Reaction of Trialkyl Phosphites with Polycyclic *p*- and *o*-Quinones. Anthraquinone, the Pyrenequinones, and the Naphthoquinones[1]

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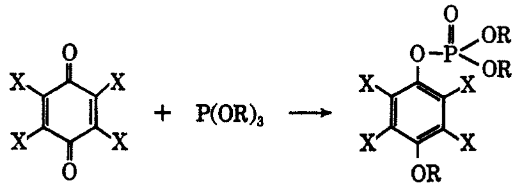
The phosphorus of trimethyl phosphite attacked the carbonyl oxygen of anthraquinone, 1,4-naphthoquinone, and 2,3-dichloro-1,4-naphthoquinone. The products were the corresponding alkyl ethers of the *p*-quinol phosphate esters. The phosphates were hydrolyzed to the corresponding alkyl ethers of *p*-quinols. Trimethyl phosphite attacked the carbonyl oxygen of 4,5-pyrenequinone, 4,5,9,10-pyrenediquinone, 1,2-naphthoquinone, and *o*-chloranil. The products were cyclic pentaoxyphosphoranes. These were converted into *o*-quinol phosphate esters by hydrogen chloride. The P^{31} nmr shifts are given.

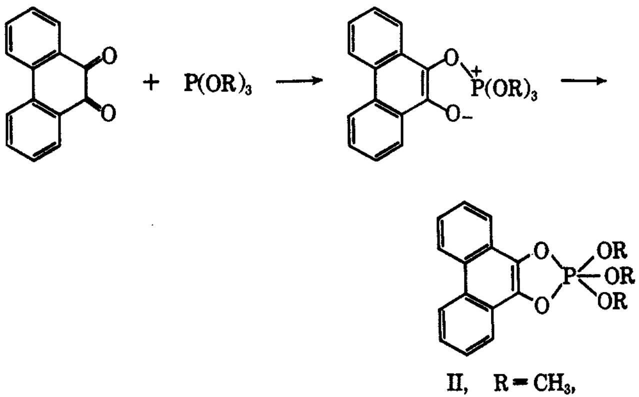
The formation of phosphorus–oxygen bonds in the reactions of trialkyl phosphites with quinones was first reported[3] in 1957. It was shown that trimethyl and triethyl phosphite converted *p*-benzoquinone and substituted *p*-quinones into alkyl ethers of *p*-quinol phosphates,[3,4] I. No chlorine substitution was observed in the case of the chlorinated *p*-quinones, contrary to previous statements in the literature.[5] However, it has been reported[6] that, for reasons that are not well understood, the reaction of triisopropyl phosphite with chloranil gave quinone phosphonates resulting from chlorine substitution.



I

The rather complex phenomena that occur during the reactions of trivalent phosphorus compounds with *p*-quinones have been studied by means of electron-spin resonance and ultraviolet and visible spectrometry.[7]

Phosphorus–oxygen bonds were also produced from the reactions of trialkyl phosphites with *o*-quinones.[8] In these cases, however, the 1:1 dipolar adducts did not undergo alkyl-group translocations; instead, they cyclized to pentaoxyphosphoranes, II. These were characterized by large positive values of the P^{31} nmr shifts,[9] relative to H_3PO_4. The X-ray analysis of one of these substances showed that the phosphorus was at the center of a regular trigonal bipyramid.[10]



II, $R = CH_3$,
$\delta P^{31} = +45.1$ ppm

The three methoxy groups of the cyclic pentaoxyphosphoranes, II, were magnetically equivalent at 25°. In a few instances, measurements were also carried out at −60°, without significant changes in the H^1 nmr spectrum. This phenomenon has been found to be quite general among related cyclic saturated pentaoxyphosphoranes.[9,11] It was recently reported[12] that at −67° the three methoxy groups of a cyclic tetraoxyalkylphosphorane[13] became magnetically nonequivalent.

The present investigation was undertaken to provide information on the behavior of polycyclic *p*- and *o*-quinones toward trialkyl phosphites.[14]

Results

Reactions of Polycyclic *p*-Quinones with Trialkyl Phosphites.—No reaction was observed between anthraquinone (III) and trimethyl phosphite at 20° after 15 hr. However, the reaction was complete at 100°

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[1] (a) Organic compounds with pentavalent phosphorus, part XXXVI; (b) F. Ramirez, A. S. Gulati, and C. P. Smith, *J. Am. Chem. Soc.*, **89**, 6283 (1967).

[2] This investigation was supported by Public Health Service Grant No. CA-04769 from the National Cancer Institute and by National Science Foundation Grant GP 3341.

[3] F. Ramirez and S. Dershowitz, *J. Org. Chem.*, **22**, 856 (1957).

[4] (a) F. Ramirez and S. Dershowitz, *ibid.*, **23**, 778 (1958); (b) F. Ramirez and S. Dershowitz, *J. Am. Chem. Soc.*, **81**, 587 (1959); (c) F. Ramirez, E. H. Chen, and S. Dershowitz, *ibid.*, **81**, 4338 (1959).

