α-Bromo-α-ketol Phosphates and Enediol Bisphosphates

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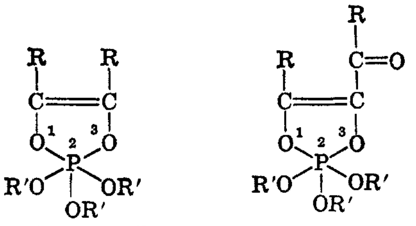
Bromination of the 1:1 adducts made from the reactions of trimethyl phosphite with α-diketones gave α-bromo-α-ketol dimethyl phosphates. This new type of phosphate ester reacted with trimethyl phosphite and gave mainly the enediol bisphosphates, resulting from an attack by phosphorus on carbonyl oxygen. In some cases, minor amounts of α-phosphonyl-α-ketol phosphates resulting from an attack by phosphorus on the α carbon were also observed. Bromination of the 1:1 adducts made from the reactions of triphenyl phosphite with α-diketones gave α,α-dibromo ketones and triphenyl phosphate. Bromination of the phenanthrenequinone–trimethyl phosphite and of the phenanthrenequinone–triphenyl phosphite adducts gave 10,10-dibromo-9(10H)-phenanthrone. Triphenylphosphine and trisdimethylaminophosphine attacked also the carbonyl oxygen of the α-bromo-α-ketol phosphates.

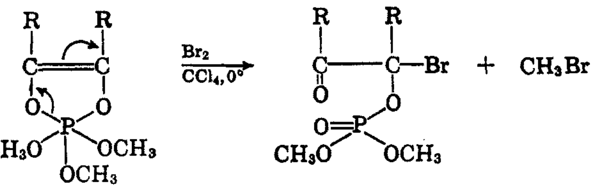
This paper is concerned with the bromination of the 2,2,2-trioxy-2,2-dihydro-1,3,2-dioxaphospholene ring system.[2] These compounds are readily available from the reaction of trialkyl and triaryl phosphites with *o*-quinones, with α-diketones, and with other vicinal polycarbonyl compounds.[3]



2,2,2-trioxy-2,2-dihydro-1,3,2-dioxaphospholenes
R′ = alkyl or aryl

Results and Discussion

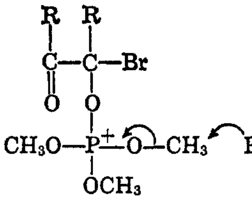
Bromination of the α-Diketone–Trimethyl Phosphite Adducts.—Bromination of the benzil–trimethyl phosphite adduct,[4] I, gave the crystalline α-bromobenzoin dimethyl phosphate (III) in 92% yield. Bromination of the biacetyl–trimethyl phosphite adduct,[4,5] II, gave α-bromoacetoin dimethyl phosphate (IV) in 95% yield.



I, R = C_6H_5, $\delta P^{31} = +49.5$ ppm *vs.* H_3PO_4
II, R = CH_3, $\delta P^{31} = +48.9$ ppm
III, R = C_6H_5, $\delta P^{31} = +4.1$ ppm
IV, R = CH_3, $\delta P^{31} = +5.5$ ppm

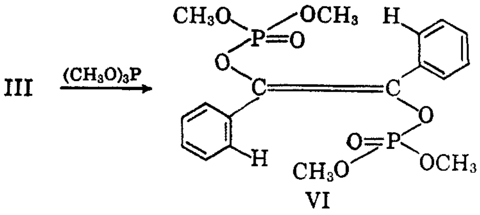
The structures of the bromoketol phosphates were based on analytical and spectral data and on rapid hydrolyses to the corresponding α-diketones, benzil and biacetyl. The aliphatic phosphate, IV, was significantly less stable than the aromatic phosphate, III.

The bromination of the phospholenes, I and II, can be pictured as an electrophilic attack by bromine leading to a tetraalkoxyphosphonium bromide,[6] V. The latter can be transformed into the products III and IV by the usual nucleophilic substitution of bromide on the activated methyl group of a phosphonium salt.



