[Contribution from the Department of Chemistry of the University of Colorado]

THE ACTION OF SODIUM ON SOME ORGANIC HALIDES IN LIQUID AMMONIA[1]

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In the course of an investigation of the action of sodium on benzyl chloride,[2] it was observed that in liquid ammonia a good yield of dibenzyl was obtained, together with toluene and other non-nitrogenous products. The work of previous investigators, particularly Lebeau,[3] Chablay,[4] Kraus,[5] Picon,[6] Dains[7] and others, has shown that, as a rule, in this solvent the organic halogen compounds yield mixtures of amines, nitriles and unsaturated hydrocarbons.

In order to determine to what extent coupling reactions in the sense of the Wurtz–Fittig synthesis might take place, the following organic halogen compounds were investigated: benzyl chloride, 1-phenyl-2-bromo-ethane, 1-phenyl-3-bromopropane, 1-phenyl-4-bromobutane, benzal chloride, benzo-trichloride, diphenyldichloromethane, diphenylchloromethane, *o*-xylylene bromide, β-bromophenylethyl ether, γ-bromophenylpropyl ether, δ-chloro-acetophenone, β-chloropropiophenone. Chlorobenzene and triphenylchloromethane, which should be considered in this group, have already been investigated by White[8] and Kraus and Kawamura,[9] respectively. The first compound yields benzene and primary, secondary and tertiary amines, while the second yields the sodium salt of triphenylmethane which, in turn, enters into various reactions.

Benzoyl chloride, which also might be considered here, reacts instantaneously with the liquid ammonia to give an almost quantitative yield of benzamide. This reaction furnishes a very convenient method for the preparation of the amide.

Apparatus and Procedure

About 250 cc. of anhydrous ammonia was placed in an unsilvered Dewar flask of 300-cc. capacity. The halide and sodium were added in small

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[1] Abstracted from a thesis presented by Gerard Berchet to the Graduate Faculty of the University of Colorado in partial fulfilment of the requirements for the Doctor of Philosophy degree.

[2] A detailed report of the action of sodium on benzyl chloride in liquid ammonia, in ether, and in the absence of solvent will be published later.

[3] Lebeau, *Compt. rend.*, **140**, 1042, 1264 (1905).

[4] Chablay, *Ann. chim.*, [9] 1, 469 (1914).

[5] Kraus and White, This Journal, **45**, 768 (1923).

[6] Picon, *Bull. soc. chim.*, **35**, 979 (1924).

[7] Dains and Brewster, This Journal, **42**, 1573 (1920).

[8] White, *ibid.*, **45**, 779 (1923).

[9] Kraus and Kawamura, *ibid.*, **45**, 2756 (1923).

portions alternately. In most of the experiments the blue color of the dissolved sodium was allowed to disappear before further addition of the metal. In those preparations in which the reaction seemed to be slow, the flask was equipped with a mechanical stirrer and mercury seal. It was not deemed necessary to protect the reaction mixture from atmospheric gases because the rapid evaporation of the ammonia prevented the entrance of air into the flask.

After the completion of the reaction, the contents of the flask were poured into a casserole and the solvent was allowed to evaporate. The residue was then treated with a mixture of ether and water, the ether layer separated, and the aqueous layer extracted several times with fresh portions of ether. The combined ether solutions were dried over calcium chloride, the ether was distilled and the residue investigated. Except in the cases of β-bromophenylethyl ether and γ-bromophenylpropyl ether the aqueous layer was not investigated further.

