[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF NOTRE DAME]

The Configuration of the Mercuric Halides

BY W. J. CURRAN AND H. H. WENZKE

The Raman spectra of the mercuric halides have been interpreted[1] to indicate a linear structure for these compounds. Bell[2] calculated the moments of the mercuric halides from solubility data. He obtained 4.0, 5.7 and 6.6 × 10^{18} for the chloride, bromide and iodide, respectively. Braekken and Scholten[3] concluded from x-ray data that the molecular configuration of mercuric chloride was linear but that of mercuric bromide was not. The solubility of the mercuric halides in benzene is so small that it is difficult to use this solvent in the determination of electric moments. These halides are more soluble in dioxane and it is for this reason that the latter solvent was used. In order to determine whether or not the dioxane formed a coördinate compound with the mercury, it was used as a solvent in the determination of the moment of mercury diphenyl. The moment of mercury diphenyl had already been determined in benzene by Hampson.[4] He obtained the value 0.41.

TABLE I

DIELECTRIC CONSTANTS AND DENSITIES OF SOLUTIONS OF MERCURIC HALIDES

(Solvent, Dioxane; *T*, 25°)

c_2	d	ϵ
	Mercury diphenyl	
0.00000	1.0270	2.3373
.04965	1.1288	2.3929
.05998	1.1489	2.4046
.06813	1.1673	2.4139
	Mercuric chloride	
0.00000	1.0260	2.2267
.00502	1.0388	2.2444
.00507	1.0390	2.2444
.00547	1.0400	2.2456
.00564	1.0405	2.2471
	Mercuric bromide	
0.00000	1.0244	2.3334
.00691	1.0478	2.2607
.00906	1.0533	2.2695
.01047	1.0578	2.2748
.01335	1.0677	2.2858
	Mercuric iodide	
0.00000	1.0260	2.2267
.01099	1.0738	2.2881
.01236	1.0802	2.2938
.01260	1.0819	2.2959
.01299	1.0832	2.2986

TABLE II

POLARIZATIONS AND MOMENTS OF MERCURIC COMPOUNDS

Comopund	P_∞	P_E[a]	P_{A+O}	$10^{18}\mu$
Mercury diphenyl	69.02	65.30[4]	3.72	0.42
Mercuric chloride	65.03	30.36[5]	34.67	1.29
Mercuric bromide	78.63	55.30[5]	23.33	1.06
Mercuric iodide	101.40	94.28[5]	7.12	0.58

[a] The electronic polarizations were obtained from the literature according to the references given.

Discussion of Results

The value of 0.42 obtained for the moment of mercury diphenyl in dioxane is practically the same as that obtained by Hampson[4] in benzene, namely, 0.41. This shows that the oxygen of the dioxane does not form a coördinate covalent link with the mercury and that the dioxane is a satisfactory solvent for these compounds. It is apparent from the moments of these compounds that the mercuric halides are not linear in structure. The decrease of the moment with increase in atomic weight of the halogen is no doubt due in part to steric effects which cause a widening of the valence angle of the mercury as the atomic weight of the halogen increases. It is no doubt also true that the moment of the mercury-to-halogen linkage decreases with increase in size of the halogen atom. Unfortunately the electric moment data do not permit the calculation of the valence angle of the mercury in these halides. The measured moments are very much smaller than those obtained in the calculations of Bell.[2] The force relationships existing between the solute and solvent are of such a complex nature that at present no quantitative relation between them and dipole moments is known.

Summary

1. Electric moments have been determined for mercury diphenyl, mercuric chloride, mercuric bromide and mercuric iodide.

2. The configuration of the mercuric halides is not linear, as has been sometimes assumed from other lines of investigation.

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(1) Kohlrausch, "Der Smekal-Raman Effekt," 1931.

(2) Bell, *J. Chem. Soc.*, 1371 (1931).

(3) Braekken and Scholten, *Z. Krist.*, **89**, 448 (1934).

(4) Hampson, *Trans. Faraday Soc.*, **30**, 877 (1934).

(5) Bergmann, Engel and Wolf, *Z. physik. Chem.*, **B17**, 81 (1932).

3. The moments obtained by direct measurement are much smaller than has been calculated from solubility data. While dipole forces undoubtedly play a part in determining solubility, apparently not enough is known about them to permit an even semi-quantitative calculation of electric moments by this method.

