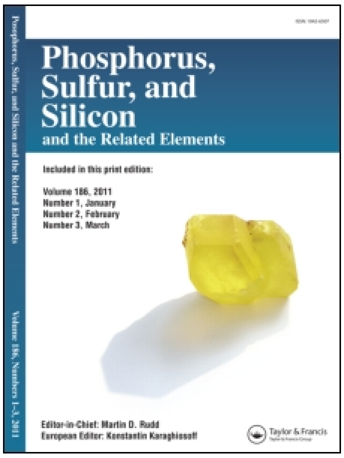

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ORGANOPHOSPHORUS COMPOUNDS, XXX

M. M. Sidky[a]; M. R. Mahran[a]; L. S. Boulos[a]
[a] National Research Centre, Dokki-Cairo, Egypt

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ORGANOPHOSPHORUS COMPOUNDS, XXX

The Reaction of Fluorenylidenetriphenylphosphorane with Maleic, Phthalic and Thiophthalic Anhydrides

M. M. SIDKY, M. R. MAHRAN and L. S. BOULOS

National Research Centre, Dokki-Cairo, Egypt.

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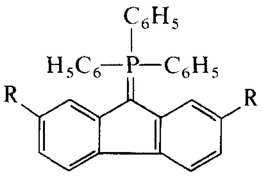
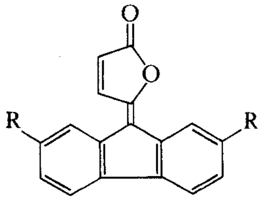
Fluoroenylidenetriphenylphosphorane (**1a**) reacts with maleic and phthalic anhydrides to give lactones **2a** and **3**, respectively. The same reagent (**1a**) extrudes sulphur from thiophthalic anhydride yielding the spiro-1,3-indandione derivative **4**. The infrared and mass spectra of the new products are discussed.

INTRODUCTION

Although fluorenylidenetriphenylphosphorane (FTP, **1a**), a stable[1] phosphinemethylene, has been found unreactive towards the carbonyl group of ketones,[2] it showed remarkable activity towards *o*-, *p*-quinones[3] and cyclic 1,2,3-tricarbonyl compounds.[4] In contribution to our work[5] on the reaction of FTP with carbonyl functions, we have now investigated its behaviour towards a number of cyclic unsaturated anhydrides, namely, maleic, phthalic and thiophthalic anhydrides. These compounds are considered as formal analogues of *p*-benzoquinone as well as 1,4-naphthoquinone.



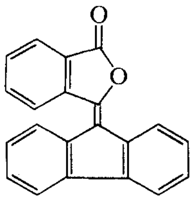
(**1a**) R = H
(**1b**) R = Br



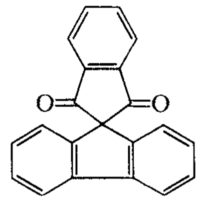
(**2a**) R = H
(**2b**) R = Br

RESULTS AND DISCUSSION

Fluorenylidenetriphenylphosphorane (FTP, **1a**) and its 2,7-dibromo-derivative (**1b**) were found to react with maleic anhydride, in dry benzene, yielding yellow products assigned structures **2a** and **2b**, respectively. Triphenylphosphine oxide (TPPO) was also isolated in each reaction. Elemental and mass spectral analyses for compound **2a**, taken as an example, corresponded to an empirical formula of $C_{17}H_{10}O_2$. Its IR spectrum, in KBr, revealed the presence of two absorption bands at 1785 cm^{-1} and 1765 cm^{-1} for a five-membered lactone-carbonyl having α—C—H grouping.[6] Strong bands at 1630 cm^{-1} (C=C, ethylenic) and at 1235 cm^{-1} (C—O, stretching) were also present in the IR spectrum of **2a**. Phthalic anhydride also reacts with FTP (**1a**) to yield a yellow product assigned the lactone structure **3**. On the other hand, when FTP was allowed to react with thiophthalic anhydride, a colourless product (**4**), devoid of sulphur (elemental analysis), was obtained. Triphenylphosphine sulphide (TPPS), was also isolated from this reaction.



