[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, DUKE UNIVERSITY]

Conductivity of Sodium Triphenylmethide in Ether. Non-conductivity of the Sodium Derivatives of Certain Active Hydrogen Compounds[1]

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The conductivity of sodium triphenylmethide in ethereal solution increases as the concentration is increased. The sodium derivatives of ketones and certain other active hydrogen compounds prepared by means of this reagent fail to conduct. Possible explanations for these results are suggested.

Schlenk and Marcus[3] have observed that sodium triphenylmethide in ether solution conducts slightly in 0.0376 molar solution but not in 0.0051 molar solution. Swift[3a] has made precise measurements of the conductance in more dilute ether solution. He found a small conductance at 10^{-8} molar solution, decreasing with increasing concentration as expected for weak electrolytes. A minimum was observed between 10^{-3} to 10^{-2} M and an increase at higher concentration.

We have extended such measurements over a higher range. In Table I are given the molar conductances of sodium triphenylmethide at various concentrations at 26°. The two results of Schlenk and Marcus (at 20°) are included in this table. It can be seen that in this range the conductance increased as the concentration of the reagent was increased. In Fig. 1 is plotted the log of the molar conductance against the log of the concentration, including the earlier work.

TABLE I

CONDUCTANCE OF ETHEREAL SODIUM TRIPHENYLMETHIDE

Concentration, mole/liter	Molar conductance, ohm^{-1}	Concentration, mole/liter	Molar conductance, ohm^{-1}
0.0051[a]	0[a]	0.0482	0.0488
.0090	.0180	.0601	.0960
.0157	.0244	.0902	.202
.0261	.0254	.1503	.417
.0376[a]	.048[a]	.2253	.792

[a] Data from Schlenk and Marcus, ref. 3.

A similar increase in conductance with increase in concentration has been observed by Fuoss and Kraus[4] with tetra-isoamylammonium nitrate in dioxane and by Evans and Pearson[5] with Grignard reagents in ethyl ether. The former system[4] showed an initial decrease in conductance at very low concentrations and the latter, a decrease at very high concentrations. However, over much of the concentrations studied the curve resembled that given in Fig. 1.

Fuoss and Kraus concluded that the ion pair of the salt has a very low degree of dissociation and that it was in equilibrium with associated, ionized complexes which conduct. On applying this multiple ion theory to the present system, the conductance would be assumed to be due not to the sodium triphenylmethide itself but to ionized complexes, the simplest of which would be the sodium ion and anion I (equation 1).[6]

$$2(C_6H_5)_3C^-Na^+ \rightleftharpoons Na^+ + \underset{\text{I}}{(C_6H_5)_3CNaC(C_6H_5)_3^-} \quad (1)$$

The conductivity of lithium triphenylmethide in ether was found to be somewhat less than that of sodium triphenylmethide. Thus, the lithium reagent showed a molar conductance of only 0.007 ohm^{-1} at a concentration of 0.0239 molar and no measurable conductance (specific conductance $< 1.5 \times 10^{-7}$ ohm^{-1}) at 0.0125 molar, whereas the sodium reagent exhibited appreciable conductance even at lower concentration (see Table I). This lower conductivity of the lithium triphenylmethide probably indicates somewhat less formation of ionized complexes.

No measurable conductivity was observed with potassium triphenylmethide in 0.005 molar ethereal solution, which was the maximum concentration obtained with this reagent. Since Schlenk and Marcus[3] reported no conductivity for sodium triphenylmethide at approximately this concentration, determination of the relative conductivities of the potassium and sodium reagents was not realized.

Incidentally, potassium triphenylmethide was considerably less soluble in ether than sodium triphenylmethide, although the latter reagent was more soluble than lithium triphenylmethide.

Non-conductivity of Sodium Derivatives of Certain Active Hydrogen Compounds.—Sodium triphenylmethide reagent is a sufficiently strong base to effect the essentially complete ionization of the α-hydrogen of ketones. For example, this reagent converts a molecular equivalent of acetophenone to its sodium derivative accompanied by the discharge of the characteristic red color of the reagent (equation 2).

$$\underset{\text{(red reagent)}}{(C_6H_5)_3CNa} + CH_3COC_6H_5 \xrightarrow{\text{ether}} (C_6H_5)_3CH + \underset{\text{(colorless)}}{Na(CH_2COC_6H_5)} \quad (2)$$

In contrast to sodium triphenylmethide reagent, such sodio ketones failed to conduct measurably in approximately 0.2 molar etheral solutions. This was readily determined by adding the ketone in small portions to a molecular equivalent of the reagent. Thus, on adding acetophenone, methyl isobutyl ketone, or methyl isovaleryl ketone, the conductance decreased roughly in proportion to the

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[1] Supported in part by the Duke University Research Council.

[2] Du Pont Fellow, 1952–1953.

[3] W. Schlenk and E. Marcus, *Ber.*, **47**, 1664 (1914).

[3a] E. Swift, Jr., THIS JOURNAL, **60**, 1403 (1938).

[4] R. M. Fuoss and C. A. Kraus, *ibid*, **55**, 2387 (1933).

[5] W. V. Evans and R. Pearson, *ibid.*, **64**, 2865 (1942).

(6) The slope of the rising portion of the curve in Fig. 1 is greater than the one half expected for dimer I, and might indicate more highly associated complexes.

