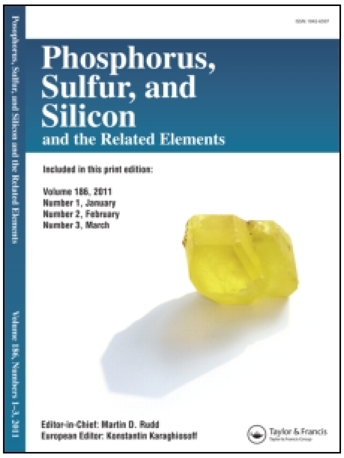

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ORGANOPHOSPHORUS COMPOUNDS

XXVII. The Reaction of Fluorenylidenetriphenylphosphorane and Triphenylphosphine with 2,3-Benzofurandione, Benzo[*b*]thiophene-2,3-dione, and Naphtho[2,1-*b*]furan-1,2-dione

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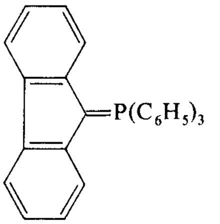
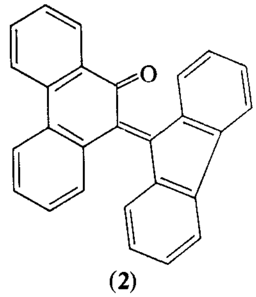
Fluorenylidenetriphenylphosphorane (**1**) reacts with 2,3-benzofurandione (**4a**), benzo[*b*]thiophene-2,3-dione (**4b**), and naphtho[2,1-*b*]furan-1,2-dione (**5**) to give the corresponding fluoren-9-ylidene derivatives (**6a**), (**6b**) and (**7**). Triphenylphosphine effects the deoxygenative dimerization of (**4b**) yielding thioindirubin (**9**), while no reaction has been observed with the furandiones (**4a**) and (**5**) respectively. Structural assignments are based on analytical, chemical, and spectroscopic results.

INTRODUCTION

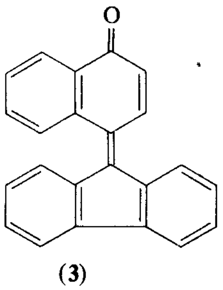
Johnson[1,2] has reported that fluorenylidenetriphenylphosphorane (**1**) reacts with aldehydes but not with ketones other than 2,4,7-trinitro-9-fluorenone. Sullivan and coworkers[3] showed that the reaction of **1** with 9,10-phenanthrenequinone and 1,4-naphthoquinone affords 10-(9-fluorenylidene)-9-phenanthrone (**2**), and 4-(9-fluorenylidene)-1-naphthone (**3**), respectively. Lately, Schönberg *et al.*[4] found that fluorenylidenetriphenylphosphorane (**1**) undergoes the Wittig reaction with a number of cyclic 1,2,3-tricarbonyl compounds to yield the corresponding ethylenes and triphenylphosphine oxide (cf. Scheme A). To obtain more information on the reaction of fluorenylidenetriphenylphosphorane (**1**) with carbonyl functions, we have examined its behaviour towards 2,3-benzofurandione (**4a**), benzo[*b*]thiophene-2,3-dione (**4b**), and naphtho[2,1-*b*]furan-1,2-dione (**5**). These compounds show in their reactions the chemical properties associated with both lactone (thiolactone) and 1,2-diketones.[5]



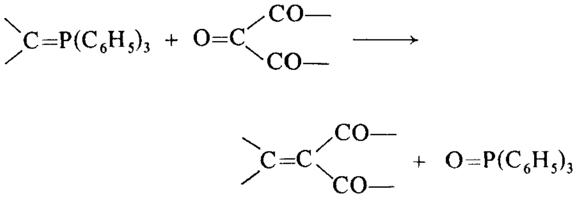
(**1**)



(**2**)

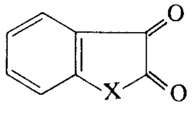


(**3**)

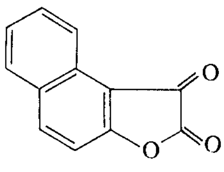


$$>C{=}P(C_6H_5)_3 + O{=}C\begin{matrix}CO-\\CO-\end{matrix} \longrightarrow >C{=}C\begin{matrix}CO-\\CO-\end{matrix} + O{=}P(C_6H_5)_3$$

SCHEME A



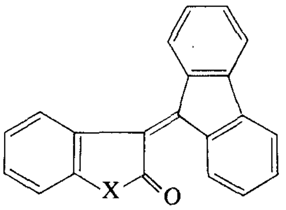
(**4a**) X = O
(**4b**) X = S



(**5**)

