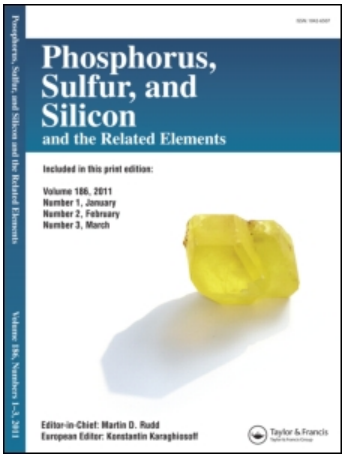

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THE REACTION OF PHOSPHONIUM YLIDES WITH 1,2-BENZO[a]PHENAZINE-8,9-DIONE, NAPHTHO[2,1-b]FURAN-1,2-DIONE, BENZO[b]THIOPHENE-2,3-DIONE AND 1,2,3-INDANTRIONE

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Dedicated to Professor Dr. Hans Jürgen Bestmann on the occasion of his 61st birthday

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When 1,2-benzo[a]phenazine-8,9-dione (**1**), was reacted with two molar amounts of phosphonium ylides (**5**), the corresponding dialkyl 1,2-dihydrobenzo[a]furo[3,2,*h*]phenazine-1,2-dicarboxylates (**9**) were obtained. Moreover, naphtho[2,1-b]furan-1,2-dione (**2**) and benzo[b]thiophene-2,3-dione (**3**) were converted by reaction with ylides (**5**) into alkyl 2-oxonaphtho[2,1-b]furan-1(2H)-ylidene acetate (10) and alkyl (2-oxobenzo[b]thien-3(2H)-ylidene)acetate (**11**). On the other hand, the spiro-compounds (**13**) were isolated from the reaction of 1,2,3-indantrione (**4**) and Wittig reagents (**5**). The structure of the new compounds **9**, **10**, **11** and **13** was confirmed on the basis of elemental analysis and spectral studies.

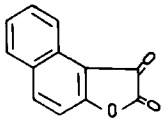
INTRODUCTION

The reaction of phosphonium ylides with certain dicarbonyl compounds is of proved synthetic utility.[1] Being stabilized carbanions, these ylides can react with electrophilic reagents to give rise to the formation of new C—C bonds.[2] Therefore, it was of interest to investigate the reaction of these ylides with some heterocyclic *o*-quinones, namely, 1,2-benzo[a]phenazine-8,9-dione (**1**), naphtho[2,1-b]furan-1,2-dione (**2**), benzo[b]thiophene-2,3-dione (**3**) and to compare their reactivities against these reagents. Moreover, the reaction of these ylides with 1,2,3-indantrione (**4**) was also studied.

RESULTS AND DISCUSSIONS

When benzophenazine-dione **1** was treated with one equivalent of methoxy- (**5a**) and/or ethoxycarbonylmethylenetriphenylphosphorane (**5b**) in THF at room temperature for three hours, dimethyl- (**9a**) and/or diethyl 1,2-dihydrobenzo[a]furo[3,2,h]phenazine-1,2-dicarboxylate (**9b**), triphenylphosphine oxide, triphenylphosphine and some unchanged benzophenazinedione (**1**) were isolated. Carrying out the reaction using two moles of the phosphonium ylide instead of one, lead to the formation of the reddish brown difuran derivatives **9a** and **9b** in

good yields. The structure of the new compounds **9a** and **9b** is assignable from their analyses, IR, ^{1}H NMR and mass spectral data. The IR spectrum of **9a**, taken as an example, shows bands at 1740 cm^{-1} (C=O, ester), 1620 cm^{-1} (C=N), 1600 cm^{-1} (C=C) and at 1225 cm^{-1} (C—O, stretching). In the ^{1}H NMR of **9a** signals at δ 3.82 (3H, $COOCH_3$, s), δ3.84 (3H, $COOCH_3$, s) and δ 7.06–8.8 ppm (8H, aromatics, m), are appeared. Protons of the dihydrofuran nucleus appeared as two doublets (each with J HH = 4 Hz) at δ 4.77 (one H, proton b) and δ 5.82 (one H, proton a). Moreover, the mass spectrum of **9a** shows the ion peaks at m/e 388 (M^+, 42%) and m/e 329 ($M^+ - COOCH_3$, base peak).