V

Reaction of α-Bromo-α-ketol Phosphates with Trimethyl Phosphite.—Trimethyl phosphite reacted with α-bromobenzoin dimethyl phosphate (III) at 45° in tetrahydrofuran solution. The major product of this reaction was isolated in crystalline state in 80% yield and proved to be one of the two possible geometrical isomers of benzoinenediol bisdimethylphosphate (VI).



VI
$\delta P^{31} = +3.1$ ppm

This isomer probably had the two benzene rings in a *trans* configuration. Molecular models showed that in this configuration the molecule can adopt a conforma-

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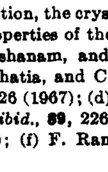
[2] *Chemical Abstracts* suggests the name 2,2-dihydro-1,3,2-dioxaphospholene for the parent ring system. This name implies a structure with pentacovalent phosphorus.



[3] References to the preparation, the crystal and molecular structure, and some physical and chemical properties of these compounds will be found in (a) F. Ramirez, M. Nagabhushanam, and C. P. Smith, *Tetrahedron*, in press; (b) F. Ramirez, S. B. Bhatia, and C. P. Smith, *J. Am. Chem. Soc.*, **89**, 3030 (1967); (c) *ibid.*, **89**, 3026 (1967); (d) W. C. Hamilton, S. J. LaPlaca, F. Ramirez, and C. P. Smith, *ibid.*, **89**, 2268 (1967); (e) F. Ramirez, *Bull. Soc. Chim. France*, 2443 (1966); (f) F. Ramirez, *Pure Appl. Chem.*, **9**, 337 (1964).

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

[5] (a) F. Ramirez, A. V. Patwardhan, N. Ramanathan, N. B. Desai, C. V. Greco, and S. R. Heller, *ibid.*, **87**, 543 (1965); (b) F. Ramirez, S. B. Bhatia, R. B. Mitra, Z. Hamlet, and N. B. Desai, *ibid.*, **86**, 4394 (1964).

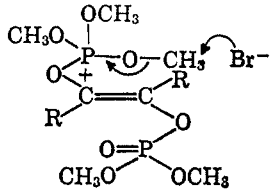
[6] (a) J. S. Cohen, *ibid.*, **89**, 2543 (1967); (b) K. D. Berlin, D. M. Hellwege, M. Nagabhushanam, and E. T. Goudy, *Tetrahedron*, **22**, 2191 (1966); (c) D. B. Denney and J. Giacine, *Tetrahedron Letters*, 1747 (1964); (d) A. Schmidpeter, B. Wolf, and K. Düll, *Angew. Chem. Intern. Ed. Engl.*,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

tion in which the benzene rings on the carbon–carbon double bond of the *trans*-stilbene system are coplanar. In this conformation, the oxygen atom attached to the olefin carbon comes close to the *o*-hydrogen of the *cis*-phenyl ring.

The ultraviolet absorption spectrum of the enediol bisphosphate, VI, had λ_{max} 260 mμ. The H^1 nmr spectrum had one doublet at a relatively high magnetic field, τ 6.73, J_{HP} = 11.4 cps, due to the four magnetically equivalent methoxy groups attached to phosphorus; the relatively high position was attributed to the *cis* relationship to the phenyl ring. Note that the two methoxy groups of α-bromobenzoin dimethyl phosphate (III) were not magnetically equivalent, and that the corresponding doublets were at τ 6.22 and 6.54, both with J_{HP} = 11.6 cps.

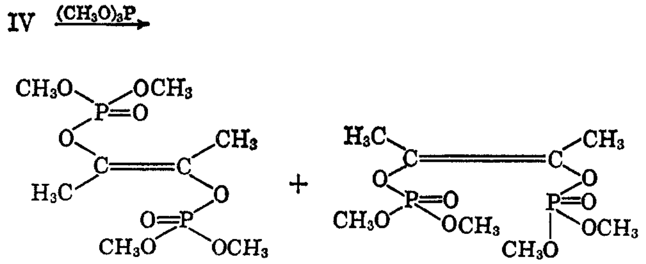
The P^{31} nmr signal due to the two equivalent phosphorus nuclei of VI was at the expected position; however, its multiplicity was unusual. The expected septet due to the coupling of the phosphorus with the six methoxy protons showed additional fine structure which is probably due to long range couplings with the *o*-phenyl protons.

