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ORGANOPHOSPHORUS INTERMEDIATES—II[a]

DEOXYGENATIVE DIMERISATION OF MALEIC ANHYDRIDES BY TRIETHYL PHOSPHITE

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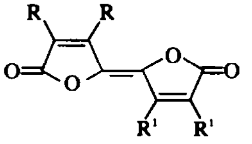
Abstract—Treatment of disubstituted maleic anhydrides with triethyl phosphite generates bifurandiones. In some instances bifurandione derivatives undergo acid-catalysed rearrangement to pyrano[3,2-b]pyran-2,6-diones.

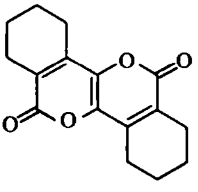
Whereas phthalic anhydride undergoes deoxygenative dimerisation reactions with triethyl phosphite initiated by attack at the carbonyl group,[1] maleic or citraconic anhydrides and triphenylphosphine react at the double bond yielding triphenylphosphoranylidenesuccinic anhydrides.[3] It occurred to us that reaction would probably not occur at the double bond in disubstituted maleic anhydrides but instead would generate, by deoxygenative dimerisation, derivatives of bifurandione[4] which are not readily accessible in most laboratories.

Treatment of diphenylmaleic anhydride with an excess of triethyl phosphite rapidly produced an excellent yield of the tetraphenylbifurandione **1a**. Dichloromaleic anhydride reacted violently with triethyl phosphite after an induction period and none of the anticipated tetrachlorobifurandione could be isolated. However, both dimethylmaleic and tetrahydrophthalic anhydrides gave modest yields of the bifurandiones (**1b** and **1c**) respectively. In the latter case a small amount of the pyronopyrone (**2**) was also formed, recalling the generation of both **3** and **4** from phthalic anhydride under similar conditions.[1] A cross-coupling reaction was effected by treating diphenylmaleic anhydride with triethyl phosphite in the presence of an excess of dimethylmaleic anhydride, and produced the dimethyldiphenylbifurandione (**1d**) together with a little **1a**.

The formulation of these compounds as *trans*-bifurandiones follows in the first instance from the high frequency CO group *ca* 1770 cm^{-1}, and in the case of **1b** and **1c** the UV spectra were almost identical to that of the known tetraethylbifurandione,[4] and quite different from that of **2**. The failure to observe a band in the IR spectra assignable to the interannular double-bond indicated the *trans*-configuration. In the case of the tetraphenyl compound a *cis*-configuration would be extremely sterically unfavourable. However, in the case of **1b** and **1c** where the steric interactions would not be so severe it appeared that *cis*-isomers might be obtainable. It is well established that in the case of the unsubstituted bifurandione the *cis*-isomer is more stable than the *trans* one, which can be converted to its geometrical isomer by treatment with conc sulphuric acid. Although the tetraphenyl and tetramethylbifurandiones were stable to prolonged heating with sulphuric acid, the bifurandione (**1c**) was rearranged into the pyronopyrone (**2**). This compound had previously been obtained by the dehydrochlorination of hexahydrophthaloyl chloride and its structure established by extensive degradations.[5]



1a: R = R' = Ph
b: R = R' = Me
c: RR = R'R' = $(CH_2)_4$
d: R = Ph, R' = Me



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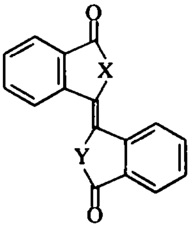
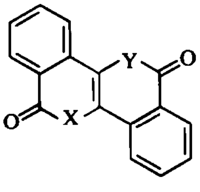
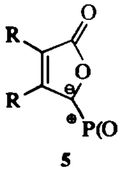


3a: X = Y = O
b: X = O, Y = S
c: X = Y = S



4a: X = Y = O
b: X = O, Y = S



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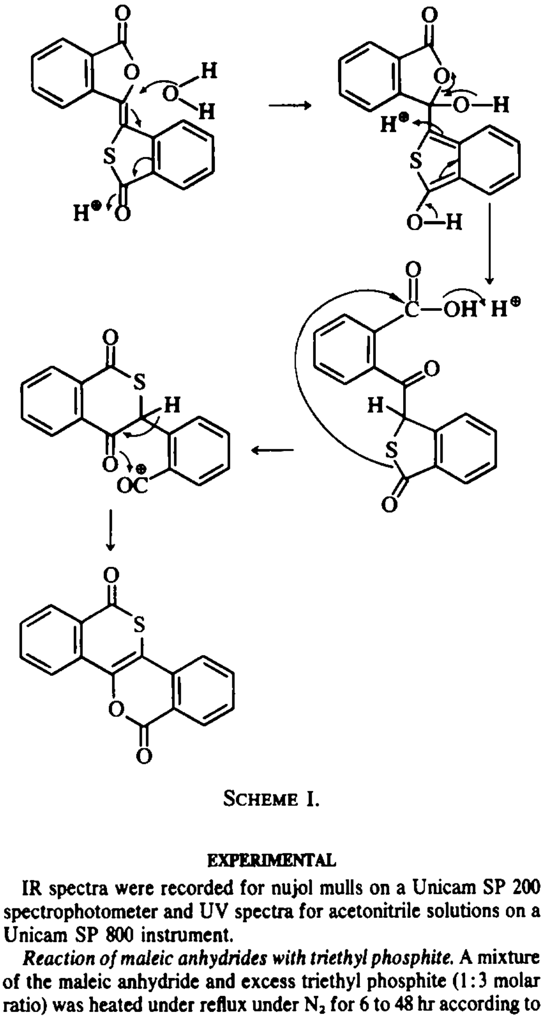
[a] A preliminary account of part of this work has already appeared (Ref 2). For the first paper in this series see Ref 1.

