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Photochemical Type II Elimination of Diisobutyl Trichloromethylphosphonate*

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The type II photo-elimination of carbonyl compounds containing γ-hydrogen to form olefins and degradated carbonyl compounds *via* a cyclic transition state is well known.[1] However, little information is available on the analogous photochemistry of phosphoryl group. In view of the strongly polar character of $P^{+}–O^{-}$ bond in ordinary phosphorus compounds, no absorption of the P=O group appears in the near UV region.[2]

We reported previously that no reduction of the phosphoryl portion occurred in photoreduction of carbonyl group of dialkyl β-ketophosphonates (I) to β-hydroxyphosphonates (II) (Eq. (1)). The quantum yield for disappearance of ketones were 0.6—0.7.[3]

$$\underset{\text{I}}{RCOCH_2P(O)(OR')_2} \rightarrow \underset{\text{II}}{RCH(OH)CH_2P(O)(OR')_2} \qquad (1)$$

a, $R=CH_3$, $R'=C_2H_5$
b, $R=C_2H_5$, $R'=C_2H_5$
c, $R=C_2H_5$, $R'=(CH_3)_2CH$

The extent of $p\pi—d\pi$ character of the P=O bond may be determined by the overlap integral and the electron affinity of the bonded atoms at phosphorus. Thus, the electronegativity of substituent on the phosphorus atom may exert a considerable effect on the $p\pi—d\pi$ overlap integral and hence on its bond energy.[4] Electron-withdrawing groups on phosphorus compete with a double-bonded oxygen atom to attract electron, resulting in a stiffer P=O bond and a higher frequency.[5]

The values of bond orders of some phosphoryl compounds have been reported, *e. g.*, $P(O)Br_3$: 1.92, $P(O)Cl_2$: 1.95, $P(O)(CF_3)_3$: 2.00, $P(O)FCl_2$: 2.05, $P(O)F_2Cl$: 2.11, and $P(O)F_3$: 2.22.[4]

Consequently, the absorption spectrum of the phosphoryl group is expected to appear in a near UV region, if a strongly electron-withdrawing group is present on phosphorus. In fact, diisobutyl trichloromethylphosphonate (III)[6] shows a new absorption (shoulder) at $\lambda_{\max}^{n\text{-hexane}}$ 253.7 nm ($\varepsilon\sim2$). The present paper reports on photochemical type II decomposition of III to give the corresponding half ester and isobutylene.

A solution of III (1.5 g, 0.25 M) in *n*-hexane was irradiated with a low-pressure Hg lamp in a quartz tube for 60 hr and the photoproducts were separated by column chromatography, giving colorless crystals (IV), mp 104—105°C, in an 11% yield and viscous liquid (V)[7] (0.18 g). The IR spectrum of IV showed strong bands of P–OH at 1640 and 1110 cm^{-1}. The mass spectrum showed the fragment ions *m/e* 83 [34%, $HP^{+}(OH)_3$], 137 (22%), 199 (12%), and 56 (100%, $C_4H_8^{+}$), although the expected parent peaks did not appear. Accurate mass numbers of

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[1] For comprehensive reviews see (a) N. J. Turro, "Molecular Photochemistry," Benjamine, New York, N. Y. (1965), p. 154; b) J. G. Calvert and J. N. Pitts, Jr., "Photochemistry," John Wiley & Sons, New York, N. Y. (1966) p. 377; c) N. C. Yang in "Reactivity of the Photoexcited Organic Molecule," John Wiley & Sons, New York, N. Y. (1967) p. 145.

[2] R. P. Buck, S. Singhadaja, and L. B. Rogers, *Anal. Chem.*, **26**, 1240 (1954).

[3] H. Tomioka, Y. Izawa, and Y. Ogata, *Tetrahedron*, **24**, 1501 (1969).

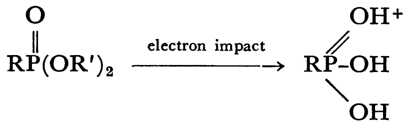
[4] O. P. Craig, A. Maccoll, R. S. Nyholm, L. E. Orgel, and L. E. Sutton, *J. Chem. Soc.*, **1954**, 332.

