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A NOVEL REDUCTIVE DIMERIZATION: THE REACTION OF 1, 2-DIBENZOYLETHYLENE WITH P(III) ESTERS[*]

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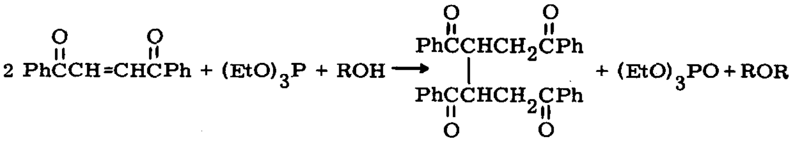
WHEN an ethanolic suspension of *trans*-1, 2-dibenzoylethylene (DBE) is treated with triethyl phosphite at ambient temperature, a deep green color forms. The DBE gradually dissolves and is replaced by a precipitate of *meso*-1, 2, 3, 4-tetrabenzoylbutane (Ia), m. p. 202-203°, identified[†] by acid-catalyzed dehydration to 2, 2', 5, 5'-tetraphenyl-3, 3'-bifuran, m. p. 195-196°. Work up of the ethanol solution yields the *d,l* form of 1, 2, 3, 4-tetrabenzoylbutane (Ib), m. p. 167-168°, and triethyl phosphate, while gas chromatography of a portion of the reaction mixture demon-



$$2\,\mathrm{Ph\overset{O}{\overset{\|}{C}}CH{=}CH\overset{O}{\overset{\|}{C}}Ph} + (\mathrm{EtO})_3\mathrm{P} + \mathrm{ROH} \longrightarrow \begin{array}{c} \mathrm{Ph\overset{O}{\overset{\|}{C}}CHCH_2\overset{O}{\overset{\|}{C}}Ph} \\ | \\ \mathrm{Ph\underset{O}{\underset{\|}{C}}CHCH_2\underset{O}{\underset{\|}{C}}Ph} \end{array} + (\mathrm{EtO})_3\mathrm{PO} + \mathrm{ROR}$$

I (a = meso; b = d, l)

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[†] All reaction products reported showed correct elementary analyses and compatable infrared spectra.

strates the presence of diethyl ether. The total yield of dimeric product is 60 to 70%, consisting of approximately 3 parts of the meso form to 2 of the racemic. A similar reaction takes place in methanol, even more readily than in ethanol.

The foregoing phenomenon represents reductive dimerization of the unsaturated ketone and oxidation of the phosphorus, with the alcoholic solvent participating in the reaction. This behavior differs considerably from the known interactions of trialkyl phosphites with α,β-unsaturated aldehydes[1], acids[2] and quinones[3], which yield phosphorus-containing products representing 1, 4 or, in the case of quinones, 1, 6 addition of the elements of trialkyl phosphite to the unsaturated carbonyl system by what may be considered an extension of the Michaelis-Arbuzov type of reaction. Further study of the reaction of DBE with various trivalent phosphorus compounds revealed that, depending on the phosphorus reagent and the solvent employed, dibenzoylethylene can participate in three general types of reaction processes, all of which take place readily at room temperature (Chart 1). In addition to reductive dimerization already described, there may be reduction to form 1, 2-dibenzoylethane (III) or phosphinylation to yield 1, 2-dibenzoylethane bearing a pentavalent phosphorus substituent (II).

The reactions of DBE with triethyl phosphite, diethyl phenylphosphonite and ethyl diphenylphosphinite in ethanol are compared in Table 1.

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[1] G. Kamai and V. A. Kukhtin, Doklady. Acad. Nauk SSSR, 112, 868 (1957).

[2] Ibid, Tr. Kazansk. Khim. -Tekhnol. Inst., 23, 133 (1957).

[3] F. Ramirez, E. H. Chen and S. Dershowitz, J. Am. Chem. Soc., 81, 4388 (1959).

TABLE 1. REACTION OF DIBENZOYLETHYLENE WITH P(III) ESTERS*

Phosphorus reagent	% Yield Dimerization (I)	Phosphinylation (II)	Time (min.) for dimer ppt.
$P(OEt)_3$	65	nil	5
$PhP(OEt)_2$	43	20	2
Ph_2POEt	34	53	1

*Phosphorus reagent (5 mmoles) added to stirred suspension of DBE (10 mmoles) in absolute ethanol (10 ml.) at 25°.

