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REARRANGEMENT REACTIONS IN FOUR-MEMBERED RING PHOSPHORUS HETEROCYCLES

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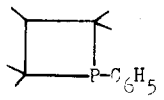
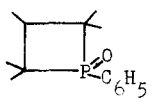
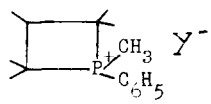
Very few examples of the preparation of phosphetanes (phosphacyclobutanes) or related derivatives have appeared in the literature (1), and relatively little is known about the chemical behavior of these systems. As recent investigations (2) have led to the synthesis of 2,2,3,4,4-pentamethyl-1-phenylphosphetane (I), the corresponding oxide II, and phosphonium salts, IIIa and IIIb, we now wish to describe the unusual behavior of II and III on treatment with phenyllithium and III with dilute sodium hydroxide.

I  II  III a)Y=Br b)Y=I 

When an ether suspension of the phosphine oxide II was treated with a slight excess of phenyllithium at 10° and then quenched with methyl iodide, an open-chain phosphine oxide IV, mp 108-120°, was formed in 81% yield.

$$C_6H_5\overset{\gamma}{C}(CH_3)_2\overset{\beta}{C}HCH_3\overset{\alpha}{C}(CH_3)_2\overset{O}{\overset{\|}{P}}(CH_3)C_6H_5 \cdot H_2O \qquad \text{IV}$$

In addition to a satisfactory elemental analysis (3), the structure was supported by its nmr spectrum and a P^{31}-H^1 decoupling experiment (4). The nmr ($CDCl_3$) showed absorption at: τ = 2.08-2.93 (10 H multiplet, aromatic); 6.69-7.33 (1 H sextet, $CH_3\underline{CH}$-); 8.32 (3 H doublet, $^2J_{PCH}$= 11.5 cps., PCH_3); 8.57 (3 H singlet, γ-CH_3); 8.83 (3 H singlet, γ-CH_3); 8.65 (3 H doublet, $^3J_{HCCH}$= 7.0 cps., β-CH_3); 8.89 (3 H doublet, $^3J_{PCCH}$= 17.0 cps., α-CH_3); and 9.50 (3 H doublet, $^3J_{PCCH}$= 19.5 cps., α-CH_3). On P^{31}-H^1 decoupling, each of the doublets collapsed to a singlet (except for the doublet at τ = 8.65), and the singlet absorption peaks (γ-CH_3 groups) remained unchanged. The unequivalence of each of the γ-methyls as well as each of the α-methyls may be due to their proximity to the asymmetric center(s) in the molecule (5). The formation of IV probably involves initial attack of phenyllithium at phosphorus to give a pentacovalent species (6) which subsequently undergoes phenyl migration

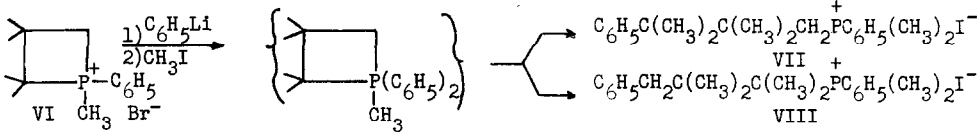
and ring opening. The timing of the latter part of the rearrangement is open to speculation.

In a similar manner, the phosphonium iodide IIIb was treated with phenyllithium in ether at 25° and then with methyl iodide to give a new phosphonium salt V (38% yield, mp 223-227°(dec)).

$$C_6H_5\overset{\gamma}{C}(CH_3)_2\overset{\beta}{C}HCH_3\overset{\alpha}{C}(CH_3)_2\overset{+}{P}(CH_3)_2C_6H_5I^- \qquad V$$

The nmr ($CDCl_3$ plus a few drops of CF_3CO_2H to increase solubility) showed absorption at: τ = 2.0-3.0 (10 H multiplet, aromatic); 6.82-7.50 (1 H multiplet, $CH_3\underline{CH}$-); 7.74 (6 H doublet, $^2J_{PCH}$= 12.2 cps., $PC\underline{H}_3$); 8.60 (3 H doublet, $^3J_{PCCH}$= 20.5 cps., α-CH_3); 8.57 (3 H singlet, γ-CH_3); 8.85 (3 H singlet, γ-CH_3); 8.99 (3 H doublet, $^3J_{HCCH}$= 7.0 cps., β-CH_3); and 9.28 (3 H doublet, $^3J_{PCCH}$= 20.5 cps., α-CH_3).

