Reactions of Carbonyl Compounds with Tervalent Phosphorus Reagents. Part III.[1] The Formation of Olefins by Deoxygenation of Carbonyl Compounds with Diphenylphosphine Oxide

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The formation of olefins from benzaldehyde or benzoylferrocene and diphenylphosphine oxide has been rationalised in terms of epoxide intermediates. These intermediates can be isolated from benzaldehyde deoxygenation reactions when the aldehyde is in excess, and it has been shown that they are readily converted into olefin by diphenylphosphine oxide. In contrast to the benzaldehyde system, the deoxygenation of benzoylferrocene gives several products in addition to olefin and the formation of some of these is rationalised in terms of an epoxide pathway.

DEOXYGENATION of organic compounds by tervalent phosphorus reagents is a useful general reaction, which has been applied to amine oxides,[2a] nitro- and nitroso-compounds,[2b] sulphoxides,[2c] and carbonyl compounds. In the last case the product is usually a dimeric olefin, such as those produced from benzaldehyde,[3a,b] benzophenone,[4] furfural,[3a] phthalic anhydride,[5] and a number of ferrocenyl carbonyl compounds.[6a,b] The phosphorus reagents employed in these reactions have been trialkyl phosphites,[3a,4,5] and the anion of diphenylphosphine oxide (1),[3b,6a,6b] generated *in situ* from triphenylphosphine oxide and sodium hydride. A number of suggestions [7] have been made about the role of the phosphorus compounds in carbonyl deoxygenations, but no conclusive evidence on this matter has been published. In particular, carbene pathways (Scheme 1, paths a and b) have been favoured, although at least one unsuccessful attempt to demonstrate carbene intermediates has been reported.[4] This paper is concerned with a reinvestigation of the reactions of diphenyl

attempts to demonstrate the existence of carbene intermediates in deoxygenations of carbonyl compounds, it seemed appropriate to test the possibility that epoxide intermediates were being formed (Scheme 1, path d), as a result of attack by the anion of (1) at the carbonyl oxygen atom of (2).

When benzaldehyde (2 mol. equiv.) reacted with diphenylphosphine oxide anion in dry bis-(2-methoxyethyl) ether at 180 °C, a mixture of *trans*-stilbene epoxide (5a) (44%), *cis*-stilbene epoxide (5b) (41%), and *trans*-stilbene (6%) was formed. Moreover, a similar result was obtained when the oxide (3) was treated with sodium hydride at 180 °C in the presence of benzaldehyde. These high-temperature deoxygenations of benzaldehyde therefore give epoxide products analogous to those isolated by several authors [9] from the more controlled deoxygenations of nitrobenzaldehydes using hexamethylphosphoric triamide.

Since epoxides are known to suffer efficient deoxygen-

The conditions used for the *in situ* generation of the diphenylphosphine oxide (1) in these experiments (hydrolysis of the corresponding chlorophosphine) were