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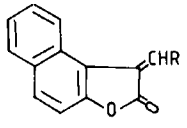
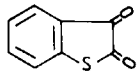


10a, R = C(O)OCH$_3$
b, R = C(O)OC$_2$H$_5$

The reaction of naphtho[2,1-b]furan-1,2-dione (**2**), with alkoxycarbonylmethylenetriphenylphosphorane (**5**) was also investigated. When **2** was allowed to react with **5a** and/or **5b** in THF at ambient temperature, methyl (**10a**) and/or ethyl 2-oxonaphtho[2,1-b]furan-1(2H)-ylidene) acetate (**10b**) accompanied with triphenylphosphine oxide were obtained respectively in good yields. Under similar conditions, however, compounds **10a** and **10b** were obtained even when two equivalents of the phosphoranes **5** were used. On the basis of IR, ^{1}H-, ^{13}C NMR, MS and elemental analyses, the structure of compounds **10** were deduced. In the ^{1}H NMR spectrum of **10a**, signals appeared at δ 3.90 ppm (3H, CH_3, s), δ 6.25 ppm (one H, =CH—, s) and δ 8.17 ppm (6H, aromatics, m). Moreover, there is no absorption in ^{13}C NMR spectrum for a ketocarbonyl-function in **10a**, which appeared in the starting material **2** at 190.167 ppm.[3] In the MS of **10a** the m/e = 254 (M^+). On the other hand, the IR spectrum of **10a** showed bands at 1670 cm^{-1} (C=O, lactone)[4], 1710 cm^{-1} (C=O, ester) and 1620 (C=C).



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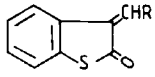
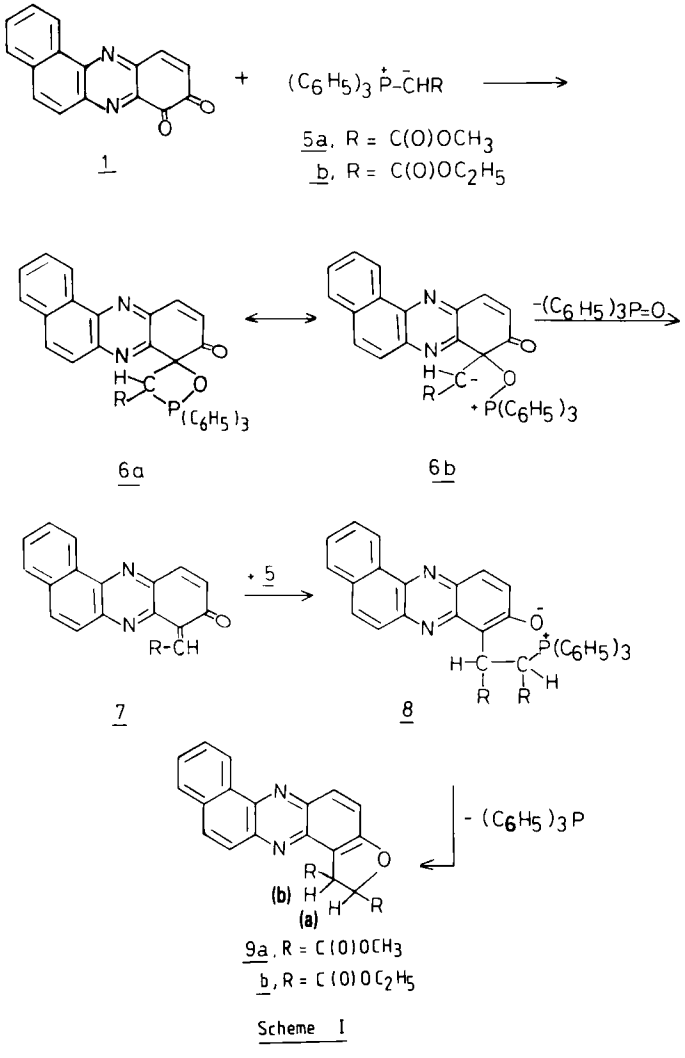


