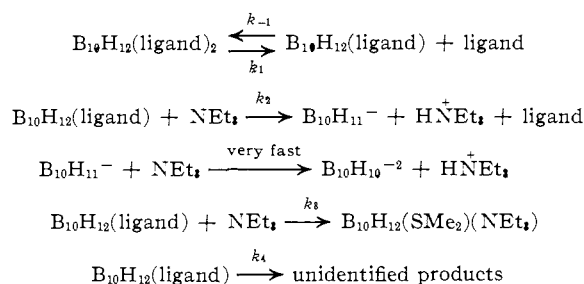


initial [II], yields decreased with decreasing initial [II] to a value of 50% at 0.01 M II.

The initial-rate method was employed and reactions were followed to approximately 5% completion. A series of rate determinations carried out at constant II concentration and varying III concentrations proved this reaction to be first order in III. A plot of pseudo-first-order rate constant *vs.* initial II concentration indicated that the reaction became essentially zero order in II at high II concentrations. The addition of dimethyl sulfide (IV) depressed the reaction rate at all concentrations of II and III. Three series of kinetic runs were carried out at different [IV], in which [II] was varied within each series and [III] was held constant. Plots of $[III]/(d[B_{10}H_{10}^{-2}]/dt)$ *vs.* $[II]^{-1}$ for each [IV] were linear and gave a common intercept of 2.1×10^{-4} sec. at $[II]^{-1} = 0$. The slopes (*z*) of each of these plots were plotted *vs.* [IV] present in each series of rate runs and a straight line described by the equation, $z = 3.45 \times 10^4 [Me_2S] + 140$ sec. mole l.⁻¹ was obtained. The intercept of the latter line was identical with the slope obtained in the first series of plots with no added IV. This intercept requires the operation of a process (*k*₄) which removes the B₁₀H₁₂(ligand) intermediate from the system without producing B₁₀H₁₀⁻² or regenerating III. The results obtained with I and III are consistent with the following rationale⁶ in which the *k*₁ process



may become rate determining at high II concentrations.

It seems probable that the *k*₂ process involves proton abstraction by II with or without the concerted ejection of the second ligand molecule.

The proposed B₁₀H₁₂(ligand) intermediate formally resembles B₁₀H₁₃⁻. That the B₁₀H₁₂(SM_e)₂ (V) reported by Knoth and Muettterties⁷ is not the intermediate involved in B₁₀H₁₀⁻² formation was shown by the fact that authentic V formed B₁₀H₁₀⁻² more than 10³ times slower than III under the same conditions. As suggested by Lipscomb,⁸ two reasonable structures exist for B₁₀H₁₃⁻ and two tautomeric B₁₀H₁₂(ligand) structures may well exist. The formation of B₁₀H₁₀⁻² from V may involve the slow conversion of V to the reactive isomer. Conversely, the *k*₄ process may involve the moderately rapid conversion of the reactive intermediate to V.

Further work is in progress and will be reported at a later date.

(6) Where L = ligand and $d[B_{10}H_{11}L]/dt = 0$, $d[B_{10}H_{10}^{-2}]/dt = k_1 [B_{10}H_{12}L_2] / \{k_2 [Et_3N] / ((k_2 + k_3) [Et_3N] + k_{-1} [L] + k_4)\}$ or $[B_{10}H_{11}L] / (d[B_{10}H_{10}^{-2}]/dt) = (1/[Et_3N]) \{ (k_{-1} [L] + k_4) / k_1 k_2 + (k_2 + k_3) / k_1 k_2 \}$. In the first series of plots, the slopes = $(k_{-1} [L] + k_4) / k_1 k_2$ sec. mole l.⁻¹, and the intercepts = $(k_2 + k_3) / k_1 k_2$ sec. In the second plot, the slope = $k_{-1} / k_1 k_2$ sec., and the intercept = $k_4 / k_1 k_2$ sec. mole l.⁻¹. Elimination of the *k*₁*k*₂ term gives $(k_2 + k_3) / k_{-1} = 0.44 \pm 0.02$ and (rate of *k*₃ process) / (rate of *k*₋₁ process) = $k_4 / (k_{-1} [L]) = 2.5 \pm 0.5 \times 10^{-4} / [L]$.

