sium oleate at 18,[11] except that in previous diagrams boundaries should be raised by a few per cent. to allow for interionic attraction and 100% dissociation of hydrochloric acid. The middle line of the diagram is given from e. m. f. and conductivity data of Figs. 1, 2 and 3. Most of the transition between simple crystalloidal and colloidal electrolytes takes place between 0.05 and 0.15 *N* for undecyl and lauryl sulfonic acids and in still more dilute solution in myristyl sulfonic acid. Above 0.1 or 0.2 *N* there can be but little else than colloid and hydrogen ions. The concentration of ionic micelles will be equal to that of the hydrogen ion, the remaining sulfonic acid forming neutral micelles.

Summary

Hydrogen-ion concentration deduced from conductivity, freezing point lowering, and electromotive force for solutions of simple sulfonic acids above 0.1 *N* are compared.

Conductivity and e. m. f. (single electrode) agree in showing that the dissociation of the colloidal electrolyte is about 50%.

If the data for thymonucleic acid and for undecyl, lauryl, myristyl, and cetyl sulfonic acids are valid, it is shown that the activity coefficients of single ions may be measured. For example, in more concentrated solutions of hydrochloric acid, the activity coefficient of the hydrogen ion appears to be about half that of the chlorine ion and $f_{H^+} < f_{HCl} < f_{Cl^-}$ where $f_{H^+} f_{Cl^-} = f_{HCl}$.

A new explanation of the genuine Hammarsten effect is given, based upon steric hindrance to close packing.

STANFORD UNIVERSITY, CALIFORNIA

RECEIVED JUNE 18, 1935

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[11] J. W. McBain and R. C. Bowden, *J. Chem. Soc.*, **123**, 2427 (1923).

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY AND PHYSICS OF THE PENNSYLVANIA STATE COLLEGE]

Nitroso Compounds. III. Reactions of Organo-metallic Compounds with Alpha Halo Nitroso Compounds[1]

BY JOHN G. ASTON AND DAVID F. MENARD

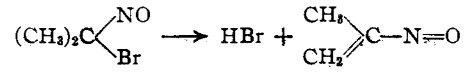
Introduction

This investigation originated in an attempt to obtain true nitroso hydrocarbons by the action of zinc alkyl on compounds of the type $CR_1R_2Br(NO)$ in a way similar to that by which Bewad had obtained nitro compounds from their alpha bromo derivatives.[2]

Although this attempt failed, certain reactions involving the nitroso group were observed which were interesting from the standpoint of possible analogies between true nitroso compounds and aldehydes or ketones.

Splitting Out of the Hydrogen Halide

When 2,2-bromonitrosopropane was treated with anhydrous ammonia, only ammonium bromide resulted along with acetoxime. To explain this splitting out of hydrobromic acid the first step in the reaction may be tentatively written

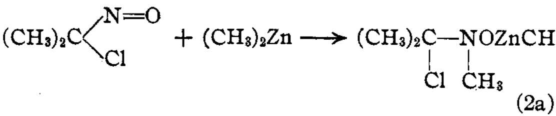


$$(CH_3)_2C\begin{matrix}NO\\Br\end{matrix} \longrightarrow HBr + \begin{matrix}CH_3\\CH_2\end{matrix}\!\!>C{-}N{=}O \qquad (1)$$

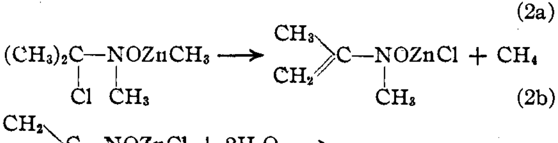
inasmuch as the unsaturated nitroso compound might well react to give acetoxime. It is not surprising therefore that the alpha halo nitroso compounds with dimethylzinc yield methane almost quantitatively by inducing the splitting out of hydrogen bromide and then reacting with it.

