The Treatment of Neopentyl Halides with Di-p-tolylmercury[1]

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The reaction of organic mercury compounds with halogen compounds to give a lengthened carbon chain is one which has received considerable attention in the past. Whitmore and Thurman[2] studied the reaction of a large variety of halogen compounds with di-p-tolylmercury. They found that in most cases no reaction took place. However, diphenylbromomethane reacted with ditolylmercury to give an 80% yield of diphenyl-p-tolylmethane. t-Butyl bromide reacted with di-p-tolylmercury to give tolylmercuric bromide, toluene and isobutylene.

All attempts to cause an alkyl halide to react with an organic mercury compound to give a lengthened carbon chain have been unsuccessful. Either there is no reaction or, as is more often the case, the mercury compound acts as a "hydrocarbo base"[3] and removes HX from the halide to give an olefin and related products.

The present work was planned in 1924 but due to peculiar difficulties encountered in the preparation of the neopentyl halides the problem was delayed until recently. It was at first hoped that the neopentyl halides might react with organic mercury compounds to give a lengthened carbon chain. Whitmore and Fleming[4] found that neopentyl chloride gave no reaction when heated with diphenylmercury. In the present work the reaction of neopentyl bromide and neopentyl iodide with ditolylmercury was attempted. The extent of reaction was determined by the iodide titration method of Whitmore and Sobatzki.[5]

Neopentyl bromide and iodide when heated for twenty hours above 200° with ditolylmercury gave less than 5 and 10% reaction, respectively. These results offer additional evidence of the unusual inactivity of the neopentyl halides.

Experimental

The di-p-tolylmercury was prepared by the reaction of p-tolylmercuric chloride and sodium iodide as described in "Organic Syntheses."[6] The neopentyl halides were pre-

pared from neopentylmercuric chloride treated with bromine and iodine.[7]

Treatment of Neopentyl Bromide with Di-p-tolylmercury.—The reactions were carried out in sealed tubes in a bomb furnace under slightly varying conditions. The following run is described but the other runs were made in essentially the same manner except for variations in the time and temperature of the heating.

A mixture of 1.5 g. of di-p-tolylmercury and 0.6 g. of neopentyl bromide was sealed in a small Pyrex bomb tube and heated at 150° for ten hours. Visual examination of the contents at the end of this time showed no evidence of reaction. The white crystals were washed out of the tube with 25 cc. of 95% ethanol and the crystals were filtered and dried. They melted at 238–240° and gave no depression with a sample of pure di-p-tolylmercury.

The titrations to determine the amount of conversion of the mercury compound were carried out according to the following procedure. About 0.1 g. of the crystalline material was placed in a 100-ml. flask equipped with a condenser having a standard taper ground glass connection. To this were added 2 cc. of chloroform, 1 g. of sodium iodide and a carefully measured excess of approximately 0.1 N iodine solution. The resulting mixture was refluxed on the steam-bath for thirty minutes, cooled to room temperature, acidified with a few drops of concentrated hydrochloric acid and titrated with a standard solution of sodium thiosulfate. From these results the amounts of di-p-tolylmercury and tolylmercuric bromide are calculated readily. The results obtained in six runs may be summarized as follows.

No reaction occurred at a temperature up to 175° in twenty-four hours. At 200 to 220° the reaction proceeded to the extent of about 3–4% during heating periods of twelve to sixty hours. At 200° about 0.66% of olefins calculated as trimethylethylene were produced and at 220° the olefins produced amounted to about 5%. Neopentyl iodide at 200° in twenty hours gave 7–9% reaction with the formation of about 0.7% olefin.

Preparation of Dineopentylmercury.—To an ethereal solution, 225 cc., 0.54 mole, of neopentylmagnesium chloride solution contained in a 1-liter three-necked flask equipped with a stirrer and reflux condenser was added during fifteen minutes 65 g. of dry mercuric chloride. The mixture which became warm and started to boil was refluxed for a total of twenty-six hours. During this time 135 cc. of dry ether was added in small portions. The entire reaction was carried out in an atmosphere of nitrogen. The reaction mixture was then cooled in a salt–ice bath while 300 cc. of ice water was added gradually through a dropping funnel. The two layers were then separated and the light brown ether layer was concentrated to about one-half volume and cooled in a salt–ice bath. The

(1) Original manuscript received November 12, 1938.
(2) Whitmore and Thurman, THIS JOURNAL, **51**, 1491 (1929).
(3) Jones and Werner, ibid., **40**, 1257 (1918).
(4) Whitmore and Fleming, ibid., **55**, 4161 (1933).
(5) Whitmore and Sobatzki, ibid., **55**, 1128 (1933).
(6) "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1932.