Herweh[4] from the pyrolysis of benzophenone with tri-isopropylphosphite, although no rationale was presented for its formation. Our experiments do not
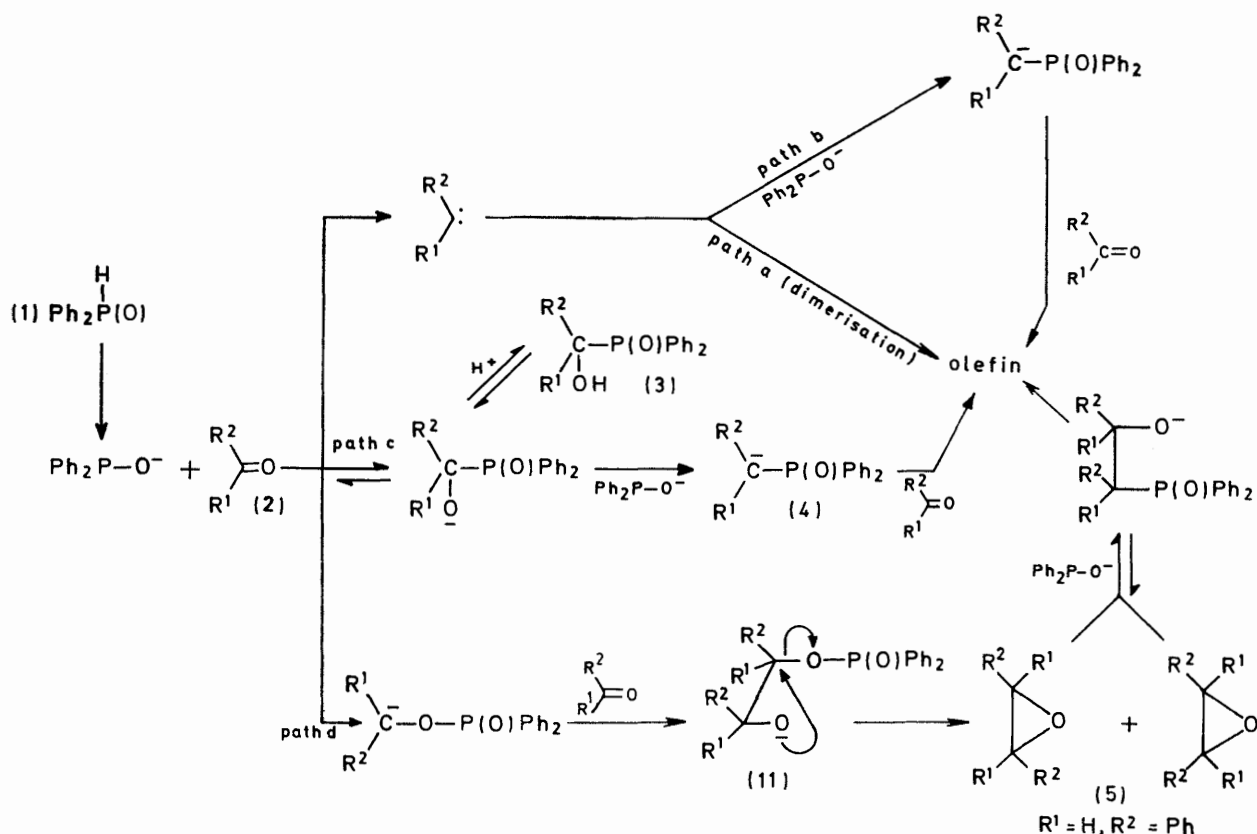

SCHEME 1 Possible routes to olefins by the deoxygenation of carbonyl compounds with diphenylphosphine oxide anion

extremely crude, and it is possible that the above stereomutation of *cis*-stilbene was acid-catalysed.

In connection with related studies, we required a sample of the olefin (6), and accordingly repeated the published synthesis [6a] from benzoylferrocene by use of the anion of (1). Although the olefin (6) was successfully prepared by this route, we found that it was a minor product (5%), formed together with five other products, none of which was present in the starting ketone. These products were separated by column chromatography of the crude reaction mixture, and identified as ferrocene (12%), benzylferrocene (4%), 1,2-diferrocenyl-1,2-diphenylethane (7) (3%), benzoyldiferrocenylphenylmethane (8) (1%), and ferrocenylcarbonyl(ferrocenyl)-diphenylmethane (9) (4%). Unchanged benzoylferrocene (11%) was also isolated, but the remainder of the product was insoluble in organic solvents, and not investigated further.

Although no rigorous mechanistic studies have been made of this reaction, we believe that a number of relevant observations may be made about the reaction products, since analogous transformations have been reported by other workers. For example, 1,1,2,2-tetraphenylethane has been isolated by Poshkus and

clarify this point. The formation of the ketones (8) and (9) also has precedent, for example in the reaction of
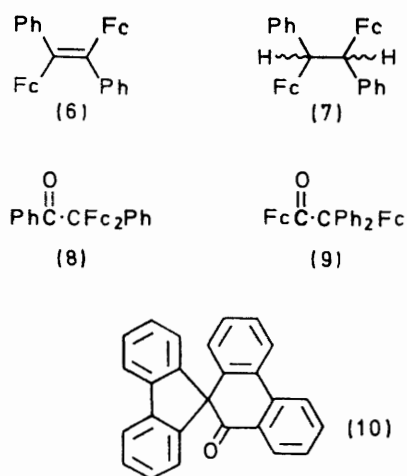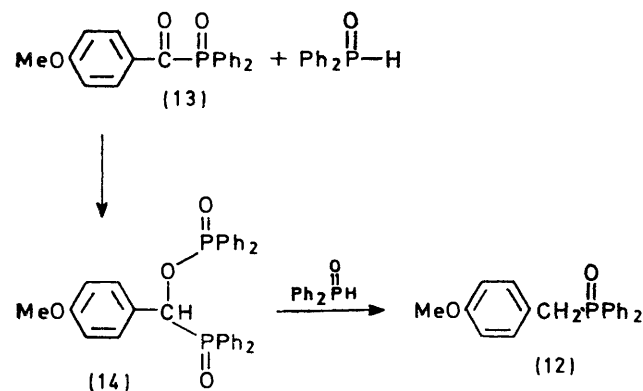

fluorenone with trialkyl phosphites to produce the spiro-ketone (10).[4] Pauson and Watts did report [6a] the formation of another reaction product, in addition to olefin (5), and its physical properties are identical with

those of the ketone (9), the major ketonic product (4%) under our experimental conditions.

