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Reactions Between (E)-5,5'-Dimesitylbifuranylidenedione and the Horner–Wittig Reagent.

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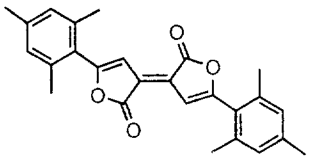
Abstract: (E)-5,5'-Dimesitylbifuranylidenedione **1** reacts with the Horner - Wittig reagent by attack at one carbonyl giving **3**; subsequent Michael addition of a second molecule of ylide leads to **4** by dehydrogenation, whilst **9** is a dimeric product.

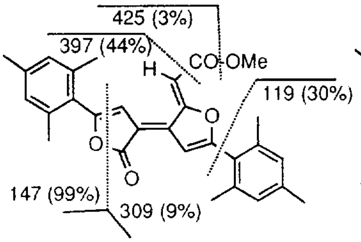
The brilliantly coloured and highly crystalline diarylbifuranylidenedione (diarylBFD) heterocycles have interesting crystallographic features,[2] but knowlege of their chemistry is limited.[2-4] As part of a more detailed study we have examined their reactions with phosphoranes. Low solubility and high m.p.s are characteristic of the series, so (E)-5,5'-dimesitylBFD **1**, rather than (E)-5,5'-diphenylBFD, was selected as the substrate on the grounds of better solubility in the Horner - Wittig reaction. It was refluxed with the stable ylide **2** (2 mol equiv) under nitrogen in toluene for 24 h. Extensive chromatographic work up, including HPLC gave a number of products, among which were triphenylphosphine along with recovered methoxycarbonylmethylene-triphenylphosphorane **2** and dimesitylBFD **1**. Interest was however concentrated on three significant products, one an orange ester **3**, m.p.124 - 128°C from hexane, the second a pale yellow crystalline compound **4**, m.p. 200 - 204°C from chloroform and methanol, and the third a red compound **9**, m.p. 246 -248°C from the same solvent mixture.

The orange ester **3** (26% yield), $C_{29}H_{28}O_5$ had IR carbonyl vibrations at 1780 and 1740 cm^{-1} assignable to a five-membered lactone ring and an α-unsaturated ester respectively, whilst the mass spectral fragmentation pattern (cf. **1A**) was readily interpreted as that of the expected mono-Horner - Wittig product **3**.[5] On the other hand, the yellow crystalline product **4** (11%), m.p. 200 - 204°C, analysed for $C_{32}H_{30}O_7$ and in the ^1H NMR spectrum six mesityl methyls and two ester methoxyls were located. In addition there was a 6H