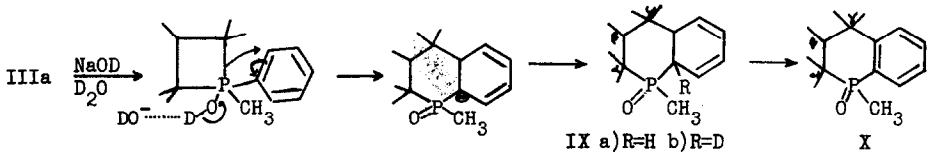
The mechanistic pathway for the phenyl migration in IIIb bears a similarity to that proposed by Zbiral (7) in which an alkylidenetriphenylphosphorane reacts with benzyne through a presumed phosphacyclobutane intermediate. Zbiral visualized the phenyl migration step (intramolecular nucleophilic substitution) as analogous to the Smiles rearrangement. As an interesting extension of this mechanism (with respect to our system), the phosphonium bromide VI was treated as below - in this unsymmetrical case two products are possible:



In actuality, the only product observed was VII (55% yield, mp 242-245°) which showed nmr (CF_3CO_2H) absorption at: τ = 2.7-3.2 (10 H multiplet, aromatic); 7.78 (2 H doublet, $^2J_{PCH}$= 15.0 cps., $PC\underline{H}_2$-); 8.35 (6 H doublet, $^2J_{PCH}$= 13.5 cps., P-$C\underline{H}_3$); 9.00 (6 H singlet) and 9.48 (6 H singlet). The clear selectivity of phenyl migration to the dimethylated position suggests that the rate controlling step is that of nucleophilic attack of the preformed carbanion upon the phenyl group (final step in Zbiral's mechanism); the more nucleophilic, tertiary carbanion would be expected to react faster than the primary carbanion. Alternatively, one can also formulate a pathway in which the polarity of the intermediate zwitterion is reversed (8).

In contrast to the stability of the oxide II to aqueous base, the salt IIIa underwent a remarkable rearrangement in the presence of 1N NaOH at 10° to give the diene (IXa), mp 133-143, in 70-80% yield. Absorption in the nmr ($CDCl_3$) was observed at: τ = 3.73-4.82 (4 H multiplet, vinyl protons); 7.02-7.49 (2 H broad doublet, allylic protons); 7.93-8.38

(1 H broad quartet, β-H); ≈ 8.62 (3 H doublet, $^{2}J_{PCH}$ ≈ 12 cps., P-CH_3); ≈ 8.81 (3 H doublet, $^{3}J_{PCCH}$ ≈ 15 cps., α-CH_3); ≈ 8.83 (3 H doublet, $^{3}J_{PCCH}$ ≈ 13 cps., α-CH_3); 9.07 (3 H doublet, $^{3}J_{HCCH}$ = 7.0 cps., β-CH_3); 8.89 (3 H singlet, γ-CH_3); and 9.20 (3 H singlet, γ-CH_3). P^{31}-H^{1} decoupling helped to confirm this assignment. In addition the relative area of the allylic region decreased by one half the original value when the reaction was run with sodium deuteroxide - a result consistent with the following pathway (to give IXb).



IX a)R=H b)R=D X

Structure proof for the diene (Calcd. mol wt, 252; Found, 258 (osmometry in benzene)) comes from its aromatization (by 30% Pd/C in refluxing decalin) to yield the tetrahydrophosphinoline (X), which showed nmr ($CDCl_3$) absorption at: τ = 1.83-2.90 (4 H multiplet, aromatic); 7.70-8.30 (1 H multiplet, β-H); 8.44 (3 H doublet, $^{2}J_{PCH}$ = 12.1 cps., PCH_3); ≈ 8.72 (3 H doublet, $^{3}J_{PCCH}$ ≈ 14.5 cps., α-CH_3); 8.86 (3 H doublet, $^{3}J_{PCCH}$ = 14.5 cps., α-CH_3); ≈ 8.88 (3 H doublet, $^{3}J_{HCCH}$ ≈ 6.5 cps., β-CH_3); and 8.68 (6 H singlet, γ-CH_3). Moreover, IXa was successively treated with trichlorosilane and methyl iodide to give a salt which underwent a Hofmann-type elimination (2N NaOH) followed by air oxidation to yield XIII. The nmr of XIII and IV were similar.

$$C_6H_5C(CH_3)_2CHCH_3C(CH_3)_2\overset{\overset{O}{\|}}{P}(CH_3)_2 \qquad \text{XIII}$$

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2. J. Org. Chem., in press.

3. The hydrate as well as the dehydrated material gave satisfactory analyses as did all of the compounds discussed in this report.

4. Nmr spectra were recorded on a Varian Associates Model A-60 spectrometer with TMSi as an internal standard. In cases where overlapping peaks occurred the values of τ and J are designated with an approximation symbol. The P^{31}-H^{1} decoupling experiments were performed using an NMR Specialties Model HD-60A heteronuclear spin decoupler in conjunction with an HR-60 spectrometer.

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8. In Zbiral's system the zwitterion is also a vinylogous ylid and the placement of the charges is logical. However, the counterparts derived from IIIb and VI are not vinylogous ylids, and phosphacyclobutane opening to give $\geq P^{\ominus}-\overset{|}{C}-\overset{|}{C}-\overset{|}{C}^{\oplus}$ must be considered. The resultant possibility of phenanion versus phenonium ion migration is suggested in: R. F. Hudson, Structure and Mechanism in Organo-Phosphorus Chemistry, Academic Press, London and New York, 1965, p. 244.

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