One of several possible mechanisms to explain the formation of the bisphosphate VI involves an attack by the trimethyl phosphite on carbonyl oxygen with the simultaneous ejection of bromide ion and formation of the tetraalkoxyphosphonium salt, VII. Nucleophilic substitution by the bromide on the activated methyl would give the product, VI. The mechanism of the reactions of trialkyl phosphites with simpler α-halo ketones (Perkow reaction) had been the subject of considerable discussion.[7] A recent view is that the phosphorus of the phosphite attacks initially the carbonyl carbon and then undergoes a rearrangement to the carbonyl oxygen.[7e]



VII

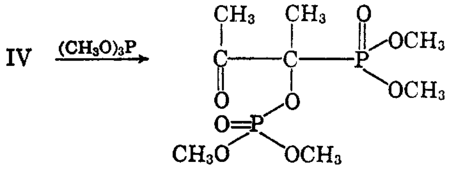
The reaction of trimethyl phosphite with α-bromoacetoin dimethyl phosphate (IV) gave the two geometrical isomers, VIIIa and VIIIb, of acetoinenediol bisdimethylphosphate. The major isomer was assigned the *trans* configuration, VIIIa, as in the case of the benzil analogue, VI. The singlet due to the magnetically equivalent methyl groups of VIIIa was at lower magnetic field (τ 7.99) than the singlet of the corresponding methyl groups of the *cis* isomer, VIIIb (τ 8.05). The isomers were not separated since VIIIb was formed in relatively small amounts and boiled closely to VIIIa.



VIIIa, major δP^{31} = +2.8 ppm

VIIIb, minor δP^{31} = +4.1 ppm

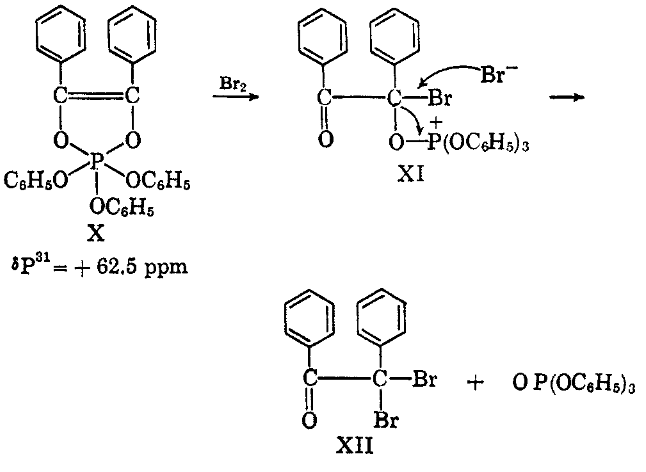
The original product of the reaction of trimethyl phosphite with α-bromoacetoin phosphate, IV, contained traces of the α-phosphonyl-α-ketophosphate, IX, which resulted from an attack by the phosphorus on the α carbon. This material was not isolated in pure state, but the spectral data are in good agreement with the suggested structure. In particular, the methyl group α to the carbonyl in IX gave a doublet at τ 8.59 with J_{HP} = 18 cps, due to H^1–P^{31} coupling with the phosphorus of a phosphonate. Note also the shifts of the two different phosphorus nuclei present in IX.