11a, R = C(O)OCH$_3$
b, R = C(O)OC$_2$H$_5$

When the ylides **5** were also allowed to react with benzo[*b*]thiophene-2,3-dione (**3**), the Wittig reaction occurred readily at ambient temperature to give methyl (**11a**) and ethyl (2-oxobenzo[*b*]thiene-3(2H)ylidene) acetate (**11b**) respectively. The structure of the α,β-unsaturated ketone **11a** was assignable from spectral and elemental analysis data. Its ^{1}H NMR absorption at δ 3.82 ppm (3H, CH_3, s); δ 7.03 ppm (1H, CH, s); δ 7.5 ppm (4H, aromatics, m). In the MS of **11a** the m/e = 220 (M^+) and its signal carbonyl-ester peak at 1680 cm^{-1}.

It could be demonstrated that the formation of the dihydrofuran derivatives **9**,

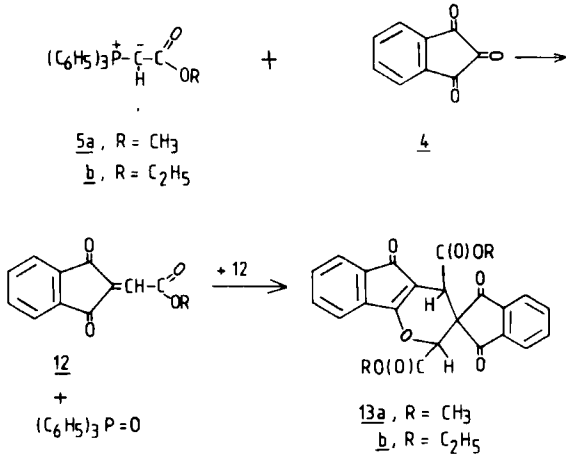
from the reaction of phosphorus ylides **5** and the benzophenazinequinone **1**, can be explained by the initial nucleophilic attack by the carbanion centre in the ylide on the reactive lactam carbonyl-carbon[5] to give the oxaphosphetane **6a**. The original ylide C—P bond of **6a** is then cleaved to give the betain **6b**. Triphenylphosphine oxide is eliminated with the formation of alkyl (9-oxobenzo[*a*]phenazine-8(9H)-ylidene) acetate (**7**). The olefinic compound **7** adds a second mole of the ylide **5**, by Michaelis addition to give dimethyl 8,9-dihydro-9-β-(triphenylphosphoranylidene)benzo[a]phenazine-8-succinate (**8**), which is followed by O-alkylation with expulsion of triphenyl phosphine to give the final product **9** (Scheme I). On the other hand, reaction of ylides **5**, thus occur with the α-diketones **2** and **3**, at the carbonyl group rather than the lactone,[6] affording the stable olefinic compounds **10** and **11**, even we use two moles of the ylide.



Scheme I

We now report also on the reaction of phosphonium ylides **5**, with 1,2,3-indantrione (**4**). Reaction of equimolecular amounts of the ylide **5** and the red trione **4** in dry THF at room temperature afforded colours crystals of 2′, 4′-dihydroxyspiro[indan-2,3′(2′H)-indeno[1,2-b]pyran]-1,3,5′(4′H)-trione diacetate (**13a**) and/or dipropionate (**13b**). The structure of the new spiro-compounds **13** was established from their elemental analyses and spectral properties which are consistent with expectation. The ^{1}H NMR spectrum of **13a**, shows two singlets for the two OCH_3 groups at δ 3.35 and 3.90 ppm. Moreover, two singlets appear at δ 4.60 and 5.24 ppm which are contributed to the two hydrogens of the dihydroaromatic ring, and the eight aromatic protons are found at δ 7.37–8.50 ppm. In the mass spectrum the M^+ appears at 432.