[5] N. B. Colthup, L. H. Daly, and S. E. Wiberley, "Introduction to Infrared and Raman Spectroscopy," Academic Press, New York, N. Y. (1964) p. 298.

[6] III: bp 109—110°C (1 mm); IR (film) 1280 (P=O), 1020 (P–O–C), 765 (P–C), 545 (C–Cl), 1370, and 1395 cm^{-1} ($CH(CH_3)_2$); NMR ($CDCl_3$) isobutyl methyl H (δ 1.10, d, J=7.5 Hz), isobutyl methine H (δ 2.11, m), and isobutyl methylene H (δ 4.20, t, J=6.6 Hz); mass *m/e*, P: 31.0 (20%), fragment ions: 199 [55%, $Cl_3CP^{+}(OH)_3$], 137 (60%, $P^{+}(OH)(O)(OC_4H_9)$], 117 (15%, CCl_3^{+}), 83 [10%, $HP^{+}(OH)_3$], and 56 (100%, $C_4H_8^{+}$).

[7] Although V showed similar IR and NMR spectra to that of III, its structure is not clear. V is not identical with III because of its mass spectrum, M+ 500.

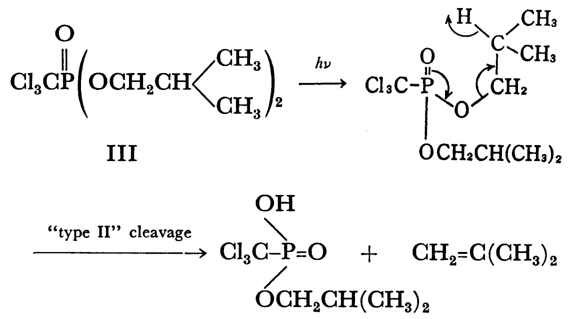
ions at *m/e* 137 and 199 were 137.037 and 198.889, respectively. Hence, the former is due to $P^{+}(O)(OH)(OC_4H_9)$ (calcd 137.036), the latter to $C^{35}Cl_3P^{+}(OH)_3$ (calcd 198.899). In the mass spectrum of III, no peak corresponding to $Cl_3CP^{+}(OH_2)(OC_4H_9)$ion was observed. In support of this, a β-scission to P=O group under electron impact is knwon.[8]



$$\mathrm{R\overset{O}{\overset{\|}{P}}(OR')_2 \xrightarrow{\text{electron impact}} R\underset{\diagdown OH}{\overset{OH^{+}}{\overset{/\!/}{P}}}\text{-}OH} \qquad (2)$$

Thus it is certain that $Cl_3CP^{+}(OH)_3$ ion for IV is produced *via* electron impact fragmentation of $Cl_3CP(O)(OH)(OC_4H_9)$. On the basis of this fact as well as in spectroscopic property, the photoproduct (IV) was identified to be $Cl_3CP(O)(OH)(OC_4H_9)$. If IV is produced *via* a type II cleavage of III, isobutylene should be simultaneously formed as a photoproduct. In fact, it was isolated by means of glpc using di-*n*-butyl maleate-β,β′-oxydipropionitrile on C-22.

Thus, it is probably valid to write the process for the photochemical cleavage of III in analogy with the type II cleavage for ketones.



III

IV

(3)

Indeed, no decomposition was observed in 54 hr irradiation of dimethyl ester, $Cl_3CP(O)(OCH_3)_2$,[9] in which a six-membered transition state for hydrogen abstraction is impossible. No isobutane was detected in the photodecomposition of III.

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[8] a) J. L. Occolowitz and G. L. White, *Anal. Chem.*, **35**, 1971 (1963); b) T. Nishikawa, *Tetrahedron*, **22**, 1383 (1966).

[9] Bp 120—126°C (12 mm); IR (film) 1280 (P=O), 1185 (P-O-CH_3), 760 (P-C), and 555 cm^{-1} (C-Cl); NMR ($CDCl_3$) methyl H (δ 4.07, d, J=10.8 Hz).