IX

δP^{31} = +6.9 ppm and *ca.* −19.7 ppm

Bromination of the Benzil–Triphenyl Phosphite Adduct, X.—Bromine converted the benzil–triphenyl phosphite adduct, X, into α,α-dibromodesoxybenzoin[8] (XII) and triphenyl phosphate. Evidently, triphenoxybenzyloxyphosphonium bromide (XI) decomposed by substitution of bromide at the benzylic position.[9]



X

δP^{31} = + 62.5 ppm

XI

XII

The formation of a geminal dibromide, XII, from the α-halotriphenoxyalkoxyphosphonium salt, XI, is entirely analogous to the formation of the geminal dihalide, XV, from the hypothetical α-halotrichloroalkoxyphosphonium salt, XIV. The latter has been suggested[10] as an intermediate in the reaction of phosphorus pentachloride with ketones.

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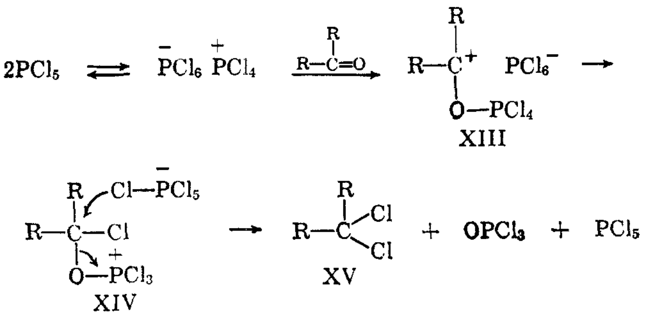
[7] For reviews and very recent discussions on this subject, see (a) R. F. Hudson, "Structure and Mechanisms in Organophosphorus Chemistry," Academic Press Inc., New York, N. Y., 1965, Chapters 4 and 5; (b) B. Miller in "Topics in Phosphorus Chemistry," Vol. 2, M. Grayson and E. J. Griffith, Ed., John Wiley and Sons, Inc., New York, N. Y., 1965, pp 133–200; (c) E. W. Lichtenthaler, *Chem. Rev.*, **61**, 607 (1961); (d) P. A. Chopard, V. M. Clark, R. F. Hudson, and A. J. Kirby, *Tetrahedron*, **21**, 1961 (1965); (e) I. J. Borowitz, M. A. Anschel, and S. Firstenberg, *J. Org. Chem.*, **32**, 1723 (1967).

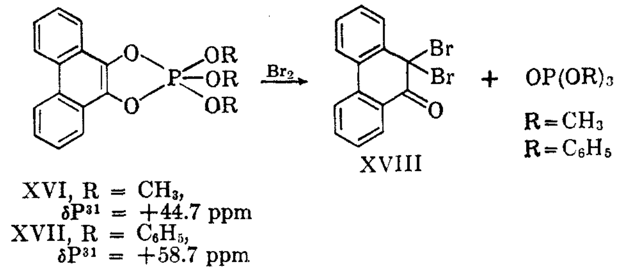
[8] W. Limpricht and A. Schwanert, *Ann.*, **155**, 70 (1870).

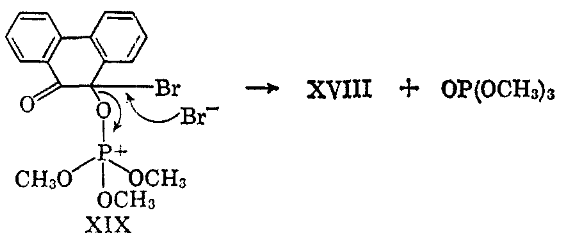
[9] For discussions of the formations of alkyl halides and of aryl halides from related phosphonium salts, see (a) G. A. Wiley, R. L. Hershkowitz, B. M. Rein, and B. C. Chung, *J. Am. Chem. Soc.*, **86**, 964 (1964); (b) L. Horner, H. Oediger, and H. Hoffmann, *Ann.*, **626**, 26 (1959); (c) H. N. Rydon and B. L. Tonge, *J. Chem. Soc.*, 3043 (1956); (d) D. G. Cox, H. N. Rydon, and B. L. Tonge, *ibid.*, 323 (1957).