(3)



(4)

Although molecular weight determination for compound **4** agreed with the same empirical formula established for compound **3** ($C_{21}H_{12}O_2$), the physical and spectral properties of both compounds were not identical. Thus, while the IR spectrum of compound **4** exhibited a strong band at 1725 cm^{-1}, characteristic for β-diketones,[7] it lacked the lactone-carbonyl absorption appearing in the spectrum of **3** at 1790 cm^{-1}. Moreover, the strong ethylenic C=C band present in the spectrum of **3** at 1630 cm^{-1} was absent in the IR spectrum of compound **4**. Besides, the mass spectrum of **4** showed a pattern of fragmentation similar to that of 1,3-indandione derivatives[8] and not like that of lactones[9,10] observed in the case of compound **3** (*vide infra*). Based upon these data, the spiro-1,3-indandione structure **4** seems likely to represent the reaction product of FTP (**1a**) with thiophthalic anhydride.

The findings of the present investigation are of particular interest since they represent a novel application of the Wittig reaction by allowing FTP (**1a**) to react with maleic and/or phthalic anhydrides. Moreover, a new method for preparing spiro-1,3-indandiones by extrusion of sulphur from thiophthalic anhydride using a phosphinemethylene, is developed.

MASS SPECTROSCOPY

The mass spectra of compounds **2**–**4** (cf. Chart 1) exhibited prominent ion peaks which would reflect their relative stability upon electron impact. In the case of compounds **2a** and **3**, the spectra revealed ejection of one neutral CO molecule from the parent ion to give ion **a** (m/e 218, 40%) and ion **b** (m/e 268, 72%), respectively. The spectrum of the brominated derivative **2b** revealed the existence of signals due to expulsion of a bromine radical from the molecular ion [M$^+$, m/e 402 (406), 85%] to give ion **c** [m/e 323 (325), 20%] followed by ejection of another Br· to give ion **d** (m/e 244, 12%). Expulsion of CO molecule from cation **c** afforded cation **e** [m/e 295 (297), 92%] while expulsion of CO from ion **d** yielded the radical cation **f** (m/e 216, 10%). This latter ion can also arise from loss of a bromine radical from cation *e*. The spectrum of compound **4** revealed successive loss of 2CO molecules from the prominent M-1 ion (m/e 295, base peak) to give cations at m/e 267 (48%) and m/e 239 (30%), respectively.

EXPERIMENTAL

All melting points are uncorrected. Benzene (thiophene-free) was dried (Na). IR spectra were recorded in KBr with a Perkin-Elmer 137 Infracord. The mass spectra were recoded at 70 eV on Varian MAT 711 Spectrometer and/or Varian MAT 112 equipment. Fragmentation reactions were supported by metastable ions.

