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TRIPHENYLPHOSPHORANYLIDENEKETENE

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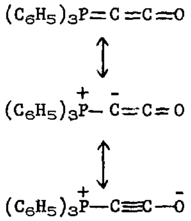
We wish to report the synthesis of triphenylphosphoranylideneketene, I, the prototype of a class of organophosphorus compounds formally related to ketenes, ylids and inner salt alkynes (1).

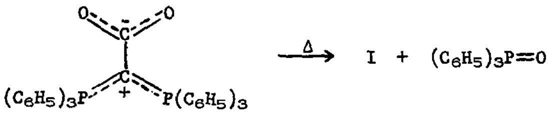


$$(C_6H_5)_3P{=}C{=}C{=}O \;\longleftrightarrow\; (C_6H_5)_3\overset{+}{P}{-}\overset{-}{C}{=}C{=}O \;\longleftrightarrow\; (C_6H_5)_3\overset{+}{P}{-}C{\equiv}C{-}\overset{-}{O}$$

I

When [(carboxy)(triphenylphosphoranylidene)methyl]triphenylphosphonium inner salt (2), II, was stirred in dry diglyme under nitrogen and warmed at 140-145° for 0.25 hour, a clear yellow solution resulted having two P^{31} n.m.r. signals of about equal intensity at -3.6 p.p.m. and -23.4 p.p.m., the latter being characteristic of triphenylphosphine oxide in diglyme. A white powder, m.p. 130-160°, that precipitated on cooling showed strong infrared absorption at 4.74μ (cumulated double bond region) and at 8.38μ

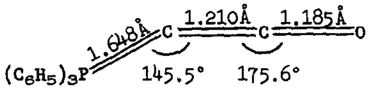
(P=O) (3). Repeated recrystallization from diglyme yielded white needles, I, m.p. 172-173.5°; triphenylphosphine oxide, m.p. 156-157°, was isolated from the filtrates. Structure I was assigned to this stable, new compound



II

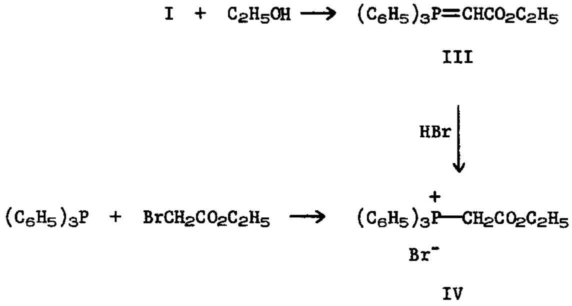
on the basis of its method of formation, infrared spectrum [4.74μ(s)], P^{31} n.m.r. spectrum (single peak at -2.6 p.p.m. in benzene at 40.5 Mc) and elemental analysis. Anal. Calcd. for $C_{20}H_{15}OP$: C, 79.44; H, 5.00; P, 10.24; M.W., 302.3. Found: C, 79.51; H, 4.93; P, 10.20; M.W., 298 (in $CHCl_3$).

Crystal structure studies (4) show that I is monomeric. The bond lengths in the cumulated chain are remarkably short and, instead of being linear as expected, the chain is bent to an angle of 145.5° at the carbon atom nearest the phosphorus. To account for this unusual molecular geometry,



a d_π-π_π type of interaction between the d orbitals of the phosphorus atom and the π orbitals of the cumulated chain is postulated (4).

When I was stirred in ethanol at room temperature, the resulting solution showed a P^{31} n.m.r. peak at -16.8 p.p.m. which is characteristic of carbethoxymethylenetriphenylphosphorane, III. Addition of aqueous HBr to the solution, followed by evaporation and purification, yielded a white solid, m.p. 155-156°, which was shown to be identical with the phosphonium salt IV obtained both by addition of HBr to an authentic sample (5) of III and by reaction of ethyl bromoacetate with triphenylphosphine (6).