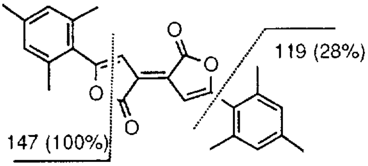


1

$Ph_3\overset{+}{P}\text{-}\overset{-}{C}HCO_2Me$ 2



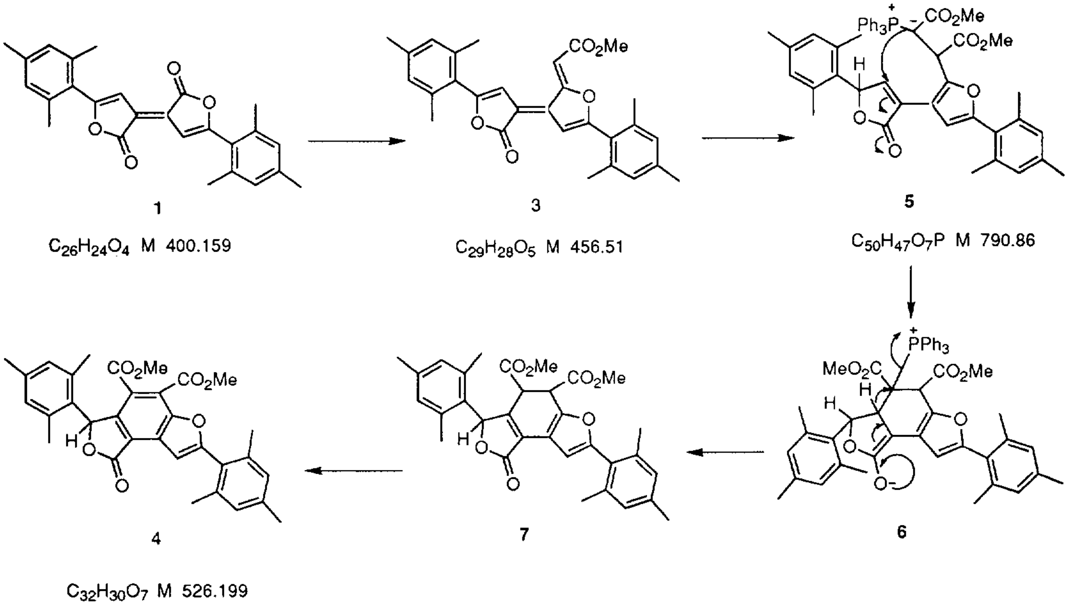
M⁺ 456 (100%) 3



M⁺ 400 (92%) 1A

multiplet containing the remaining four aromatic protons and two non-aromatic protons. The IR spectrum showed absorption bands at 1760, 1740 and 1730 cm^{-1} which might be assigned to a five membered lactone and two ester groups. The mass spectrum showed the expected losses of 119 and and 147. There was also a cleavage of two methoxycarbonyl groups.

A suitable single crystal for X-ray structure determination was obtained from methanol / chloroform and the resulting hexasubstituted benzene structure **4** is shown in Fig. 1 The lactone and benzofuran central portion is virtually planar, with the mesityl rings twisted out of plane. The ester groups are differently oriented with respect to the central benzene ring, in agreement with the IR deduction of two different ester groups. A possible



Scheme 1. Formation of two Horner - Wittig products from dimesitylBFD.

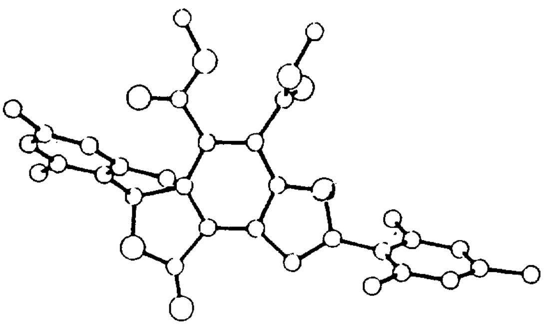


Fig. 1 .X-Ray structure of the Horner-Wittig diester 4.

rationale of the formation of **4** is shown in Scheme 1. Wittig reaction leading to **3** is followed by Michael addition of a further molecule of ylide to the newly formed double bond, and proton transfer, giving **5**. A second Michael addition leads to **6** which eliminates triphenylphosphine with an accompanying 1,2-hydride shift. The product **7** would be expected to dehydrogenate readily to give **4** and this presumably occurs through hydrogen transfer to other components of the reaction mixture or through aerial oxidation.

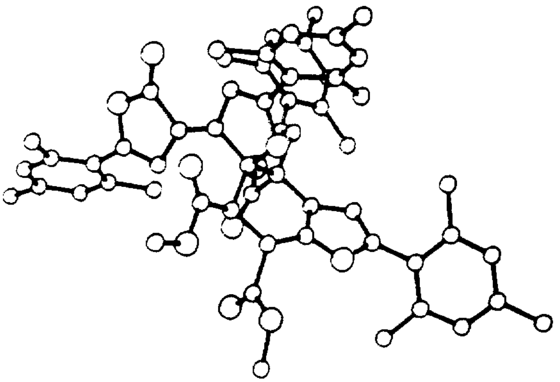
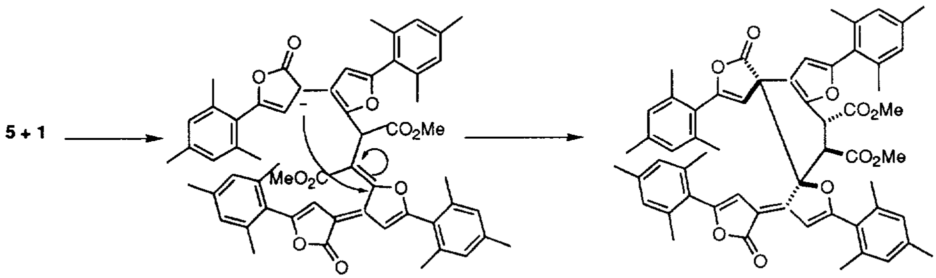