[5] E. C. Ladd and M. R. Harvey, U. S. Patent 2,609,376 (Sept 2, 1952); *Chem. Abstr.*, **47**, P7540 (1953).

[6] (a) Th. Reetz, J. F. Powers, and G. R. Graham, Abstracts, 37th National Meeting of the American Chemical Society, Chicago, Ill., Sept 1958, p 86P. (b) For a recent discussion, see C. Walling and M. S. Pearson in "Topics in Phosphorus Chemistry," Vol. 3, E. J. Griffith and M. Grayson, Ed., Interscience Publishers, Inc., New York, N. Y., 1966, p 23.

[7] E. A. C. Lucken, F. Ramirez V. P. Catto, D. Rhum, and S. Dershowitz, *Tetrahedron*, **22**, 637 (1966).

[8] (a) F. Ramirez and N. B. Desai, *J. Am. Chem. Soc.*, **82**, 2652 (1960); (b) F. Ramirez and N. B. Desai, *ibid.*, **85**, 3252 (1963).

[9] (a) F. Ramirez, *Pure Appl. Chem.*, **9**, 337 (1964); (b) F. Ramirez, *Bull. Soc. Chim. France*, 2443 (1966).

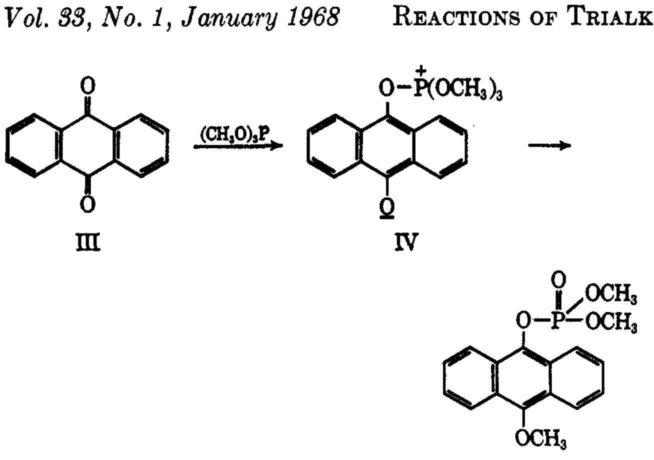
[10] (a) W. C. Hamilton, S. J. LaPlaca, and F. Ramirez, *J. Am. Chem. Soc.*, **87**, 127 (1965); (b) W. C. Hamilton, S. J. LaPlaca, F. Ramirez, and C. P. Smith, *ibid.*, **89**, 2268 (1967); (c) R. D. Spratley, W. C. Hamilton, and J. Ladell, *ibid.*, **89**, 2272 (1967).

[11] (a) F. Ramirez and N. Ramanathan, *J. Org. Chem.*, **26**, 3041 (1961); (b) F. Ramirez, N. Ramanathan, and N. B. Desai, *J. Am. Chem. Soc.*, **85**, 3465 (1963); (c) F. Ramirez, A. V. Patwardhan, and C. P. Smith, *J. Org. Chem.*, **30**, 2575 (1965); (d) F. Ramirez, A. V. Patwardhan, and C. P. Smith, *ibid.*, **31**, 474 (1966); (e) F. Ramirez, A. V. Patwardhan, and C. P. Smith, *ibid.*, **31**, 3159 (1966).

[12] D. G. Gorenstein and F. H. Westheimer, *J. Am. Chem. Soc.*, **89**, 2762 (1967).

[13] F. Ramirez, O. P. Madan, and S. R. Heller, *ibid.*, **87**, 731 (1965).

[14] For other work on the reactions of trialkyl phosphites with quinones, see (a) V. A. Kukhtin and K. M. Orekhova, *Dokl. Akad. Nauk SSSR*, **124**, 819 (1959); (b) V. A. Kukhtin, N. S. Garif'yanov, and K. M. Orekhova, *J. Gen. Chem. USSR*, **31**, 1070 (1961); (c) A. Mustafa, M. M. Sidky, and F. M. Saliman, *Tetrahedron*, **22**, 393 (1966).