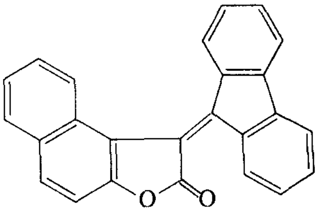
RESULTS AND DISCUSSION

We have found that phosphorane (**1**) reacts with compounds (**4a**), (**4b**), and (**5**), in dry benzene, to give coloured crystalline substances. Based on the following considerations, we assign structures (**6a**), (**6b**), and (**7**), respectively, for these Wittig-reaction products. 1-Fluoren-9-ylidenenaphtho[2,1-*b*]furan-2(1*H*)-one (**7**), taken as example, is an orange-yellow crystalline substance, which elemental and mass spectroscopic analyses confirmed to be $C_{25}H_{14}O_2$. Its ir spectrum showed an absorption band at 1800 cm^{-1} (lactone),[6] while the strong $>C=O$ absorption band at 1715 cm^{-1} (five ring-ketone) recorded for the parent compound (**5**) was absent in the spectrum of (**7**). Similarly, the orange-red 3-fluoren-9-ylidenbenzo[*b*]thiophen-2(3*H*)-one (**6b**), had the molecular formula $C_{21}H_{12}OS$; mass spectral data confirmed the elemental composition. The ir spectrum of (**6b**) showed the presence of an absorption at 1700 cm^{-1}, attributed to the thiolactone grouping.[7] Further evidence for the formation of (**6b**) was obtained by allowing thiofluorenone to react with 2-oxo-diazo-dihydrothionaphthene (**8**), followed by treatment with copper bronze. The orange-red crystalline compound, thus formed, proved to be identical with (**6b**) (mp, mixed, mp, and comparative ir spectra). From the above results, it can be seen that fluorenylidenetriphenylphosphorane (**1**) undergoes the Wittig reaction[8] with the diones of the present study, thus establishing a potential method of introducing a new disubstituted carbon into the C_9-position of fluorene. Meanwhile, this reaction adds a further example to what is already known about the reactivity of the C-3 (C-1) carbonyl group in compounds (**4**) and (**5**) towards diazoalkanes,[9] diaryldiazoalkanes[10,11] and active hydrogen-containing compounds.[12–14]

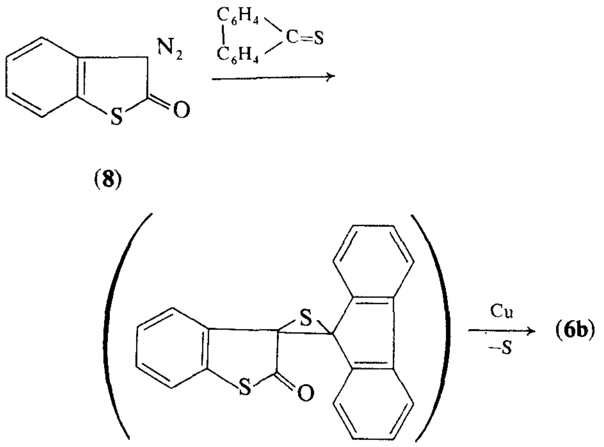


(**6a**) X = O, Yellow

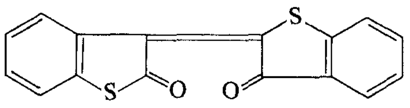
(**6b**) X = S, Orange-red



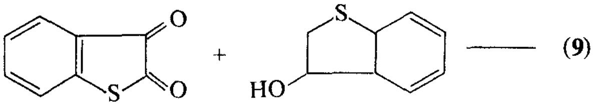
(**7**) Orange-yellow



It appeared of interest, also, to extend this study to include the behaviour of compounds (**4a**), (**4b**), and (**5**) towards triphenylphosphine. Whereas the furandiones (**4a**) and (**5**) were found to be stable towards the action of triphenylphosphine, in boiling benzene, benzo[*b*]thiophene-2,3-dione (**4b**) has been converted into [$\Delta^{2,3'}$ (2'*H*, 3*H*)-bibenzo[*b*]thiophene]-2',3-dione (**9**), almost quantitatively, under similar reaction conditions. The identity of **9** was established by comparison of its properties (mp, mixed mp and ir) with an authentic sample of thioindirubin[15] prepared by the condensation of benzo[*b*]thiophene-2,3-dione (**4b**) and 3-hydroxythionaphthene (**10**). The significance of this finding is not only the



(**9**)



(**4b**) (**10**)

discovery of a new pattern for deoxygenative dimerization of benzo[*b*]thiophene2,3-dione (**4b**) by TPP but also the establishment of a novel method for preparing the known indigo-type dye; thioindirubin (**9**).

EXPERIMENTAL

All melting points are uncorrected. Benzene (thiophene-free) was dried (Na). Reactions were conducted under prepurified dry nitrogen. Microanalyses were performed by Beller, microanalytisches Laboratorium, 34 Göttingen, Germany, and the laboratory of microanalysis, National Research Centre. Ir spectra were recorded in KBr discs, with a Perkin-Elmer 137 Spectrophotometer, and mass spectra were determined on a Varian MAT 711.