Replacement of ethoxy groups by phenyl in the phosphorus reagent favors phosphinylation at the expense of dimerization, although the shorter time required for dimer precipitation suggests that the rates of both reactions are enhanced by phenyl substitution. The product, 1-phenylethoxyphosphinyl-1, 2-dibenzoylethane (II, R_1=Ph, R_2=OEt), m. p. 169-171°, is stable, but 1-diphenylphosphinyl-1, 2-dibenzoylethane (II, R_1=R_2=Ph) dehydrates during recrystallization from cyclohexane to yield 2, 5-diphenyl-3-diphenylphosphinylfuran, m. p. 193-194°. Triphenyl phosphite and triphenyl phosphine do not react with DBE at room temperature, but in boiling ethanol these reagents produce a low yield of the dimer (I), accompanied by some dibenzoylethane (III) and other products.

Although the usual reaction of DBE with triethyl phosphite in methanol or ethanol yields dimer exclusively, reduction and phosphinylation can be promoted and dimerization diminished by adding the ketone slowly to triethyl phosphite in methanol over the period of several hours so that the concentration of DBE is kept low. Under these conditions the yield of dimer (I) was only 47% accompanied by 10% of dibenzoylethane

(III), m.p. 145-145.5°, and 13% of 1-diethoxyphosphinyl-1,2-dibenzoylethane (II, $R_1=R_2=OEt$), m.p. 122-123°. When the reaction of DBE with triethyl phosphite is carried out in phenol rather than alcohol, the reduction product (III) is formed in 70% yield, accompanied by a smaller amount of a dimer containing an enol phosphate substituent (IV, $R_1=R_2=OEt$), m.p. 116.5-117.5°.

The origin of the various reaction products can be explained by the mechanistic scheme of Chart 1. Nucleophilic attack of the trivalent phosphorus ester on DBE probably takes place at the double bond to produce the intermediate (A), although attack at a carbonyl oxygen to give (C)

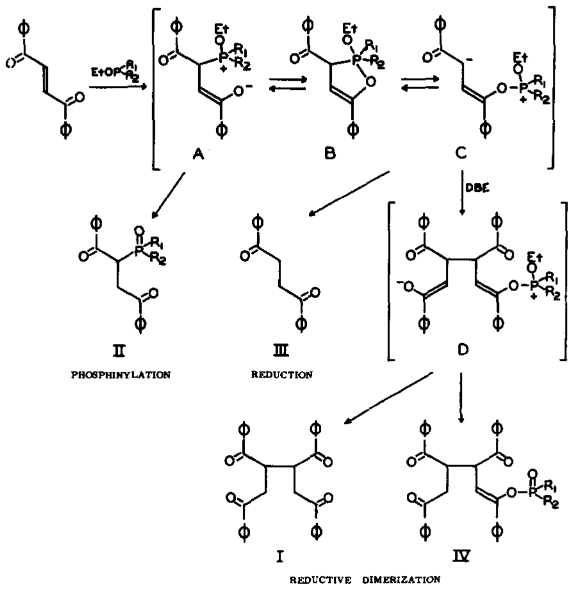

Chart 1

would lead to the same results since these structures are interconvertible through the phosphorane (B). Electron withdrawing substituents (Ph) on the phosphorus favor the intermediate A with an intact carbon to phosphorus bond, so that nucleophilic cleavage of the ethoxy linkage by the hydroxylic solvent yields the phosphinylated product (II). Electron donating substituents (OEt) on the phosphorus favor the carbanionic intermediate (C)* which can lead to either reduction or reductive dimerization depending on the environment. If the concentration of DBE is high and the acidity low, the carbanion adds to a double bond to give the dimeric intermediate (D) which, on ester interchange with the solvent, yields tetrabenzoylbutane (I). But if the concentration of DBE is low, or if the reaction is carried out in more acidic medium (phenol), the carbanion (C) is protonated before dimerization can occur, and ester interchange yields dibenzoylethane (III) as the major product. The enol phosphorus ester (IV) arises when cleavage of the ethoxy linkage in (D) takes place in preference to ester interchange.

Experimental support for the proposed intermediates is provided by isolation of the analytically pure phosphorane (B, $R_1=R_2=Ph$), m.p. 116-118°, from the reaction of DBE with ethyl diphenylphosphinite in dry 1,2-dimethoxyethane. On warming in ethanol, this intermediate was smoothly transformed to the phosphinylated product (II), while treatment with additional DBE in ethanol at 25° gave a 20% yield of the dimer (I).

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*Stabilization of the carbanion by the adjacent benzoyl group plays an important role. Studies in the chalcone series by E. R. DeSombre indicate that replacement of the benzoyl group by phenyl abolishes dimerization and reduction so that phosphinylation is the exclusive reaction pathway.