III IV

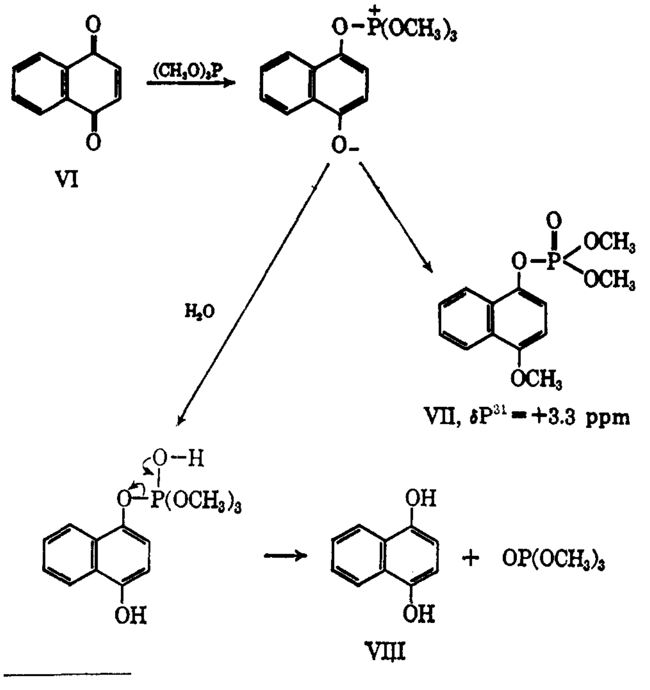
V, $\delta P^{31} = +2.8$ ppm

within 24 hr. The only observable product of this reaction was 10-methoxy-9-hydroxyanthracene dimethyl phosphate (V). The ether phosphate, V, was formed presumably from the intermediate 1:1 dipolar ion IV formed by initial attack of the phosphite on carbonyl oxygen. The conversion of the dipolar ion into the ether phosphate was a nucleophilic attack by a phenoxy anion on an activated methyl group of a trimethoxyaryloxyphosphonium salt.[15]

The structure followed from the value of the P^{31} nmr shift[9] and from the H^1 nmr spectrum, which showed the presence of a methoxy group on the anthracene ring at τ 5.96 and two equivalent methoxy groups of a phosphate ester at 6.20 (J_{HP} = 11.2 cps). The infrared spectrum was consistent with the ether phosphate structure.

The reaction of 1,4-naphthoquinone (VI) with trimethyl phosphite occurred in boiling benzene. The major product of the reaction, which was isolated in over 80% yield, was 4-methoxy-1-hydroxynaphthalene 1-dimethyl phosphate (VII). The structure was based mainly on the P^{31} and H^1 nmr and infrared spectra. A minor product of the reaction, which was isolated in approximately 5% yield, was 1,4-dihydroxynaphthalene (VIII). This product was probably due to hydrolysis of the dipolar intermediate, precursor of the ether phosphate. (See Scheme I.)

SCHEME I

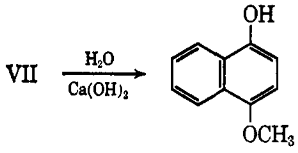


VI

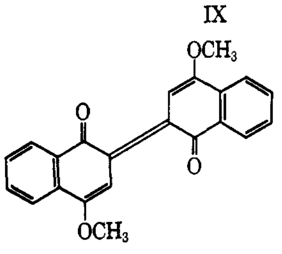
VII, $\delta P^{31} = +3.3$ ppm

VIII

The ether phosphate, VII, was converted into 1-hydroxy-4-methoxynaphthalene (IX) by hydrolysis using $Ca(OH)_2$ as the base. When the alkaline hydrolysis of the ether phosphate, VII, was carried out without protection against oxygen, the previously reported[16] high melting, blue substance assumed to be the dimer X was observed.

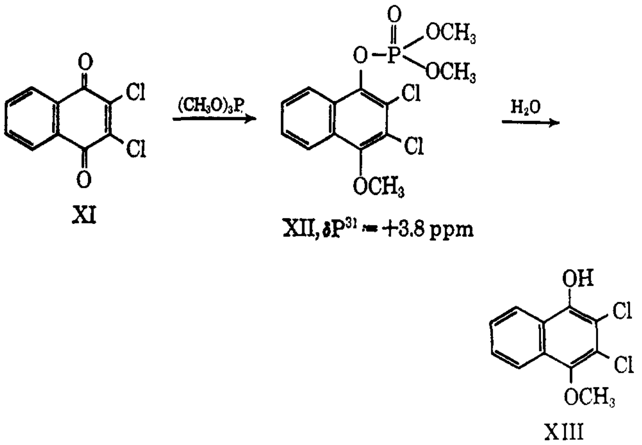


IX



X

The reaction of 2,3-dichloro-1,4-naphthoquinone (XI) with trimethyl phosphite occurred also in boiling benzene and gave mainly 2,3-dichloro-4-methoxy-1-hydroxynaphthalene 1-dimethyl phosphate (XII). The ether phosphate, XII, was hydrolyzed to 2,3-dichloro-4-methoxy-1-hydroxynaphthalene (XIII). The phenolic ether was isolated in high yield when the hydrolysis was carried out in the absence of air and with $Ca(OH)_2$ as the base.



XI

XII, $\delta P^{31} = +3.8$ ppm

XIII

We observed none of the 3-chloro-1,4-naphthoquinone-2-phosphonate (XIV) from the reaction of 2,3-dichloro-1,4-naphthoquinone (XI) with trimethyl phosphite. The chloro quinone phosphonate, XIV, was said to be the product of the reaction of dichloronaphthoquinone (XI) with triethyl phosphite.[5]

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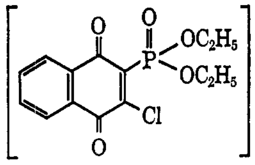
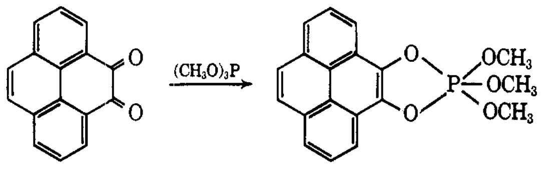
(15) (a) J. S. Cohen, *J. Am. Chem. Soc.*, **89**, 2543 (1967); (b) K. D. Berlin, D. M. Hellwege, M. Nagabhushanam, and E. T. Gaudy, *Tetrahedron*, **22**, 2191 (1966); (c) D. B. Denney and J. Giacine, *Tetrahedron Letters*, 1747 (1964); (d) A. Schmidpeter, B. Wolf, and K. Düll, *Angew. Chem. Intern. Ed. Eng.*, **4**, 712 (1965); (e) H. Teichmann, M. Jatkowski, and G. Hilgetag, *ibid.*, **6**, 372 (1967).