The unexpected rearrangement of **1c** to **2** led us to examine the behaviour of the biphthalylidenes (**3a**), **3b** and **3c** under similar conditions. Indeed yellow biphthalylidene was readily converted to the colourless di-isocoumarin (**4**). Review of the literature revealed that this reaction had been observed previously,[6] but had been interpreted as isomerisation of the *trans*-biphthalylidene to the sterically unfavourable *cis*-isomer. Rearrangement of either the mono-**3b** or dithiabiphthalylidene (**3c**) gave solely the monothiadiisocoumarin (**4b**). A mechanism for the rearrangement which accommodates this feature is indicated in Scheme I.

We assume that the deoxygenative dimerisations follow the pathway previously adumbrated[1] for phthalic anhydrides, so that bifurandione formation entails generation of the phosphorane (**5**), which then undergoes a Wittig type reaction with a further maleic anhydride molecule. Analogous reactions of phosphoranes with maleic anhydrides have been reported.[7]



Scheme I.

EXPERIMENTAL

IR spectra were recorded for nujol mulls on a Unicam SP 200 spectrophotometer and UV spectra for acetonitrile solutions on a Unicam SP 800 instrument.

Reaction of maleic anhydrides with triethyl phosphite. A mixture of the maleic anhydride and excess triethyl phosphite (1:3 molar ratio) was heated under reflux under N_2 for 6 to 48 hr according to the anhydride used. The mixture was cooled and in the case of the diphenylmaleic anhydride reaction the product could be filtered off directly. In the other cases triethyl phosphite and phosphate were distilled off *in vacuo* and the residue chromatographed on silica gel in benzene. The following bifurandiones were thus obtained:

3,4,3',4'-*Tetraphenylbifurandione* (6 h, 50%) m.p. 390° from EtOH. ϑ_{max} 1770 cm^{-1}, λ_{max} 399 nm (45,170). (Found: C, 81·4; H, 4·4. Calc. for $C_{32}H_{20}O_4$: C, 82·0; H, 4·3%).

3,4,3',4'-*Tetramethylbifurandione* (48 h, 5%) m.p. 238–239° from EtOH, ϑ_{max} 1760 cm^{-1}, λ_{max} 340 nm (39,280). (Found: C, 65·6; H, 5·5. Calc. for $C_{12}H_{12}O_4$: C, 65·5; H, 5·5%).

3,4:3',4'-*Bis(tetramethylene)bifurandione* (48 h, 15%) m.p. 308–310° from EtOH, ϑ_{max} 1770 cm^{-1}, λ_{max} 344 nm (41,000). (Found: C, 70·3; H, 5·8. Calc. for $C_{16}H_{16}O_4$: C, 70·5; H, 5·9%).

The last mentioned bifurandione was accompanied by the isomeric 3,4:7,8-bis(tetramethylene)pyrano[3,2-b]pyran-2,6-dione (1%) m.p. 318–320° from EtOH (lit. m.p. 303–305 ϑ_{max} 1700 cm^{-1}, λ_{max} 343 nm (15,000), 360 nm (19,520), 380 nm (15,000).

Deoxygenative codimerisation

Diphenylmaleic anhydride (0·4 g) and dimethylmaleic anhydride (1·6 g) in triethyl phosphite (10 ml) were heated under reflux under N_2 for 1 h. The cooled mixture was diluted with light petroleum. The ppt was filtered off and separated by preparative TLC into a small amount of tetraphenylbifurandione and 3,4-*dimethyl*-3',4'-*diphenylbifurandione* (22%) m.p. 166–168° from EtOH. ϑ_{max} 1750 cm^{-1}, λ_{max} 368 nm (41,970). (Found: C, 76·3; H, 4·6. Calc. for $C_{22}H_{16}O_4$: C, 76·7; H, 4·65%).

Acid-catalysed isomerisation reactions

The bifurandione derivative (1 g) in conc H_2SO_4 (80 ml) was kept at 120–140° for 2 to 14 h until rearrangement was complete. The progress of the reaction was followed by IR spectroscopy of small aliquots processed in the same way as adopted for the large-scale work-up. The final mixture was poured onto ice, the ppt filtered off, washed with water, dried and recrystallised. Thus: biphthalylidene gave [2]-benzopyrano[4,3-c]-[2]benzopyrano-6,12-dione (92%) after 2 h m.p. 330–332° from toluene (lit.[1] m.p. 330–332°); monothio- and dithiobiphthalylidene gave 5-thia-[2]-benzopyrano[4,3-c] - [2]benzopyrano-6,12-dione in yields of 44 and 27% after 12 and 14 h respectively, m.p. 334–336° from toluene (lit. m.p.[1] 334–336°); 3,4;3'4'-bis(tetramethylene)bifurandione gave 3,4;7,8-bis(tetramethylene)pyrano[3,2-b]pyran-2,6-dione in 64% yield after 12 h, m.p. 318–320° from EtOH (lit.[5] m.p. 303–305°).

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