Experimental

Benzyl Chloride.[10]—Three hundred grams of benzyl chloride was treated with the calculated amount of sodium—1 mole of sodium to 1 mole of chloride—in several runs and the residues were combined. Brightly colored red and purple intermediate products formed and disappeared during the course of the reaction. The combined residues were taken up with a mixture of ether and water, after which treatment a solid—4.5 g.—was left. After separating the ether layer, the aqueous solution was extracted several times with fresh portions of ether. The combined ether solutions were then dried over calcium chloride. The ether was distilled through a Vigreux column, after which 25 g. of toluene came over between 95 and 110° at 629 mm. The residue—181 g.—was then fractionated under reduced pressure. At first a few drops of unchanged benzyl chloride came over; then the temperature rose rapidly. At 150–155° under 17 mm. pressure, 94 g. of dibenzyl came over. The residue in the flask, a viscous oil, was treated with ether. A solid weighing 5.1 g. separated. This proved to be identical with the 4.5 g. of white solid separated in the first phase of the reaction. This substance was referred to as "Solid A." It proved to be a hydrocarbon which crystallized from chloroform–alcohol and melted at 183–184°. After distilling the ether, the viscous oil was again fractionated under reduced pressure. An additional 14 g. of dibenzyl was obtained, together with 37 g. of a liquid—"Liquid B"—which distilled at 200–240° under a pressure of 10 mm., and finally 13 g. of a very viscous oil which distilled between 240 and 270° under 10 mm. pressure. This was referred to as "Liquid C." The residue in the flask weighed 9 g. All of the products were nitrogen and halogen free. The yields were as follows: toluene, 25 g.; dibenzyl, 108 g.; Solid A, 9.5 g.; Liquid B, 37 g.; Liquid C, 13 g.; residue, 9 g.

1-Phenyl-2-bromo-ethane.—This compound was prepared from phenylethyl alcohol by the Norris[11] method. It reacted rapidly with sodium in liquid ammonia in the ratio of 1 mole of halide to 1.9 moles of sodium. The following products were obtained from the ether extracts of the reaction products of 66 g. of the halide: ethyl-

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[10] Since this paper was submitted, an article by Wooster and Mitchell has appeared in which an account of the action of sodium and potassium on benzyl bromide in liquid ammonia is given [This Journal, **52**, 693 (1930)].

[11] Norris, Watt and Thomas, *ibid.*, **38**, 1071 (1916).

benzene, 14.5 g.; styrene, 0.5 g.; residue (nitrogen free), 7 g. The residue consisted of high-boiling hydrocarbons from which no 1,4-diphenylbutane could be obtained.

1-Phenyl-3-bromopropane.—Fifty g. of the halide required 6.6 g. of sodium—ratio 1:1.5. The residue weighing 28 g. yielded the following products: propylbenzene, 8.5 g.; phenylpropylamine, 5.9 g.; high-boiling hydrocarbons, 3 g.; residue containing nitrogen, 7 g.; diphenylhexane, none.

1-Phenyl-4-bromobutane.—This substance reacted with the sodium in the ratio 1:1.5. From 9.3 g. of the halide the following products were obtained: butylbenzene, 2.5 g.; unsaturated hydrocarbons, 0.05 g.; phenylbutylamine, 1.04 g.; hydrocarbons and amines, 1.6 g.

Benzal Chloride.—The reaction in the case of benzal chloride was more violent than in that of benzyl chloride. The sodium was used in the ratio 2:1. During the course of the reaction a bright red coloration developed which did not disappear until the ether–water mixture was added at the end of the experiment. Sixty grams of the chloride was used. The following products were obtained from the residue: dibenzyl, 2.5 g.; benzylamine, 15.0 g.; higher-boiling amines and residue, 14.0 g.

Benzotrichloride.—In this reaction the trichloride required approximately 3 moles of sodium. A rather large amount of tarry matter, insoluble in ether, along with about 5% of dibenzyl, was obtained. The tarry matter contained nitrogen.

Diphenylchloromethane.—On account of the slight solubility of the chloride in the ammonia, the reaction was slow. The addition of anhydrous ether considerably hastened the reaction. Twenty-four grams of the halide required 4.3 g. of sodium—ratio 1:1.59. It was difficult to determine the end-point of the reaction on account of the dark brown color of the mixture. On treatment of the residue with the ether–water mixture, a white solid, identified as *sym.*-tetraphenylethane, separated. From the ether layer a second portion of this hydrocarbon together with diphenylmethane was obtained. The total yield of these two compounds was 13 and 5.5 g., respectively. No other products were obtained from the ether layer.

Diphenyldichloromethane.—As in the case of diphenylchloromethane the reaction was slow until dry ether was added to the reaction mixture. In this experiment 31.5 g. of the halide was treated with sodium in the molecular ratio of 1:2. Care was taken to keep the halide in excess until the end of the reaction. After treating the residue with the ether–water mixture, 16 g. of a solid remained which on purification proved to be tetraphenylethylene. An additional 3.8 g. of tetraphenylethylene was obtained from the ether extract. The 19.8 g. of tetraphenylethylene obtained from the 31.5 g. of the diphenyldichloromethane corresponds to a yield of 90% of the theoretical. This method of preparation compares favorably with that of Norris.[12] The conversion of the tetraphenylethylene into tetraphenylethane seems to be effectively prevented by the method of procedure in which the sodium is added in small portions to an excess of halide until the ratio 1:2 is reached.