(16) (a) S. Goldschmidt and H. Wessbecher, *Ber.*, **61**, 372 (1928); (b) J. E. Leffler, "The Reactive Intermediates of Organic Chemistry," Interscience Publishers, Inc., New York, N. Y., 1956, p 54.



XIV, not observed

Reaction of Polycyclic *o*-Quinones with Trialkyl Phosphites.—Trimethyl phosphite was treated with 4,5-pyrenequinone[17] (XV) at 20° in benzene solution. The only product observed in this reaction was the 1:1 adduct with pentavalent phosphorus, XVI. This crystalline derivative of the 2,2-dihydro-1,3,2-dioxaphospholene ring system was isolated in quantitative yield. The pentacovalency of the phosphorus was based on the positive value of the P^{31} nmr shift.[8-10] The value of the shift was very similar to that previously observed in the case of the phenanthrenequinone–trialkyl phosphite adducts.[8,18]

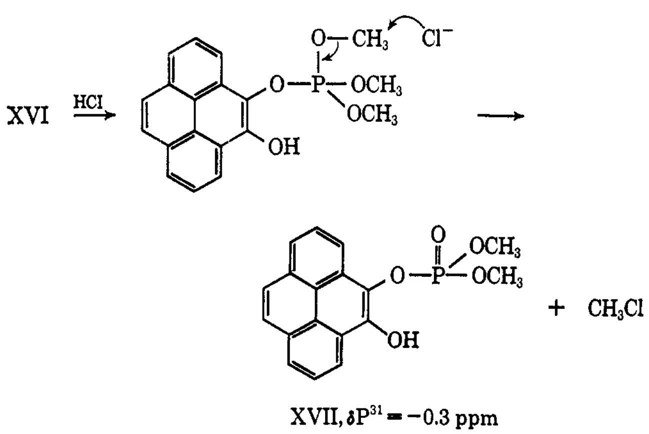


XV XVI, $\delta P^{31} = +44.5$ ppm

The three methoxy groups attached to the phosphorus gave rise to one H^1 nmr doublet at τ 6.24. The doublet with J_{HP} = 13.2 cps was due to the coupling between the protons and the phosphorus. The appearance of one doublet indicated that the three methoxy groups were either magnetically equivalent or indistinguishable under the conditions of the H^1 nmr experiment as discussed in the introduction.

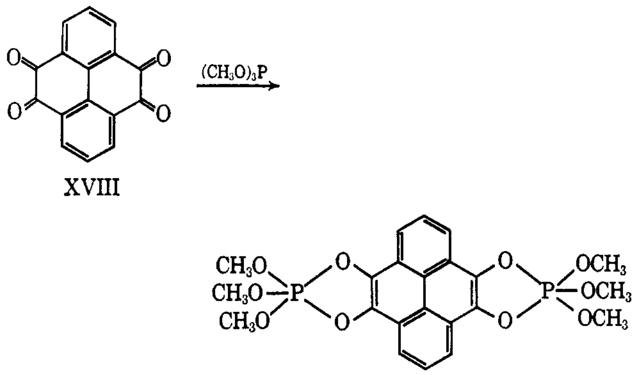
The infrared spectrum of adduct XVI had a band at 6.06 μ which seems to be characteristic of the C=C bond in the phospholenes with pentavalent phosphorus.[10] This type of band, with a rather high infrared frequency of 1650 cm^{-1}, was also observed in the phenanthrenequinone–triisopropyl phosphite adduct. The X-ray analysis of the latter compound showed that the 9,10 C=C distance is shorter (1.33 A) than the corresponding distance in phenanthrene itself (1.37 A).[10]

The pyrenequinone–phosphite adduct, XVI, was converted into 4,5-dihydroxypyrene-4-dimethyl phosphate (XVII) by hydrogen chloride. This reaction involves presumably a nucleophilic attack by chloride ion on the activated methyl group of a trimethoxyaryloxyphosphonium salt.[15]



XVII, $\delta P^{31} = -0.3$ ppm

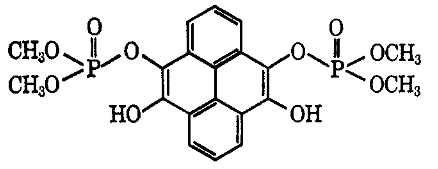
Trimethyl phosphite converted 4,5,9,10-pyrenediquinone,[17] XVIII, into the crystalline bispentaoxyphosphorane (XIX) at 20°. No intermediate was detected in this reaction. The two phosphorus nuclei in XIX gave one P^{31} nmr signal. The six methoxy groups gave rise to one doublet at τ 6.17 (J_{HP} = 13.5 cps).



