

point 146–149° of the triphenylbismuth dichloride, for which the literature values range from 136 to 150°, would not rule out such a possibility for the bismuth compound, but the fairly sharp melting point of the antimony compound is not indicative of a mixture.

Another possibility to consider is that the differences of 29 and 28 cm.³ between the molar refraction and the total polarization from which the small moment values have been calculated are not dipole polarizations but atomic polarizations. Antimony pentachloride, which might be expected to have this trigonal bipyramidal structure, which has been found also for phosphorus pentachloride, has been reported to have a polarization¹² of about 54 in the pure liquid and about 49 in carbon tetrachloride solution. The molar refraction MR_D calculated for it by the method used in obtaining the refraction in Table II is 47 which indicates an atomic polarization not greater than 8 or much less than 3. As the atomic polarization of triphenylantimony dichloride would, probably, arise largely from its two Sb–Cl dipoles, it should not be greater than that of antimony pentachloride. It, therefore, appears extremely improbable that triphenylantimony dichloride should have an atomic polarization of 29, a value altogether abnormal in any case. It seems reasonable, therefore, to regard these two moment values as real, although they may be somewhat high because of

(12) Simons and Jessop, *THIS JOURNAL*, **53**, 1263 (1931).

neglect of atomic polarization. The conclusion to be drawn from these data is, therefore, that the molecular structures of triphenylantimony dichloride and triphenylbismuth dichloride are slightly unsymmetrical or that the specimens here measured were mixtures of a symmetrical with an unsymmetrical structure. It is to be regretted that it has thus far been impossible to obtain a sufficient concentration in solution of the ethylbismuth dichloride and dibromide very kindly sent to us by Dr. George Calingaert of the Ethyl Gasoline Corporation for measurement.

Summary

The dipole moments of triphenylgermanium bromide, triphenyltin chloride, benzylmercury chloride, triphenylantimony dichloride, and triphenylbismuth dichloride have been measured in benzene solution. Minimum values have been calculated for the metal-to-halogen bond moments in the first three compounds and used to estimate the minimum amounts of ionic character in the three bonds. The small moments found for triphenylantimony dichloride and triphenylbismuth dichloride are smaller than would be expected for unsymmetrical arrangements at the apices of a trigonal bipyramid, but argue against the expected symmetrical, trigonal bipyramidal arrangement as the only structure for these molecules.

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NOTES

Note on the Specific Gravity of Sodium Dichromate Solutions

BY DAVID F. ALTIMIER

The "International Critical Tables" and similar reference handbooks have based their tables for the density of sodium dichromate solutions on the erroneous work of Stanley.¹ The specific gravity of sodium dichromate solutions has been more accurately determined in the low concentration ranges by Jones and Bassett.²

(1) Arthur Stanley, *Chemical News and Journal of Industrial Science*, **54**, 194–195 (1886).

(2) H. C. Jones and H. P. Bassett, *Am. Chem. J.*, **24**, 290–349 (1906).

The results of recent determinations in this Laboratory are presented in the accompanying table.

Experimental.—The customary experimental procedure was followed in determining the specific gravity. The sodium dichromate, granular dihydrate, was prepared by recrystallization of the technical grade and the impurities were less than those specified by the American Chemical Society for c. p. potassium dichromate.³ The solutions were made by dissolving weighed amounts of sodium dichromate in distilled water and then deaerating the solutions. The temperature of the bath was maintained at $15.6 \pm 0.1^\circ\text{C}$. ($60 \pm 0.2^\circ\text{F}$). After weighing, the di-

(3) Committee on Analytical Reagents, American Chemical Society, *Ind. Eng. Chem.*, **17**, 756 (1925); *Ind. Eng. Chem., Anal. Ed.*, **1**, 171 (1929); **3**, 221 (1931); **13**, 639 (1940).

chromate content of each solution was checked by electro-metric titration according to the method described by Kelley.⁴ All weighings were made in air and calculated to weights *in vacuo*.

It will be noted that the specific gravity determinations made with technical $\text{Na}_2\text{Cr}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$ in tap water⁵ are in good agreement with the data for c. p. $\text{Na}_2\text{Cr}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$ and consequently the data may be used for determining the dichromate content of solutions of technical sodium dichromate without introducing any appreciable error.