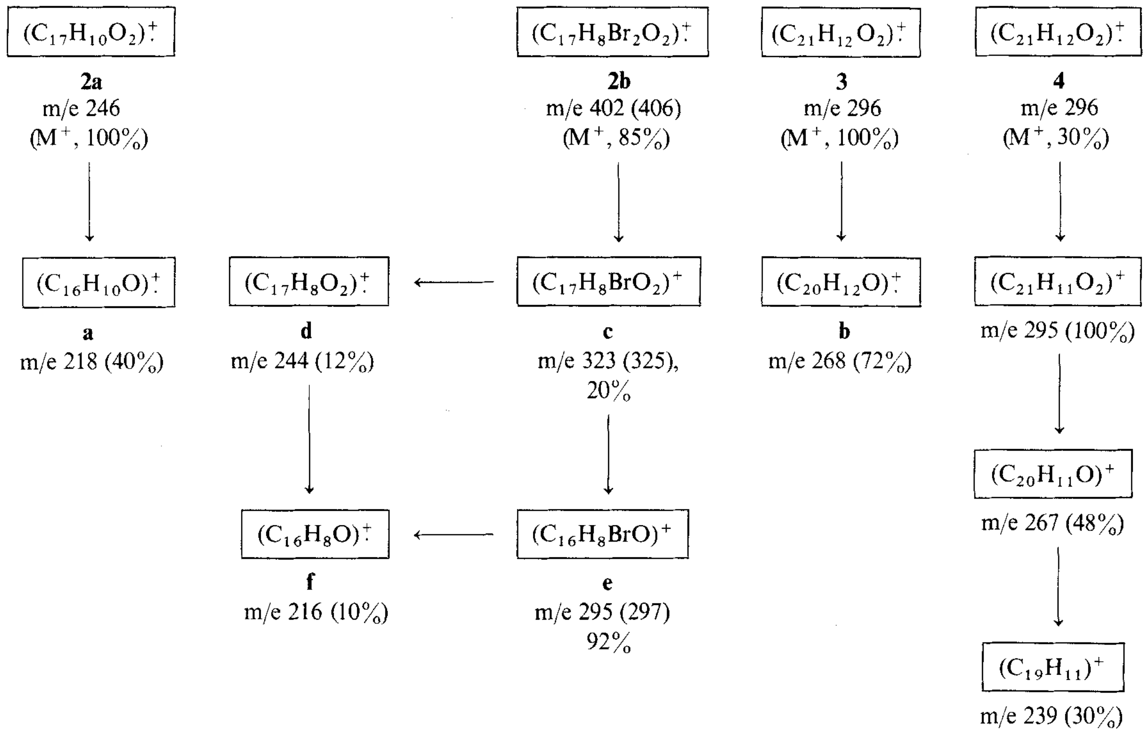


Chart 1

Reaction of Fluorenylidenetriphenylphosphorane (FTP, 1a) with maleic anhydride

To a solution of FTP[11] (**1a**) (0.64 g, 0.0015 mol) in dry benzene (25 ml) was added a solution of maleic anhydride (0.1 g, 0.001 mol) in benzene (25 ml) and the mixture left at ambient temperature for 24 hr. The precipitated material was filtered off, recrystallized from benzene to give compound **2a** as yellow crystals (0.28 g, 75%), mp 175–177° (dec.). Anal. Calcd for $C_{17}H_{10}O_2$: C, 82.95; H, 4.09. Found: C, 82.93; H, 3.97. Benzene was evaporated from the filtrate and the residual substance (0.30 g, 72%) was recrystallized from benzene petroleum ether (b.r. 60–80°) to give colourless needles proved to be triphenylphosphine oxide (TPPO) (mp and mixed mp 152°)[12].

Similarly, the reaction of phthalic anhydride (0.001 mol) with FTP (0.0015 mol) in boiling benzene (50 ml) for 6 hr at room temperature, afforded compound **3** as yellow crystals (75%), mp 203–205 (dec.). Anal. Calcd for $C_{21}H_{12}O_2$: C, 85.13; H, 4.08. Found: C, 85.26; H, 4.31. TPPO (80%) was also separated from the reaction mixture and identified (mp and mixed mp).

Reaction of 2,7-dibromofluorenylidenetriphenylphosphorane (**1b**) *with maleic anhydride*

A solution of compound **1b**[13] (0.9 g, 0.0015 mol) in benzene (25 ml) was added to a solution of maleic anhydride (0.1 g, 0.001 mol) in the same solvent (25 ml) and the mixture left at room temperature for 24 hr. The precipitated material was filtered off (0.45 g, 70%) and recrystallized from chloroform to give compound **2b** as orange crystals, mp 285–287° (dec.). Anal. Calcd for $C_{17}H_8Br_2O_2$: C, 50.53; H, 2.00; Br, 39.55. Found: C, 50. 58; H, 2.19; Br, 39.41. Triphenylphosphine oxide (ca. 85%) was isolated after evaporation of the benzene filtrate till dryness and identified (mp and mixed mp).

The reaction of FTP (**1a**) *with thiophthalic anhydride*

A mixture of FTP (0.0015 mol) and thiophthalic anhydride[14] (0.001 mol) in benzene (30 ml) was refluxed for 6 hr. After cooling, the precipitated material was filtered off, recrystallized from benzene-ethanol mixture to give compound **4** (85%) as colourless needles, mp 178–180° (dec.). Anal. Calcd for $C_{21}H_{12}O_2$: C, 85.13; H, 4.08. Found C, 85.35; H, 4.14. The benzene filtrate was evaporated till dryness and the residual substance was twice crystallized from ethanol to give colourless needles (80%) proved to be triphenylphosphine sulphide (mp and mixed mp 156°).[15]

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