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REACTIONS WITH ORGANOPHOSPHORUS COMPOUNDS—IV

REACTION OF DI-, AND TRIALKYL PHOSPHITES WITH 1,2-BENZOPHENAZINE-3,4-QUINONE

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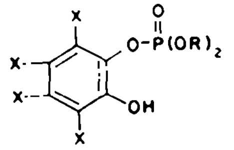
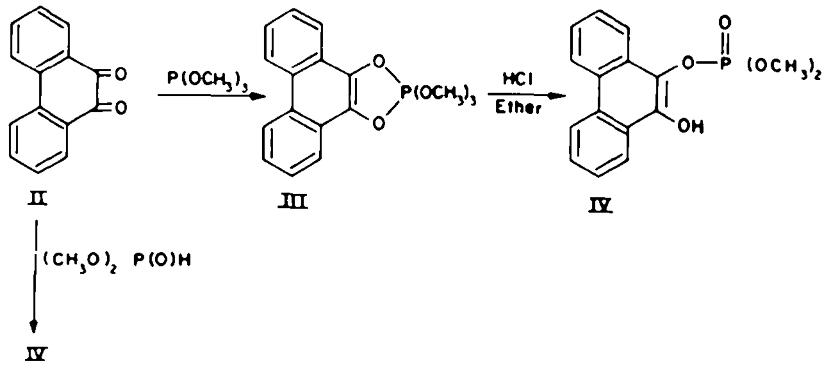
Abstract—Phenanthraquinone (II) reacts with dimethyl phosphite to give the corresponding *o*-quinol-monophosphate (IV). The action of dialkyl phosphites on 1,2-benzophenazine-3,4-quinone (V) in benzene solution has been investigated, and the colourless 1:1-adducts, formed on the cold, believed to have structure similar to IX or X. In boiling benzene, a mixture of yellow 1:1-adducts (VIf–h) and red-violet 1:1-adducts (VIIc–e) is obtained. Trimethyl phosphite as well as *o,o*-dimethyl hydrogen phosphorodithioate $(CH_3O)_2P(S)SH$ effects the reduction of the quinone (V) to 3,4-dihydroxy-1,2-benzophenazine (VIa). The IR spectra of the adducts are recorded.

DIEFENBACH[1] has reported the formation of hydroxyaryl phosphates (I) when dialkyl phosphites react with symmetrical halogenated *o*-quinones. In extension of our studies[2] on the behaviour of α-dicarbonyl compounds towards the action of di-, and trialkyl phosphites, we would like to report our results. When phenanthraquinone (II) was reacted with dimethyl phosphite, IV was formed and its identity with that, obtained by Ramirez *et al.*[3] via III (cf. Scheme A), has been confirmed.[4] We now have also



I, X = Halogen, R = Alkyl



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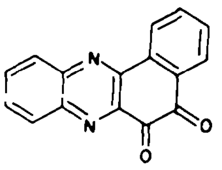
[1] E. Diefenbach, Ger. Pat. 937,956 (1956).

[2] A. Mustafa, M. M. Sidky and F. M. Soliman, *Tetrahedron* **22**, 393 (1966).

[3] F. Ramirez and N. B. Desai, *J. Amer. Chem. Soc.* **82**, 2652 (1960).



V

reacted the yellow 1,2-benzophenazine-3,4-quinone (V) with dialkyl phosphites, namely, dimethyl, diethyl, diisopropyl phosphite, and have found that addition takes place in molecular proportions. When the reaction was carried out in dry benzene, at room temp for 48 hr, colourless 1:1-adducts designated as "A" were isolated. On the other hand, when the reaction mixture in dry benzene was refluxed for 12 hr, a mixture of yellow 1:1-adducts "B" and red-violet 1:1-adducts "C" was obtained. Refluxing of the benzene solution of either A or B effected their conversion to C.

