

XXXIII.—*Dicyanates and Dibenzoates of Triphenylbismuthine and Triphenylstibine.*

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FROM a consideration of the stability to heat of halogen and similar derivatives of the type Ph_3BiX_2 , it was shown (J., 1926, 1648) that the halogens and pseudo-halogens could be arranged in an electrochemical order almost identical with that deduced by Birckenbach and Kellermann (*Ber.*, 1925, 58, 786, 2377) from a study of the decomposition potentials of the potassium salts in aqueous solution.

Further evidence is now adduced as to the similarity of the conclusions reached by these entirely different modes of approach. Birckenbach and Kellermann showed that the electronegative properties of these elements and radicals decrease from fluorine thus: F, ONC, OCN, Cl, N_3 , Br, CN, SCN, I, SeCN, TeCN. The position of the cyanate radical, OCN, is particularly interesting, since it is widely separated from the thiocyno- and selenocyanogroups. This difference has also been brought to light by a study of the properties of *triphenylbismuthine dicyanate*, $(\text{C}_6\text{H}_5)_3\text{Bi}(\text{OCN})_2$. It is quite stable at the ordinary temperature, in marked distinction to the corresponding dithiocyanate and diselenocyanate, which lose phenyl pseudohalide. Its temperature of decomposition is about 150° , which is very close to that of triphenylbismuthine dichloride. The reaction is probably complex. Phenyl cyanate, $\text{Ph}-\text{O}-\text{CN}$, which should be produced according to the general equation $\text{Ph}_3\text{BiX}_2 = \text{Ph}_2\text{BiX} + \text{PhX}$ (J., 1922, 121, 91), is unknown. If formed, it would doubtless undergo polymerisation and possibly other changes.

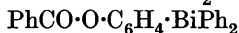
In comparing our results with those of Birckenbach and Kellermann, it has been assumed that triphenylbismuthine dicyanate has the normal cyanate structure, $\text{Ph}_3\text{Bi}(\text{O}-\text{C}\equiv\text{N})_2$. Kaufmann and Kögler (*Ber.*, 1926, 59, 184), from a comparison of the stabilities of the lead halides and pseudohalides, PbX_4 , have reached identical conclusions as to the electrochemical order of F, OCN, and Cl, which give relatively stable derivatives. The thiocyanate, iodide and selenocyanate of this type decompose immediately according to the equation $\text{PbX}_4 = \text{PbX}_2 + \text{X}_2$.

The relative electrochemical positions of iodine and thiocyanogen were first investigated by Soderbäck (*Annalen*, 1919, 419, 283). In aqueous or ethereal solution, an equilibrium exists between $\text{K}(\text{or Ag})\text{SCN}$, $\text{K}(\text{or Ag})\text{I}$, I_2 , and $(\text{SCN})_2$ and the results were inconclusive. Nitrosyl thiocyanate, however, has a transitory

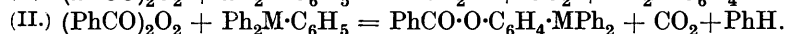
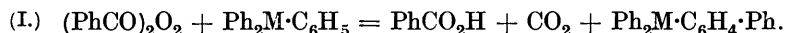
existence in the deep red solutions obtained from nitrous acid and thiocyanates, or from nitrosyl chloride and silver thiocyanate. No evidence of the existence of the corresponding iodide can be obtained, but nitrosyl bromide is stable below -2° . On these grounds, he considered iodine to be the more positive radical. By a comparison of the times required for the development of the odour of iodobenzene and phenyl thiocyanate when triphenylbismuthine dichloride is mixed with aqueous solutions of potassium iodide and thiocyanate, results are obtained in agreement with those of Soderbäck and of Birckenbach and Kellermann (compare J., 1926, 1648). The observed times were 3 and 40 seconds, respectively, at the ordinary temperature, the theoretical quantities of the different salts being employed. The slower production of phenyl thiocyanate has been noted on several occasions and, indicating the slower decomposition of the dithiocyanate, is evidence of the more positive nature of iodine.

Wilkinson and one of us have shown (J., 1924, 125, 856) that nitration of triphenylbismuthine dinitrate yields a meta-derivative. Owing to the oxidation of the triaryl derivatives (R_3M) of bismuth, antimony, arsenic, and phosphorus to compounds of the type $R_3M(O\cdot NO_2)_2$ during nitration, it was impossible to determine the orienting influence of the metal or metalloid in the tervalent condition.