On the basis of the above observations and data, the spiro-compound **13** apparently arise by Wittig reaction of the trione **4** and ylide **5**, to the reactive intermediate **12**, with expulsion of triphenylphosphine oxide. Dimerization of **12** by Diels–Alder type, afforded the final product **13** (Scheme II). Formation of six-membered dihydroaromatic ring from 1,2,3-indantrione is a new reaction of phosphoranes.



Scheme II

EXPERIMENTAL

All melting points are uncorrected. THF was peroxide-free and absolutely dry. All reactions were carried out under N_2 atmosphere. The IR spectra were measured in KBr, on a Carl Zeiss Infracord Spectrometer Model UR 10. The ^{1}H NMR spectra were run in $CDCl_3$, at 90 MHz on a varian Spectrometer using TMS as an internal reference. ^{13}C NMR were performed on Spectrometer JNM-PS Jeol Tokio, in $CDCl_3$. MS were carried at 70 eV on Karatos equipment provided with data system.

Dimethyl 1,2-dihydrobenzo[a]furo[3,2-h]phenazine-1,2-dicarboxylate (**9a**). To a solution of methoxycarbonylmethylenetriphenylphosphorane (**5a**)[7] (3,34 g, 0.01 mole) in 20 ml tetrahydrofuran, was added drop by drop with stirring at room temperature, a solution of 1,2-benzo[a]phenazine-8,9-dione (**1**)[8] (1.22 g, 0.005 mole) in 15 ml THF. The reaction mixture was left for three hours during which the colour was changed from yellow to red. After THF was distilled under reduced pressure, the residue that left behind was dissolved in 20 ml chloroform, followed by 20 ml *n*-hexane and left overnight in the refrigerator. The precipitate that formed was filtered off and crystallized from

benzene/pet. ether (b.p. 40–60) to give dimethyl 1,2-dihydrobenzo[a]furo[3,2-h]phenazine-1,2-dicarboxylate (**9a**), as reddish brown crystals, m.p. 230°C (1.7 g, 87%). Calcd. for $C_{22}H_{16}N_2O_5$: C, 68.04; H, 4.12; N, 7.21. Found: C, 68.14; H, 4.17; N, 7.9.

The chloroform/*n*-hexane filtrate, was chromatographed on alumina, affording triphenylphosphine as colourless crystals m.p. and mixed m.p. 80°C (0.91 g, 70%), and colourless crystals of triphenylphosphine oxide, m.p. and mixed m.p. 151°C[9] (0.97 g, 69%).

When the reaction was performed using equimolar amounts from the ylide **5a** and the *o*-quinone **1**; the dihydrofuran **9a**, triphenylphosphine oxide and triphenylphosphine were obtained together with some unchanged quinone **1**.

In a similar manner, diethyl 1,2-dihydrobenzo[a]furo[3,2,h]phenazine-1,2-dicarboxylate (**9b**) was obtained from the reaction of ethoxycarbonylmethylenetriphenylphosphorane (**5b**)[7] (3.48 g, 0.01 mole) and benzophenazine-quinone **1** (1.22 g, 0.005 mole) as reddish brown crystals, m.p. 195°C, from benzene/pet. ether (1.76 g, 85%). Calcd. for $C_{24}H_{20}N_2O_5$: C, 69.23; H, 4.80; N, 6.73. Found: C, 69.05; H, 4.69; N, 6.65. IR cm^{-1}: 1740 (C=O, ester); 1620 (C=N); 1600 (C=C). ^1H NMR δ 1.30 (3H, CH_3, t); 1.40 (3H, CH_3, t); 4.30 (2H, CH_2, q); 4.40 (2H, CH_2, q); 4.70 (1H, C—H, d); 5.80 (1H, C—H, d, J HH = 4 Hz); 7.92 (8H, aromatics, m). m/e = 416 (M^+).