The reaction of dimethyl phosphite with 1,2-benzophenazine-3,4-quinone (V) in benzene has been found to be catalysed by the action of sunlight and the red-violet adduct C was isolated. The colourless adduct A was also formed, but in minor quantities. 1,2-Benzophenazine-3,4-quinone (V) is known to give a violet photo-addition product (VIIb) with benzaldehyde.[4] The reactions between dialkyl phosphites and the quinone (V) are regarded as radical chain processes.[5] It seems likely that the photochemical effect is due to the excitation of V to its diradical (or triplet state). The photo-dissociation $(RO)_2P(O)H \rightarrow (RO)_2\dot{P}(O) + \dot{H}$ cannot provide the required radicals.[6]

Badger *et al.*[7] have shown that the substance, formerly believed to be present in the lactim form (VIa), obtained from the quinone (V) by the action of phenyl hydrazine, is in reality the lactam modification (VIIa) which explains its blue-violet colour. Lactam–lactim tautomerism has been confirmed with the photo-addition product (VId) and the blue-violet colour of this substance in the solid state probably indicates that the compound exists in the lactam form (VIIb).[4]

In analogy with the violet compounds (VIIa) and (VIIb), the red-violet quinone–phosphite adducts C are assigned structure similar to VIIc–e. These adducts are soluble in alkali and react in their lactim form with ethereal diazomethane to give, e.g. the yellow methylated product (VIi) (*vide infra*). Consequently, the red-violet colour of the quinone–phosphite adducts in the solid state is in favour of the proposed lactam structure (cf. VIIc–e); (cf. also the violet photo-adduct VIIb).[4] The alternative lactam structure (VIIIa–c) for (VIIc–e) is probably unimportant, at least under the conditions studied, for it involves an unstable 2,3-naphthaquinone type of bond structure.[7]

The IR spectrum of VIIe, taken as an example, in KBr shows bands at 3100 cm^{-}; (N—H band); 1730 cm^{-1} and 1680 cm^{-1} (C=O group); 1590 cm^{-1} (aromatic band)[1] 1248 cm^{-1} ($\geqslant P \rightarrow O$) and 990 cm^{-1} which appears to be of P-O-C (isopropyl). The solubility of the adduct in $CDCl_3$ is too small to obtain satisfactory NMR spectrum. In favour of the proposed structure, the red-violet quinone-dimethyl phosphite

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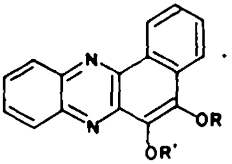
[4] A. Schönberg, A. Mustafa and S. M. A. D. Zayed, *J. Amer. Chem. Soc.* 75, 4302 (1953).

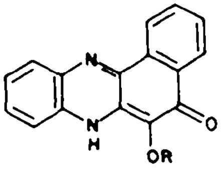
[5] R. F. Moore and W. A. Waters, *J. Chem. Soc.* 238 (1953).

[6] F. Ramirez and S. Dershowitz, *J. Org. Chem.* 22, 1282 (1957).

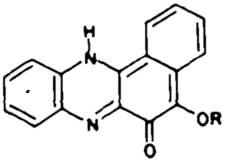
[7] G. Badger, R. S. Pearce and R. Pettit, *J. Chem. Soc.* 3204 (1951).



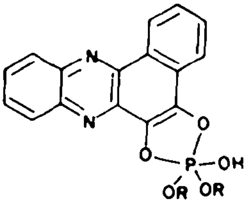
VIa, $R = R' = H$
VIb, $R = CH_3, R' = H$
VIc, $R = R' = CH_3$
VId, $R = H, R' = COC_6H_5$
VIe, $R = CH_3, R' = COC_6H_5$
VIf, $R = H, R' = P(O)(OCH_3)_2$
VIg, $R = H, R' = P(O)(OC_2H_5)_2$
VIh, $R = H, R' = P(O)(OC_3H_7\text{-}i)_2$
VIi, $R = CH_3, R' = P(O)(OCH_3)_2$