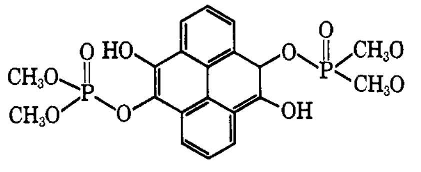
XVIII

XIX, $\delta P^{31} = +44.3$ ppm

Treatment of bisphosphorane XIX with hydrogen chloride gave a bisphosphate ester of 4,5,9,10-tetrahydropyrene, XX. The phosphoryl groups could be at positions 4,10 or 4,9 as in XXa and XXb, respectively; the data did not distinguish between the two structures.



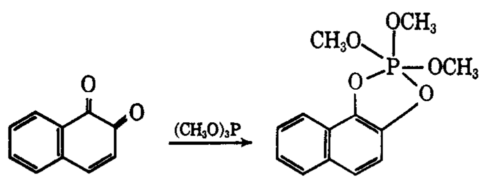
XXa



XXb

$\delta P^{31} = +1.0$ ppm

The reaction of trimethyl phosphite with 1,2-naphthoquinone (XXI) took place at 20° and gave the corresponding cyclic phosphorane, XXII. This reaction was also reported by Kukhtin[14] and coworkers while the present work was in progress. The Russian investigators did not fully characterize the product of their reaction.



XXI XXII, $\delta P^{31} = +45.5$ ppm

Reaction of *o*-Chloranil (XXIII) with Trimethyl Phosphite.—The outcome of this reaction depended on the reaction conditions. The pentaoxyphosphorane, XXIV, was obtained in high yield when a benzene

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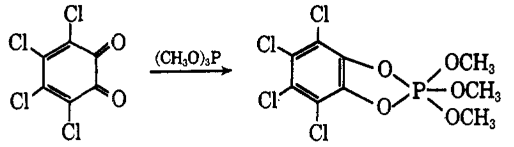
(17) H. Vollmann, H. Becker, M. Corell, and H. Streek, *Ann.*, **531**, 1 (1937).

(18) F. Ramirez, S. B. Bhatia, R. B. Mitra, Z. Hamlet, and N. B. Desai, *J. Am. Chem. Soc.*, **86**, 4394 (1964).

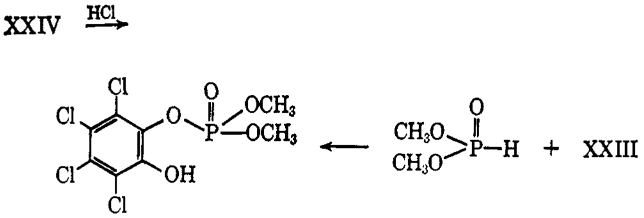
solution of *o*-chloranil (XXIII) was added very slowly to the phosphite at 20°. Kukhtin, *et al.*,[14] also reported having performed this reaction.



XXIII

XXIV, $\delta P^{31} = +46.2$ ppm

The phosphorane, XXIV, was converted into tetrachlorocatechol dimethyl phosphate (XXV) by means of hydrogen chloride. The same phosphate ester was made from the reaction of *o*-chloranil with dimethyl phosphite.



XXV, $\delta P^{31} = +2.7$ ppm

Experimental Section

The analyses were performed by Schwarzkopf Microanalytical Laboratories, Woodside, N. Y. All P^{31} nmr are given in parts per million from 85% H_3PO_4 as zero; they were determined at 40.5 Mc. The H^1 nmr are given in parts per million from TMS = 10 (τ values); they were determined at 60 Mc.

Reaction of Anthraquinone with Trimethyl Phosphite. A.—No evidence of reaction was observed when a suspension of anthraquinone (2.7 g) in trimethyl phosphite (8 g) was kept 15 days at 20° under N_2.

B.—A suspension of anthraquinone (4.3 g) in trimethyl phosphite (25 g) was kept 24 hr at 95° under N_2. The clear solution was evaporated at 20° and 1 mm. The yellow viscous oil was mixed with cold water (10°), and the mixture was stirred 8 hr at this temperature and 10 hr at 20°. This treatment allowed crystallization of the low melting anthrahydroquinone ether phosphate, V. The latter was collected by filtration; the crude material (6.4 g, 93%) had mp 50–60°. One recrystallization from benzene–hexane gave 4.8 g of 10-methoxy-9-hydroxy-anthracene-9-dimethyl phosphate (V), mp 65–68°. The analytical sample of V had mp 74-75° (from hexane).

Anal. Calcd for $C_{17}H_{17}O_5P$: C, 61.4; H, 5.1; P, 9.3. Found: C, 61.6; H, 5.3; P, 9.1.

The H^1 nmr spectrum (in $CDCl_3$) had multiplets at τ 1.8 and 2.5 (aromatics), a singlet at 5.96 (CH_3O), and a doublet at 6.20 (J_{HP} = 11.2 cps, $POCH_3$ or phosphate).