Reaction with Zinc Alkyls

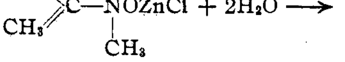
In the reaction of one mole of dimethylzinc and one mole of 2-chloro-2-nitrosopropane, one mole of methane is evolved per mole of chloronitroso compound. In the products of hydrolysis of the solid addition product methylhydroxylamine, acetone and acetoxime were observed. The first two arise from addition. The net reaction may be written



$$(CH_3)_2C\begin{matrix}N{=}O\\Cl\end{matrix} + (CH_3)_2Zn \longrightarrow \underset{Cl}{(CH_3)_2C}{-}\underset{CH_3}{N}OZnCH_3 \qquad (2a)$$



$$\underset{Cl}{(CH_3)_2C}{-}\underset{CH_3}{N}OZnCH_3 \longrightarrow \begin{matrix}CH_3\\CH_2\end{matrix}\!\!>C{-}\underset{CH_3}{N}OZnCl + CH_4 \qquad (2b)$$



$$\begin{matrix}CH_2\\CH_3\end{matrix}\!\!>C{-}\underset{CH_3}{N}OZnCl + 2H_2O \longrightarrow$$

$$(CH_3)_2CO + CH_3NHOH + Zn(OH)Cl \qquad (2c)$$

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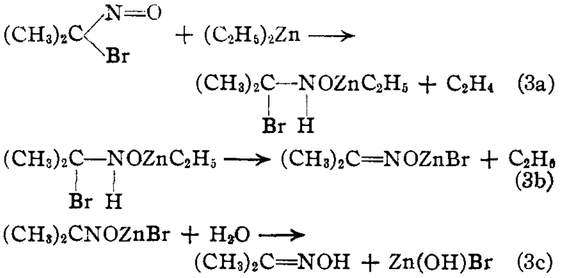
[1] From a thesis presented by David F. Menard in partial fulfilment of the requirements for the Ph.D. degree, June, 1934.

[2] Bewad, *J. prakt. Chem.*, [2] **48**, 368 (1893).

In this reaction and following ones, HX is represented as splitting out after addition and then reacting with the remaining zinc methyl linkage in the addition product. The reaction might as well have been represented as occurring by first splitting out HX and then adding of zinc methyl to the unsaturated nitroso compound. Indeed the presence of acetoxime indicates that some splitting out of HX from the chloronitroso compound does occur directly, followed by decomposition of the unsaturated nitroso compound. The yields of the various products show that no other reaction of importance occurs.

Diethyl zinc reacted with 2-bromo-2-nitrosopropane in the same way that dimethylzinc reacted on the chloro compound, yielding ethane with acetone and ethylhydroxylamine as the hydrolysis products. However, only about 70% reacted in this way while the remaining 30% was reduced as shown by the presence of ethylene in the gaseous mixture. It was assumed that one mole of ethane was formed for each mole of ethylene and the secondary reaction written



$$(CH_3)_2C\begin{smallmatrix}N{=}O\\ Br\end{smallmatrix} + (C_2H_5)_2Zn \longrightarrow (CH_3)_2\underset{Br}{C}-\underset{H}{N}OZnC_2H_5 + C_2H_4 \quad (3a)$$

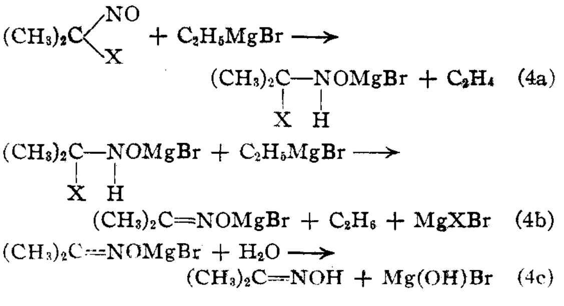
$$(CH_3)_2\underset{Br}{C}-\underset{H}{N}OZnC_2H_5 \longrightarrow (CH_3)_2C{=}NOZnBr + C_2H_6 \quad (3b)$$

$$(CH_3)_2CNOZnBr + H_2O \longrightarrow (CH_3)_2C{=}NOH + Zn(OH)Br \quad (3c)$$

In keeping with this, acetoxime was also found in the products of hydrolysis of the mixed insoluble addition product.

