With *n*-heptyl bromide, methylene iodide, *β*-bromostyrene, *p*-bromotoluene and triphenylchloromethane some of the expected hydrocarbon was isolated in each case but the yields varied over a wide range. The other halogen compounds in general gave unexpected compounds or tarry products from which nothing definite could be isolated.

It was noticed in nearly every case that a marked color developed when the lithium *n*-butyl solution and the halogen compound were mixed. This color usually disappeared if the mixture was allowed to stand for several days. The development of color was particularly noticeable when *β*-bromostyrene was used. When it was first treated with lithium *n*-butyl solution a deep red color appeared. This color changed to a purple and then gradually faded out entirely. When this tube was opened,

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[1] Schlenk and Holtz, *Ber.*, **50**, 271 (1917).

[2] Grosse, *Ber.*, **59**, 2653 (1926).

[3] Hager with Marvel, THIS JOURNAL, **48**, 269 (1926).

the products isolated from the reaction were phenyl-1-hexene-1 and *trans-trans*-diphenyl-1,4-butadiene-1,3.

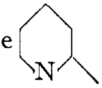
The production of color and the isolation of diphenylbutadiene suggested that probably the reaction between lithium *n*-butyl and β-bromostyrene gave first two free radicals, the *n*-butyl radical and the group $C_6H_5CH{=}CH{-}$. These free radicals could then react subsequently in the following manners.

I $C_4H_9{-} + C_6H_5CH{=}CH{-} \longrightarrow C_6H_5CH{=}CH{-}C_4H_9$
II $2\,C_4H_9{-} \longrightarrow C_4H_9{-}C_4H_9$
III $2\,C_6H_5CH{=}CH{-} \longrightarrow C_6H_5CH{=}CH{-}CH{=}CH{-}C_6H_5$
IV $2\,C_4H_9{-} \longrightarrow C_4H_8 + C_4H_{10}$
V $2\,C_6H_5CH{=}CH{-} \longrightarrow C_6H_5C{\equiv}CH + C_6H_5CH{=}CH_2$
VI $C_4H_9{-} + C_6H_5CH{=}CH{-} \longrightarrow C_4H_8 + C_6H_4CH{=}CH_2$
VII $C_4H_9{-} + C_6H_5CH{=}CH{-} \longrightarrow C_4H_{10} + C_6H_5C{\equiv}CH$

The products isolated indicate that reactions I and III actually had taken place. Probably reaction IV also occurs and the butyl group is lost as gaseous butene-1 and butane. There is no indication that either octane, phenylethylene or phenylacetylene was produced.

If the reaction really proceeds through the formation of free radicals, it would be expected that if lithium *n*-butyl were allowed to react with triphenylchloromethane, the characteristic color of triphenylmethyl would appear. When this reaction was carried out a highly colored solution was obtained. The color deepened on heating the mixture and faded on cooling as it should if hexaphenylethane were produced. When the reaction vessel was opened the color was discharged. The products isolated from the reaction mixture were triphenyl-1,1,1-pentane, triphenylcarbinol and *n*-butyl alcohol. The triphenylcarbinol was a secondary product obtained by the action of sulfuric acid on a mixture of the hydrocarbon and some sulfuric acid soluble product which could not be isolated by crystallization from inert solvents. This substance was presumably triphenylmethylperoxide, the presence of which indicates that a reaction analogous to II above occurred to give hexaphenylethane, which was then oxidized in the air, when the tube was opened, to give the peroxide. The *n*-butyl alcohol must have been formed from a smaller amount of unreacted lithium *n*-butyl by oxidation with air.

The formation of very complex products from compounds containing more than one halogen would be predicted if free radicals are intermediate products in this reaction. Of the polyhalogen compounds studied, only methylene iodide gave enough of the expected hydrocarbon for isolation, and a large high-boiling portion was produced as a side product. *o*-Dichlorobenzene and hexabromobenzene gave very complex insoluble compounds. Trimethylene bromide and carbon tetrachloride gave high-boiling products from which no definite pure substances could be isolated. Tetrachloro-ethylene was used in only one reaction and when it was mixed with the lithium *n*-butyl solution a very violent explosion occurred.