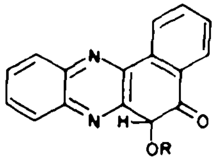
VIIa, $R = H$
VIIb, $R = COC_6H_5$
VIIc, $R = P(O)(OCH_3)_2$
VIId, $R = P(O)(OC_2H_5)_2$
VIIe, $R = P(O)(OC_3H_7\text{-}i)_2$



VIII a, $R = P(O)(OCH_3)_2$
VIII b, $R = P(O)(OC_2H_5)_2$
VIII c, $R = P(O)(OC_3H_7\text{-}i)_2$



IXa, $R = CH_3$
IXb, $R = C_2H_5$
IXc, $R = C_3H_7\text{-}i$



Xa, $R = P(O)(OCH_3)_2$
Xb, $R = P(O)(OC_2H_5)_2$
Xc, $R = P(O)(OC_3H_7\text{-}i)_2$

adduct, taken as an example, gave VIi upon methylation with ethereal diazomethane. Compound VIi has also been obtained by the sequence of the following reactions: methylation of the photo-addition product (VIIb, and or its lactim form VId)[4] with ethereal diazomethane in presence of methanol gave the yellow 3-methoxy-4-benzoyloxy-1,2-benzophenazine (VIe). The latter, upon treatment with alcoholic alkali, yielded 3-methoxy-4-hydroxy-1,2-benzophenazine (VIb). Compound VIb, golden yellow in colour, dissolves in absolute ethanol with yellow colour, unchanged upon addition of water.[7] Thus, it seems that its lactam form is unimportant, at least under the conditions studied, favouring the stabilization of the lactim form (cf. VIb) via hydrogen bonding to the adjacent nitrogen. The IR spectrum of compound VIb confirms such a deduction. In Nujol, at the 1500 cm^{-1}–1800 cm^{-1} region, no bands corresponding to the normal carbonyl frequency were detected. Furthermore, characteristic band for a free OH absorption is absent, which may be attributed to the presence of intramolecular hydrogen bonding.[8] Compound VIb gave a violet absorbate when its alcoholic solution was treated with MgO.[9] Moreover, VIb has been found to be converted to VIc by the action of diazomethane in presence and not in absence of methanol.[10] Phosphorylation of VIb with dimethyl phosphorochloridate in presence of potassium carbonate and ethyl methyl ketone afforded VIi, now obtained via action of diazomethane on VIIc.

In connection with the proposed structure (cf. VIf–h) for the yellow quinone–phosphite adducts B and IXa–c or Xa–c for the colourless quinone–phosphite adducts A, we would like to mention that such structures cannot yet be considered as rigidly proven. Further work is in progress, but we present now the available experimental results. Methylation of the colourless adduct A and the yellow adduct B, obtained by action of dimethyl phosphite on V (see experimental part), with ethereal diazomethane in presence of methanol gave only one and the same methylated product, proved to be identical with VIi (as inferred from their IR spectra). The fact that VIi is yellow in colour may throw light on the importance of VIf structure for the yellow adduct B, rather than the unimportant structure VIIIa under the conditions studied. The IR spectrum of the yellow adduct, assigned structure similar to VIh, in KBr shows broad band at 3200 cm^{-1} (strong intramolecularly bonded OH)[11] and sharp band at 3000 cm^{-1} (probably N-H group). The bands in the 1625 cm^{-1} and 1600 cm^{-1} region cannot be assigned unequivocally to the carbonyl group, since phenyl in plane-skeletal vibration can occur here.[12] Bands at 1275 cm^{-1} ($\geqslant P \rightarrow O$, free); at 1238 cm^{-1} ($\geqslant P \rightarrow O$, hydrogen bonded) and 1100 cm^{-1} appears to be of P—O—C (isopropyl) are shown by the IR spectrum. The ready transformation of VIh to VIIe may be attributed to the possible lactam–lactim tautomerism exhibited by VIa or VId. In CS_2, the exhibition of bands at 3550 cm^{-1} (OH group); 3400 cm^{-1} (N—H group) and 1625 cm^{-1} (C=O group) are in favour of such equilibrium (VIh $\rightleftharpoons$ VIIe). Also, in solution, the possible structure IXa or Xa for the colourless adduct may be found in tautomerism with VIf; a fact which may account for the formation of VIi by the action of diazomethane on the colourless quinone–dimethyl phosphite adduct (IXa, and or Xa). The IR spectrum of the colourless adduct IXc shows in KBr strong bands at 3450 cm^{-1} (OH, hydrogen bonded); 1700 cm^{-1} (C=O group) and 1600 cm^{-1} (aromatic band). This may illustrate that the possible tautomeric form, e.g. Xc cannot be ruled out. The NMR spectrum[13] of the colourless quinone–diisopropyl phosphite adduct shows a broad resonance at 4·55 ppm which may be attributable to acidic OH proton, presumably P—OH. Moreover, worthy