***o*-Xylylene Bromide.**—On account of the slowness of the reaction even in the presence of anhydrous ether, the Dewar flask was fitted with a mechanical stirrer and mercury seal. Two moles of sodium were required for 1 mole of the bromide. The yield obtained from 25 g. of *o*-xylylene bromide consisted of 3.1 g. of *o*-xylene and 5.8 g. of a residue containing nitrogen.

β-Bromophenylethyl Ether.—In this case the reaction took place vigorously and smoothly, without the formation of intermediate colored compounds. The ratio of halide to sodium was 1:2. From 21 g. of β-bromophenylethyl ether the following compounds were obtained: 1,4-diphenoxybutane, 2.9 g.; phenol, 7.0 g.

γ-Bromophenylpropyl Ether.—This compound reacted rapidly and smoothly with

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[12] Norris, *Ber.*, **47**, 473 (1914).

sodium in the ratio 1:1.82. No intermediate colored compounds were observed. From 52 g. of the bromide a residue weighing 25.5 g. was obtained. This consisted of a mixture of colorless crystals and a mobile liquid, both of which were nitrogen free. From this mixture the following products were obtained: phenoxypropane,[13] 14.8 g.; phenol, 6.0 g.; 1,6-diphenoxyhexane, 4.4 g.

α-Chloro-acetophenone.—The halide reacted with sodium in the ratio 1:2.2. From 30 g. of the chloro-acetophenone, 13.5 g. of a reddish oil was obtained. This was nitrogen and halogen free. Four grams of acetophenone was separated from this oil; 0.4 g. of a colorless solid, melting at 73–74°, was also obtained, but was not identified. The residue yields, for the most part, tarry matter when it is distilled.

β-Chloropropiophenone.—In this case the reaction with sodium is rapid although the β-chloropropiophenone is not very soluble in the ammonia. The reaction takes place in the ratio of halide to sodium of 1:1.53. From 16 g. of the chloride a residue weighing 11 g. was obtained. This was a viscous oil, slightly fluorescent in solution, and nitrogen and halogen free. It did not boil at 380° under 20 mm. pressure. On cooling it solidified to a hard resin.

Conclusions

The limited number of halogen compounds studied does not permit one to draw definite conclusions regarding the relation of the structure of the molecule to the products formed. In the cases of the monohalogen compounds the following reactions indicate a possible mechanism

$$\begin{array}{rcll}
MCH_2X + 2Na & \longrightarrow & (MCH_2Na) + NaX & (I) \\
(MCH_2Na) + MCH_2X & \longrightarrow & MCH_2CH_2M + NaX & \\
MCH_2Na + NH_3 & \longrightarrow & MCH_3 + NaNH_2 & (II) \\
MCH_2X + NaNH_2 & \longrightarrow & MCH_2NH_2 + NaX & (III) \\
2C_6H_5O(CH_2)_2Br + 2Na & \longrightarrow & 2NaBr + C_6H_5O(CH_2)_4O(C_6H_5) & (IV) \\
C_6H_5O(CH_2)_2Br + 2Na & \longrightarrow & NaBr + C_6H_5ONa + C_2H_4\text{[14]} &
\end{array}$$

The reactions must be much more complicated in the cases of the polyhalogen compounds, as, for example, when nitriles are formed.[15]

Summary

1. The action of sodium in liquid ammonia on thirteen organic halogen compounds has been studied.

2. In eight cases a reaction in the sense of the Wurtz–Fittig synthesis took place to some extent.

3. Convenient methods for the preparation of benzamide, tetraphenylethylene and tetraphenylethane have been suggested.

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[13] Dionneau, *Ann. chim.*, **3**, 201 (1915).

[14] Hamonet, *Compt. rend.*, **136**, 96 (1903).

[15] Dains and Brewster, THIS JOURNAL, **42**, 1573 (1920).