Reaction with Grignard Reagents

When 2-chloro or 2-bromo-2-nitrosopropane was treated with ethylmagnesium bromide (2 moles of Grignard per mole of compound), no addition was observed; the principal reaction was a reduction similar to the secondary reaction observed with diethylzinc

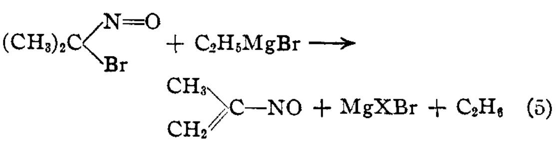


$$(CH_3)_2C\begin{smallmatrix}NO\\ X\end{smallmatrix} + C_2H_5MgBr \longrightarrow (CH_3)_2\underset{X}{C}-\underset{H}{N}OMgBr + C_2H_4 \quad (4a)$$

$$(CH_3)_2\underset{X}{C}-\underset{H}{N}OMgBr + C_2H_5MgBr \longrightarrow (CH_3)_2C{=}NOMgBr + C_2H_6 + MgXBr \quad (4b)$$

$$(CH_3)_2C{=}NOMgBr + H_2O \longrightarrow (CH_3)_2C{=}NOH + Mg(OH)Br \quad (4c)$$

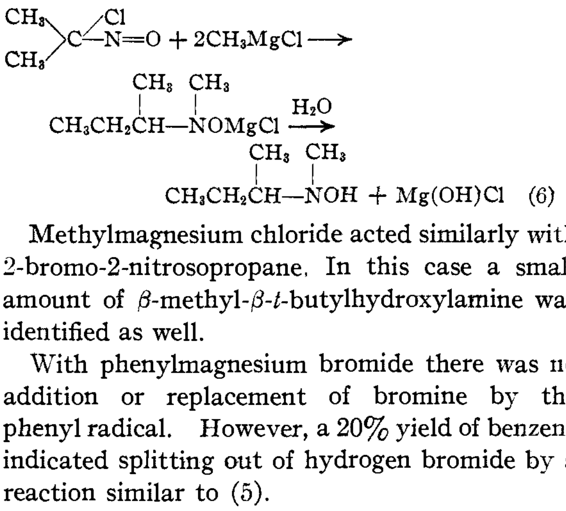
The products were ethane and ethylene and after hydrolysis of the insoluble addition compound, acetoxime and its hydrolysis products (acetone and hydroxylamine). Whereas reactions (4a and 4b) require equal molal quantities of ethane and ethylene, the ethane produced in both cases considerably exceeded the ethylene. This indicated a reaction



$$(CH_3)_2C\begin{smallmatrix}N{=}O\\ Br\end{smallmatrix} + C_2H_5MgBr \longrightarrow \begin{smallmatrix}CH_3\\ CH_2\end{smallmatrix}\!\!>C-NO + MgXBr + C_2H_6 \quad (5)$$

involving the splitting out of hydrogen bromide, which reacted with the Grignard to yield ethane while the hypothetical unsaturated nitroso compound after hydrolysis yielded hydroxylamine as in the reaction with ammonia (1).