The infrared spectrum had bands at 6.20 (vw), 6.95 (vw), 7.35 (s), 7.8–7.9 (m), 8.45 (w), and 9.55 μ (vs).

Reaction of 1,4-Naphthoquinone with Trimethyl Phosphite.—A mixture of 1,4-naphthoquinone, VI (13.9 g, mp 123–124°, freshly crystallized from benzene), trimethyl phosphite (14.0 g), and benzene (120 ml) was kept 20 hr at reflux under N_2. The solution was evaporated at 20°, first at 20 mm and then at 0.1 mm. This crude material was dissolved in benzene (150 ml) and was extracted with 5% aqueous NaOH, (4 × 50 ml). The benzene solution was evaporated at 20° and 20 mm giving a yellow oil (20 g, 78%) with spectral characteristics identical with those of purified 4-methoxy-1-hydroxynaphthalene 1-dimethyl phosphate (VII). The ether phosphate, VII, was purified by molecular distillation at 155° and 0.1 mm.

Anal. Calcd for $C_{13}H_{15}O_5P$: C, 55.3; H, 5.3. Found: C, 55.0; H, 5.3.

The H^1 nmr spectrum in CCl_4 had five aromatic protons as multiplets at τ 1.9 and 2.6, one aromatic proton as a doublet at 3.42 (J_{HH} = 8.5 cps), three protons as a singlet at 6.25 (CH_3O), and six protons at 6.22 (J_{HP} = 11.2 cps, $POCH_3$).

The infrared spectrum had bands at 6.12 (w), 6.25 (w), 6.82 (m), 7.21 (m), 7.80 (m), 7.90 (s), 8.20 (m), 8.40 (w), 9.10 (m), 9.55 (vs), 10.10 (m), 10.90 (m), 11.10 (m), and 11.65 μ (m).

Hydrolysis of 4-Methoxy-1-hydroxy-1-naphthalene 1-Dimethyl Phosphate (VII).—The known[19] 4-methoxy-1-hydroxynaphthalene (IX) was obtained in 65% yield when VII was hydrolyzed with aqueous $Ca(OH)_2$ at 90° for 5 hr.

Reaction of 2,3-Dichloro-1,4-naphthoquinone with Trimethyl Phosphite.—A mixture of the quinone, XI (10.0 g, mp 192–193°, freshly crystallized from acetone), trimethyl phosphite (10.0 g), and benzene (100 ml) was kept 20 hr at reflux under N_2. The solution was evaporated at 20° and 20 mm; the pale yellow residue failed to crystallized and was redissolved in benzene (200 ml). The solution was extracted with 5% aqueous NaOH, and the benzene was evaporated to give a yellow oil. The latter was extracted into 150 ml of warm hexane, leaving approximately 2 g of hexane-insoluble material, not characterized further. The hexane solution gave on cooling 10.3 g (67% yield) of colorless 2,3-dichloro-4-methoxy-1-hydroxynaphthalene 1-dimethyl phosphate (XII), mp 53–54°.

Anal. Calcd for $C_{13}H_{13}O_5Cl_2P$: C, 44.5; H, 3.7; Cl, 20.2; P, 8.8. Found: C, 44.6; H, 3.9; Cl, 19.8; P, 8.9.

The H^1 nmr spectrum had aromatic protons as multiplets at τ 2.0 and 2.5, a singlet at 6.15 (CH_3O), and a doublet at 6.18 (J_{HP} = 11.3 cps, $POCH_3$ of phosphate).

The infrared spectrum (CH_2Cl_2) had bands at 6.38 (w), 6.90 (m), 7.35 (s), 7.8–7.9 (s), 8.40 (w), 9.50 (vs), 10.15 (s), and 10.90 μ (s).

Hydrolysis of 2,3-Dichloro-4-methoxy-1-hydroxynaphthalene 1-Dimethyl Phosphate.—The ether phosphate, XII (2.5 g), was added to 320 ml of degassed water containing 0.5 g of $Ca(OH)_2$ at 80° under N_2. After 5 hr at 80°, the solution was cooled to 0° and was made acidic with 6 ml of 1:1 HCl. The crude 2,3-dichloro-4-methoxy-1-hydroxynaphthalene (XIII) (1.8 g) was extracted into 30 ml of hexane. On cooling, the hexane solution afforded the ether, XIII (1.3 g, 75% yield), mp 110–111°. The analytical sample had mp 115–116°.

Anal. Calcd for $C_{11}H_8O_2Cl_2$: C, 54.3; H, 3.3; Cl, 29.3. Found: C, 53.4; H, 3.3; Cl, 27.8.

The H^1 nmr spectrum in $CDCl_3$ had 4 H^1 multiplets at τ 2.0 and 2.5, a 1 H^1 singlet at 3.98 (OH), and 3 H^1 singlet at 6.00 (CH_3O).

The infrared spectrum in CH_2Cl_2 had bands at 2.90 (m), 6.38 (s), 6.90 (s), 7.30 (s), 7.45 (s), 8.25 (m), 9.12 (m), 9.25 (s), 10.18 (s), and 11.20 μ (s).