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[8] A. Albert and R. Goldacre, *J. Chem. Soc.* 454 (1943).

[9] F. Feigl, *Spot Tests in Organic Analysis* p. 188. Elsevier (1965).

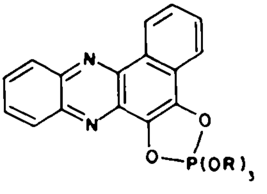
[10] Cf. the expected hydrogen bonding between the 4-OH group and the ring nitrogen atom which also accounts for its difficult solubility in aqueous alkali; A. Schönberg and A. Mustafa, *J. Chem. Soc.* 746 (1946).

[11] L. J. Bellamy, *The infra-red Spectra of Complex Molecules* p. 96. John Wiley (1958).

[12] A. Mustafa, M. M. Sidky, S. M. A. D. Zayed and F. M. Soliman, *Tetrahedron* **19**, 1335 (1963).

[13] We wish to acknowledge our thanks to Dr. N. S. Bhacca, NMR Application Laboratory Instrument Division, Varian associates, Palo Alto, Calif. for carring out the NMR and for helpful discussions.

to mention, whereas, the above-described adducts A and B are readily cleaved by HCl or alkali hydroxide to yield VIa, the corresponding red-violet form C (e.g. VIIc) is only converted to VIa by the action of HCl and acetic acid mixture. In dry dioxan, the adduct A gave an almost colourless solution, and the adduct B a yellow solution. On the other hand, in aqueous dioxan, both forms gave reddish-violet solutions which may be attributed to the increased proportion of the corresponding lactam form C.[7] Treatment of an almost colourless benzene solution of the adduct A and yellow benzene solution of the adduct B with freshly activated silica gel results in acquiring of the surface of the inorganic material with a red-violet colour. Similar adsorptiochromism was also observed with activated alumina. The colour of the adsorbates on alumina is similar to the colour shown when alumina is placed into the colourless benzene solution of 1,3-diketohydrindene; a violet adsorbate is formed, believed to be due to the enol form.[14] We believe that the adsorption may be reminiscent of similar ones by Weitz *et al.*[15] or may be attributed to the possible lactam–lactim tautomerism (*vide supra*). It is proposed that the lactim form (VIf), as an example, for the yellow adduct B is rather important than the possible red-violet lactam form (cf. VIIc). The alternative cyclic structure IXa, as an example, may represent the colourless adduct A which in solution may be found in equilibrium with the yellow adduct VIf and/or Xa which may also be in equilibrium with the red-violet lactam form VIIc. The formation of the lactam form VIIc, as an example, appears to be favoured by polar solvents or by the action of heat, associated with a considerable deepening in the colour of the solution.