(7) Whitmore, Wittle and Harriman, THIS JOURNAL, **61**, 1585 (1939).

crystalline material which separated was collected and dried to give 40 g. of crude material. This was recrystallized from ether to give 10 g. of white needles melting at 116–116.5° which gave no depression with an authentic sample of neopentylmercuric chloride.

The mother liquors were concentrated carefully and the semisolid residue distilled in vacuum twice through a side-arm flask. The dineopentylmercury boiled at 67–69° at 3 mm. and melted at 31–33°. The yield was 23.5 g., about 28.5% on the basis of the mercuric chloride used. An iodine titration indicated an impurity of approximately 7% of neopentylmercuric chloride.

Summary

1. Neopentyl bromide and neopentyl iodide react only slightly with ditolylmercury even under drastic conditions.

2. No evidence of a lengthening of the carbon chain was found.

3. Further evidence is given for the unusual inactivity of the neopentyl halides.

4. Dineopentylmercury has been prepared.

[Contribution from the Department of Chemistry, Technical College]

The Electrolytic Condition of Aniline Hydrochloride, Aniline Hydriodide and α-Naphthylamine Hydriodide in Aniline Solution

By Herbert H. Hodgson and Ewart Marsden

In connection with a study of the mechanism of the phenylation of α-naphthylamine,[1] it appeared reasonable to expect that the conductivities of the various aniline solutions employed
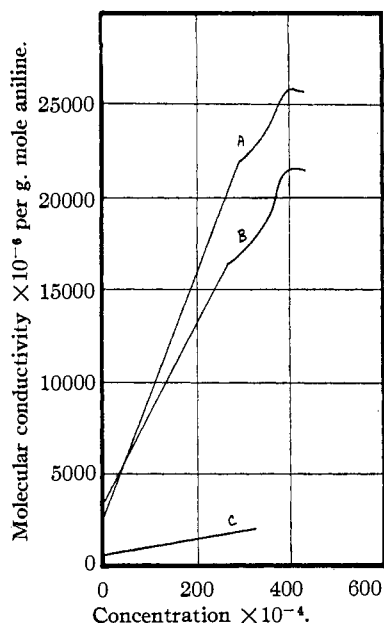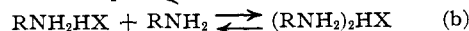

Fig. 1.—A, aniline hydriodide; B, α-naphthylamine hydriodide; C, aniline hydrochloride.

would throw light on the condition of the solute prior to phenylation. Accordingly, the conductivities of aniline hydrochloride, aniline hydriodide and α-naphthylamine hydriodide, dissolved in aniline, have been measured and plotted with

(1) Hodgson and Marsden, *J. Chem. Soc.*, 1365 (1939); 1181 (1939).

respect to concentration. The curves thereby obtained all exhibit the same general form, and consequently the deductions made therefrom should be valid for each solution. Previous work by Pound[2] on the electrolytic behavior of solutions of aniline hydrochloride in aniline has been generally confirmed.

The chemical behavior of iodine during the catalytic phenylation process[1] would appear to indicate that a double compound is first formed between two molecules of aniline and one molecule of hydriodic acid in the case of diphenylamine formation, and a similar compound between one molecule each of α-naphthylamine and aniline for that of phenyl-α-naphthylamine, with subsequent expulsion of ammonium iodide and regeneration of hydriodic acid to continue the process. Such a type of double compound actually has been isolated by Mandel[3] from a solution of aniline hydrochloride in aniline.

If the assumption of double compound formation be valid, the various equilibria in solution would then be

$$RNH_2HX \rightleftarrows RNH_3^+ + X^- \qquad (a)$$
$$RNH_2HX + RNH_2 \rightleftarrows (RNH_2)_2HX \qquad (b)$$
$$(RNH_2)_2HX \rightleftarrows (RNH_2)_2H^+ + X^- \qquad (c)$$

From the graph of the conductivities plotted with respect to concentration (Fig. 1), it is found that over most of the concentration ranges measured, the conductivity decreases linearly with dilution. Since the conductivity of the active (ionizable) part of the total concentration of the

(2) Pound, *J. Phys. Chem.*, **31**, 547 (1927).
(3) Mandel, *Ber.*, **53**, 2216 (1920).