The reaction of one mole of methylmagnesium chloride on one mole of 2-chloro-2-nitrosopropane resulted in addition to the N=O group as the main reaction. Hydrolysis yielded methylhydroxylamine. The reaction of two moles of methylmagnesium chloride resulted in addition to the N=O group and simultaneous replacement of the halogen by the methyl group with rearrangement, yielding 68% of β-*s*-butyl-β-methylhydroxylamine



$$\begin{smallmatrix}CH_3\\ CH_3\end{smallmatrix}\!\!>\overset{Cl}{C}-N{=}O + 2CH_3MgCl \longrightarrow CH_3CH_2\overset{CH_3}{C}H-\overset{CH_3}{N}OMgCl \xrightarrow{H_2O} CH_3CH_2\overset{CH_3}{C}H-\overset{CH_3}{N}OH + Mg(OH)Cl \quad (6)$$

Methylmagnesium chloride acted similarly with 2-bromo-2-nitrosopropane. In this case a small amount of β-methyl-β-*t*-butylhydroxylamine was identified as well.

With phenylmagnesium bromide there was no addition or replacement of bromine by the phenyl radical. However, a 20% yield of benzene indicated splitting out of hydrogen bromide by a reaction similar to (5).

Kohler and Tishler[3] have discussed the analogous α-halo-ketone problem and have shown that Grignard reagents often react with ketones of the type $R_2C(X)COR$ to replace halogen by magnesium with the simultaneous production of the alkyl halide

$$R_2C(X)COR + R^1MgX^1 \longrightarrow R^1X + R_2C(MgX^1)COR \quad (7)$$

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(3) Kohler and Tishler, This Journal, **54**, 1595 (1932); **57**, 217 (1935).

In none of our experiments was there ever a detectable amount of alkyl halide which might have been produced by an analogous reaction.

Experimental

Preparation of 2-Bromo-2-nitrosopropane.[4]—Four hundred and twenty-seven grams (3.15 moles) of $NaAc \cdot 3H_2O$ dissolved in 500 cc. of water was added to a solution of 110 g. (1.5 moles) of acetoxime dissolved in 200 cc. of water. Five hundred grams of ice was added. With constant stirring and cooling, 239 g. (1.5 moles) of bromine was dropped in at such a rate that the solution was kept below 0°.

The dark blue oil was separated after standing for twenty minutes, washed with ice water and dried over 10 g. of anhydrous sodium sulfate in the cold. The last traces of water were removed by cooling in ether–carbon dioxide snow and filtering off the ice; yield, 46–54 g. (20–30%). The product was over 90% pure (bromine analysis).

Preparation of 2-Chloro-2-nitrosopropane.[5]—The procedure was as described for the bromo compound, the chlorine being introduced as a rapid stream; yield, 62%.

Reaction of 2-Bromo-2-nitrosopropane with Ammonia.—Dry ammonia was bubbled through a solution of 32 g. of 2-bromo-2-nitrosopropane in 50 cc. of anhydrous ether at 20–25° for four hours, when no further precipitation of ammonium bromide took place. The 2-bromo-2-nitrosopropane, carried over into a condenser cooled in ice-salt, was returned to the reaction flask from time to time. Fourteen grams of solid ammonium bromide (identified by analysis) was filtered off. The ether solution was fractionated, yielding 4.2 g. of bromo acetone, 2.8 g. of acetoxime and 2.4 g. of tar.

Reaction of Dimethylzinc with 2-Chloro-2-nitrosopropane.—The apparatus and procedure already described[6] were used. To a solution of 21.8 g. (0.204 mole) 2-chloro-2-nitrosopropane in 150 cc. of anhydrous ether at 0° was added 19.4 g. (0.204 mole) of dimethylzinc. The resulting mixture stood at room temperature for twenty-five hours. Analyses of the gas showed that 2.64 g. (0.165 mole) of methane was formed, or 81% based on reaction (2b).

No products were found in the ether solution. An insoluble solid addition product was hydrolyzed with dilute sulfuric acid. Analysis of the gas corresponded to a yield of 0.67 g. (0.042 mole) of methane, or 10.3% based on the zinc methyl used.