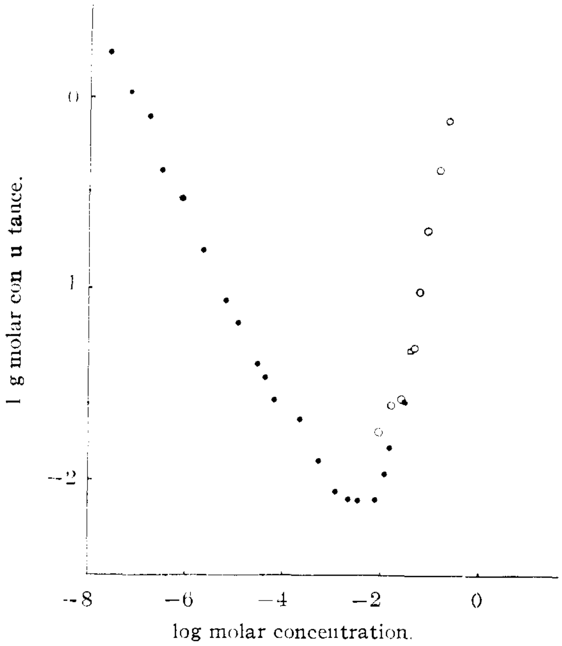
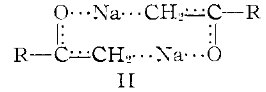


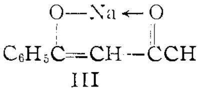
Fig. 1.—Open circles, this work; solid circles Swift,[3a] square, Schlenk and Marcus[3].

amount of the ketone added and became immeasurably small at equivalence (resistance $>2.5 \times 10^6$ ohms). At the concentration used all the sodio ketones were soluble.

Zook and Rellahan[7] have presented evidence that at least certain sodio ketones exist as dimers in ethereal solution. Since these dimers do not conduct, we suggest that they exist as ring structures such as II. Such a ring structure would not be possible with sodium triphenylmethide, which conducts.



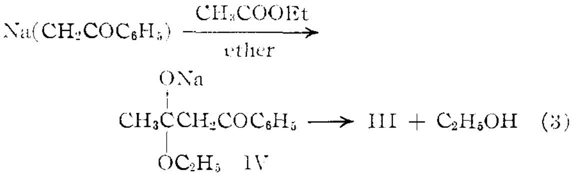
II



III

Similarly, on adding benzoylacetone to a molecular equivalent of sodium triphenylmethide reagent, the red color was discharged and the conductance became immeasurably small. The sodio β-diketone, which precipitated after 15 minutes, is suggested to have the six-atom ring structure III, although no evidence for such a monomer appears to have been reported.

Recently[8] bimolecular rate constants were obtained for the Claisen type of acylation of sodioacetophenone with ethyl acetate in dilute ethereal solution. This condensation appeared to involve the intermediate formation of the addition complex IV (equation 3).



$$\mathrm{Na(CH_2COC_6H_5)} \xrightarrow[\text{ether}]{\mathrm{CH_3COOEt}} \mathrm{CH_3\overset{ONa}{\underset{OC_2H_5}{C}}CH_2COC_6H_5} \longrightarrow \mathrm{III} + \mathrm{C_2H_5OH} \quad (3)$$

IV

This reaction has now been found to take place without producing a detectable amount of intermediate ions. Thus, no conductance was observed on adding ethyl acetate to a molecular equivalent of the sodio ketone in ethereal solution. The sodio β-diketone III precipitated after about 30 minutes.

Also, phenylacetonitrile, 2,2-diethyldecanoic acid, 2-ethyl-2-butyldecanoic acid, ethanol, octanol-1 and phenylacetylene were added to molecular equivalents of ethereal sodium triphenylmethide reagent. In each case the conductance became immeasurably small, although in the first two cases the bridge was unsteady as though the resistance was near the 2.5×10^6 ohms limit of the instrument. Precipitates were formed except with the two carboxylic acids.

It is interesting that even the sodium salt of 2-ethyl-2-butyldecanoic acid, which is fairly soluble in ether,[9] failed to conduct. The state of aggregation of this salt or of the other salts was not determined.

Experimental

Sodium triphenylmethide was prepared in ethyl ether solution essentially as described previously.[10] The concentration of the solution was determined by decomposition of appropriate samples with water and titration with standard acid.

Conductivity of Sodium Triphenylmethide (Table I, Fig. 1).—The solvent, ethyl ether, dried over sodium, showed no conductivity.

Ethereal solutions of this reagent were contained in a closed conductivity cell of the usual type with platinized platinum electrodes. The cell constant (0.360) was determined with KCl solution in conductivity water. Resistance was measured at 26° by a conductivity bridge manufactured by Industrial Instruments Inc., with which a maximum resistance of 2.5×10^6 ohms could be determined. The cell was filled with the triphenylmethide solution, and dilutions were made in a dry-box (over P_2O_5) in an atmosphere of purified nitrogen. The concentration of the diluted solutions was determined as described above after the resistance measurements were made.

Treatment of Sodium Triphenylmethide with Active Hydrogen Compounds.—The active hydrogen compounds were purified by appropriate procedures, and weighed samples of them added to a molecular equivalent of approximately 0.2 molar sodium triphenylmethide reagent in the cell in the dry-box at 26°. The results are given in the discussion.

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(7) H. D. Zook and W. L. Rellahan, THIS JOURNAL, **79**, 881 (1957).

(8) D. G. Hill, J. Burkus and C. R. Hauser, *ibid.*, **81**, 602 (1959).

(9) See C. R. Hauser and W. J. Chambers, *ibid.*, **78**, 3837 (1956).

(10) C. R. Hauser and B. Hudson, "Organic Reactions," Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1942, Chap. 9.