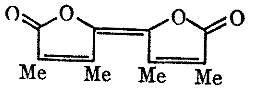
The Deoxygenative Dimerisation of Carboxylic Anhydrides

By C. W. BIRD* and D. Y. WONG

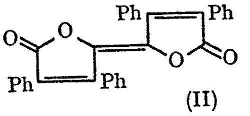
(*Department of Chemistry, Queen Elizabeth College, Campden Hill, London, W.*8)

Summary Evidence is presented for the formation of a phosphorane intermediate during the deoxygenative dimerisation of carboxylic anhydrides by triethyl phosphite.

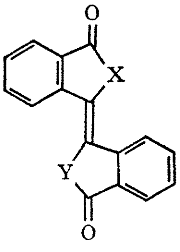
MALEIC ANHYDRIDE and its monosubstituted derivatives have been shown[1] to react with triphenylphosphine at the double bond yielding triphenylphosphoranylidenesuccinic anhydrides. We have now found that dimethyl- and diphenyl-maleic anhydrides are converted into the corresponding bifurandiones, (I) and (II), on heating under reflux with triethyl phosphite. The behaviour of these disubstituted maleic anhydrides† is analogous to that of phthalic anhydride which is converted into (III) under these conditions.[2]



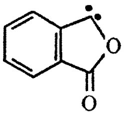
(I)



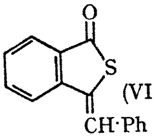
(II)



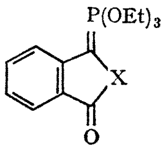
(III) X=Y=O
(IV) X=Y=S
(V) X=O; Y=S



(VI)



(VIII)



(VII) a; X=O
b; X=S

The mechanism postulated for this deoxygenative dimerisation entailed attack of the phosphorus atom of the phosphite on the carbonyl oxygen of the anhydride leading to the carbene (VI), followed by dimerisation. Our experiments show that thiophthalic anhydride reacts some thousand times faster with triethyl phosphite, yielding (IV), than does phthalic anhydride, whereas both *N*-methyl- and *N*-phenyl-phthalimide do not react. Thus the reactivity sequence $S > O \gg NR$ is that expected for nucleophilic attack of triethyl phosphite on the carbonyl carbon atom. It appears most unlikely that a free carbene, *e.g.* (VI), would exist as such in the presence of an excess of triethyl phosphite, as it would undoubtedly be converted into the phosphorane (VIIa). Evidence for such an intermediate (VII) is provided by two reactions. Brief treatment of thiophthalic anhydride with triethyl phosphite in the presence of phthalic anhydride yields predominantly the monothiabiphthalidylidene (V). A similar reaction in which benzaldehyde was substituted for phthalic anhydride generated the benzylidenethiaphthalide (VIII).

The relatively low reactivity of either phthalic anhydride or benzaldehyde towards triethyl phosphite under the reaction conditions precludes formation of sufficient quantities of the appropriate carbenes to couple with the thiaphthalidylidene species and so generate (V) or (VIII). However formation of the intermediary phosphorane (VIIb), followed by normal Wittig reactions accounts satisfactorily for these products.

(*Received, June* 24*th*, 1969; *Com.* 913.)

---

† Dichloromaleic anhydride reacts violently with triethyl phosphite but none of the expected bifurandione has yet been isolated.

[1] A. Schonberg and A. F. A. Ismail, *J. Chem. Soc.*, 1940, 1374; G. Aksnes, *Acta Chem. Scand.*, 1961, **15**, 692; R. F. Hudson and P. F. Chopard, *Helv. Chim. Acta*, 1963, **46**, 2178; C. Osuch, J. E. Franz, and F. B. Zienty, *J. Org. Chem.*, 1964, **29**, 3721.

[2] F. Ramirez, H. Yamanaka, and O. H. Basedow, *J. Amer. Chem. Soc.*, 1961, **83**, 173.