[10] (a) M. S. Newman and B. C. Ream, *J. Org. Chem.*, **31**, 2175 (1966); (b) M. S. Newman and G. Kaugars, *ibid.*, **31**, 1379 (1966); (c) M. S. Newman and L. L. Wood, Jr., *J. Am. Chem. Soc.*, **81**, 4300 (1959).



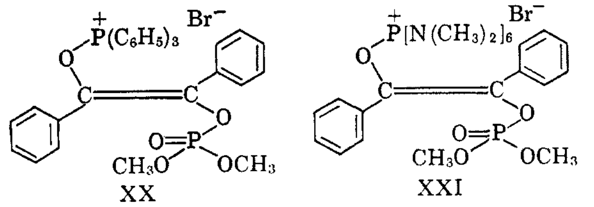
Bromination of the Phenanthrenequinone–Phosphite Adducts.—The bromination of the phenanthrenequinone–trimethyl phosphite adduct, XVI, was significantly different from the bromination of other adducts made from the reactions of trimethyl phosphite with α-diketones. In the quinone case, the products were 10,10-dibromo-9(10H)-phenanthrone[11] (XVIII) and trimethyl phosphate. The intermediate tetraoxyphosphonium bromide, XIX, decomposed by substitution of bromide at the phenanthrene ring rather than by substitution at a methyl group.





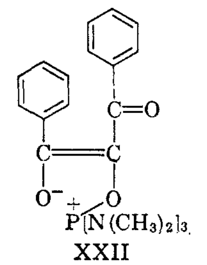
As expected, the bromination of the phenanthrenequinone–triphenyl phosphite adduct, XVII, gave the same dibromophenanthrone, XVIII.

Reactions of α-Bromo-α-ketol Phosphates with Tertiary Phosphines and Amino Phosphines.—Several experiments were performed to compare the behavior of the trialkyl phosphites and of tertiary phosphines, $(C_6H_5)_3P$, and triaminophosphines, $[(CH_3)_2N]_3P$, toward the α-bromo-α-ketol phosphates. The results clearly showed that in all of these cases, the *end product of the reactions*, XX and XXI, had a new P–O bond and not a new P–C bond. The conclusions reached from the P^{31} nmr data are unequivocal since the P^{31} nmr shifts of triphenyloxyphosphonium salts[12] (enolphosphonium salts) analogous to XX and of triaminooxyphosphonium salts[13] analogous to XXI are known.



δP^{31} = +4.3 and −65.9 ppm δP^{31} = +4.2 and −34.2 ppm

The two phosphorus signals in compounds XX and XXI were of equal intensities. The values at +4 ppm were due to the phosphates, and the values at −65 ppm and at −34 ppm were due to the two types of phosphonium salts. Note the shift of a triaminooxyphosphonium inner salt, XXII, made from the reaction of trisdimethylaminophosphine with diphenylpropanetrione.[13]



XXII

δP^{31} = −35.9 ppm

Experimental Section

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/sec. All H^1 nmr are given in parts per million *vs* TMS as 10 (τ values); they were determined at 60 Mc.

Reaction of the Benzil–Trimethyl Phosphite Adduct, I, with Bromine.—A solution of bromine (11.8 g) in CCl_4 (60 ml) was added dropwise to a solution of the benzil-phosphite adduct,[4] I, (24.7 g, 1 mole equiv) in CCl_4 (80 ml) at 0° with stirring. The bromoketol phosphate crystallized and was filtered, washed with cold hexane (100 ml), and dried at 20° under vacuum. The phosphate, III, (27 g, 92% yield) was recrystallized from a mixture of hexane and tetrahydrofuran (1:2.5 v/v) (0.22 g/ml) giving colorless α-bromobenzoin dimethyl phosphate (III), mp 119–120°.

Anal. Calcd for $C_{16}H_{16}O_5BrP$: C, 48.0; H, 4.0; Br, 20.0. Found: C, 48.2; H, 4.1; Br, 20.0.