Continuous ether extraction of the aqueous solution yielded 5.67 g. (0.079 mole) of acetoxime and 0.60 g. of tar. In the aqueous portion 0.204 mole of zinc and 0.204 mole of chloride were identified. This was distilled and 5.58 g. (0.96 mole) of acetone was identified in the distillate. The residue, which reduced ammoniacal silver nitrate and iodine solutions, was reduced with 20 g. of zinc dust and 50 cc. of 6 *N* hydrochloric acid. It was then made alkaline and distilled into standard hydrochloric acid (free methylhydroxylamine is decomposed in hot aqueous alkali),[7] yielding 0.109 mole of methylamine hydrochloride, identified by analysis and by conversion to N-methyl-*p*-toluene-sulfonamide, m. p. 78–78.5°,[8] (confirmed by mixed melting point).

Reaction of Diethylzinc with 2-Bromo-2-nitrosopropane.—Thirty-five grams (0.289 mole) of diethylzinc was added to a solution of 44 g. (0.289 mole) of 2-bromo-2-nitrosopropane in 125 cc. of anhydrous ether as above; 2.09 g. (0.075 mole) of ethylene and 6.28 g. (0.209 mole) of ethane were found in the gases.

In the ether solution, 2.0 g. of bromoacetone and 1.7 g. of tar were identified.

On hydrolysis of the addition product 0.17 g. (0.006 mole) of ethylene, 2.61 g. (0.087 mole) of ethane, 9.4 g. (0.127 mole) of acetoxime, 2.89 mole of zinc, 0.265 mole of bromide, 8.0 g. (0.138 mole) of acetone and 0.118 mole of ethylhydroxylamine were found. The ethylhydroxylamine was reduced and converted to N-ethyl-*p*-toluenesulfonamide, m. p. 63°,[8] and identified by a mixed melting point.

Reaction of Two Moles of Ethylmagnesium Bromide with 2-Chloro-2-nitrosopropane.—An ether solution containing 0.748 mole of ethylmagnesium bromide was added to a solution of 40 g. (0.374 mole) of 2-chloro-2-nitrosopropane in 150 cc. of anhydrous ether as above except that nitrogen replaced the carbon dioxide; 4.15 g. (0.148 mole) of ethylene and 6.05 g. (0.201 mole) of ethane were found in the gas.

From the ether 3.9 g. of unreacted 2-chloro-2-nitrosopropane was obtained. No gas was evolved on hydrolysis of the insoluble addition product. From the ether extract 6.8 g. of liquid (b. p. 60–120°), 6.6 g. (0.90 mole) of acetoxime and 4.1 g. of tar were obtained. In the aqueous portion, 1.03 moles of halide, 11.0 g. (0.189 mole) of acetone and 0.123 mole of hydroxylamine[9] were identified. No other products were found.

Reaction of Two Moles of Ethylmagnesium Bromide with 2-Bromo-2-nitrosopropane.—An ether solution containing 0.0528 mole of ethylmagnesium bromide was added to a solution of 40 g. (0.264 mole) of 2-bromo-2-nitrosopropane in 170 cc. of anhydrous ether; 2.60 g. (0.294 mole) of ethane was found in the gas.

No products were found in the ether and no gas was evolved on hydrolysis of the insoluble addition product. From the ether extract 5.6 g. of unidentified liquids (b. p. 60–120°), 3.2 g. (0.044 mole) of acetoxime and 4.2 g. of tar were obtained. In the aqueous portion, 0.796 mole of bromide, 0.68 g. (0.012 mole) of acetone and 0.042 mole of hydroxylamine were identified.

Reaction of Two Moles of Methylmagnesium Chloride with 2-Chloro-2-nitrosopropane.—An ether solution containing 0.546 mole of methylmagnesium chloride was added to a solution of 29 g. (0.268 mole) of 2-chloro-2-nitrosopropane in 50 cc. of anhydrous ether. No gas was evolved.

The entire reaction mixture was hydrolyzed and continuously extracted with ether as previously. In the ether portion, after hydrolysis and continuous extraction of the entire reaction mixture, only 0.4 g. of chloroacetone

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(4) Following the method of Piloty [*Ber.*, **31**, 454 (1898)], the yields were erratic and the material very impure.