XI, R = CH_3

Whereas, dialkyl phosphites $(RO)_2P(O)H$ effected the formation of 1:1-adducts with the quinone V, *o,o*-dimethyl hydrogen phosphorodithioate $(CH_3O)_2P(S)SH$ now has been found to effect reduction, yielding 3,4-dihydroxy-1,2-benzophenazine (VIa). Similar results has been also observed upon treatment of V with trimethyl phosphite, whereby VIa was formed. It is believed that the latter compound is formed via cleavage of a cyclic intermediate adduct similar to XI.[16] The IR spectrum of VIa in Nujol shows absorption at 3400 cm^{-1} (N—H group) and 1665 cm^{-1} (C O group).

EXPERIMENTAL

All m.ps are uncorrected. The benzene was thiophene-free and dried (Na). The photo-experiments were carried out in Schlenk tubes[17] of Pyrex glass. The tubes were sealed while a stream of dry N_2 was passing through. The IR spectra were taken in a Perkin–Elmer 137 spectrophotometer.

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[14] A. Schönberg, A. Mustafa and W. Asker, *J. Amer. Chem. Soc.* **73**, 2876 (1951); *Ibid.* **74**, 5640 (1952); *Ibid.* **75**, 4645 (1953).

[15] F. Weitz and F. Schmidt, *Ber. Dtsch. Chem. Ges.* **72**, 2099 (1939); E. Weitz *et al.*, *Z. Elektro Chem.* **47**, 65 (1941).

[16] Cf. the reducing action of trialkyl phosphites, F. Ramirez, H. Yamanaka and O. H. Basedow, *J. Amer. Chem. Soc.* **83**, 173 (1961).

[17] W. Schlenk and A. Thal, *Ber. Dtsch. Chem. Ges.* **46**, 2840 (1913).

Reaction of phenanthraquinone (II) *with dimethyl phosphite*

A mixture of phenanthraquinone (0·5 g) and dimethyl phosphite (0·4 g) in dry benzene was refluxed under N_2 for 12 hr. The excess of dimethyl phosphite and benzene was removed under red. press. The oily residue, thus obtained, was washed several times with pet. ether (b.p. 40–60°) and crystallized from benzene–pet. ether (b.p. 40–60°) to give IV as colourless crystals, m.p. 130° (85%). There was no depression of the m.p. on admixture with the compound IV prepared according to Ramirez *et al.*[8]

Reaction of 1,2-*benzophenazine*-3,4-*quinone* (V) *with dimethyl phosphite*

(a) *At room temperature. Formation of the adduct A.* To a suspension of phenazinequinone (V)[18] (1·3 g) in dry benzene (20 ml) was added dimethyl phosphite[19] (0·80 g). The reaction mixture was kept at room temp. (25°) for 48 hr. The almost colourless adduct, so obtained, was filtered, washed with pet. ether and crystallized from $CHCl_3$–pet. ether (b.p. 40–60°) to give IXa (or Xa) as almost colourless crystals, m.p. 173–175° (dec.) (1·4 g; 77%). (Found: C, 58·40; H, 4·04; N, 7·52; P, 8·35; OCH_3, 16·37; $C_{18}H_{15}N_2O_5P$ requires: C, 58·36; H, 4·08; N, 7·56; P, 8·36; OCH_3, 16·76%.)

In a similar manner, the following compounds were obtained respectively by the action of diethyl and diisopropyl phosphites. The colourless quinone–diethyl phosphite adduct (IXb or Xb) (75%), m.p. 180–182° from $CHCl_3$–pet. ether (b.p. 40–60°). (Found: C, 59·98; H, 4·80; N, 6·84; P, 7·93; OC_2H_5, 20·64. $C_{20}H_{19}N_2O_5P$ requires: C, 60·30; H, 4·80; N, 7·03; P, 7·77; OC_2H_5, 20·36%.) The colourless quinone–diisopropyl phosphite adduct (IXc or Xc) (63%), m.p. 162–164° (dec.) from $CHCl_3$–pet. ether (b.p. 40–60°). (Found: C, 61·98; H, 5·58; N, 6·26; P, 7·46. $C_{22}H_{23}N_2O_5P$ requires: C, 61·96; H, 5·43; N, 6·57; P, 7·26%.)