(7) W. H. Knoth and E. L. Muettterties, *J. Inorg. Nucl. Chem.*, **20**, 66 (1961).

(8) W. N. Lipscomb, *Advanc. Inorg. Chem. Radiochem.*, **1**, 117 (1959).

(9) Alfred P. Sloan Research Fellow.

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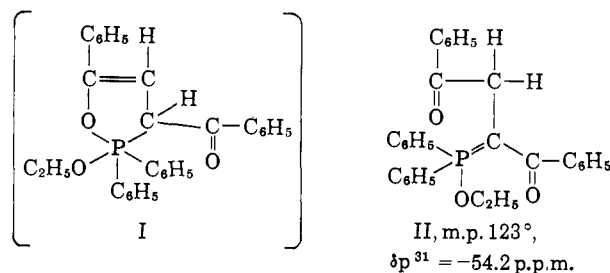
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RECEIVED SEPTEMBER 30, 1964

A Crystalline Alkoxydiarylalkylidenephosphorane from the Reaction of Ethyl Diphenylphosphinite with an α - β -Unsaturated Ketone¹

Sir:

Harvey and Jensen² ascribed the *cyclic dialkoxydiarylalkylphosphorane* structure³ I to the adduct, "m.p. 116–118°," which is formed from ethyl diphenylphosphinite and *trans*-dibenzoyl ethylene in an ether solution.⁴ We should like to report that this substance is actually the *alkoxydiarylalkylidenephosphorane*⁵ II, a moderately stable phosphinitemethylene.



Equimolar amounts of ethyl diphenylphosphinite⁵ and *trans*-dibenzoyl ethylene were allowed to react at 20° in anhydrous 1,2-dimethoxyethane (*ca.* 1.6 M). The infrared spectrum of the resulting clear, red solution after 3 hr. showed that the reaction was nearly complete. The 1:1 adduct crystallized and was filtered after 2 days; yield, 42%; m.p. 118–120° (crude). Recrystallization from benzene–hexane gave II, m.p. 122–123°. Spectral characteristics are: infrared bands, (CH₂Cl₂, μ): 5.97 (strong C=O) and 6.65 (broad and strong "enolate" C=O⁶); $\delta_{P_{31}}$ = -54.2 p.p.m.⁷ (CH₂Cl₂); H¹ n.m.r. (CDCl₃; p.p.m. in the τ -scale): multiplet at 2.65 (aromatic), 2H¹

(1) This investigation was supported by the National Science Foundation (G 19509) and by Public Health Service Research Grant No. CA-04769-05 from the National Cancer Institute.

(2) R. G. Harvey and E. V. Jensen, *Tetrahedron Letters*, **No. 26**, 1801 (1963).

(3) Structure I: 2-ethoxy-2,2-diphenyl-3-benzoyl-5-phenyl- Δ^4 -oxaphospholene; structure II: ethoxydiphenyl-(benzoyl-, phenacyl-) methylenephosphorane.

(4) For other reactions of α - β -unsaturated carbonyl compounds with trivalent phosphorus compounds: (a) V. A. Kukhtin and K. M. Orekhova, *J. Gen. Chem. U.S.S.R.*, **30**, 1539 (1960); (b) G. Kamai and A. V. Kukhtin, *ibid.*, **31**, 1621 (1961), and earlier papers; (c) V. A. Ginsburg and A. Ya. Yakubovich, *J. Gen. Chem. U.S.S.R.*, **30**, 3944 (1960); (d) E. R. DeSombre, R. G. Harvey, and E. V. Jensen, Abstracts, Division of Organic Chemistry, 146th National Meeting of the American Chemical Society, Denver, Colo., Jan., 1964, p. 21C.

(5) R. Rabinowitz and J. Pellon, *J. Org. Chem.*, **26**, 4624 (1961).