Reaction of 4,5-Pyrenequinone with Trimethyl Phosphite.—Trimethyl phosphite (1.67 g, 1.1 mole equiv) was added to a suspension of the pyrene quinone, XV (2.85 g, crystallized from chlorobenzene), in benzene (25 ml) at 20° under N_2. The mixture was stirred 24 hr at 20°, and the clear solution was triturated with hexane (30 ml) and filtered, yielding 3.6 g, 88% yield, of the quinone–phosphite adduct, XVI, sample of mp 81–82°. Recrystallization from hexane gave the analytical sample of the adduct, mp 86–87°.

Anal. Calcd for $C_{19}H_{17}O_5P$: C, 64.0; H, 4.8; P, 8.7. Found: C, 63.7; H, 5.1; P, 9.1.

The H^1 nmr spectrum in $CDCl_3$ had aromatic protons as multiplets at τ 1.9 and 2.2, and a doublet at 6.24 (J_{HP} = 13.2 cps).

The infrared spectrum in CH_2Cl_2 had bands at 6.03 (w), 6.20 (w), 6.24 (w), 6.40 (vw), 6.80 (w), 6.92 (w), 7.16 (m), 7.25 (s), 7.63 (m), 8.20 (w), 8.50 (m), 9.28 (vs), and 10.90 μ (s).

Reaction of 4,5-Pyrenequinone–Trimethyl Phosphite Adduct, XVI, with Hydrogen Chloride.—A solution of the adduct, XVI (1.98 g) in benzene (35 ml) was treated with an excess of hydrogen chloride gas at 10°. The solution was evaporated at 20° and 25 mm, affording a crystalline residue (1.7 g) which was recrystallized from benzene (25 ml) and hexane (40 ml). The resulting 4,5-dihydroxypyrene 4-dimethyl phosphate, XVII (1.6 g), had mp 117–120°. The analytical sample had mp 119–120°.

Anal. Calcd for $C_{18}H_{15}O_5P$: C, 63.2; H, 4.4; P, 9.0. Found: C, 63.8; H, 4.5; P, 9.0.

The H^1 nmr spectrum in $CDCl_3$ had a 1 H^1 singlet at τ 0.5 (OH), an 8 H^1 multiplet at 2.2 (aromatic), and a 6 H^1 doublet at 6.20 (J_{HP} = 11.5 cps, $POCH_3$ of phosphate).

The infrared spectrum in CH_2Cl_2 had bands at 2.9–3.4 with a minimum at 3.0, 6.10 (w), 6.20 (m), 6.68 (w), 7.45 (w), 7.62 (m), 8.50 (m), 9.52 (vs), and 10.62 μ (ms).

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[19] F. Russig, *J. Prakt. Chem.*, **62**, 50 (1900).

Reaction of 4,5,9,10-Pyrenediquinone, XVIII, with Trimethyl Phosphite.—Trimethyl phosphite (5.6 g, 3 mole equiv) was added to a suspension of the diquinone, XVIII (4.04 g), in benzene (35 ml) at 20° under N_2. The mixture became a solution and then deposited crystals (6.8 g, 87%) of the diquinone–bisphosphite adduct, XIX, mp 206–211°. Concentration of the benzene filtrate gave additional adduct XIX (1.2 g).

Anal. Calcd for $C_{22}H_{24}O_{10}P_2$: C, 51.9; H, 4.7; P, 12.1. Found: C, 51.4; H, 4.7; P, 12.5.

The H^1 nmr spectrum in $CDCl_3$ had six protons as a multiplet at τ 1.7 and 18 protons as a doublet at 6.17 (J_{HP} = 13.5 cps, $POCH_3$).

The infrared spectrum in CH_2Cl_2 had bands at 6.10 (m), 6.25 (w), 7.60 (w), 6.90 (w), 7.40 (s), 8.46 (m), 8.65 (m), 9.30 (vs), 10.45 (mw), and 11.45 μ (s).

Reaction of the 4,5,9,10-Pyrenediquinone–Bisphosphite Adduct, XIX, with Hydrogen Chloride.—Anhydrous hydrogen chloride was passed through a solution of the adduct XIX (7.1 g) in methylene chloride (80 ml) at 0°. The colorless crystals of 4,5,9,10-tetrahydroxypyrene-4,9-bisdimethyl phosphate or -4,10-bisdimethylphosphate (XX) crystallized from the solution (first crop, 3.5 g, mp 164–165°). Evaporation of the solvent gave a second crop of the bisphosphate, XX (3 g, mp 162–164°).

Anal. Calcd for $C_{20}H_{20}O_{10}P_2$: C, 49.8; H, 4.1; P, 12.9. Found: C, 49.7; H, 4.2; P, 12.0.

The H^1 nmr spectrum in deuterio dimethyl sulfoxide had a multiplet at τ 1.8 and a doublet at 6.05 (J_{HP} = 12 cps). Integration of these signals gave the proportion 8:12 protons.