We believe that the formation of the ketonic and olefinic products can be explained in terms of Scheme 1, path d. The olefin may well arise *via* epoxide intermediates, as was found with *trans*-stilbene. The ketones could arise from the intermediate (11) by a 1,2-shift of either a ferrocenyl or a phenyl group with elimination of diphenylphosphinate anion. Since ferrocenyl epoxides are generally unstable—the authors are aware of only one such compound having been characterised [11]—it is not surprising that no epoxides have been isolated from this rather vigorous reaction.

The formation of benzyl ferrocene was more unexpected. However, its formation may be akin to that of *p*-methoxybenzyldiphenylphosphine oxide (12) from *p*-anisic acid and tetraphenyldiphosphine.[12] This oxide is believed to result from the addition of diphenylphosphine oxide (1) to the carbonyl oxygen atom of

benzylferrocene is possible. Since the ferrocenyl group is recognised [15] to be an electron donor of effect comparable to that of the *p*-methoxyphenyl group, we suggest that the reduction of (17b) could be facilitated by ferrocene, in a fashion similar to the cases already cited.

The major identified product of the deoxygenation of benzoylferrocene is ferrocene. A number of similar cleavage reactions of diaryl ketones,[16] and of benzoylferrocene [17] itself, under basic conditions, have been

(15)   (16)   (17)

a; $R^1 = OH$, $R^2 = PPh_2$
b; $R^1 = H$, $R^2 = Fc$

(13)

(14)   (12)

SCHEME 2

p-anisoyldiphenylphosphine oxide (13) to produce compound (14), and subsequent reduction of (14) represented as in Scheme 2. Diphenylphosphine oxide is known [13] to be a reducing agent [and indeed may account for the formation of (7), possibly from (6)] and the final reductive step in Scheme 2 only occurs when the *p*-methoxy-group of (14) is present. A similar electronic requirement has been observed [14] in the reaction of substituted methyl benzoates with compound (1), since only the aroyldiphenylphosphine oxide (15) from methyl salicylate was found to be reduced to the corresponding benzyl oxide (16). It is thus apparent that electron release to the benzylic position in intermediates of the type (17a) is essential for reduction to occur. In our reaction, if an intermediate of type (17b) were formed, by attack of phosphorus on the carbonyl oxygen atom, followed by protonation, then subsequent reduction to
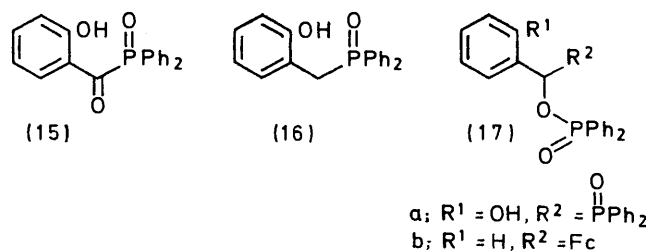
reported. An acceptable explanation of these reactions (with alkali) has been proposed by Kenner *et al.*,[16a] who suggested that an addition–elimination sequence *via* an intermediate (18) is responsible for the loss of an aryl group. A similar intermediate (19) could result from the addition of the anion of (1) to the carbonyl carbon atom of benzoyl ferrocene. The formation of such an intermediate has ample precedent in the general reactions of tervalent phosphorus compounds with carbonyl compounds, as discussed earlier in this paper. It may be that breakdown of the intermediate (19) sometimes results in loss of the ferrocenyl anion, and

(18)   (19)   (20)   (21)
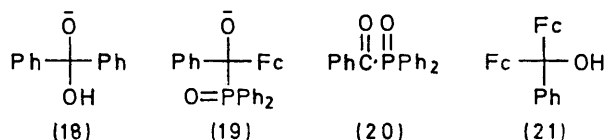
formation of benzoyldiphenylphosphine oxide (20), which would certainly not survive the conditions of the reaction and work-up.[1,12]

An alternative explanation is that any residual sodium hydride might, at the elevated temperatures, attack the benzoylferrocene. The feasibility of this was demonstrated by heating a mixture of sodium hydride and benzoylferrocene to 180°, by which time the mixture had melted and resolidified. Work-up of this gave ferrocene (19%), αα-diferrocenylbenzyl alcohol (21) (9%), unchanged benzoylferrocene (2) (12%), and α-ferrocenylbenzyl alcohol (50%). This reaction shows

[11] A. A. Koridze, *Zhur. obshchei Khim.*, 1969, **39**, 1649 (*Chem. Abs.*, 1969, **71**, 91,615j).