(b) *In boiling benzene. Formation of the adducts B and C.* A mixture of the quinone (V) (2·6 g), dimethyl phosphite (1·6 g) and benzene (30 ml) was kept at reflux temp for 12 hr. The cooled reaction mixture was filtered off and the solid product, thus obtained, was found to be a mixture of yellow and red-violet crystals. After treatment with $CHCl_3$, the undissolved red-violet precipitate was collected and crystallized from glacial AcOH to give VIIc as red-violet crystals, m.p. 236–238° (dec.) (1·8 g, 50%). (Found: C, 58·12; H, 3·92; N, 7·73; P, 8·58. $C_{18}H_{15}N_2O_5P$ requires: C, 58·36; H, 4·08; N, 7·56; P, 8·36%.) The $CHCl_3$ filtrate afforded a yellow crystalline product after addition of pet. ether. Recrystallization from $CHCl_3$–pet. ether (b.p. 40–60°) gave VIf as yellow crystals, m.p. 146–148° (dec.) (1·5 g, 41%). (Found: C, 58·21; H, 4·11; N, 7·37; P, 8·59. $C_{18}H_{15}N_2O_5P$ requires: C, 58·36; H, 4·08; N, 7·56; P, 8·36%.)

In the case of diethyl phosphite, the cooled reaction mixture was filtered off, and the dark red quinone–diethyl phosphite adduct was crystallized from glacial AcOH to give red-violet crystals of VIId, m.p. 223–225° (dec.). (Found: C, 60·11; H, 4·60; N, 7·27; P, 8·00. $C_{20}H_{19}N_2O_5P$ requires: C, 60·30; H, 4·80; N, 7·03; P, 7·77%.) The benzene filterate, afforded upon concentration under red. press. a yellow precipitate and this was crystallized from $CHCl_3$–pet. ether (b.p. 40–60°) as yellow crystals of VIg, m.p. 144–146° (dec.) (35%). (Found: C, 60·03; H, 4·84; N, 6·92; P, 8·01. $C_{20}H_{19}N_2O_5P$ requires: C, 60·30; H, 4·80; N, 7·03; P, 7·77%.)

Similarly, diisopropyl phosphite reacted with V to give a mixture of yellow and red-violet crystals, separated from each other in a manner similar to that described for diethyl phosphite (see above). The quinone–diisopropyl phosphite adduct C was crystallized from $CHCl_3$ to give VIIe as red-violet crystals, m.p. 208–210° (dec.) (42%). (Found: C, 61·66; H, 5·33; N, 6·54; P, 7·06. $C_{22}H_{23}N_2O_5P$ requires: C, 61·96; H, 5·43; N, 6·57; P, 7·26%.)

The yellow adduct B gave on recrystallization from pet. ether (b.p. 40–60°) VIh as yellow crystals, m.p. 138–140° (dec.) (51%). (Found: C, 61·68; H, 5·63; N, 6·63; P, 7·37. $C_{22}H_{23}N_2O_5P$ requires: C, 61·96; H, 5·43; N, 6·57; P, 7·26%.)

Transformation of the yellow adduct (VIh) *to the red adduct* (VIIc)

The yellow quinone–diisopropyl phosphite adduct (VIh) (0·5 g) was refluxed in dry benzene (30 ml) for 6 hr. After cooling, the red-violet precipitate was collected and recrystallized from $CHCl_3$ to give VIIe as red-violet crystals (91%) (m.p. and mixed m.p.)

On similar treatment, the colourless quinone–diisopropyl phosphite adduct (IXc or Xc) was converted into the red-violet compd VIIc (m.p. and mixed m.p.).

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[18] O. Fischer, *Ber. Dtsch. Chem. Ges.* 36, 3622 (1903).