From the work of Gelissen and Hermans (*Ber.*, 1925, 58, 287) it appeared probable that, by the action of benzoyl peroxide on the triphenyl derivatives of the elements of the nitrogen group, mixed organo-derivatives such as $Ph_2Bi\cdot C_6H_4\cdot Ph$ or



might be obtained, according to the equations



The first reaction might be expected to predominate (Gelissen).

The dibromide or dichloride of a substance of the type $Ph_2M\cdot C_6H_4\cdot Ph$ might yield on suitable decomposition a halogen derivative of diphenyl, $C_6H_5\cdot C_6H_4X$ (J., 1915, 107, 21, 23; 1924, 125, 857): $(Ph\cdot C_6H_4)MPh_2X_2 = Ph\cdot C_6H_4X + Ph_2MX$. By orientation of the halogen atom in this compound, the directing influence of the tervalent element M might be determined. In boiling light petroleum, however, triphenylbismuthine and benzoyl peroxide gave *triphenylbismuthine dibenzoate*. The corresponding *stibine dibenzoate* was prepared in a similar manner. No other products could be isolated. The two dibenzoates were identical with the compounds obtained from silver benzoate and the bismuthine and

stibine dichlorides. Gelissen and Hermans (*Ber.*, 1926, 59, 666) obtained a dibenzoate from *cyclohexene* and the peroxide.

Triphenylphosphine and benzoyl peroxide in light petroleum at the ordinary temperature give triphenylphosphine oxide and benzoic anhydride, but no perbenzoic acid could be detected (compare Gelissen and Hermans, *Ber.*, 1926, 59, 66). This illustrates the great tendency of the phosphorus atom in the phosphines to become quinquevalent, and is analogous to the action of thiocyanogen and thiocyanic acid giving the sulphide, Ph_3PS (*J.*, 1923, 123, 1054).

Difficulties in the preparation of triphenylphosphine (*J.*, 1924, 125, 864) may be avoided by using the method of Gilman and Vernon (*J. Amer. Chem. Soc.*, 1926, 48, 1066), the crude undistilled triphenyl phosphite being treated directly with magnesium phenyl bromide. This method is much less troublesome than that involving the use of sodium and gives a much better yield.

EXPERIMENTAL.

Triphenylbismuthine dicyanate was prepared by shaking the dichloride (2.4 g.; 1 mol.) and silver cyanate (1.4 g.; 2 mols.) in dry ether (40 c.c.) for 4 hours. Extraction of the insoluble residue with chloroform yielded a solid which was crystallised twice from chloroform-light petroleum; m. p. 128.5—129°. A further quantity was obtained from the ether. The weight of silver chloride obtained was 1.30 g. (calc., 1.32 g.) (Found: C, 45.8, 45.8; H, 3.1, 3.2; N, 5.5, 5.4; Bi, 39.4, 39.1. $\text{C}_{20}\text{H}_{15}\text{O}_2\text{N}_2\text{Bi}$ requires C, 45.8; H, 2.9; N, 5.35; Bi, 39.9%).

When the dicyanate is warmed with aqueous alcohol (1:1), ammonia is evolved. On heating with excess of water, it gives a turbid, frothing liquid resembling an alkaline solution of the dichloride, and probably containing the unstable dihydroxide or oxide (*J.*, 1920, 117, 765). On heating to 150°, the dicyanate decomposes and an oil with an intensely pungent odour distils and partly solidifies. No definite product could be isolated from the minute amount available.

In one experiment, the silver cyanate used contained carbonate. The silver chloride precipitate then contained some insoluble triphenylbismuthine carbonate, which remained after removal of the dicyanate with chloroform and of silver salts with ammonia. With hydrochloric acid, it gave the dichloride, recognised by m. p. and mixed m. p.

Triphenylstibine Dicyanate.—Triphenylstibine dichloride (3.2 g.) and silver cyanate were shaken in dry ether for 14 hours. The solid was then washed with ether, leaving 2 g. of silver chloride (calc., 2.16 g.). The ether yielded 2.5 g. of white crystals, m. p. 105—113°. After two crystallisations from chloroform-light

petroleum, these melted at 111—112° (Found: N, 6.5, 6.4; Sb, 27.4, 28.1. $C_{20}H_{15}O_2N_2Sb$ requires N, 6.4; Sb, 27.9%).