Methyl *2*-oxonaphtho[*2,1*-b]furan-*1*(*2*H)-ylidene) acetate (**10a**). To a solution of the ylide **5a** (3.34 g, 0.01 mole) in 20 ml THF, was added drop by drop at room temperature, a solution of naphtho[2,1-b]furan-1,2-dione (**2**)[10] (1.98 g, 0.01 mole) in 30 ml THF. The reaction mixture was stirred for one hour, during which yellow crystals appeared. Filtration gave **10a**, m.p. 208°C, from benzene (2.33 g, 92%). Calcd. for $C_{15}H_{10}O_4$: C, 70.86; H, 3.93; Found: C, 70.58; H, 3.85.

Even when two equivalents of the ylide **5a** were used under severe reaction conditions, **5a** reacted with only one carbonyl group in the α-diketone **2**, to form **10a**.

The THF filtrate afforded upon concentration and dilution with pet. ether (40–60°C), triphenylphosphine oxide, m.p. and mixed m.p. 151°C (2.2 g, 80%).

Ethyl 2-oxonaphtho[2,1-b]furan-1(2H)-ylidene) acetate (**10b**), was isolated from the reaction of the ylide **5b** (2.68 g, 0.01 mole) and the α-diketone **2** (1.98 g, 0.01 mole), as yellow crystals, m.p. 135°C (2.4 g, 90%). Calcd. for $C_{16}H_{12}O_4$: C, 71.64; H, 4.47. Found: C, 71.58; H, 4.45. IR cm^{-1}: 1705 (C=O, ester); 1670 (C=O, lactone); 1630 (C=C). ^1H NMR δ: 1.40 (3H, CH_3, t); 4.40 (2H, CH_2, q), 6.25 (1H, C—H, s); 8.05 (6H, aromatics, m). m/e = 268 (M^+).

Methyl (2-oxobenzo[b]thiene-3(2H)ylidene) acetate (**11a**). A solution of benzo[b]thiophene-2,3-dione (**3**)[11] (1.64 g, 0.01 mole) in 20 ml THF, was added dropwise under stirring to a solution of the ylide **5a** (3.34 g, 0.01 mole) in 20 ml THF. The reaction mixture was kept at room temperature for three hours during which the colour changed to orange. After the solvent was distilled off, the residue that left behind, was triturated with benzene and the orange precipitate was crystallized from benzene to give **11a** as orange crystals, m.p. 160°C (2 g, 91%). Calcd. for $C_{11}H_8O_3S$: C, 60.00; H, 3.63; S, 14.54. Found: C, 60.16; H, 3.65; S, 14.39.

The benzene filtrate afforded triphenylphosphine oxide m.p. and mixed m.p. upon adding *n*-hexane.

Ethyl (2-oxobenzo[b]thiene-3(2H)ylidene acetate (**11b**). This compound was obtained in 88% yield, as orange crystals, m.p. 118°C. Calcd. for: C, 61.53; H, 4.27; S, 13.67. Found: C, 61.40; H, 4.25; S, 13.46. ^1H NMR δ 1.33 (3H, CH_3, t); 4.30 (2H, CH_2, q); 7.03 (1H, C—H, s); 7.5 (4H, aromatics, m). m/e = 234 (M^+).