The infrared spectrum in CH_2Cl_2 had bands at 3.0–3.3 with a minimum at 3.15, 6.18 (m), 6.65 (m), 8.20 (m), 8.40 (w), 8.55 (w), 9.00 (m), 9.30 (s), 9.50 (s), 9.70 (s), 10.60 (m), 10.70 (m), 11.50 (ms), and 12.40 μ (ms).

Reaction of 1,2-Naphthoquinone, XXI, with Trimethyl Phosphite.—Trimethyl phosphite (24.2 g, 2 mole equiv) was added, dropwise (2 hr) to a solution of 1,2-naphthoquinone, XXI (15.5 g, freshly recrystallized), in 200 ml of methylene chloride at 20° under N_2 with stirring. The solvent and excess phosphite were removed after 15 hr (20°, 25 mm and 0.1 mm, respectively). The residue was distilled: (1) bp 120–146° (1 mm), 1.8 g; (2) 148–150° (1 mm), 11.2; (3) 150–155° (1 mm), 4.6 g; (4) undistillable up to 290° (1 mm), 7.5 g.

Fractions 1,2, and 3 had very similar infrared spectra. The analytical sample, fraction 2, was pale yellow.

Anal. Calcd for $C_{13}H_{15}O_5P$: C, 55.3; H, 5.3; P, 11.0. Found: C, 55.3; H, 5.3; P, 10.9.

The H^1 nmr spectrum in CCl_4 had a 6 H^1 multiplet at *ca.* τ 2.7 and a 9 H^1 doublet at 6.35 (J_{HP} = 13.0 cps).

The infrared spectrum in CH_2Cl_2 had bands at 6.06 (w), 6.23 (m), 6.80 (s), 7.12 (m), 7.30 (m), 7.68 (ms), 7.75 (ms), 8.47 (m), 9.18 (vs), 9.30 (vs), 9.70 (vs), 9.95 (vs), and 11.27 μ (m).

Reaction of *o*-Chloranil with Trimethyl Phosphite.—A solution of *o*-chloranil (XXIII) (8.58 g) in benzene (70 ml) was added dropwise over a 1.5-hr period to a solution of trimethyl phosphite (4.75 g, 1.1 mole equiv) in 10 ml of benzene at 20° under N_2. The reaction was exothermic, and the temperature was maintained at 20° by external cooling. After 2 hr at 20°, the solution was evaporated at 20° and 25 mm and then at 1 mm. The residue was recrystallized from hexane yielding a first crop of the *o*-chloranil–trimethyl phosphite adduct, XXIV (9.6 g, 80%), mp 65–66°. The mother liquid afforded more of adduct XXIV (2.3 g, mp 63–65°).

Anal. Calcd for $C_9H_9O_5Cl_4P$: C, 29.2; H, 2.4; Cl, 38.4; P, 8.3. Found: C, 29.1; H, 2.5; Cl, 38.4; P, 8.6.

The H^1 nmr spectrum in CCl_4 had a doublet at τ 6.36 (J_{HP} = 13.0 cps).

The infrared spectrum in CH_2Cl_2 had bands at 6.23 (w, shoulder), 6.32 (vw), 6.80 (s), 7.20 (m), 7.70 (w), 8.12 (w), 8.50 (m), 9.20 (vs), 9.42 (vs), and 9.90 μ (vs).

Reaction of *o*-Chloranil–Trimethyl Phosphite Adduct, XXIV, with Hydrogen Chloride.—Anhydrous hydrogen chloride was passed through a solution of adduct XXIV (2.2 g) in benzene (35 ml) at 0°. The solvent was evaporated at 20° and 25 mm, affording crystalline tetrachlorocatechol dimethyl phosphate, XXV, mp 146–147°. Recrystallization from benzene–hexane gave the analytical sample of the same melting point; the yield was quantitative.

Anal. Calcd for $C_8H_7O_5Cl_4P$: C, 26.9; H, 2.0; P, 8.7. Found: C, 26.6; H, 2.1; P, 8.8.

The H^1 nmr spectrum in deuterio dimethyl sulfoxide had a singlet at τ −1.00 (OH) and a doublet at 5.96 (J_{HP} = 12 cps, $POCH_3$ of phosphate).

Reaction of *o*-Chloranil with Dimethyl Phosphite.—Solid *o*-chloranil (2.0 g) was added in small proportions over a 15-min period to an excess of dimethyl phosphite [$(CH_3O)_2P(O)H$] (4 ml) at 0°. The mixture was kept 12 hr at 0° and was then evaporated at 20° and 1 mm. The colorless crystals (2.9 g) were crystallized from benzene (20 ml) and hexane (50 ml) giving the same catechol XXV that was previously obtained.

Registry No.—II (R = CH_3), 4903-06-4; III, 821-65-1; V, 15052-38-7; VII, 15052-39-8; XII, 15052-40-1; XIII, 15052-41-2; XVI, 15156-54-4; XVII, 15052-42-3; XIX, 15052-43-4; XXa, 15052-44-5; XXb, 15052-45-6; XXII, 15052-46-7; XXIV, 15052-47-8; XXV, 15052-48-9.