[Contribution from the Department of Chemistry, Duke University]

METALATIONS OF DI- AND TRI-PHENYLMETHIDES WITH ALKALI AMIDES, AND SOME REVERSIONS. CARBONATIONS AND NITROSATIONS[1]

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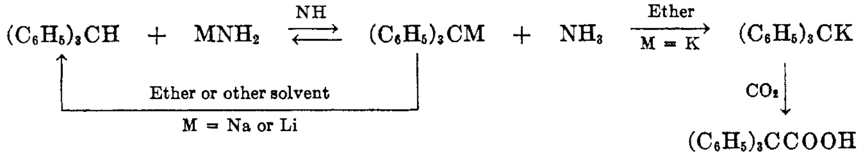
It has previously been observed (1) that, although both sodium and potassium amides metalate triphenylmethane in liquid ammonia, only the potassium triphenylmethide is stable on replacing the ammonia with ether, in which medium carbonation may be effected to form triphenylacetic acid. The sodium triphenylmethide reverts to the hydrocarbon as the last portion of the liquid ammonia is evaporated. It has now been found that the reversion (ammonolysis) of sodium triphenylmethide to triphenylmethane occurs also on replacing the ammonia with dibutyl ether, dioxane, toluene, or triethylamine. In each case the characteristic red color of the triphenylmethide ion was discharged, and no triphenylacetic acid was obtained on attempted carbonation. Similarly lithium triphenylmethide, when formed from lithium amide and triphenylmethane in liquid ammonia, underwent reversion on replacing the ammonia by ether. This difference between potassium triphenylmethide and sodium or lithium triphenylmethide may be illustrated by the following scheme.



$$(C_6H_5)_3CH + MNH_2 \xrightleftharpoons{NH} (C_6H_5)_3CM + NH_3 \xrightarrow[M = K]{Ether} (C_6H_5)_3CK \xrightarrow{CO_2} (C_6H_5)_3CCOOH$$

$$(C_6H_5)_3CM \xrightarrow[M = Na \text{ or } Li]{\text{Ether or other solvent}} (C_6H_5)_3CH$$

Even when sodium triphenylmethide was prepared in ether solution from triphenylchloromethane and sodium amalgam and then treated with liquid ammonia, it underwent, on evaporating the ammonia, complete ammonolysis to form triphenylmethane and sodium amide. The sodium amide, which precipitated from the ether, was isolated as benzamide. Schlenk and Ochs (2) have reported such an ammonolysis but no details were given.

$$\underset{\text{(in ether)}}{(C_6H_5)_3CNa} + \text{liq. } NH_3 \xrightarrow{NH_3 \text{ evaporated}} (C_6H_5)_3CH + NaNH_2$$

Also, a similar difference in stability has previously been observed between sodium and potassium diphenylmethides (3). Thus, sodium diphenylmethide, when formed by metalating diphenylmethane with sodium amide in liquid ammonia, undergoes reversion on replacing the ammonia with ether. Under similar conditions potassium diphenylmethide is obtained as a deep red suspension which has been carbonated to form diphenylacetic acid (90%) (3). We have similarly obtained a deep red suspension in ether of the potassium derivative of

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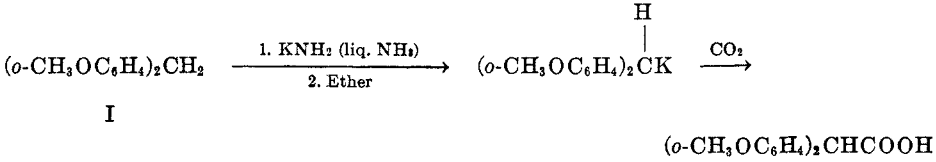
bis(2-methoxyphenyl)methane (I) which was carbonated to give bis(2-methoxyphenyl)acetic acid (II, 61%).



$$(o\text{-}CH_3OC_6H_4)_2CH_2 \xrightarrow[\text{2. Ether}]{\text{1. KNH}_2\text{ (liq. NH}_3\text{)}} (o\text{-}CH_3OC_6H_4)_2\overset{H}{C}K \xrightarrow{CO_2} (o\text{-}CH_3OC_6H_4)_2CHCOOH$$

