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SOME REACTIONS OF 5-PHOSPHONIASPIRO-[4,4]-NONANE IODIDE - A SPIRO PHOSPHONIUM RING SYSTEM

B. D. Cuddy, J. Charles F. Murray and Brian J. Walker[1]
Department of Chemistry, David Keir Building,
Queen's University of Belfast, Belfast BT9 5AG,
N. Ireland.

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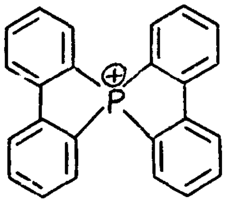
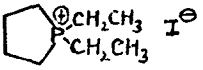
There has been considerable recent interest in compounds containing a phosphorus atom in small (four or five) ring systems, since the geometrical restraints imposed by these rings often modify reaction pathways[2]. The effect of two such rings on the reactivity of phosphonium salts, for example (1), would be of current interest.

(1) n = 2,3 or 4



(2)

Most compounds prepared containing a spiro phosphonium group have been without α-protons, for example (2)[3], and so one facet of their reactions, that of ylid formation, is precluded. However, Russian workers have recently prepared 5-phosphoniaspiro-[4,4]-nonane iodide (1; n=4)[4] and, since we were able to prepare its monocyclic (3) and acyclic (4)[5] analogues, this seemed a suitable compound to study.



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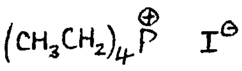
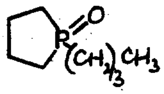


$(CH_3CH_2)_4\overset{\oplus}{P}\quad I^{\ominus}$

(4)

The salts (1; n=4), (3) and (4) show a progressive change in ^{31}P n.m.r. chemical shift, -72, -59.5 and -39.9 ppm^{6} respectively from 85% ortho phosphoric acid. The value for the spiro compound (1; n=4) is especially large for a phosphonium salt and since ^{31}P chemical shifts are thought to be related to *d*-orbital participation^{7} it may be that considerable modification of bonding has taken place to accommodate the spiro ring system.

Salts (1; n=4), (3) and (4) are all hydrolysed by refluxing in 4 molar KOH in 95% ethanol for four days. Tetraethylphosphonium iodide gives triethylphosphine oxide (92%) while both (1; n=4) and (3) undergo ring opening to give phosphine oxides (5) and (6) respectively, in high yield. That the oxide obtained from salt (3) is the ring opened, rather than the alternative ring retained, product was deduced from its mass spectrum ($^{m}/_{e}$ 162, 133, 105), although the presence of minor amounts of ring retained product cannot be ruled out. Preliminary rate studies suggest the rate of hydrolysis is $(1) > (3) > (4)$. Although the enhancement of hydrolysis rate for the monocyclic salt (3) over (4) is expected^{8}, the further enhancement for (1; n=4) is perhaps surprising. The formation of a pentavalent intermediate from (1; n=4) by attack of hydroxide ion should be unfavourable, either from electronegativity criteria ($O^{\ominus}$ axial) or from diequatorial ring bridging, depending on the position of initial attack^{9}. Presumably these factors are overcome by the extra relief of ring strain. These results will be discussed more fully elsewhere.



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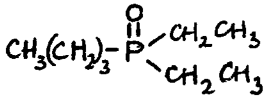
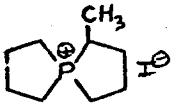


(6)

Derkach and Kirsanov^{4} were unable to prepare an ylid from the salt (1; n=4), which suggests that the geometric constraints imposed by the ring system may reduce the extent of d_{π} overlap with the adjacent carbanion. However, we have found that the α-protons in salt (1; n=4) could be exchanged to the extent of 74% (from n.m.r.; J_{PCCH}=18Hz) in 0.5 molar $Na^{\oplus}\ \overset{\ominus}{O}Et/EtOD$ during one week at room temperature, presumably *via* an intermediate ylid. Salts (3) and (4), under the same conditions, gave 58% and 68% exchange respectively.

These experiments suggest that ylid formation from (1; n=4) is possible and treatment of this salt with phenyl lithium at room temperature, followed by the addition of methyl iodide, gave the methylated salt (7) (30%); m.p. 163-165°; m.s. $^{m}/_{e}$ 157 (M^{+}), 101, 87; n.m.r. τ($CDCl_3$)

6.90-8.20 m (15H), 8.55 dd (3H; J_{HCCH}=7Hz, J_{PCCH}=18Hz). Similar treatment of salts (3) and (4) gave the analogous methylated products (8) and (9).



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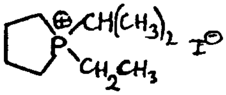

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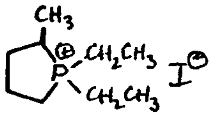

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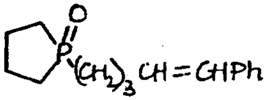

(11)

In the case of the monocyclic salt (3) the product appears to be, from its mass spectrum ($^m/_e$ 159 116, no appreciable peak due to $^m/_e$ 101) and n.m.r. (multiplet centred at 8.9τ is a superimposed quartet and two triplets) the acyclic methylated structure (8) rather than the alternative (10).

Ylids generated from salts (1; n=4), (3) and (4) will also undergo Wittig Reactions with aldehydes and ketones. Salt (1; n=4) refluxed for two days with benzaldehyde in $K^{\oplus}\overset{\ominus}{O}C(CH_3)_3$/ $(CH_3)_3COH$ gave an oil; i.r. 1,680 1,450 1,160 740 and 690 cm^{-1}; n.m.r.τ($CDCl_3$) 7.5-8.6 m (14H), 3.3-4.0 m (2H), 2.7 m (5H); m.s. $^m/_e$ 248 (M^+), 157, 118, 117, 104, 90; which appears to have structure (11).

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