Fixation and Deoxygenation of Carbon Dioxide to form Furans using Organophosphorus Intermediates

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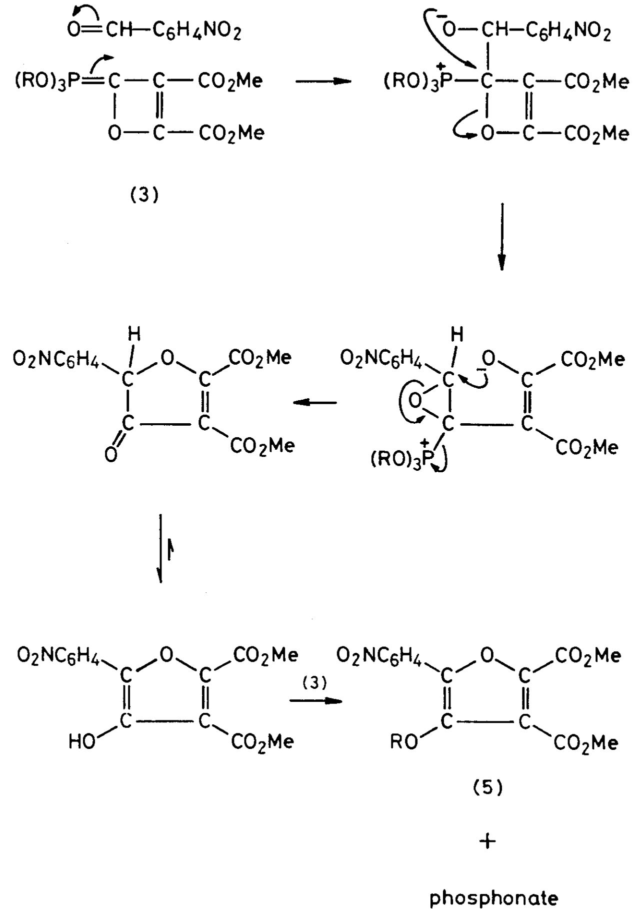
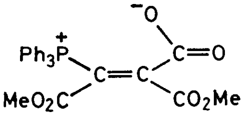
Summary The passage of carbon dioxide through a solution of dimethyl acetylenedicarboxylate during the addition of two equivalents of a trialkyl phosphite leads to the formation of an ylide (**3**) which reacts with 4-nitrobenzaldehyde to give a furan (**5**) in which the heterocyclic oxygen and one of the β-carbon atoms in the furan ring are derived from the carbon dioxide.

CARBON DIOXIDE is known to react with the 1:1 intermediate initially formed in the reaction of triphenylphosphine with dimethyl acetylenedicarboxylate to form a mixture of the carboxylate betaines (**1a**) and (**1b**).[1] We now report that carbon dioxide can also be rapidly and efficiently trapped when the reaction is carried out using a trialkyl phosphite in place of the triphenylphosphine. The product formed, however, is no longer ionic but has the cyclic form (**2**), as shown by ^{31}P n.m.r. spectroscopy [*e.g.* (**2**, R = Et): $\delta(^{31}P)$ −53·8 p.p.m.].† Furthermore, unlike the betaine (**1**), the phosphorane (**2**) reacts rapidly with a second molecule of trialkyl phosphite to form the ylide (**3**) with the simultaneous elimination of a molecule of phosphate. The ^{31}P n.m.r. spectrum of (**3**, R = Et) showed a signal at $\delta(^{31}P)$ 40·4 p.p.m. and its ^{13}C n.m.r. spectrum showed, among other features, a characteristically large phosphorus coupling to the α-carbon [$\delta(^{13}C)$ 48·12 p.p.m., J_{PC} 250 Hz].[2] We have shown by ^{31}P n.m.r. studies that the phosphate produced during the formation of (**3**) is derived entirely from the phosphorane (**2**) and that the phosphite added to (**2**) provides the phosphorus atom for the ylide (**3**). It is interesting to note that the phosphate oxygen is derived originally from the carbon dioxide.

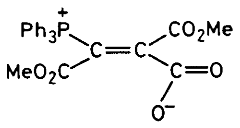
The ylide (**3**) reacts rapidly with water to form various diastereoisomers of the phosphonate (**4**).‡ Ylide (**3**) also reacts with 4-nitrobenzaldehyde in toluene solution at 80 °C over 30 min to regenerate trialkyl phosphite and give an organophosphorus compound [$\delta(^{31}P)$ 21·3 p.p.m. from (**3**, R = Me)] which closely resembled the phosphonate (**4**), together with a yellow crystalline compound which has been shown to be the furan (**5**).‡ This material was stable to dilute acid, and n.m.r. spectroscopy indicated that only one isomer was present. We believe that the ylide (**3**) does not undergo the normal Wittig reaction to give an alkylidene oxete because the formation of an exocyclic double bond to the oxete ring is unfavourable. Instead we propose that the reaction occurs as shown in the Scheme. It is interesting



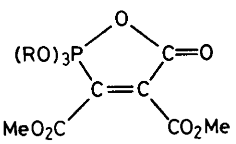
SCHEME



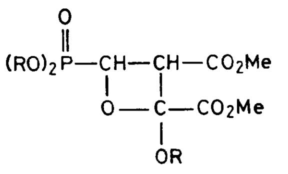
(**1a**)



(**1b**)



(**2**)



(**4**)

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† Positive shifts are downfield with respect to 85% phosphoric acid.

‡ The structure was identified by ^{1}H, ^{13}C, and ^{31}P n.m.r. spectroscopy and combustion analysis of a purified sample.

to note that the carbon atom and the oxygen atom derived from the carbon dioxide are not only part of the furan ring but are also no longer directly bonded. The formation of the furan ring accounts for the unusual expulsion of the phosphite molecule, and dealkylation of a second molecule of ylide explains the origin of the observed alkoxy-substituent on the furan ring and the production of phosphonate. Thus, one molecule of aldehyde reacts with two molecules of ylide. Use of this ratio of reactants gave the furan (**5**, R = Me) in 60% yield. Preliminary studies indicate that this reaction also occurs with other aldehydes.

The use of carbon dioxide as a starting material in the reaction offers obvious potential for producing isotopically labelled materials. The scope of the reaction for producing isotopically labelled furans and their subsequent conversion into other organic molecules is currently under investigation.

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[1] A. W. Johnson and J. C. Tebby, *J. Chem. Soc.*, 1961, 2126; M. A. Shaw, J. C. Tebby, J. Ronayne, and D. H. Williams, *J. Chem. Soc. C*, 1967, 944.

[2] J. C. Tebby, S. E. Willetts, and D. V. Griffiths, *J. Chem. Soc., Chem. Commun.*, 1981, 420.