I

II

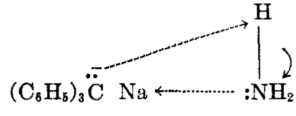
However, the potassium derivative of bis(4-methoxyphenyl)methane (III), when similarly formed with potassium amide in liquid ammonia, failed to be obtained in ether. Instead, the characteristic red color of the anion became lighter, and on attempted carbonation only the starting material was recovered. Similarly the potassium derivatives of mesityl phenylmethane (IV) and of tetraphenylethane (V) underwent reversion, and only the starting compounds IV and V were recovered on attempted carbonation or nitrosation (butyl nitrite).

$$\underset{\text{III}}{(p\text{—}CH_3OC_6H_4)_2CH_2} \qquad \underset{\text{IV}}{\text{Mes—}CH_2\text{—}C_6H_5} \qquad \underset{\text{V}}{(C_6H_5)_2CH\text{—}CH(C_6H_5)_2}$$

The nitrosation of the potassium derivative of IV was carried out as a possible synthesis of mesityl phenyl ketoxime which has apparently been prepared only through the ketimine (4). The feasibility of the method was demonstrated with potassium diphenylmethide from which benzophenone oxime was obtained.

$$(C_6H_5)_2CH_2 \xrightarrow[\text{2. Ether}]{\text{1. KNH}_2\text{ liq. NH}_3\text{)}} (C_6H_5)_2CHK \xrightarrow{C_4H_9ONO} (C_6H_5)_2C{=}NOH$$

These reversions on replacing the ammonia with ether or other inert solvents appear to be dependent not only on the formation of relatively insoluble products but also on the tendency of the metallic cation to coordinate with the ammonia, and on the relative reactivity of the active hydrogen of the hydrocarbon (or basicity of the carbanion of the metallic derivative). Although insufficient evidence is at hand to evaluate these factors, it should be mentioned that Kraus and Rosen (5) observed that sodium triphenylmethide crystallizes from ammonia with one molecule of the solvent, while potassium triphenylmethide crystallizes free from ammonia. This suggests that the reversion observed with sodium triphenylmethide involves an acid-base reaction within complex VI. The reversion of lithium triphenylmethide would presumably be similar.



VI

EXPERIMENTAL

Reversion of sodium triphenylmethide. To each of five suspensions of 0.028 mole of sodium amide in 150 ml. of liquid ammonia was added 0.028 mole of triphenylmethane, and the ammonia was replaced by an equal volume of each of the following solvents, ether, dibutyl ether, toluene, dioxane and triethylamine. In each case the characteristic red color was discharged leaving a gray suspension which failed to yield triphenylacetic acid on treatment with powdered Dry Ice.

Reversion of lithium triphenylmethide. When triphenylmethane (0.028 mole) was metalated with lithium amide in 150 ml. of liquid ammonia (red solution) and the ammonia replaced by ether, the color was discharged and no acid was obtained on treating the resulting gray suspension with Dry Ice. The triphenylmethane was recovered in 95% yield.

Ammonolysis of sodium triphenylmethide. To 75 ml. of redistilled liquid ammonia was added 65 ml. of 0.48 *M* (0.031 mole) of a bright red ethereal solution of sodium triphenylmethide, prepared from triphenylchloromethane and sodium amalgam (6) and the ammonia was evaporated (red color discharged). The resulting ethereal suspension of sodium amide was refluxed 4 hours to remove dissolved ammonia and 4.8 g. (0.035 mole) of benzoyl chloride then was added. After refluxing 1 hour the ether was evaporated and the residue was triturated with sodium hydroxide followed by ligroin to give 2.7 g. (74%) of benzamide, m.p. 127.5–128°; reported m.p. 128° (7). This melting point was not depressed on admixture with an authentic sample of benzamide.

