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TRIALKYL- AND TRIARYL-ALKYLIDENEPHOSPHORANES FROM THE REACTION OF TERTIARY PHOSPHINES WITH TRANS-DIBENZOYLETHYLENE

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Kuwajima and Mukaiyama[2] assigned O-phosphonium betain structures, Ia and Ib (Table I), to the adducts formed in the reaction of <u>trans</u>-dibenzoylethylene (DBE) with tri-<u>n</u>-butylphosphine and triphenylphosphine, respectively. This type of structure, Ic, had been previously suggested by Horner and Klupfel[3]. Kukhtin and Orekhova[4] proposed a cyclic oxyalkylphosphorane structure, IId, for the DBE-triethyl phosphite adduct, which they did not characterize.

Harvey and Jensen[5] postulated the existence of an equilibrium between the cyclic and the open structures, IId and Id, but since they carried out their reactions in alcohol, could not shed further light on the matter. They, however, claimed[5] the isolation of a cyclic adduct, IIe, from the reaction of DBE with ethyl diphenylphosphinite in dimethoxyethane as solvent. Structures like I and II have found their way into recent reviews[6] without any experimental justification. Therefore, it seems desirable to summarize at this time the results of our investigations in this field. These results are at variance with previous proposals[2,3,4,5,6].

TABLE I

a, R = R' = n-C_4H_9; b, R = R' = C_6H_5; c, R = R' = C_2H_5;
d, R = R' = OR''; e, R = C_6H_5, R' = OC_2H_5

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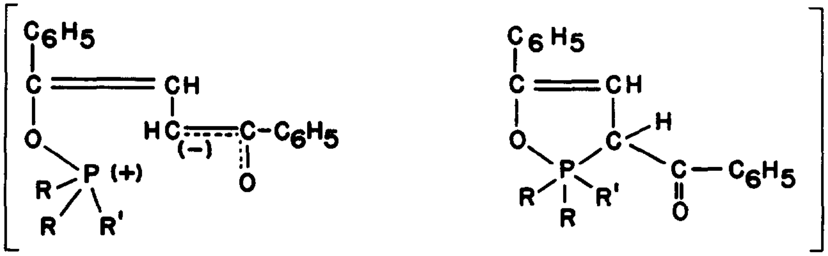

I a,b,c,d,e II a,b,c,d,e

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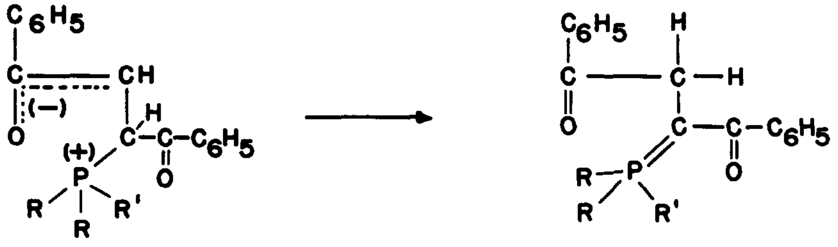


III a,b,c,d,e IV a,b,c,d,e

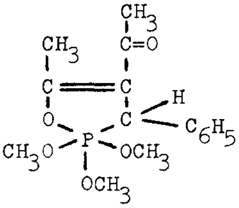
COMPD.	δ P^{31}	COMPD.	δ P^{31}
IV a	− 21.3	$(n\text{-}C_4H_9)_3P$	+ 32
IV b	− 16.9	$(C_6H_5)_3P$	+ 5.7
IV d R'' = CH_3	− 56.2	$(CH_3O)_3P$	− 140.0
IV e	− 54.2	$(C_6H_5)_2POC_2H_5$	− 109.8

(1) Tri-n-butylphosphine reacted rapidly with DBE in methylene chloride at 0°. The reaction was complete within 30 minutes when equimolar amounts of the reagents were mixed in 2M concentration. The adduct was a rather stable alkylidenephosphorane or ylid, IVa, which was isolated in over 80% of the theory. Presumably, the phosphorus of the phosphine attacked the β-carbon of DBE to form the C-phosphonium betain, IIIa, which then underwent a rapid proton transfer to the more stable ylid, IVa. This is entirely analogous to the behavior of p-benzoquinone with triphenylphosphine elucidated in 1956 by Ramirez and Dershowitz[7,8].

(2) The reaction of triphenylphosphine with DBE was quite slow at 20°. Furthermore, the reaction is complicated by subsequent transformations of the initial adduct. These will be described in the forthcoming paper, but is clear that the initial 1:1 adduct has the ylid structure, IVb (*cf.* the P^{31} n.m.r. shift in Table I).

(3) The reaction of trimethyl phosphite[9] with DBE and the reaction of ethyl diphenylphosphinite[10] with DBE produce the corresponding ylids, IVd and IVe, respectively, and not the cyclic oxyphosphoranes, IId and IIe[4,5,6].

(4) The reaction of trimethyl phosphite with 3-benzylidene-2,4-pentanedione[9,11] yielded the first authentic example of a cyclic oxyalkylphosphorane, V, derived from the reaction of a trivalent phosphorus compound with an α,β-unsaturated carbonyl compound. Now, the initial C-phosphonium betain, similar to IIId, does not undergo a proton shift, since the anion that would result from this shift is less stable than the original anion; the latter, therefore, cyclizes to a compound having pentacovalent phosphorus, V.



V, M.P. 49-51°

$\delta P^{31} = +27.9$ P.P.M.

The ylids, IVa, b, d, e, are characterized by: (a) strong infrared bands at 6.6μ ("enolate" C=O) and 5.9μ (benzoyl C=O); (b) at $2H^1$ doublet in the n.m.r. spectrum at $\tau = 6.2$ to 6.3 p.p.m., with J_{HP}=17 to 21 c.p.s. (equivalent phenacyl protons); (c) negative P^{31} n.m.r. shifts[12] (Table I). The ylid $(C_6H_5)_3P{=}CH.CO.C_6H_5$ had an infrared band at 6.63μ and a P^{31} shift at -16.7 p.p.m. $(CHCl_3)$[13]. The magnitude of the shifts in the ylids are related to the shifts in the trivalent phosphorus compounds, $R_2R'P$ (Table I).

The DBE-tributylphosphine adduct IVa, had m.p. 96-97° (from benzene-hexane). Found: C, 76.4; H, 8.8; P, 6.2. $C_{28}H_{39}O_2P$ requires: C, 76.7; H, 8.9; P, 7.0. The ylids, IVa,b,d,e reacted with water in methylene chloride solution and gave mostly 1,2-dibenzoylethane and the corresponding oxides, phosphate ester or phosphinate, $R_2R'PO$.

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6. R. G. Harvey and E. R. DeSombre in "Topics in Phosphorus Chemistry", Vol. 1, M. Grayson and E. J. Griffin, Ed., Interscience Publishers, New York, N. Y., 1964. None of the formulas given after line 19 of p. 59 of this review represent the correct structure of the DBE-ethyl diphenylphosphinite adduct. The claim in footnote (*) of p. 95 is erroneous. There is no experimental justification for formulas (35) in p. 92, (37) in p. 95, (38) and (39) in p. 96. The paper by Horner and Klupfel (Ref. 3) was omitted.

7. F. Ramirez and S. Dershowitz, J. Am. Chem. Soc., 78, 5614 (1956).

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