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SYNTHESIS OF A PENTACOVALENT ARSENIC HETEROCYCLE

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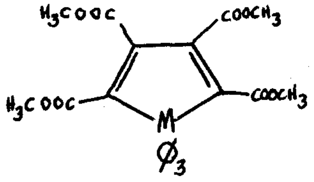
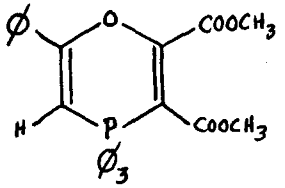
THE recent publication[1] of the preparation of a phosphole (Ia) containing pentacovalent phosphorus prompts us to report the results of similar research into heterocycles of pentacovalent fifth-row atoms containing five single bonds to carbon.[2] We have independently prepared the phosphole reported by Johnson and wish now to announce as well the arsenic analog (Ib). When triphenylarsine is mixed with a slight excess of pure dimethyl acetylenedicarboxylate in ether and allowed to stand several days, the mixture deposits in over 50% yield white crystals of tetramethyl 1,1,1-triphenylarsole-2,3,4,5-tetracarboxylate (Ib), m.p. 212° (Found: C, 61.9; H, 4.9. Calc. for $C_{30}H_{27}AsO_8$: C, 61.0; H, 4.6%).[3] The infrared spectrum shows two ester peaks



Ia, M = P
b, M = As



II

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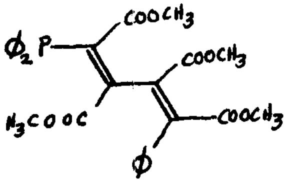
[1] Johnson and Tebby, J.Chem.Soc. 2126 (1961).

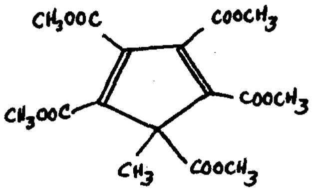
[2] J.B. Hendrickson, J.Amer.Chem.Soc. 83, 2018 (1961).

[3] The high carbon values in the analyses are apparently due to some arsenical trapped in the soda-lime trap, as shown by positive Gutzeit tests on the soda-lime.

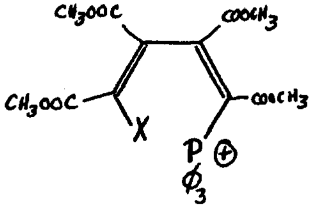
of about equal intensity at slightly different wavelengths (5.80 and 6.00), similar in this respect to the phosphole, Ia, and our recent oxaphosphorin, II[2], as well as to dimethyl 2,3-diphenylpyrrol-4,5-dicarboxylate.[4] The ultraviolet spectrum shows a large peak at 220 m (log $\varepsilon = 4.63$) and a family of three at 259 m (3.99), 264 m (3.99), and 270 m (3.88), very similar to the spectra of triphenylphosphine and arsine oxides[5] and tetraphenylphosphonium ion[6] but increased in intensity. The latter spectra are said to be little more than that expected from the multiple phenyl absorption and differ notably from the simple triphenyl compounds ($\emptyset_3P$, $\emptyset_3As$, etc.) which are trivalent and bear an unshared electron pair.[5] The spectrum of the phosphole, Ia, was not obtainable[1] owing to its ready reversion in solution to the stable rearrangement product, III.



III



IV



Va, X = -
b, X = H

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[4] J.B. Hendrickson and Rees, J.Amer.Chem.Soc. 83, 1250 (1961).

[5] Jaffe, J.Chem.Phys. 22, 1430 (1954).

[6] Unpublished observations.

These spectra are important for the light they throw on the bonding properties of the pentacovalent atoms, for the spectrum of the butadiene-tetra-ester portion of the molecule has been reported by Cookson[7] for his penta-ester, IV, which shows maxima at 223 mμ (log ε = 3.92) and 295 mμ (3.78). The shift from these values in the present compounds clearly requires some resonance participation by outer orbitals of the pentacovalent atom, despite the fact that the pentacovalency itself would be expected to afford complete saturation of the bonding capacity of these atoms.

Evidence for the attachment of the three phenyl groups to arsenic, apart from the mode of formation, is provided by the reaction of the heterocycle with ozone, followed by thiosulfate reduction and sublimation, which yielded authentic triphenylarsine, m.p. and mixed m.p. 59-61°. Similarly, warming with methanolic KOH saponified one ester group to a mono-acid, $C_{29}H_{25}AsO_8$ (Found: C, 61.08; H, 4.3. Calc.: C, 60.4; H, 4.34%),[3] which on pyrolysis yielded triphenylarsine oxide, m.p. 180-200° (subl.), identical in infrared spectrum to an authentic sample, as well as triphenylarsine, similarly identified. Diazomethane converted this acid back to the starting ester.

The nuclear magnetic resonance spectrum provides several features of interest for it consists of only three clean sharp peaks at τ = 2.78; 6.34; 6.87; with intensities of about 5:2:2. Thus the correspondence with expectation is striking. Triphenylarsine shows a clean peak at 2.92 whereas the peak of triphenylphosphine at the same place is split and complex owing to splitting of aromatic hydrogens (primarily ortho) by the phosphorus nucleus (nuclear spin 1/2),[2] a splitting not observed with the arsenic nucleus (nuclear spin 3/2). Accordingly, while the 2.78τ peak is clean in the arsole, Ib, it is split in the phosphole, Ia, centering at 2.70, as in the oxaphosphorin, II (2.65). The stable rearrangement product, III, shows the complex peak of

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[7] R.C. Cookson, J. Hudec and Whitear, Proc.Chem.Soc. 117 (1961).

$\text{Ø}_2\overset{\text{"}}{\text{P}}$-centering at 2.82 with the single phenyl bonded to the olefin absorbing at 2.44, reminiscent of the cinnamoyl absorption; all four ester methyls show up as separate peaks (6.08, 6.64, 6.67, and 6.98). The freshly-prepared unstable phosphole, Ia, always shows a complex absorption between $\tau = 6\text{-}7$ containing these four peaks (increasing with impurity of the sample or with time) and two others at 6.31 and 6.37, as well as the unified complex $\text{Ø}_3\text{P}$ peak.

The thermal stability of this heterocycle is in remarkable contrast to that of the phosphole, which readily decomposes at room temperature,[1] for vacuum pyrolysis up to 300° served only to cause clean sublimation of the arsole. This thermal instability in the phosphorane case was offered[1] as one reason for its formulation as the acyclic zwitterion, Va, but the similarity of the other physical properties between the two compounds seems to us to provide a more compelling rationale for the true phosphole formulation, Ia. Furthermore, if a solution of the freshly-prepared phosphole in methanol is treated with HCl in methanol, an immediate precipitation of the stable rearrangement product, III, occurs. Since there is no reason to expect that the protonated form of the zwitterion, Vb, should not be a stable salt as it stands nor that it should rearrange instantly to III, the zwitterionic formulation seems untenable to us and we prefer Ia, rearrangement of which to III by acid catalysis (cf. initial protonation of a β-ester carbonyl) is mechanistically sound. The differences in stability are nevertheless so striking as to require explanation, for which we tentatively proffer the larger size of arsenic and the greater availability of low-energy d-orbitals for its bonding as reasons for the greater stability of Ib.

Further studies of these interesting heterocycles are in hand.