(6) Triphenylbenzoylmethylenephosphorane [F. Ramirez and S. Der-showitz, *J. Org. Chem.*, **22**, 41 (1957)] has an "enolate" carbonyl at 6.63 μ . The P³¹ n.m.r. shift (*vs.* 85% H₃PO₄) is -16.7 p.p.m. (CHCl₃). Its hydrochloride has -20.7 p.p.m. (CHCl₃). A. J. Speziale and K. W. Ratts [*J. Am. Chem. Soc.*, **85**, 2790 (1963)], however, reported -21.6 p.p.m. for the former *ylid*, and -18.9 p.p.m. for the latter *hydrochloride* (both in CHCl₃).

(7) All P³¹ n.m.r. spectra were determined at 40.5 Mc./sec. and are expressed in p.p.m. *vs.* 85% H₃PO₄.

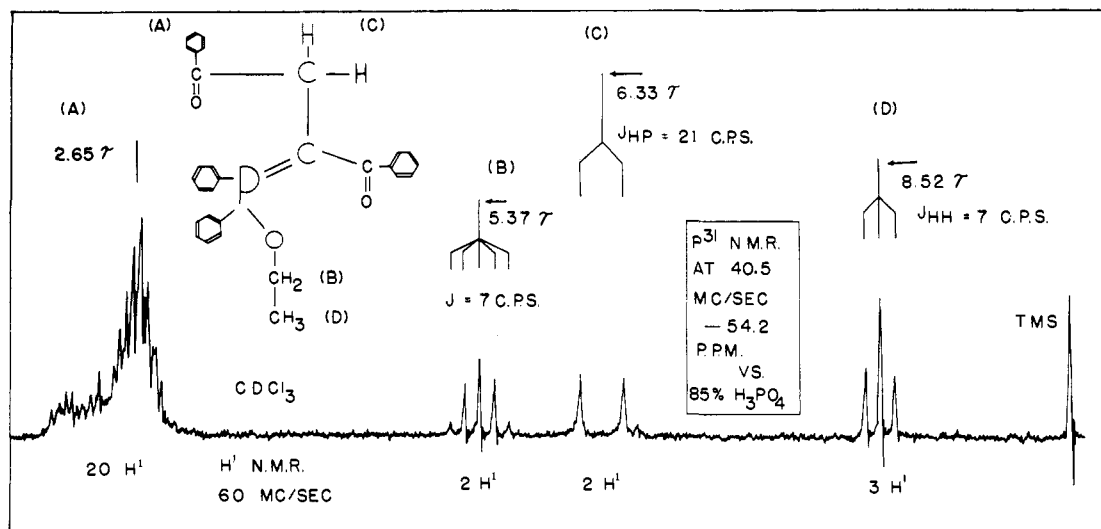
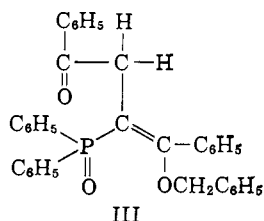


Figure 1.

quintet at 5.37, $J = 7$ c.p.s. (POCH_2CH_3); 2H^1 doublet at 6.33, $J_{\text{HP}} = 21$ c.p.s. (equivalent phenacyl protons); 3H^1 triplet at 8.52, $J = 7$ c.p.s. (CH_3CH_2-) (Fig. 1). The reaction was nearly complete in 10 min. in methylene chloride solution (ca. 1.7 M). II was isolated in 32% yield when this solution was evaporated after 5 days. II is very susceptible to moisture.

Structure I should give a positive P^{31} shift,^{8,9} while structure II would be expected to give a negative P^{31} shift.^{6,9}

The phosphinimethylenic II reacted with benzyl bromide at 20° and gave the phosphine oxide enol ether III in quantitative yield. III had m.p. $179-180^\circ$ (benzene). *Anal.* Calcd. for $\text{C}_{28}\text{H}_{29}\text{O}_3\text{P}$: C, 79.5; H, 5.5; P, 5.9. Found: C, 79.8; H, 5.6; P, 5.9. Spectral properties are infrared bands (CH_2Cl_2 , μ): 5.95 ($\text{C}=\text{O}$), 6.15 ($\text{C}=\text{C}$), and 8.48 (PO); $\delta_{\text{P}^{31}} = -28.6$ p.p.m. (CDCl_3); ^1H n.m.r. (CDCl_3 , τ): 25H^1 multiplet at 2.70 (aromatics); 2H^1 singlet at 6.00 ($\text{C}_6\text{H}_5\text{CH}_2\text{O}$); 2H^1 doublet at 6.10, $J_{\text{HP}} = 16$ c.p.s. (two equivalent phenacyl protons).