Carbonation of the potassium derivative of bis(2-methoxyphenyl)methane (I). Bis(2-hydroxyphenyl)methane[2] was methylated with an excess of dimethyl sulfate to give, after several recrystallizations from methanol, a 73% yield of bis(2-methoxyphenyl)methane (I), m.p. 62–63°; reported m.p. 66° (8).

To 0.056 mole of potassium amide in 100 ml. of liquid ammonia was added with stirring 11.4 g. (0.056 mole) of I in anhydrous ether, and the ammonia replaced by ether essentially as described previously for diphenylmethane (3). The resulting red suspension of the potassium derivative was treated with 200 g. of powdered Dry Ice to give, after recrystallization from ethanol, 8.2 g. (50%, 74% conversion) of bis(2-methoxyphenyl)acetic acid (II), m.p. 149–149.5°, Neut. equiv., Calc'd 272, Found 271.

Anal.[3] Calc'd for $C_{16}H_{16}O_4$: C, 70.57; H, 5.93.
Found: C, 70.63; H, 5.97.

Attempted carbonation of bis(4-methoxyphenyl)methane (III). Bis(4-hydroxyphenyl)-methane[2] was methylated in 71% yield with dimethyl sulfate to give bis(4-methoxyphenyl)-methane (III), b.p. 152–154° at 3 mm., m.p. 48–49°; reported m.p. 47–48° (9), 51–51.5° (10).

When compound III was added to potassium amide in liquid ammonia a red color developed but on replacing the ammonia with ether, the color changed to light pink. On adding Dry Ice no appreciable amount of the corresponding carboxylic acid was obtained, and 85% of III was recovered.

Nitrosation of potassium diphenylmethide. To a stirred red suspension of potassium diphenylmethide in 200 ml. of ether, prepared from 0.11 mole of potassium amide and 0.1 mole of diphenylmethane as described previously (3) was added slowly 10.3 g. (0.1 mole) of butyl nitrite. The red color changed to green which changed to a light tan after 30 minutes. There was isolated, through the hydrochloride salt, 6.8 g. (37%) of benzophenone oxime, m.p. 142–143°; reported m.p. 141–142° (11). This melting point was not depressed on admixture with an authentic sample of benzophenone oxime.

Attempted carbonation or nitrosation of compounds IV *and* V. Mesityl phenylmethane (IV) was prepared in 55% yield by the Freidel-Crafts benzylation of mesitylene. It boiled at 130–132° at 8 mm. and melted at 35°; reported m.p. 36° (12).

When compound IV was metalated with potassium amide in liquid ammonia (red color), the ammonia replaced by ether (color discharged), and the resulting gray suspension treated with butyl nitrite, no oxime was obtained. The hydrocarbon was recovered (80%).

Similarly tetraphenylethane (V) produced a red color with potassium amide in liquid ammonia, but on replacing the ammonia with ether the color was discharged, and only the starting compound was recovered after treatment with Dry Ice or butyl nitrite.

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[2] We are indebted to the Bakelite Corporation, Bloomfield, N. J., for a generous sample of this compound.

[3] Analysis by Clark Microanalytical Laboratory, Urbana, Illinois.

SUMMARY

1. In contrast to potassium triphenylmethide, sodium and lithium triphenylmethides, when prepared by the metalations of triphenylmethane with sodium or lithium amides in liquid ammonia, underwent reversion to the hydrocarbon on replacing the ammonia with ether or other solvents. The reversion of sodium triphenylmethide was shown to involve an ammonolysis by preparing it from triphenylchloromethane and sodium amalgam and treating it with ammonia.

2. Like potassium diphenylmethide, potassium bis(2-methoxyphenyl)methide formed in ether a stable, red suspension which was carbonated to give bis(2-methoxyphenyl)acetic acid. The potassium diphenylmethide was nitrosated with butyl nitrite to form benzophenone oxime.

3. The potassium derivatives of bis(4-methoxyphenyl)methane, mesityl phenylmethane, and tetraphenylethane reverted to the corresponding hydrocarbons in attempts to prepare them similarly in ether.

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