Fig. 2. X-Ray structure of the Horner-Wittig 'dimeric' compound 9.

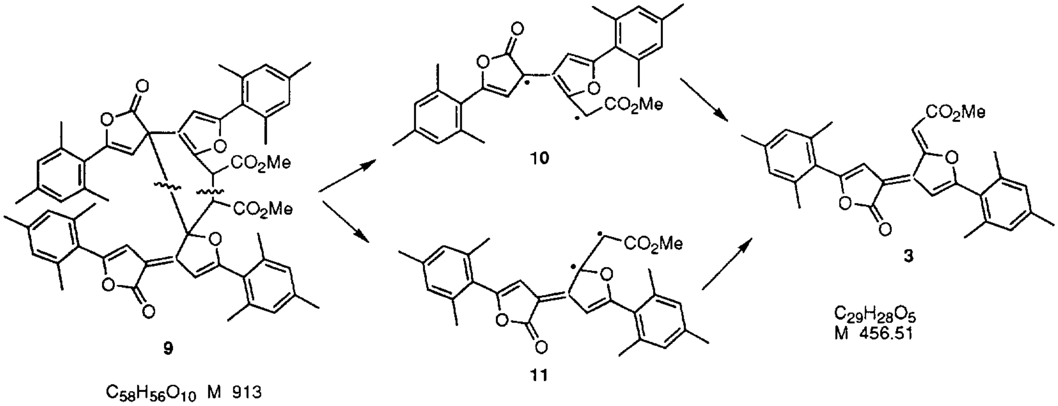


8

9 $C_{58}H_{56}O_{10}$ M 913

Scheme 2. Formation of third Horner - Wittig product from dimesitylBFD

Since the third reaction product, the red compound m.p. 246 - 248°C, formed a suitable crystal for X-ray analysis, this was undertaken forthwith and led to structure **9** (stereochemistry relative), see Fig 2. This showed that the molecular formula was not $C_{29}H_{28}O_5$ as indicated by initial mass spectrometry, but $C_{58}H_{56}O_{10}$. Its presence could be explained as a Diels-Alder product from 2 mols of **3** or by the formation mechanism given in Scheme 2. In this, involvement of the phosphorane intermediate **5** in a Wittig reaction with a



Scheme 3. Mass spectral breakdown of the Horner - Wittig product **9**, m.p. 246 - 248°C.

second mol of dimesitylBFD leads to **8**, shown as the anion which now undergoes an intramolecular Michael addition to give the final product **9**. The mass spectrometric clevage is intelligible as a retro-Diels-Alder reaction, or cleaving as in Scheme 3.[6]

References and Notes:

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3. Klingsberg, E., Chem. Rev., 1954, 54, 59.
4. Rahmani, M. and Crombie, L., Pertanika, 1987, 81.
5. ^{1}H NMR spectroscopy indicates that the compound is not stereochemically homogeneous as there are two methyl ester signals. The (E)-isomer of the unsaturated ester (Z)-**3** appears hindered and atropisomerism is a possibility. The dimesityl BFD molecule is non-planar with the mesityl rings twisted out of plane to the extent of 39^{0} in the blue crystalline form and 56^{0} in the red crystalline form.[2]
6. We thank a Referee for his helpful comments on the formation and breakdown of compound **9**.

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