(5) This method is superior to that of Ponzio, *Chem. Zentr.*, **77**, 1, 1692 (1906).

(6) Menard and Aston, THIS JOURNAL, **56**, 1601 (1934).

(7) Kjellin, *Ber.*, **26**, 2382 (1893).

(8) Remsen and Palmer, *Am. Chem. J.*, **8**, 241 (1886).

(9) Acree and Johnson, *ibid.*, **38**, 316 (1907).

and 4.0 g. of tarry residue were identified. In the aqueous portion, 0.751 mole of chloride and 3.0 g. of acetone (0.054 mole) were identified.

The free base was steam distilled from the aqueous portion into hydrochloric acid solution after making alkaline without reduction. Evaporation of the distillate yielded a very hygroscopic hydrochloride which was entirely soluble in absolute alcohol. It reduced ammoniacal silver nitrate. Nineteen grams (0.14 mole) of this hydrochloride was reduced with 40.0 g. of stannous chloride (0.21 mole) and 40 cc. of concd. hydrochloric acid in the cold. After making alkaline, distilling the base into hydrochloric acid and evaporating to dryness, a solid hydrochloride was obtained; recrystallized twice from absolute alcohol, m. p. 242–244° in a sealed tube. *Anal.* Calcd. for $C_5H_{14}NCl$: Cl, 28.63. Found: (Volhard) Cl, 28.68.

The hydrochloride was converted into the oxalate (twice recryst. from absolute alcohol) m. p. 109–110°. *Anal.* Calcd. for $C_7H_{15}O_4N$: C, 46.90; H, 8.57. Found: C, 46.84, 46.75; H, 8.76, 8.60.

This was identified as N-methyl-*s*-butylamine oxalate by a mixed melting point with a known sample of oxalate. The known sample was prepared by the methylation of *s*-butylamine obtained by the reduction of methyl ethyl ketoxime.[10] The base[11] thus obtained was purified through the *p*-toluenesulfonamide, and converted into the oxalate, m. p. 110–111° (from absolute alcohol). (The oxalate of N-methyl-*t*-butylamine melts with decomposition at 166°.[12])

β-*s*-Butyl-β-methylhydroxylamine.—The reaction of methylmagnesium chloride with 2-chloro-2-nitrosopropane was repeated and the free β-*s*-butyl-β-methylhydroxylamine was extracted with ether after making alkaline, without previous reduction or distillation. A solid product, m. p. 59–60°, b. p. 86° at 101 mm., was obtained, but was difficult to keep pure. *Equivalent weight.* Calcd. for $C_5H_{12}ON$: 103.1. Found: 102.5–103.0.

In handling, this compound apparently absorbed water of recrystallization. *Anal.* Calcd. for $C_5H_{12}ON{\cdot}H_2O$: C, 49.54; H, 12.48. Found: C, 48.80, 48.81; H, 12.29, 12.49.

Reaction of Two Moles of Methylmagnesium Chloride with 2-Bromo-2-nitrosopropane.—An ether solution containing 0.474 mole of methylmagnesium chloride was added to 36 g. (0.237 mole) of 2-bromo-2-nitrosopropane dissolved in 100 cc. of dry ether.

After hydrolysis and extraction, in the ether layer were identified 0.3 g. of bromoacetone, 1.8 g. of acetoxime and 4.3 g. of tar. In the aqueous portion, 0.413 mole of halide and 1.3 g. of acetone were identified, and 4 g. of impure β-*s*-butyl-β-methylhydroxylamine, b. p. 85–93° at 115 mm. (a yield of 17%), and 3.4 g. of tar were extracted from it after making alkaline.