TABLE I

$\text{Na}_2\text{Cr}_2\text{O}_7$, wt. per cent.	Specific gravity 15.6°/15.6°C. (60°/60°F.)
1.50	1.0105
4.50	1.0344
13.41	1.1076
22.61	1.1921
31.44	1.2833
39.48	1.3763
44.10	1.4356
47.38	1.4790
48.10	1.4886
53.07 ^a	1.5683 ^a
56.28 ^a	1.6200 ^a
56.68 ^a	1.6259 ^a
57.23	1.6352
60.25 ^a	1.6849 ^a
61.40 ^a	1.7056 ^a
63.92	1.7464

^a These values obtained by using technical grade sodium dichromate in tap water.

(4) Kelley and co-workers, *Ind. Eng. Chem.*, **9**, 780 (1917).

(5) These determinations were made by W. H. Hartford of this Laboratory.

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On the Mechanism of "Aromatizing" Diene Reactions in Nitrobenzene

BY F. BERGMANN

Diels-Alder reactions in nitrobenzene allow one to obtain in a single step an aromatic condensation product.¹ The mechanism and the general applicability of this modified method of diene synthesis have now been investigated with the following results.

(a) If the isolated tetrahydro product, which is obtained in the usual solvents, is boiled in nitrobenzene for different periods, aromatization occurs. Therefore, no active intermediary stage, as has been observed in diene reactions, is responsible for the easy dehydrogenation with nitrobenzene.

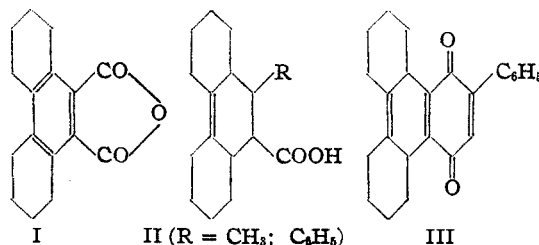
(b) Other nitro compounds, *e. g.*, *p*-chloro-, *p*-bromonitrobenzene and *m*-dinitrobenzene, when

(1) E. Bergmann, L. Haskelberg and F. Bergmann, *J. Org. Chem.*, in press.

added to the xylene solution of the two components, do not influence the results of the condensation in the instances investigated so far.

(c) Dicyclohexenyl and maleic anhydride are easily condensed in nitrobenzene with simultaneous aromatization (I). However, with cinnamic or crotonic acid the tetrahydro products (II) were obtained. It is evident that nitrobenzene acts only on systems capable of double ortho-enolization, as in the adducts with quinones or maleic anhydrides. In these cases the di-enolic form is dehydrogenated and one new double bond established in the newly formed six-membered ring. The removal of the remaining two "hydroaromatic" hydrogen atoms now depends on the stability of the intermediary dihydrobenzene nucleus, which in most cases undergoes spontaneous dehydrogenation. At times the intermediary stage can be isolated, as in the condensation of dicyclohexenyl and phenylquinone (III).² The possibility of double enolization is, however, not sufficient for the aromatizing effect of nitrobenzene, as anthracene endosuccinic anhydride is not affected by this solvent. Here only the two hydrogens in α -position to the carboxyls would be removable for steric reasons and the intermediary IV would not be stable under the experimental conditions, but would be converted into V.³ The only other case recorded in literature where nitrobenzene failed to dehydrogenate the addition product, is the work of Weidlich⁴ on *bis*-(1,1'-dialin). This latter reaction is now under investigation.

As a final proof for the above assumed reaction mechanism, we have now found that *meso*-diphenylsuccinic acid (VI), when heated for twelve hours in nitrobenzene, yields diphenylmaleic anhydride (VII) in about 40% yield. The di-enolic system involved in all these reactions, $-\text{C}(\text{OH})=\text{C}=\text{C}(\text{OH})-$, may be regarded as the vinylog



(2) Ch. Weizmann, E. Bergmann and T. Berlin, *THIS JOURNAL*, **60**, 1331 (1938).

(3) Diels and Friedrichsen, *Ann.*, **513**, 145 (1934).

(4) Weidlich, *Ber.*, **71**, 1203 (1938).