The only halogen compound used which was not a hydrocarbon derivative was α-chloropyridine. It gave a very tarry product from which nothing definite could be isolated. A free radical of the type  would not be expected to be very stable.

The products isolated from the reaction of lithium *n*-butyl and *o*-, *m*- and *p*-bromotoluene were the most unexpected. *p*-Bromotoluene and lithium *n*-butyl gave a 76% yield of *p*-*n*-butyltoluene. On the other hand *o*- and *m*-bromotoluenes gave nearly quantitative yields of toluene. In the case of *p*-bromotoluene the reaction is almost entirely of the type illustrated by Equation I. With the *ortho* and *meta* isomers the reaction is almost entirely of the type illustrated by Equation VI. This difference in reaction between *ortho*, *meta* and *para* isomers would not be predicted.

While no butene or butane has been isolated from any of the reaction mixtures, as would be required to establish definitely the exact course of the reaction, there seems to be little doubt that free radicals are first produced when a halogen compound reacts with a lithium alkyl. A very similar mechanism for the Wurtz-Fitting reaction for the synthesis of hydrocarbons has been recently advanced by Bachmann and Clarke.[4]

Experimental Part

Apparatus and General Procedure.—About 1 liter of 1 molar lithium *n*-butyl solution in petroleum ether was prepared and analyzed according to the procedure of Hager and Marvel[3] and then transferred from the reservoir C to a series of small reaction flasks as shown in Fig. 1. The reaction flasks were made in two compartments, separated by a glass valve easily broken. In one (D) the lithium *n*-butyl solution was measured. In the other compartment (E) was placed the halogen compound dissolved or suspended in purified petroleum ether. The compartment containing the lithium *n*-butyl solution was sealed off, the glass valve between the two compartments was broken and the two solutions were slowly mixed. In order to avoid accidents the reaction flask was placed behind a heavy glass shield before the valve was broken.

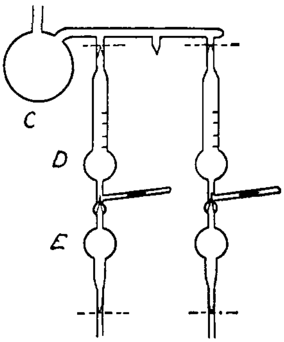


Fig. 1.

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[4] Paper presented before the Organic Section of the American Chemical Society at the meeting in Richmond, April, 1927, THIS JOURNAL, **49**, 2089 (1927).

The petroleum ether was purified as described in the earlier paper.[3] The fraction boiling at 35–50° was used. Air was removed from the reaction flasks by displacement with solvent vapors or by evacuating the flask with a mercury vapor pump. All of the liquid halogen compounds were purified by distillation and the material used boiled over only a one-half degree range in most cases. The solid halogen compounds were recrystallized until their melting points were constant.

After the reactions were complete, the reaction flasks were opened and the contents poured into ice water. The aqueous solution was saved and analyzed for halogen and for alkalinity. This gave a rough check on the completeness of the reaction. In nearly every case the reactions ran to completion as far as removal of halogen was concerned. The petroleum ether solutions were carefully distilled and the higher-boiling residues of hydrocarbons were separated as far as possible by distillation or crystallization.

The reaction between lithium *n*-butyl and triphenylchloromethane was carried out in the apparatus shown in Fig. 2. This change in style of apparatus seemed desirable because of the low solubility of the halogen compound in low-boiling petroleum ether. The lithium alkyl solution was placed in one bulb (A) and the dry triphenylchloromethane in the other (B). Some of the petroleum ether was then distilled over into the bulb containing the halogen compound. Some of the triphenylchloromethane dissolved. The apparatus was tilted and this solution was filtered into the lithium *n*-butyl solution. These processes were repeated until all of the triphenylchloromethane was carried into the bulb containing the lithium *n*-butyl.