To our knowledge, II is the first isolated, crystalline member of this family. Some phosphinimethylenes have been reported.¹⁰⁻¹²

(8) The crystalline 2,2,2-trimethoxy-3-phenyl-4-acetyl-5-methyl- Δ^4 -oxaphospholene, made from trimethyl phosphite and 3-benzylidene-2,4-pentanedione, has $\delta_{\text{P}^{31}} = +27.9$ p.p.m.; cf. F. Ramirez, A. V. Patwardhan, and S. R. Heller, *J. Am. Chem. Soc.*, **86**, 514 (1964), compound VI, Table I.

(9) $\delta_{\text{P}^{31}}$ in p.p.m.: $(\text{CH}_3\text{O})_3\text{P}$, -140.0 ; $\text{C}_2\text{H}_5\text{OP}(\text{C}_6\text{H}_5)_2$, -109.8 ; $\text{P}(\text{C}_6\text{H}_5)_3$, $+6$.

(10) W. J. Middleton, U. S. Patent 3,067,233 (Dec. 4, 1962).

(11) F. Ramirez and O. P. Madan, Abstracts, Division of Organic Chemistry, 148th National Meeting of the American Chemical Society, Chicago, Ill., Aug., 1964, p. 13S.

(12) G. H. Birum, U. S. Patent 3,058,876 (Oct. 16, 1962).

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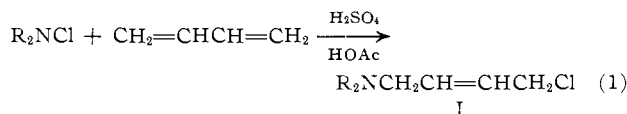
O. P. MADAN
C. P. SMITH

RECEIVED AUGUST 18, 1964

The Chemistry of Ion Radicals. The Free-Radical Addition of N-Chloramines to Olefinic and Acetylenic Hydrocarbons

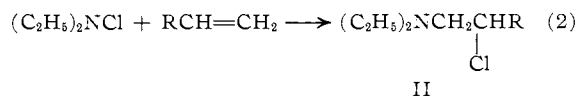
Sir:

We recently reported¹ the free-radical addition in acidic media of N-chloramines to butadiene, which afforded 1-chloro-4-dialkylamino-2-butenes (I) (eq. 1). Minisci and Galli² have subsequently suggested that

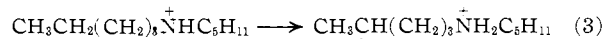


the addition of an aminium radical $\text{R}_2\text{N}^+\text{H}$ to an unsaturated hydrocarbon is limited to conjugated dienes. We therefore wish to report that chloramines undergo free-radical addition to terminal olefins and allenes and to terminal and internal acetylenes in sulfuric acid-acetic acid in yields of 30-60%, thereby demonstrating the applicability of the chloramine addition reaction to these classes of unsaturated hydrocarbons.

We reported previously^{1,3} that 1,1-diphenylethylene and norbornadiene reacted with chloramines *via* ionic rather than radical pathways; our further results now demonstrate that aliphatic terminal monoolefins undergo the desired radical addition (eq. 2) to afford β -chloramines (II) (Table I, entries 1, 2), although internal



olefins apparently undergo only ionic reactions (entry 4). However, intramolecular hydrogen abstraction by an aminium radical (eq. 3), which leads ultimately to a pyrrolidine (the Hofmann-Loeffler reaction⁴), precludes addition of the aminium radical to terminal olefinic bonds when the chloramine contains an appropriately placed methylene group (entry 3).



(1) R. S. Neale and R. L. Hinman, *J. Am. Chem. Soc.*, **85**, 2666 (1963).

(2) F. Minisci and R. Galli, *Tetrahedron Letters*, 167 (1964).

(3) R. S. Neale and E. B. Whipple, *J. Am. Chem. Soc.*, **86**, 3130 (1964).

(4) M. E. Wolff, *Chem. Rev.*, **63**, 55 (1963).