[19] For the preparation of dimethyl-, diethyl-, and diisopropyl phosphite, cf. H. McCombie, B. C. Saunders and G. J. Stacey, *J. Chem. Soc.* 380 (1945).

Photochemical reaction between V *and dimethyl phosphite*

Compound V (1·3 g) and freshly distilled dimethyl phosphite (0·8 g), in dry benzene (20 ml), were exposed to sunlight for 10 hr (January). At the end of the experiment, a mixture of red-violet crystals and colourless crystals formed, which was filtered off, washed thoroughly with $CHCl_3$ and crystallized from glacial AcOH as red-violet crystals of VIIc (66%) (m.p. and mixed m.p.). The $CHCl_3$ filrate afforded on addition of pet. ether (b.p. 40–60°) colourless crystals of IXa (or Xa) (20%) (m.p. and mixed m.p.).

Action of diazomethane on VId

To a suspension of VId (1 g) in dry ether (20 ml) and MeOH (5 ml) was added an etheral solution of diazomethane (prepared from 6 g nitrosomethylurea). The reaction mixture was kept at 0° for 48 hr. The violet crystals of VId were transformed into a yellow substance which was filtered off and washed with ether. Recrystallization from benzene gave VIe as golden yellow crystals, m.p. 217–219° (84%). (Found: C, 75·60; H, 4·46; N, 7·24. $C_{24}H_{16}N_2O_3$ requires: C, 75·77; H, 4·23; N, 7·36%.) VIe gave a negative ferric chloride colour reaction, and was insoluble in 10% NaOHaq.

3-*Methoxy*-4-*hydroxy*-1,2-*benzophenazine* (VIb)

Compound VIe (0·4 g) was refluxed for 3 hr with a mixture of EtOH (10 ml) and 10% NaOHaq (10 ml). After the addition of 10% HCl, the precipitated solid was crystallized from benzene–pet. ether (b.p. 40–60°) to give VIb as golden yellow crystals, m.p. 199–200° (0·18 g, 66%). (Found: C, 74·00; H, 4·52; N, 10·17. $C_{17}H_{12}N_2O_2$ requires: C, 73·90; H, 4·37; N, 10·13%.)

Compound VIb gives a violet ferric chloride colour reaction, dissolves in alcoholic NaOH (5%) (NaOH 0·5 g dissolved in 10 ml EtOH) but is insoluble in 10% NaOHaq. VIb gives blue-violet adsorbate when its alcoholic solution is treated with MgO.[8] Methylation with diazomethane in presence of MeOH (as described for VId, see above) gave 3,4-dimethoxy-1,2-benzophenazine (VIc)[7] (m.p. and mixed m.p.).

3-*Methoxy*-4-*dimethoxyphosphinyloxy*-1,2-*benzophenazine* (VIi)

Compound VIb (0·3 g) was stirred with dry powdered K_2CO_3 (0·5 g) in dry ethyl methyl ketone (20 ml) for 2 hr. Dimethyl phosphorochloridate[10] (0·2 g) was added and the reaction mixture was gently refluxed for 24 hr. After separating the inorganic residue, the excess ketone and other volatile materials were removed under red. press. The residue was washed several times with pet. ether and then crystallized from benzene–pet. ether (b.p. 40–60°) to give VIi as yellow crystals, m.p. 159–160° (65%). (Found: C, 59·49; H, 4·36; N, 7·24; P, 8·20. $C_{19}H_{17}N_2O_5P$ requires: C, 59·47; H, 4·44; N, 7·27; P, 8·04%.) Compound VIi gives no colour with ferric chloride and is insoluble in 10% NaOHaq.