Triphenylbismuthine and Benzoyl Peroxide.—An intimate mixture of these compounds reacted violently at 68°, white fumes and a strong odour of diphenyl being produced. Extraction with hot water and sodium hydroxide and crystallisation of the residue from alcohol yielded triphenylbismuthine and bismuth hydroxide. Other conditions were therefore employed.

The bismuthine (4 g.), benzoyl peroxide (2.2 g.; 1 mol.), and light petroleum (b. p. 60—80°; 50 c.c.) were heated under reflux. The clear solution soon deposited 3.3 g. of a faintly yellow solid, m. p. 164.5—166.5°. This was repeatedly crystallised from benzene—light petroleum, the last three operations giving products of m. p. 171.5—173.5°, 172—173.5°, 171—172.5°, taken simultaneously. The compound decomposed a few degrees above the m. p. With hot hydrochloric acid, it gave no benzene, indicating the absence of tervalent bismuth, but was converted into benzoic acid and triphenylbismuthine dichloride, m. p. 139—141°. When it was mixed with potassium iodide or thiocyanate in aqueous suspension, the characteristic odours of iodobenzene and phenyl thiocyanate were produced, thus affording conclusive proof of the presence of a derivative of quinquivalent bismuth (J., 1922, **121**, 92; 1924, **125**, 854). Analysis showed the substance to be *triphenylbismuthine dibenzoate*, and it did not depress the m. p. of the product obtained from the dichloride and silver benzoate (Found: Bi, 30.8, 30.5. $C_{32}H_{25}O_4Bi$ requires Bi, 30.6%).

The petroleum mother-liquor from the original reaction was concentrated, yielding successively benzoyl peroxide, triphenylbismuthine dibenzoate, and triphenylbismuthine.

Triphenylstibine and Benzoyl Peroxide.—From the stibine (5 g.) and the peroxide (3.4 g.; 1 mol.) in light petroleum (b. p. 60—80°; 100 c.c.), a solid, m. p. 170.5—173.5°, separated after 20 minutes' heating (7.3 g.). After two crystallisations from benzene—light petroleum, it melted at 171.5°, the purification being less troublesome than that of the corresponding bismuth compound. With hot hydrochloric acid, the stibine dichloride (m. p. and mixed m. p. 142—143°) and benzoic acid, m. p. 121°, were obtained. The original petroleum filtrate yielded a trace of triphenylstibine.

Analysis showed the product to be *triphenylstibine dibenzoate*. It did not depress the m. p. (170.5—172.5°) of the compound obtained from the dichloride and silver benzoate (Found: Sb, 20.4, 20.6. $C_{32}H_{25}O_4Sb$ requires Sb, 20.5%).

A comparison of the m. p.'s of the dichlorides and dibenzoates of triphenylbismuthine and triphenylstibine is of interest:

	Dibenzoate.	Dichloride.
Bismuthine	172—173°	141°
Stibine	171—171·5	143

Preparation of the Bismuthine and Stibine Dibenzoates from the Corresponding Dichlorides.—(a) Bismuthine dichloride, 2 g.; (b) stibine dichloride, 0·9 g. Silver benzoate (2 mols.) (a) 1·8 g., (b) 0·95 g. Reaction occurred on shaking in chloroform over-night. The product, purified as described above, had m. p. (a) 171·5°, (b) 170·5—172·5°.

Triphenylphosphine and Benzoyl Peroxide.—The phosphine (2·9 g.) and the peroxide (2·7 g.; 1 mol.) were separately and completely dissolved in light petroleum, and the cold solutions mixed. A precipitate quickly formed which melted at 140—148°, and after three crystallisations from chloroform–light petroleum had the constant m. p. 153·5°. It did not depress the m. p. (153·5°) of an authentic specimen of triphenylphosphine oxide.

The original petroleum filtrate on concentration deposited white crystals, m. p. 37·5—39·5°. These were free from phosphorus (and from perbenzoic acid, as shown by the odour and by the behaviour to both aniline and potassium iodide) and when mixed with benzoic anhydride (m. p. 42·5—43·5°) also melted at 37·5—39·5°. The compounds appeared to be identical. With warm aniline, the product from the reaction quickly gave benzanilide, m. p. and mixed m. p. 159—160°, but no nitrosobenzene.

When the phosphine and the peroxide were shaken in the minimum of light petroleum for an hour, heat was developed. The products of the reaction were the same.

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