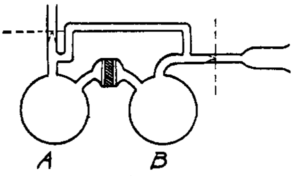

Fig. 2.

Lithium *n*-Butyl and *n*-Heptyl Bromide.—Approximately 0.25 mole of lithium *n*-butyl was mixed with 0.25 mole of *n*-heptyl bromide. After 90 days the tube was opened and the contents poured into ice water. Careful fractionation of the petroleum ether layer resulted in the isolation of 4 g. of nearly pure *n*-undecane. The observed constants were, b. p. 192–197°; d^{20}_{0} 0.7966, n^{22}_{D} 1.4220. The constants reported in the literature[5] are: b. p. 195°; d^{20}_{0} 0.741; n^{20}_{D} 1.4184.

Lithium *n*-Butyl and Methylene Iodide.—This reaction was run with 0.50 mole of lithium *n*-butyl and 0.25 mole of methylene iodide. The reaction mixture stood for 23 days before it was opened. About 2 g. of impure *n*-nonane was isolated from a considerable quantity of higher-boiling material which could not be separated into definite fractions. The observed physical constants were: b. p. 147–149°; d^{20}_{0} 0.7486; n^{18}_{D} 1.412; whereas those given in the literature[6] are: b. p. 150.6°; d 0.718; n^{20}_{D} 1.405.

Lithium *n*-Butyl and β-Bromostyrene.—The reaction was run with 0.25 mole of each reagent. The reaction mixture stood for 38 days before opening. The petroleum ether was distilled under ordinary pressure and then a fraction was removed under

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[5] International Critical Tables, Vol. I. McGraw-Hill Book Co., **1926**, page 243.

[6] Ref. 5, p. 230.

reduced pressure. The residue solidified. The fraction which was distilled under reduced pressure had the following physical constants: b. p. 97–100° at 8 mm.; d_0^{25} 0.9455; n_D^{25} 1.5377; M_D, calcd. for phenyl-1-hexene-1, 53.55; found, 52.96.

Anal. (total carbon). Subs. 0.4123: 809.1 cc. CO_2 at 26° and 738.4 mm. Calcd. for $C_{12}H_{16}$: C, 89.93. Found: 89.65.

The solid residue in the distilling flask was recrystallized from ethyl alcohol and then melted at 145–146°. It added bromine readily to give a product which melted with decomposition at 235–242°. The *trans-trans* isomer of diphenyl-1,4-butadiene-1,3 melts at 147–148° and adds bromine to give a tetrabromo addition product which melts with decomposition at 230°.[7]

Lithium *n*-Butyl and Triphenylchloromethane.—The reaction was run for 9 days using 0.20 mole of triphenylchloromethane and 0.23 mole of lithium *n*-butyl. In working up the product some material crystallized from the petroleum ether. This was separated and found to consist of more than one substance. On treatment with sulfuric acid part of the material went into solution. This was poured into ice water and a solid separated. On recrystallization from alcohol pure triphenylcarbinol melting at 160–161° was obtained. Since the original material would not give triphenylcarbinol on recrystallization alone, this must have been produced from triphenylmethyl peroxide by the action of sulfuric acid.

On distilling the petroleum ether about half a gram of material boiling at 105–116° with the characteristic odor of *n*-butyl alcohol was isolated. Its identification as *n*-butyl alcohol was confirmed by making the 3,5-dinitrobenzoate, which melted at 61°.

The residue after removal of the petroleum ether and *n*-butyl alcohol was distilled under 0.01 mm. pressure and a fraction boiling at 170–180° was isolated. After a few days this fraction solidified and on recrystallization from petroleum ether, acetone or ethyl alcohol gave crystals melting at 153–154°.

Anal. Subs. 0.1642, 0.1680: CO_2, 0.5536, 0.5649; H_2O, 0.1230, 0.1225. Calcd. for $C_{23}H_{24}$: C, 91.94; H, 8.06. Found: C, 92.09, 91.73; H, 8.39, 8.16.

