Synthesis of a Dialkyl Phosporoisocyanidate

By WOJCIECH J. STEC, ANDRZEJ KONOPKA, and BOGDAN UZNAŃSKI
(*Centre of Molecular and Macromolecular Studies, Polish Academy of Sciences,* 90–362 *Łódź, Poland*)

Summary The first compound with the $>P(O)NC$ structure and its rearrangement to a dialkyl phosphorocyanidate, as shown by i.r. and ^{31}P n.m.r. spectroscopy, are described.

THE synthesis of diaryl phosphoroisoselenocyanatidates has been described only recently.[1] We find that the reaction of equimolar amounts of the dioxaphosphorinan[2] (I), δ (^{31}P) + 1·8 p.p.m. (MeCN, H_3PO_4 ext. standard; +ve shift to higher field) with KSeCN in dry MeCN solution gives the isoselenocyanatodioxaphosphorinan (II), m.p. 64—67° (from benzene–n-heptane, 1 : 1) δ (^{31}P + 29·0 p.p.m. (C_6H_6), ν_{NCSe} (KBr) 1295br,s and ν_{PO} 1305br,s cm^{-1}.† Treatment of (II) with triethyl phosphite in benzene

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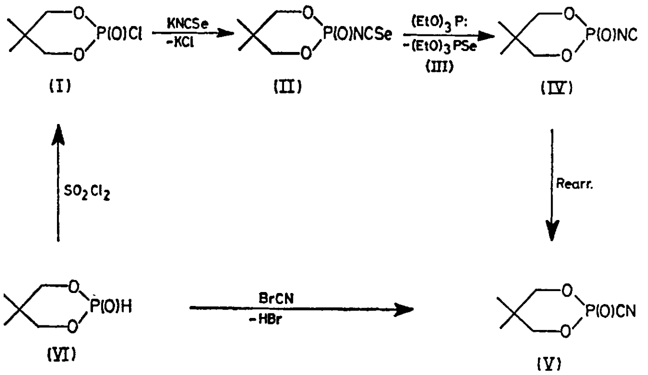
† All operations with (II), (IV), and (V) have to be carried out under dry nitrogen under scrupulously dry conditions. Compounds (II), (IV), and (V) gave mass spectra fully consistent with their postulated structures.

caused cleavage of the C=Se bond[3] with formation of the phosphoroselenoate[4] (III) and the isocyanodioxaphosphorinan (IV), the first compound with the >P(O)NC structure, m.p. 70·5—72° (from ether–n–heptane, 1 : 1), δ (^{31}P) + 34·5 p.p.m. (C_6H_6) |^1J (^{31}P–^{14}N)| 13·9 Hz, ν_{NC} (C_6H_6) 2080sh,m and ν_{PO} 1340br,s cm^{-1}. Compound (IV) is very reactive and unstable and readily isomerizes to the cyano-compound (V), m.p. 79—81°, δ (^{31}P) + 28·5 p.p.m. (C_6H_6), ν_{CN} (C_6H_6) 2210sh,m and ν_{PO} 1330br,s cm^{-1}. Compound (V) was obtained independently by reaction of the dioxaphosphorinan (VI)[5] with BrCN.‡ The rearrangement (IV) → (V) was followed by i.r. and ^{31}P n.m.r. spectroscopy.



The proton-noise decoupled ^{31}P n.m.r. spectrum of (IV) shows a 1 : 1 : 1 triplet, resulting from the coupling of ^{31}P with ^{14}N ($I = 1$). Such splitting, to our knowledge, has not been observed in the spectra of other >P(O)–N< compounds and strongly supports the presence of the NC-group.[6]

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‡ Yamada *et al.* (S. Yamada, Y. Kasai, and V. Shioiri, *Tetrahedron Letters*, **1973**, 1595) have claimed on the basis of i.r. data that in the reaction of triethyl phosphite with BrCN both phosphoro-cyanide and -isocyanide are formed and after several weeks at room temperature the isocyanide had decomposed. Our ^{31}P n.m.r. results showed that the reaction of 2-methoxy-5,5-dimethyl-1,3,2-dioxaphosphorinan (R. S. Edmundson, *Tetrahedron*, 1964, **20**, 2781) with an equimolar amount of BrCN in benzene solution gave a mixture of the 2-cyano-compound (V) and the corresponding 2-bromo-compound δ(^{31}P) + 14·7 p.p.m. (C_6H_6), (W. J. Stec and A. Zwierzak, *Canad. J. Chem.*, 1967, **45**, 2513), in a 57:43 ratio. Traces of (IV) (< 5%) were evident from the ^{31}P n.m.r. spectrum of the reaction mixture recorded immediately after the exothermi creaction of (VI) with BrCN.

[1] T. Gabrio and G. Barnikow, *Z. Chem.*, 1969, **9** (5), 183.
[2] R. S. Edmundson, *Tetrahedron*, 1968, **21**, 2379.
[3] L. I. Stangeland, T. Austad, and J. Songstad, *Acta Chem. Scand.*, 1973, **27**, 3919.
[4] W. J. Stec, A. Okruszek, B. Uznanski, and J. Michalski, *Phosphorus*, 1972, **2**, 95.
[5] A. Zwierzak, *Canad. J. Chem.*, 1967, **45**, 2502.
[6] 'Isonitrile Chemistry,' ed. I. Ugi, Academic Press, New York, London, 1971, p. 5.