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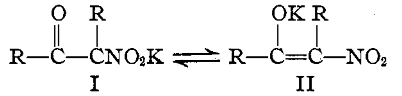
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

Asymmetric Syntheses. IV. The Action of Optically Active Nitrates on 2-Bromofluorene

BY J. T. THURSTON AND R. L. SHRINER

The reaction between optically active nitrates and cyclic ketones[1] led to the formation of salts which could possess either structure[2] I or II. In

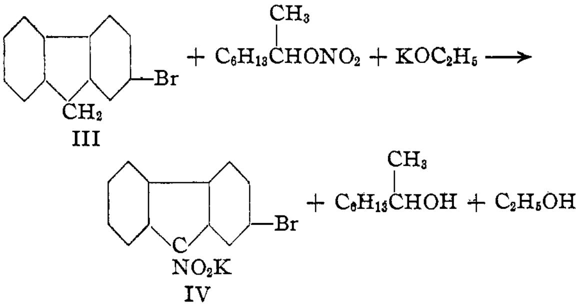


$$R-\overset{\overset{O}{\|}}{C}-\overset{\overset{R}{|}}{C}NO_2K \rightleftharpoons R-\overset{\overset{OK}{|}}{C}=\overset{\overset{R}{|}}{C}-NO_2$$

I II

order to avoid this, a study has been made of the action of optically active nitrates on an active methylene compound which cannot undergo such tautomerization.

Since Wislicenus and Waldmüller[3] showed that fluorene would react with ethyl nitrate in the presence of potassium ethoxide to give the potassium salt of 9-nitrofluorene, it was decided to study the reaction between the optically active 2-octyl nitrates and 2-bromofluorene (III).

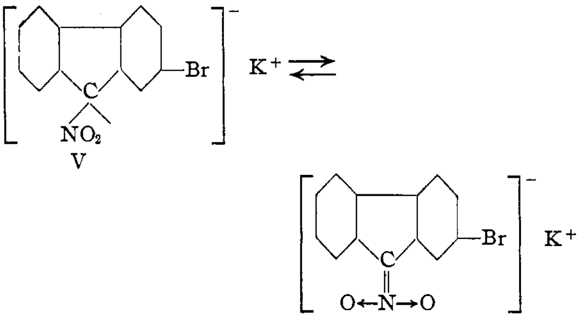


III

IV

The latter compound (III) contains an active methylene group but cannot undergo enolization. The presence of the bromine in one ring renders the molecule unsymmetrical so that carbon atom 9 in the product (IV) may be asymmetric.

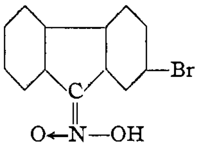
Treatment of 2-bromofluorene with *d*-2-octyl nitrate in the presence of potassium ethoxide yielded the potassium salt of 9-nitro-2-bromofluorene which possessed a very slight optical activity. Two independent preparations gave specific rotations[4] of +4.48 and +4.33°. The observed rotations were very low, +0.06 ± 0.01° and +0.05 ± 0.01°, but the absolute alcohol solutions of the salts were distinctly optically active. The *l*-2-octyl nitrate gave a very low specific rotation of −1.71°. The salts racemized readily. The activity of these salts indicates that at least a partial asymmetric synthesis was achieved by the optically active reagents. At least part of the salt must exist as the asymmetric ion (V) since the other form of the ion (VI) is not asymmetric.



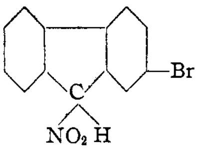
V

VI

Immediate treatment of the *d*-potassium salt with acid gave the *aci*-9-nitro-2-bromofluorene (VII) which was optically inactive. This *aci*-form (VII) was a solid, m. p. 132°. It was



VII



VIII

readily soluble in sodium carbonate solution, and gave a green color with ferric chloride. This *aci*-form was transformed into the *normal*-nitro compound (VIII) by heating it in alcoholic solution. The *normal*-nitro compound (VIII) gave

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(1) Shriner and Parker, THIS JOURNAL, 55, 766 (1933).

(2) Horne and Shriner, *ibid.*, 55, 4652 (1933).

(3) Wislicenus and Waldmüller, *Ber.*, 41, 3334 (1908).

(4) All specific rotations reported in this paper were determined at 25° with sodium D light.