2',4'-Dihydroxyspiro[indan-2,3'(2'H)-indeno[1,2-b]pyran]-1,3,5'(4'H)-trione diacetate (**13a**). To a cooled suspension of the red 1,2,3-indantrione (**4**)[12] (1.6 g, 0.01 mole) in THF (20 ml) was added dropwise with stirring, a solution of the ylide **5a** (3.34 g, 0.01 mole) in THF (20 ml). The reaction mixture was kept at room temperature for three hours. The colourless product, so obtained, was filtered off and crystallized from THF/benzene to the spiro-compound **13a**, m.p. 189°C (1.95 g, 90.2%). Calcd. for $C_{24}H_{16}O_8$: C, 66.66; H, 3.70. Found: C, 66.42; H, 3.72.

The THF filtrate, afforded upon concentration and addition of *n*-hexane, a colourless precipitate. Recrystallization from benzene/*n*-hexane gave triphenylphosphine oxide m.p. and mixed m.p. 151°C (2.5 g, 90%).

In a similar manner, 2',4'-dihydroxyspiro[indan-2,3'(2'H)-indeno[1,2-b]pyran]-1,3,5'(4'H)-trione dipropionate (**13b**), was obtained by the action of ylide **5b** (3.48 g, 0.01 mole) on the red trione **4** (1.6 g, 0.01 mole). It was crystallized from THF/*n*-hexane as colourless crystals, m.p. 184°C (3.79 g, 82.6%). Calcd. for: $C_{26}H_{20}O_8$: C, 67.82; H, 4.34. Found: C, 67.85; H, 4.33. ^1H NMR δ: 1.30 (3H, CH_3, t); 1.40 (3H, CH_3, t); 4.35 (2H, CH_2, q); 4.40 (2H, CH_2, q); 4.22 (1H, C—H, s); 4.93 (1H, C—H, s); 8.00 (8H, aromatics, m). In the MS of **13b** the m/e = 460 (M^+).

REFERENCES

1. H. J. Bestmann and H. J. Lang, *Tetrahedron Letters,* **25,** 2101 (1969).
2. J. I. G. Cadogan, "Organophosphorus Reagents in Organic Synthesis", Academic Press (London), 1979; H. J. Bestmann, R. Zimmermann, "Organic Phosphorus Compounds", Vol. 3, G. M. Kosolapoff, L. Maier, Ed., John Wiley and Sons, Inc., New York, N.Y. 1972; A. Wm. Johnson, "Ylide Chemistry in Organic Chemistry. A series of Monographs", Ed., A. T. Blomquist, Academic Press (London) 1966.
3. H. Günther, *Chemie im unserer Zeit,* **8,** 84 (1974).
4. K. Heusler, J. Kebrle, G. Meystre, H. Ueberwasser, P. Wieland, G. Anner and A. Wettstein, *Helv. Chim. Acta,* **42,** 2043 (1959).
5. A. Mustafa, M. M. Sidky and F. M. Soliman, Tetrahedron **23,** 107 (1967); A. Schönberg, A. Mustafa and S. M. A. D. Zayed, *J. Am. Chem. Soc.,* **75,** 4302 (1953).
6. M. M. Sidky, W. M. Abdou, A. A. El-Kateb, F. H. Osman and N. M. Abd-El-Rahman, *Egypt J. Chem.,* **27,** 817 (1984); A. Mustafa, M. M. Sidky and F. M. Soliman, *Tetrahedron* **22,** 393 (1966).
7. For the preparation of compounds **5,** cf. H. J. Bestmann and O. Kratzer, *Chem. Ber.,* **95,** 1894 (1962).
8. For the preparation of **1,** cf. O. Fischer, *Chem. Ber.,* **36,** 3622 (1903).
9. A. Michaelis and L. Gleichmann, *Chem. Ber.,* **15,** 801 (1882).
10. For the preparation of **2,** cf. K. Fries and R. Frellstedt, *Chem. Ber.,* **54,** 719 (1921).
11. For the preparation of **3,** cf. F. Koeniger, *Chem. Ber.,* **41,** 235 (1908).
12. For the preparation of **4,** cf. A. Schönberg and R. Moubacher, *J. Chem. Soc.,* **71** (1943).