The H^1 nmr spectrum had a multiplet between τ 2.2 and 2.7 (ten aromatic protons), a doublet at 6.22, J_{HP} = 11.6 cps, and a doublet at τ 6.54, J_{HP} = 11.6 cps (6 H^1 of two methoxy groups).

The infrared spectrum in $CHCl_3$ had bands at 5.88 (C=O), 7.8 (P=O), and 9.5 μ ($POCH_3$).

The ultraviolet spectrum in $CHCl_3$ had λ_{max} 258 mμ.

Reaction of α-Bromobenzoin Dimethyl Phosphate with Trimethyl Phosphite.—Trimethyl phosphite (1.76 g) was added at once to a suspension of α-bromobenzoin dimethyl phosphate (II) (5.13 g) in anhydrous tetrahydrofuran (25 ml). The mixture was kept 2 hr at 50°, and the resulting clear, colorless solution was kept 32 hr at 20°. The solvent was removed at 20° (15 mm), and the residue was triturated with hexane (30 ml), giving 4.5 g (82%) of benzoinenediol bisdimethylphosphate (1,2-dihydroxy-1,2-diphenylethylene bisdimethylphosphate) (VI), mp 78–87°. Recrystallization from benzene–hexane gave VI of mp 111–112° (>75% yield), δP^{31} + 3.1 ppm (in CH_2Cl_2).

Anal. Calcd for $C_{18}H_{22}O_8P_2$: C, 50.5; H, 5.2; P, 14.4. Found: C, 50.4; H, 5.2; P, 14.0.

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[11] A preliminary communication on the preparation of this compound has appeared; *cf.* ref 4. Subsequently, the same compound was prepared by bromination of 9-methoxyphenanthrene; see J. van de Linde and E. Havinga, *Rec. Trav. Chim.*, **84**, 1047 (1965).

[12] (a) R. D. Partos and A. J. Speziale, *J. Am. Chem. Soc.*, **87**, 5068 (1965); (b) H. Hoffmann and H. J. Diehr, *Tetrahedron Letters*, 583 (1962); (c) H. Hoffmann and H. J. Diehr, *Angew. Chem. Intern. Ed. Engl.*, **3**, 737 (1964); (d) I. J. Borowitz and L. I. Grossman, *Tetrahedron Letters*, 471 (1962); (e) I. J. Borowitz, K. C. Kirby, Jr., and R. Virkhaus, *J. Org. Chem.*, **31**, 4031 (1966); (f) F. Ramirez and C. P. Smith, unpublished observations.

[13] (a) F. Ramirez, A. V. Patwardhan, and C. P. Smith, *J. Am. Chem. Soc.*, **87**, 4973 (1965); (b) F. Ramirez, A. V. Patwardhan, H. J. Kugler, and C. P. Smith, *Tetrahedron Letters*, 3053 (1966); (c) F. Ramirez, A. V. Patwardhen, H. J. Kugler, and C. P. Smith, *J. Am. Chem. Soc.*, **89**, 6276 (1967).

The septet with J_{PH} = 11.4 cps showed a complex fine structure which could not be completely resolved, but which showed a coupling of 1.9 cps.

The H^1 nmr spectrum had a multiplet between τ 2.3 and 2.6 (ten aromatic protons) and a doublet at 6.73, J_{HP} = 11.4 cps (12 H^1 of four methoxy groups).

The infrared spectrum in $CHCl_3$ had bands at 7.78 (P=O), 8.85, and 9.50 μ ($POCH_3$). The ultraviolet spectrum in $CHCl_3$ had λ_{max} 260 mμ.

Reaction of the Biacetyl–Trimethyl Phosphite Adduct with Bromine.—A solution of bromine (24.2 g) in CCl_4 (80 ml) was added dropwise over a 2-hr period to a solution of the biacetyl-trimethyl phosphite adduct,[5] II (31.8 g) in CCl_4 (80 ml) at 0°. The mixture was kept 30 min at 0° and was evaporated at 20° (first at 15 mm, then at 0.1 mm). The colorless oil (41 g) was subjected to short-path distillation giving α-bromoacetoin dimethyl phosphate (IV) (5.1 g, 76%) which was collected at a bath temperature of 80–92° at 0.08 mm. This material underwent decomposition on standing and was not analyzed; it was utilized as soon as it was prepared.