This material is undoubtedly triphenyl-1,1,1-pentane. The total amount isolated was 16 g., or about 26% of the calculated amount.

Lithium *n*-Butyl and α-Chloropyridine.—The quantities used in this experiment were 0.35 mole of lithium *n*-butyl and 0.30 mole of α-chloropyridine. The reaction mixture stood for 7 days. Only tarry, insoluble products could be isolated.

Lithium *n*-Butyl and *o*-Bromotoluene.—A mixture of 0.25 mole of *o*-bromotoluene and 0.27 mole of lithium *n*-butyl was allowed to stand for 4 days. On fractionation of the petroleum ether a 65% yield of toluene boiling at 109–113° was isolated. It was further identified by oxidation to benzoic acid, m. p. 121°, and nitration to 2,4-dinitrotoluene, m. p. 70–71°.

Lithium *n*-Butyl and *m*-Bromotoluene.—A mixture of 0.24 mole of *m*-bromotoluene and 0.25 mole of lithium *n*-butyl was allowed to stand for 4 days. An 87% yield of toluene was isolated.

Lithium *n*-Butyl and *p*-Bromotoluene.—A mixture of 0.25 mole of each reagent was allowed to stand for 30 days. From the petroleum ether was obtained 28 g. (75% of the calculated amount) of *p*-butyltoluene, b. p. 197–200°; n_D^{14} 1.5009; d_4^{14} 0.9452. The constants given in the literature[8] are: b. p. 198–199°; $d_4^{14.2}$ 0.8618; $n_D^{14.2}$ 1.4912. Since the constants did not check as closely as might be desirable, a sample of the hydrocarbon was oxidized to terephthalic acid and this then converted to the dimethyl ester, which melted at 137–138°.

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[7] Rebuffat, *Gazz. chim. ital.*, **15**, 107 (1885); **20**, 155 (1890).

[8] Niemczycki, *Chem. Zentr.*, **71**, 468 (1900).

Lithium *n*-Butyl and Polyhalogen Compounds.—When lithium *n*-butyl solutions were allowed to react with trimethylene bromide and carbon tetrachloride, complex liquid hydrocarbon mixtures were obtained. With *o*-dichlorobenzene heavy, tarry products slightly fluorescent in solution were produced. Hexabromobenzene gave a dark insoluble powder. A similar powder was obtained when lithium phenyl was used instead of lithium *n*-butyl. When tetrachloro-ethylene was used a violent explosion occurred.

Summary

1. The reaction between lithium *n*-butyl and various halogen compounds has been studied.
2. In general the simple reaction of replacement of halogen by the *n*-butyl group does not occur.
3. The products which were formed suggest that the first step in the reaction of lithium *n*-butyl and a halogen compound is the formation of free radicals. These then undergo further reactions which differ widely for different groups.

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MAGNESIUM DIETHYL AND ITS REACTION WITH ACETYL CHLORIDE

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Introduction

Magnesium diethyl was apparently first prepared by Hallwachs and Schafarik[1] by heating magnesium with ethyl iodide. They described it as a solid, although the reactions of the liquid or oily fraction indicate that some magnesium diethyl was contained in the excess ethyl iodide. Later, Cahours[2] carried out the preparation from the same materials but he described his product as a liquid. Löhr[3] then prepared magnesium diethyl by heating magnesium with ethyl iodide and also by heating magnesium with mercury diethyl. His product was a solid. Fleck[4] extended Löhr's work on magnesium dialkyls, and, among other reactions, made a careful study of the reaction between magnesium diethyl and acetyl chloride.

We have prepared magnesium diethyl by the preferred method of Löhr[3] and Fleck,[4] namely, by heating magnesium with mercury diethyl

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[1] Hallwachs and Schafarik, *Ann.*, **109**, 206 (1859).

[2] Cahours, *Ann.*, **114**, 227 (1860).

[3] Löhr, *Ann.*, **261**, 48 (1891).

[4] Fleck, *Ann.*, **276**, 129 (1893).