A Bismuthonium Ylid

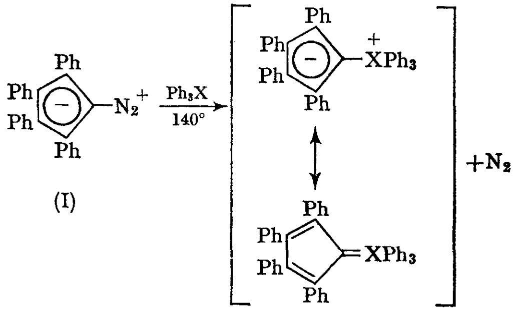
By DOUGLAS LLOYD* and M. I. C. SINGER
(*Department of Chemistry, United College, University of St. Andrews, St. Andrews, Fife*)

No bismuthonium ylid has hitherto been described, although a bismuthonium-*N*-tosylimine has been prepared.[1]

Cyclopentadienylids (II; X = P, As, Sb) of other Group V elements have proved to be readily obtainable by carbenic decomposition of diazotetraphenylcyclopentadiene (I) in the molten triphenyl derivatives of these elements:[2]

When a mixture of the diazo-compound (I) and triphenylbismuth is heated to 140° under nitrogen, a deep blue product results, which dissolves in ether and can be reprecipitated, m.p. 195° (decomp.), on addition of light petroleum (b.p. 40—60°). Thin-layer chromatography indicates that the blue product is contaminated by small amounts of triphenylbismuth (only), but attempts to prepare an analytical sample by chromatographic methods or by recrystallisation have failed owing to the ready decomposition of this blue product in solution. However, from its mode of preparation and from its spectra we believe it to be triphenylbismuthonium tetraphenylcyclopentadienylid (II; X = Bi).

It is interesting that whereas the corresponding phosphonium, arsonium, and stibonium ylids are yellow, the bismuthonium analogoue (like the corresponding pyridinium ylid) is deep blue; there is a similar difference between pentaphenylantimony, -arsenic, and -phosphorus which are colourless or yellow, and pentaphenylbismuth



(I)

(II)

which is deep violet.[1,3] Also unlike the phosphorus, arsenic, and antimony ylids, but like pyridinium cyclopentadienylids,[4] this bismuth ylid gives solutions whose colours vary markedly with the polarity of the solvent, *e.g.*, solutions in benzene or ether are deep blue, in acetone blue-purple, and in methanol red-purple. In methanol there are absorption maxima at 240, 335, 528 mμ; in benzene at 280, 345 596 mμ. These maxima are almost coincident with those shown by pyridinium tetraphenylcyclopentadienylid in the same solvents.[5] It seems probable that the vacant 6*d*-orbitals of bismuth, unlike the 4*d*- or 5*d*-orbitals of arsenic or antimony, cannot effectively overlap the 2*p*-orbitals of the anionic moiety.

Unlike the other Group V cyclopentadienylids, the bismuthonium ylid does not form isolable salts with picric or perchloric acids, decomposition intervening. It is also rapidly decomposed by methanolic sodium hydroxide, tetraphenylcyclopentadiene being among the products.

We are grateful to our colleagues G. S. Harris and F. Inglis for a gift of triphenylbismuth.

(*Received, August* 14*th*, 1967; *Com.* 862.)

---

[1] G. Wittig and D. Hellwinkel, *Chem. Ber.*, 1964, **97**, 789.

[2] I. B. M. Band, D. Lloyd, M. I. C. Singer, and F. I. Wasson, *Chem. Comm.*, 1966, 544; D. Lloyd, M. I. C. Singer, M. Regitz, and A. Liedhegener, *Chem. and Ind.*, 1967, 324; D. Lloyd and M. I. C. Singer, *ibid.*, pp. 510, 787.

[3] G. Wittig and M. Rieber, *Annalen*, 1949, **562**, 187; G. Wittig and K. Clauss, *ibid.*, 1952, **577**, 26; G. Wittig and D. Hellwinkel, *Chem. Ber.*, 1964, **97**, 741, 769.

[4] D. Lloyd and J. S. Sneezum, *Chem. and Ind.*, 1955, 1221; *Tetrahedron*, 1958, **3**, 234; E. M. Kosower and B. G. Ramsey, *J. Amer. Chem. Soc.*, 1959, **81**, 856.

[5] D. Lloyd and M. I. C. Singer, unpublished work (quoted, in part, in D. Lloyd, "Carbocyclic Non-benzenoid Aromatic Compounds", Elsevier, Amsterdam, 1966, p. 67).