3-Fluoren-9-ylidene-2(3H)-benzofuranone (**6a**)

Fluorenylidenetriphenylphosphorane (**1**)[16] (0.86 g, 0.002 mol) was added to a suspension of 2,3-benzofurandione (**4a**)[10] (0.15 g, 0.001 mol) in benzene (25 ml). The reaction mixture was left at room temperature under stirring (magnetic) for 48 hr. After filtration, the solid material (0.26 g; 88%) was crystallized from benzene to give (**6a**) as yellow crystals, mp 170–172°. Ir (1765 cm^{-1}, lactone). Anal. Calcd for $C_{21}H_{12}O_2$: C, 85.12; H, 4.08. Found: C, 85.38; H, 4.32. The filtrate gave, upon evaporation, triphenylphosphine oxide (mp, and mixed mp 152°).[17]

3-Fluoren-9-ylidenebenzo[b]thiophen-2(3H)-one (**6b**)

A mixture of 1 (0.86 g, 0.002 mol), and benzo[*b*]thiophene-2,3-dione (**4b**)[18] (0.16 g, 0.001 mol) in benzene (25 ml) was allowed to stir at room temperature for 24 hr. The crystals that separated (0.28 g, 90%) were recrystallized from benzene to give (**6b**) as orange red crystals, mp 202–204°. Anal. Calcd for $C_{21}H_{12}OS$: C, 80.76; H, 3.87; S, 10.25. Found: C, 80.44; H, 3.80; S, 10.56. Triphenylphosphine oxide (0.24 g, 85%) was isolated after evaporation of the benzene filtrate till dryness and identified (mp, and mixed mp).

Reaction of 2-Oxo-3-diazo-dihydrothionaphthene (**8**) *with thiofluorenone*

A mixture of diazo compound (**8**)[19] (1.8 g, 0.01 mol) and thiofluorenone[20] (1.96 g, 0.01 mol) in petroleum ether (50 ml, bp 100–140°) was refluxed for 4 hr. Copper bronze (2 g) was added and refluxing continued for 2 hr further, whereby, the yellow colour of the reaction mixture turned red. The mixture was filtered while hot and the solvent was removed under reduced pressure. The residue that left (2.2 g, 70%) was crystallized from benzene to give orange red crystals proved to be (**6b**) (mp, mixed mp and comparative ir spectra).

1-Fluoren-9-ylidenenaphtho[2,1-b]furan-2(1H)-one (**7**)

Phosphorane (**1**) (0.86 g, 0.002 mol) was allowed to react with naphtho[2,1-*b*]furan-1,2-dione (**5**)[21] in benzene (25 ml) at room temperature for 24 hr. The substance that separated after cooling was collected (0.29 g, 85%) and recrystallized from benzene to give **7** as orange-yellow crystals, mp 250–252°. Anal. Calcd for $C_{25}H_{14}O_2$: C, 86.69; H, 4.07. Found: C, 86.50; H, 4.12. Triphenylphosphine oxide was also isolated from the filtrate, and identified (mp and mixed mp).

Action of triphenylphosphine on benzo[b]thiophene-2,3-dione (**4b**)

A mixture of triphenylphosphine[22] (0.52 g, 0.002 mol) and compound (**4b**) (0.16 g, 0.001 mol) in benzene (25 ml) was refluxed for 6 hr, whereby the yellow colour of the solution turned deep red. After concentration and cooling, the substance that separated was collected (0.27 g, 92%) and recrystallized from benzene to give (**9**) as deep red crystals, mp 205°. Ir (1700 cm^{-1} thiolactone, 1666 cm^{-1} 5-ring ketone). Anal. Calcd for $C_{16}H_8S_2O_2$: C, 64.86; H, 2.72; S, 21.62. Found: C, 64.5; H, 2.81; S, 21.98. Compound 9 was found identical (mp, mixed mp and ir spectra) with authentic thioindirubin (**9**) prepared according to Friedländer.[15]

Triphenylphosphine oxide (0.24 g, 85%) was isolated from the above benzene filtrate and identified.

Attempted reaction of triphenylphosphine with 2,3-benzofurandione (*4a*) *and naphtho[2,1-b]furan-1,2-dione* (**5**)

A mixture of triphenylphosphine (1.3 g) and 2,3 benzofurandione (**4a**) (0.75 g) in benzene (25 ml) was boiled under reflux for 12 hr. After cooling, the resulting precipitate (0.65 g) was collected and proved to be unchanged 2,3-benzofurandione by mp and mixed mp. From the filtrate, triphenylphosphine was recovered (mp, and mixed mp) in an almost quantitative yield.

Under similar reaction conditions, naphtho[2,1-*b*]furan-1,2-dione (*5*) was recovered almost quantitatively when allowed to react with triphenylphosphine.

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