Action of diazomethane on VIIc

To a mixture of VIIc (1 g) and MeOH (5 ml) was added an ethereal solution of diazomethane (from 6 g nitrosomethylurea). The reaction vessel was kept in the ice-chest for 24 hr and then treated with a fresh amount of ethereal diazomethane and left overnight at 0°. The solid phase (red-brown in colour) was filtered off, dissolved in hot benzene and treated with activated alumina. After removing the inorganic material, the benzene solution was concentrated under red. press. Addition of pet. ether (b.p. 40–60°) afforded VIi as yellow crystals, m.p. 159–160°. There was no depression of the m.p. on admixture with the material prepared by the action of dimethyl phosphorochloridate on VIb (see above) and the IR spectra were identical.

Similarly, the action of diazomethane on the yellow quinone–dimethyl phosphite adduct (VIf), as well as, on the colourless quinone–dimethyl phosphite adduct (IXa or Xa) gave VIi (m.p. and mixed m.p.) and the IR spectra were identical.

Acid hydrolysis of VIIc

A mixture of the adduct VIIc (0·2 g) in glacial AcOH (15 ml) and HCl (sp. gr. 1·18, 0·5 ml) was refluxed for 3 hr. The blue-violet precipitate formed, was collected and crystallized from AcOEt to give VIIa[7] (m.p. and mixed m.p.). The dimethoxy derivative (VIc) was obtained upon methylation of

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[10] E. E. Hardy and A. Anniston, U.S. Pat. 2,409,039 (1946); *Chem. Abstr.* **41**, 1233 (1947); F. R. Atherton, H. T. Howard and A. R. Todd, *J. Chem. Soc.* 1106 (1948).

VIIa with methyl sulphate and NaOH, in the usual way. There was no depression of the m.p. on admixture with the material prepared according to Badger *et al.*[7] The colourless adduct (IXc or Xc) and the yellow adduct VIf, gave on similar treatment the dihydroxy derivative VIa or its tautomer VIIa (see above).

Action of alcoholic KOH *on* VIh *and* IXc

A mixture of each of VIh and IXc (0·2 g) in MeOH (10 ml) and 5% KOHaq (5 ml) was refluxed for 3 hr. It was then cooled, acidified with cold dil. HCl. The product (0·1 g) was crystallized from AcOEt to give VIa (m.p. and m.p.). This was also identified through the formation of the corresponding diacetate[7] (VI, R = R′ = $COCH_3$) (m.p. and mixed m.p.).

Compounds VIIc–e were recovered unchanged or almost unchanged upon similar treatment with alcoholic KOH.

Adsorption colour experiments with* VIf *and* IXa

(a) *With activated alumina.* When a freshly prepared yellow benzene solution of VIf or almost colourless benzene solution of IXa (orXa) was treated with activated alumina (E. Merck, Darmstadt, for chromatography), the inorganic material acquired an orange colour after a short time.

(b) *With dried silica gel.* When the above experiment was repeated with dried silica gel (E. Merck) in place of alumina, the colour of the adsorbates on silica gel was deep red (after few min) and the benzene solution acquired an orange colour.

Reaction of V *with trimethyl phosphite*

A mixture of the yellow quinone V (1·3 g) and trimethyl phosphite[21] (0·7 g) in dry benzene (20 ml) was kept at room temp for 12 hr under N_2. The resulting blue-violet precipitate was filtered off and washed with EtOH. This was identified as VIIa (80%) through the formation of the corresponding diacetate[7] (VI, R = R′ = $COCH_3$) (m.p. and mixed m.p.).

Similarly compd VIIa was obtained upon treatment of V with *o,o*-dimethyl hydrogen phosphorodithioate.[22]

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* In all cases, decolorization was effected by treating the coloured surface of the active material with MeOH (elution). The experiments were carried out at room temp. Both alumina and silica gel were heated (½ to 1 min) with a free flame before use.

[21] The trimethyl phosphite was purified by treatment with Na followed by fractional distillation. For the preparation of trimethyl phosphite, see B. A. Arbusov and K. V. Nikonov, *Zh. Obsh. Khim.* 17, 2139 (1947).

[22] R. B. March, T. R. Fukuto and R. L. Metcalf and M. G. Maxon, *J. Economic Entomology* 49, 185 (1956).