The entire portion (b. p. 85–93°) was reduced as in the previous experiment. The hydrochloride of the resulting amine, melting at 190–200°, was converted into the oxalate. Fractional recrystallization of the product from alcohol (2.0 g.) yielded (in order of increasing solubility) 0.1 g. of oxalic acid, m. p. 187°, 0.1 g. of oxalate, decomp. 166–167° (probably N-methyl-*t*-butylamine oxalate) and 1.4 g. of N-methyl-*s*-butylamine oxalate, m. p. 110–111°.

Reaction of One Mole of Methylmagnesium Chloride with One Mole of 2-Chloro-2-nitrosopropane.—An ether solution containing 0.400 mole of methylmagnesium chloride was added to a solution of 43 g. (0.400 mole) of the chloronitrosopropane. After standing overnight the blue ether solution was decanted from the solid addition product. Fractional distillation yielded only 4.0 g. of chloronitrosopropane. The solid addition product was hydrolyzed in the cold with dilute sulfuric acid. By continuous extraction with ether 0.78 g. of acetone, 3.40 g. of unreacted chloronitrosopropane, 0.07 g. of acetoxime (m. p. 60°), 3.0 g. of tar were obtained and separated by distillation. The aqueous portion after extraction was distilled to half its volume to remove 0.041 mole of acetone as ascertained by analysis of the distillate. The residue was reduced with zinc dust and hydrochloric acid, made alkaline, and the volatile bases (0.115 mole) distilled into standard hydrochloric acid. Evaporation of the distillate yielded a hygroscopic reducing salt. This was further reduced with stannous chloride and concentrated hydrochloric acid. The hydrochloride obtained after the usual procedure was crystallized from absolute alcohol (m. p. 137–159°). *Anal.* Calcd. for CH_6NCl: Cl, 52.50. Found: Cl, 47.1. This salt was undoubtedly methylamine hydrochloride while the impurity was probably N-methyl-*s*-butylamine.

Reaction of Phenylmagnesium Bromide with 2-Bromo-2-nitrosopropane.—This reaction was carried out in the same manner as the methyl Grignard experiments. To a solution of 54 g. (0.363 mole) of 2-bromo-2-nitrosopropane was added an ether solution containing 0.495 mole of phenylmagnesium bromide. The resulting mixture contained no excess phenylmagnesium bromide. It was worked up as before. Upon distillation the following products were identified in the ether layer, 13.1 g. of bromoacetone, a little diphenyl (corresponding only to that found originally present in the phenylmagnesium bromide solution) and 5.0 g. of tar.

The addition product was hydrolyzed and continuously extracted for sixty-eight hours to dissolve all tar and colored material. The following products were identified from the ether extract of the aqueous portion: 5.6 g. (0.096 mole) of acetone, 0.096 mole of hydroxylamine, 4.16 g. (0.057 mole) of acetoxime, 5.8 g. (0.074 mole) of benzene and 14.1 g. of tar.

Summary

1. The reactions of dimethyl- and diethylzinc on 2-bromo and 2-chloro-2-nitrosopropane have been studied and found to involve the nitroso group.

2. The reactions of methyl and ethyl Grignard reagents have also been studied with these same compounds and found to involve the nitroso group.

3. The β-*s*-butyl-β-methylhydroxylamine obtained by the reaction of two moles of methyl

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[10] "Organic Syntheses," Vol. X1, p. 58.

[11] See also Löffler, *Ber.*, **43**, 2041 (1910), for another method of preparation.

[12] Sabatier and Mailhe, *Ann. chim. phys.*, [3] **16**, 87 (1909).

Grignard reagent and both nitroso compounds is a rearrangement product. It is the only case where the bromine is replaced by the action of the organometallic compound.