[12] R. S. Davidson, R. A. Sheldon, and S. Trippett, *J. Chem. Soc.* (*C*), 1967, 1547.

[13] A. J. Floyd, K. C. Symes, G. I. Fray, G. E. Gymer, and A. W. Oppenheimer, *Tetrahedron Letters*, 1970, 1735; M. J. Gallacher and I. D. Jenkins, *J. Chem. Soc.* (*C*), 1971, 210; J. A. Miller, G. M. Stevenson, and B. C. Williams, *J. Chem. Soc.* (*C*), 1971, 2714.

[14] J. A. Miller, unpublished results.

[15] M. Cais, *Organometallic Chem. Rev.*, 1966, **1**, 435.

[16] (*a*) G. W. Kenner, M. J. T. Robinson, C. M. B. Taylor, and B. R. Webster, *J. Chem. Soc.*, 1962, 1756; (*b*) R. Delange, *Bull. Soc. chim. France*, 1903, **29**, 1131; (*c*) G. Lock and E. Rödiger, *Ber.*, 1939, **72**, 861.

[17] (*a*) P. L. Pauson and W. E. Watts, *J. Chem. Soc.*, 1962, 3880; (*b*) N. Weliky and E. S. Gould, *J. Amer. Chem. Soc.*, 1957, **79**, 2742.

that the alkoxide formed by attack of hydride on benzoyl-ferrocene in a melt can eliminate ferrocenyl anion, which either remains until quenched or in part adds to un-changed benzoylferrocene to afford the alcohol (21). A similar formation of triphenylmethanol has been observed [15a-c] in reactions of benzophenone with potassium hydroxide at elevated temperatures.

Although these studies demonstrate the formation of epoxide intermediates in the benzaldehyde reaction, the benzoylferrocene reaction pathway is less well defined. However, some of the reaction products do suggest that there is a similarity in the pathways to olefin formation. While it is recognised that epoxides would arise *via* carbene intermediates, it does not seem likely that benzaldehyde would be an efficient carbene trap compared with a tervalent phosphorus compound. It has already been mentioned that the reactions described here bear a formal similarity to those of hexamethyl-phosphoric triamide, in that epoxides have been isolated from nitrobenzaldehyde deoxygenations with this reagent. In these systems, intermediate dioxaphos-phoranes have been isolated, and the epoxides have been shown to result from their thermal decomposition. It is therefore possible that similar intermediates exist in the reactions described here. In view of the severity of our reaction conditions, it is not surprising that phosphoranes have not been isolated, or even observed, and we feel that the more direct rationale presented in Scheme 1, path d, is adequate to explain our experimental results.

EXPERIMENTAL

I.r. spectra were recorded on a Perkin-Elmer 137 spectrometer. N.m.r. spectra were recorded for deuteriochloroform solutions on a Perkin-Elmer R-10 spectrometer at 60 MHz with tetramethylsilane as internal standard. T.l.c. was performed on Kieselgel G$_{254}$ (Merck).

Reactions of Diphenylphosphine Oxide (1).—The oxide was generated *in situ* by the following procedure. Diphenylphosphinous chloride was dissolved in dry bis-(2-methoxyethyl) ether (5 vol) under nitrogen, and water (1 mol. equiv.) was added to the stirred solution. After the initial exothermic reaction had subsided (*ca.* 5 min), sodium hydride (2 mol. equiv. as 50% dispersion in oil) was added in small batches and the resultant paste was stirred under nitrogen until effervescence ceased (*ca.* 15 min). This paste contained diphenylphosphine oxide (1 mol. equiv.) as its sodium salt, and was generally used in 20% excess.

(a) *With excess of benzaldehyde*. Benzaldehyde (2·12 g, 0·02 mol) was added to diphenylphosphine oxide (0·012 mol) and the mixture was stirred at 180 °C under nitrogen for 1 h. It was then taken up in a mixture of ether (100 ml) and water (100 ml). The ether layer was washed with saturated sodium hydrogen carbonate solution (100 ml), dried (MgSO$_4$), and evaporated. The residue (4·5 g) showed no carbonyl absorption in the i.r., and was chromatographed on silica, with petroleum (b.p. 40—60°) as eluant, to give *trans*-stilbene (0·10 g, 6%), *cis*-stilbene epoxide (0·78 g, 40%), and *trans*-stilbene epoxide (0·86 g, 44%), identified by comparison (m.p., t.l.c., and n.m.r.) with authentic samples.