The H^1 nmr spectrum in CCl_4 had two doublets at τ 6.15 and 6.20, both with J_{HP} = 11.6 cps. The spectrum had a singlet at τ 7.58 (acetyl) and a singlet at 7.75 (methyl).

The infrared spectrum in CCl_4 had bands at 5.72 (C=O), 7.78 (P=O), 8.20, and 9.55 μ($POCH_3$).

Reaction of α-Bromoacetoin Dimethyl Phosphate with Trimethyl Phosphite.—Trimethyl phosphite (1.14 g) was added to α-bromoacetoin dimethyl phosphate (IV) (2.24 g) under N_2. The mixture was kept 1.5 hr at 100°, and the residue was distilled at 20° (first at 15 mm, then at 0.1 mm). The residue from this distillation (2.5 g) was submitted to short-path distillation at a bath temperature of 100–125° and 0.07 mm. A colorless distillate (2.0 g, 78%) consisted mostly of *trans*-acetoinenediol bisdimethylphosphate (2,3-dihydroxy-2-butene bisdimethylphosphate) (VIIIa) which had the following spectral characteristics: δP^{31} = +2.8 ppm (in CH_2Cl_2), a septet.

The H^1 nmr spectrum (in CCl_4) had signals at τ 7.99 (singlet of CH_3C) and 6.21, J_{HP} = 11.3 cps (doublet due to CH_3O).

The infrared spectrum in CCl_4 had bands at 7.81 (P=O), 8.50, and 9.62 μ ($POCH_3$).

A minor component of this mixture was the *cis*-acetoinenediol bisdimethylphosphate (VIIIb) with the following spectral characteristics: δP^{31} = +4.1 ppm (in CH_2Cl_2), a septet.

The H^1 nmr spectrum (in CCl_4) had signals at τ 8.05 (singlet of CH_3C), and 6.25, J_{HP} = 11.5 cps, (doublet due to CH_3O).

Traces of α-dimethoxyphosphonylacetoin dimethyl phosphate (IX) were detected in the distilled liquid as indicated by the following spectral data.

Two signals of equal intensities, δP^{31} = +6.9 ppm (phosphate) and *ca.* −19.7 ppm (phosphonate), were noted.

The H^1 nmr spectrum had a doublet at τ 8.59, J_{HP} = 18 cps, (CH_3C) and 7.69 (singlet due to acetyl).

The infrared spectrum in CCl_4 had bands at 5.80 with a shoulder at 5.88 μ.

The liquid was submitted to short-path redistillation, and a fraction was collected at a bath temperature of 125–128° (0.08 mm). This material was nearly pure *trans* isomer, VIIIa, with only traces of the *cis* isomer, VIIIb, and no phosphonate, IX; it had $n^{25}D$ 1.4380.

Spectral characteristic were as indicated above.

Anal. Calcd for $C_8H_{18}O_8P_2$: C, 31.6; H, 5.9; P, 20.4; mol wt, 304. Found: C, 30.4; H, 5.8; P, 20.5; mol wt, 356 (thermoelectric method in benzene).

Reaction of the Benzil–Triphenyl Phosphite Adduct with Bromine.—The adduct, X, was prepared as follows. A mixture of benzil (2.1 g) and freshly distilled triphenyl phosphite (4.0 g) was kept several hours at 110° under N_2. The mixture was dissolved in boiling hexane (50 ml), filtered, and cooled. The adduct, X, had mp 98–100°.

A solution of the adduct, X (14.0 g) in CCl_4 (60 ml) was treated with a solution of bromine (4.7 g, 1 mole equiv) in CCl_4 at 0° with stirring. The color of the bromine was discharged instantaneously. The solvent was removed under vacuum; the residue was treated with 15 ml of methanol. The colorless, crystalline material (6.2 g, mp 108–111°) was recrystallized from hexane giving α,α-dibromodesoxybenzoin[8] (XII), mp 111–112°. The methanol filtrate was evaporated giving an oil which soon solidified to a material which was identified as triphenyl phosphate by comparison with an authentic sample.