4. All the organometallic compounds except the methyl Grignard reagent, tended to some extent to split out HX.

STATE COLLEGE, PA. RECEIVED JULY 22, 1935

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

The Conductance of Non-aqueous Solutions. I. Sodium Triphenylboron and Disodium Tri-α-naphthylboron in Diethyl Ether

BY HENRY E. BENT AND MAURICE DORFMAN

Considerable work has been published recently from this Laboratory dealing with the alkali metal derivatives of various organic compounds. These compounds are salt-like in their character and conduct an electric current in non-aqueous solutions. The dissociation constants of these salts are not known but the assumption has been made that they are all of the same order of magnitude.[1,2] The data of this paper will be used later to test this assumption and are of immediate interest in establishing the structure of disodium tri-α-naphthylboron. A preliminary report of the experimental method[3] is given.

Sodium triphenylboron is a peculiar compound.[4] Triphenylboron is saturated as far as primary valence forces are concerned. It is true that it may readily add other molecules such as ammonia by means of a coördinate covalence but this can hardly be the case for sodium. The sodium addition compound conducts an electric current in diethyl ether solution and therefore presumably the sodium ion is held to the triphenylboron ion by electrostatic force.[5] The stability of sodium triphenylboron is therefore apparently due to a large electron affinity of triphenylboron. This in turn is probably due to the fact that the negative ion may be represented by a large number of structures, which result in a stabilization as a result of the phenomenon of resonance.[6]

The compound disodium tri-α-naphthylboron is still more curious. The second sodium is held rather loosely.[7] It was not possible, however, to measure ΔF for the addition of the second sodium due to the fact that an amalgam which might be in equilibrium with the compound would be solid at ordinary temperatures.

It seemed quite possible that a study of the conductance of solutions of these compounds, especially when compared with sodium triphenylmethyl, might shed some light on their structure and properties.

The method used experimentally was the ordinary a. c. procedure for resistances up to about 10^6 ohms. For higher resistance a d. c. method was adopted. The two methods were found to check in the region in which they overlapped.

Experimental Part

The cell "A," buret "B," and the tube in which the sodium addition compound was prepared are shown in Fig. 1. Two sheets of platinum, 1 cm. wide by 2 cm. long, were held rigidly about 1 mm. apart as indicated at the right in Fig. 1. Six holes were drilled in the sheets and soft glass rods pulled down to the size of the holes. A small bead was placed at the middle of each rod, the platinum sheets slipped over the ends and then by means of a small flame the end heated until sufficiently soft to allow it to be mashed down with a graphite rod. Heavy platinum wires were welded to the sheets of bright platinum and these in turn welded to No. 40 platinum ribbon, the latter being sealed into Pyrex as described by Bent and Gilfillan.[8] The cell constant was 0.00898.

The sodium addition compound was prepared in "C" by shaking a known weight of the boron compound with 40% sodium amalgam. The product was poured into the buret quantitatively by distilling ether back into "C"

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[1] Bent, *et al.*, THIS JOURNAL, **52**, 1498 (1930); **53**, 1786 (1931); **54**, 1393, 3250 (1932); **57**, 1217, 1242, 1259 (1935).

[2] Conant and Wheland, *ibid.*, **54**, 1212 (1932); McEwen, work soon to be published.

[3] This work was in progress before the first paper of Fuoss and Kraus [*ibid.*, **55**, 476 (1933)] appeared. In order to minimize the importance of polarization potentials they found it convenient to work with potentials as high as 150 v. In order to avoid the same difficulty we used potentials as small as possible, in most cases not more than 20 mv. A high sensitivity galvanometer made possible the use of these small potentials. Under these conditions polarization potentials gave no trouble.

[4] The stability of this compound has been reported in an earlier communication, Bent and Dorfman, *ibid.*, **57**, 1259 (1935).

[5] Krause and Polack [*Ber.*, **59**, 777 (1926)] state that sodium triphenylboron has a small conductivity in ether solution but give no quantitative data.

[6] Pauling and Wheland, *J. Chem. Phys.*, **1**, 362 (1933).

[7] Bent and Dorfman, *loc. cit.*

[8] Bent and Gilfillan, THIS JOURNAL, **55**, 3989 (1933).