$$\mathrm{I} + C_2H_5OH \longrightarrow \underset{\mathrm{III}}{(C_6H_5)_3P{=}CHCO_2C_2H_5}$$

$$\Big\downarrow \mathrm{HBr}$$

$$(C_6H_5)_3P + BrCH_2CO_2C_2H_5 \longrightarrow \underset{\mathrm{IV}}{(C_6H_5)_3\overset{+}{P}{-}CH_2CO_2C_2H_5\ \ Br^-}$$

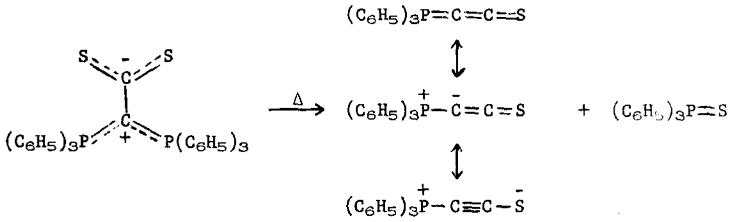
The addition of methanol-d to I at room temperature yielded the deuterated ylid V, isolated as white crystals, m.p. 166-169°, having a P^{31} n.m.r.

$$\mathrm{I} + CH_3OD \longrightarrow (C_6H_5)_3P{=}CDCO_2CH_3$$

V

chemical shift at -17.6 p.p.m. (in $CDCl_3$) and a H^1 n.m.r. spectrum with peaks only at -3.52 p.p.m. (methyl protons) and -7.58 p.p.m. (center of aryl proton multiplet) in the expected 1:5 area ratio. These facile additions of active hydrogen (or deuterium) compounds provide further evidence for the proposed skeletal structure of I and illustrate a general method for forming a variety of β-ketoalkylidenetriphenylphosphoranes, ylids that have been shown to be versatile synthetic intermediates (7). Imidazole, methyl mercaptan and malononitrile, for example, add readily to I to yield ylids that are not readily obtainable by other methods.

Triphenylphosphoranylidenethioketene, VI, together with triphenylphosphine sulfide, was obtained by the analogous thermal cleavage of [(dithiocarboxy)(triphenylphosphoranylidene)methyl]triphenylphosphonium inner salt, VII, in dry diglyme under nitrogen at 120-130°. Recrystallization of the mixture from benzene yielded light tan needles, VI, m.p. 224-226°, having infrared absorption bands at 4.73μ(m) and 5.10μ(s), and a



VII

VI

single P^{31} n.m.r. peak at +7.7 p.p.m. (in CH_2Cl_2 at 24.3 Mc). *Anal.* Calcd. for $C_{20}H_{15}PS$: C, 75.43; H, 4.75; P, 9.73; S, 10.07; M.W., 318.3. Found: C, 75.49; H, 4.68; P, 9.69; S, 10.06; M.W., 315 (in $CHCl_3$).

Other interesting addition reactions of these cumulated organophosphorus compounds have been observed and are being further investigated.

REFERENCES

1. For convenience we are using the name triphenylphosphoranylideneketene for I rather than a name based on possible ionic contributing structures such as those shown.
2. C. N. Matthews, J. S. Driscoll, and G. H. Birum, to be published. The mesomeric inner salt was obtained by treating a diglyme solution of hexaphenylcarbodiphosphorane with carbon dioxide.
3. Diphenylketene absorbs at 4.74μ, phenylacetylene at 4.70μ, and triphenylphosphine oxide at 8.38μ.
4. J. J. Daly and P. J. Wheatley, Monsanto Research SA, Zurich, Switzerland, in press. We thank these authors for communicating the results of a three-dimensional X-ray diffraction study of I.
5. Purchased from Aldrich Chemical Company, Inc., Milwaukee, Wis.
6. G. Wittig and W. Haag, *Chem. Ber.*, **88**, 1654 (1955).
7. (a) H. J. Bestmann, *Angew. Chem. Intl. Ed.*, **4**, 583, 645, 830 (1965).
   (b) A. Maercker, *Organic Reactions*, **14**, 270 (1965).
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