(b) *With* trans-*stilbene epoxide*. *trans*-Stilbene epoxide (1·96 g, 0·01 mol) was added to diphenylphosphine oxide (0·012 mol). The mixture was stirred at 180 °C under nitrogen for 1 h, then worked up as in (a) to give a slushy residue (2·0 g), which was shown (t.l.c. and n.m.r.) to contain no *trans*-stilbene epoxide, *cis*-stilbene epoxide, or *cis*-stilbene. Crystallisation of the residue yielded pure *trans*-stilbene (1·51 g, 85%).

(c) *With* trans-*stilbene epoxide in the presence of* cis-*stilbene*. *trans*-Stilbene epoxide (1·96 g, 0·01 mol) and *cis*-stilbene (1·80 g, 0·01 mol) were added to diphenylphosphine oxide (0·012 mol). The mixture was stirred at 180 °C under nitrogen for 1 h, then worked up as in (a); the residue (3·95 g) crystallised from petroleum to give *trans*-stilbene (3·20 g, 88%). No *cis*-stilbene or stilbene epoxides were present in the crude residue from the work-up.

Reaction of Benzaldehyde with α-*Hydroxybenzylphosphine Oxide* (3).—α-Hydroxybenzyldiphenylphosphine oxide (3·24 g, 0·01 mol) was suspended in a mixture of benzaldehyde (1·06 g, 0·01 mol) and bis-(2-methoxyethyl) ether (10 ml). Sodium hydride (0·48 g of a 50% dispersion in oil, 0·01 mol) was added. The stirred slurry was heated at 160 °C under nitrogen for 1 h, and then poured into water (200 ml). Ether extracts (2 × 50 ml) were washed with saturated sodium hydrogen carbonate solution and then with water (5 × 100 ml), dried, and evaporated. The oily residue (2·2 g) did not contain any benzaldehyde or any significant amounts of stilbenes (n.m.r., i.r., and t.l.c.). Chromatography of the residue as in the previous experiment (a) yielded *cis*-stilbene epoxide (38%) and *trans*-stilbene epoxide (46%).

Reaction of α-*Hydroxybenzyldiphenylphosphine Oxide* (3) *with Sodium Hydride*.—α-Hydroxybenzyldiphenylphosphine oxide (1·62 g, 0·005 mol) was suspended in bis-(2-methoxy-ethyl) ether (10 ml) under nitrogen at 160 °C. Addition of sodium hydride (0·24 g of a 50% dispersion in oil, 0·005 mol) resulted in vigorous effervescence. Once all the hydride had been added, the mixture was cooled, and then poured into water. Extraction with ether yielded benzaldehyde (88%).

Reaction of Benzoylferrocene with Diphenylphosphine Oxide at 200 °C.—Triphenylphosphine oxide (15·5 g, 0·055 mol) and sodium hydride (2·7 g, 0·055 mol, as a 50% dispersion in mineral oil) were heated at 200° for 1 h under nitrogen. Benzoylferrocene (11·5 g, 0·04 mol), purified by chromatography and crystallisation, was added. The mixture was heated for a further 3 h at 200°, then allowed to cool, and the solid was leached several times with ether. The combined ethereal extracts yielded a black viscous material which was chromatographed on alumina (Spence grade H) and separated into five components as follows. Light petroleum eluted ferrocene (0·78 g, 12%); light petroleum–ether (23 : 2) gave benzylferrocene (0·41 g, 4%); light petroleum–ether (4 : 1) gave a mixture (0·97 g) of the ethylene (6) and the ethane (7); light petroleum–ether (1 : 1) gave a mixture (0·52 g) of the two ketones (8) and (9); and ether gave unchanged benzoylferrocene (1·30 g, 11%).

Rechromatography of the mixture of the ethylene (6) and the ethane (7) with benzene–light petroleum (3 : 1) as eluant gave 1,2-diferrocenyl-1,2-diphenylethylene (6) (0·45 g, 5%), m.p. 275—278° (lit.,[18] 278—280°), and 1,2-diferro-cenyl-1,2-diphenylethane (7) (0·30 g, 3%), m.p. 215—218°

[18] S. I. Goldberg, W. D. Bailey, and M. L. McGregor, *J. Org. Chem.*, 1971, **36**, 761.

(softening from 190°) (lit. [18] m.p. 220—222° for the achiral   cool and water was added to destroy unchanged sodium