The dibromo ketone, XII, was hydrolyzed to benzil in boiling 5% aqueous HCl.

Reaction of the Phenanthrenequinone–Trimethyl Phosphite Adduct with Bromine.—The adduct, XVI, was prepared as follows. A suspension of freshly crystallized phenanthrenequinone in dry benzene was treated with 1.1 mole equiv of trimethyl phosphite. The resulting solution was stirred 6 hr at 20° under N_2. The solvent was removed under vacuum; the residue was dissolved in hexane; and the solution was cooled to −10°. The adduct, XVI, had mp 71–73° and was obtained in 90% yield.

A solution of the adduct, XVI, (4.95 g) in CCl_4 (25 ml) was treated with a solution of bromine (2.4 g) in CCl_4 (24 ml) at 20°. The mixture was kept 24 hr at 0°, and the resulting needles (3.4 g, mp 105–106°) were collected. The 10,10-dibromo-9(10H)-phenanthrone[11] (XVIII) was recrystallized from benzene–cyclohexane without an increase in the melting point.

Anal. Calcd for $C_{14}H_8Br_2O$: C, 47.8; H, 2.3; Br, 45.4. Found: C, 48.0; H, 2.4; Br, 46.0.

The dibromo ketone, XVIII, was hydrolyzed to phenanthrenequinone in boiling aqueous methanol containing small amounts of concentrated H_2SO_4.

Reaction of the Phenanthrenequinone–Triphenyl Phosphite Adduct with Bromine.—The adduct, XVII, was prepared as follows. A mixture of phenanthrenequinone (2.1 g) and freshly distilled triphenyl phosphite (12.4 g) was kept several hours at 110° under N_2 with stirring. The mixture was cooled, treated with hexane, and filtered. The hexane-insoluble adduct, XVII, (4.5 g) had mp 143–145°. One recrystallization from benzene–hexane gave the adduct, XVII, mp 146–147°.

A solution of bromine (0.8 g) in CCl_4 was added slowly to a solution of the adduct, XVII, (2.6 g, 1 mole equiv) in 20 ml of CCl_4 at 20° with stirring. The mixture was filtered, and the filtrate was concentrated somewhat until crystals appeared. The mixture was cooled to 0° and was filtered to give 10,10-dibromo-9(10H)-phenanthrone (XVIII) (800 mg, mp 96–97°) which was identical with the sample described above.

Reaction of the α-Bromobenzoin Dimethyl Phosphate with Trivalent Phosphorus Compounds.—In these experiments, equimolar amounts of the trivalent phosphorus compound were added to a solution of α-bromobenzoin dimethyl phosphate (III) in CH_2Cl_2 at 20°. The P^{31} nmr spectrum of the resulting solutions were examined after several hours. The reaction with triphenyl phosphine and with trisdimethylaminophosphine were exothermic. In each case, the corresponding solutions contained only two phosphorus nuclei with the shifts indicated in formulas XX and XXI, respectively. For comparison purposes, the signals of triphenyl phosphine oxide, $(C_6H_5)_3PO$, δP^{31} = −26.5 ppm, and hexamethylphosphoramide, $[(CH_3)_2N]_3PO$, δP^{31} = −23.2 ppm, were also measured.

Registry No.—I, 4850-55-9; II, 1665-79-8; III, 15023-93-5; IV, 15023-94-6; VI, 15023-95-7; VIIIa, 15023-96-8; VIIIb, 15023-98-0; IX, 15023-97-9; X, 4850-59-3; XII, 15023-99-1; XVI, 4903-06-4; XVII, 4850-60-6; XVIII, 4061-20-5; XX, 15024-03-0; XXI, 15024-04-1; XXII, 5969-58-4.