Novel Dimeric Products from 10-Methyleneanthrone[1]

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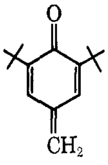
1,2-Dihydro-7-ethoxy-3H-benz[*de*]anthracene-3-spiro-10′-anthrone (**7a**) is shown to be a major by-product (14% yield) of the reaction of 10-methyleneanthrone (**4**) with triethyl phosphite (1 molar equiv) at 95°. Mechanistic studies suggest that **7a** is formed *via* a path involving Diels–Alder dimerization of **4**, abstraction of a proton from the dimer, and alkylation of the resulting anion with a phosphonium betaine generated *in situ*. In contrast to a literature report, oxidation of 9-methoxy-10-methylanthracene (**13**) with anhydrous cupric chloride (2 molar equiv) in refluxing benzene or carbon tetrachloride gives 1,2-dihydro-7-methoxy-3H-benz[*de*]anthracene-3-spiro-10′-anthrone (**7b**) as the major product (*ca.* 60–70% yield). Spiroanthrones **7a** and **7b** can also be prepared in *ca.* 50% yield by reaction of **4** with an excess of ethyl iodide or methyl iodide in hot methanolic sodium methoxide. Oxidation of **4** with molecular oxygen occurs readily in benzene at 24–25° and gives anthraquinone (**17**), spiro[anthracene-9(10H),2′-oxiran]-10-one (**18**), and other products. The dimerization tendency and autoxidative susceptibility of **4** thus appear to be greater than has been realized heretofore.

The reaction of triethyl phosphite with quinone methide **1** was described in the previous paper of this series.[1b] Phosphite-catalyzed dimerization of **1** was shown to be the major reaction path, and betaine **2** and ylide **3** were implicated as key intermediates.[1b] During the course of this work,[1b] the reaction of triethyl phosphite with another *p*-quinone methide, 10-methyleneanthrone (**4**), was described in two independent reports.[2] In both cases the only identified product was phosphonate **6** (yield, 61[2a] or 18%[2b]),[3] a substance whose precursor was evidently betaine **5**.[2a] A product analogous to **6** had not been obtained from betaine **2**;[1b] however, this result did not seem particularly surprising, since it appeared readily rationalizable in terms of steric factors. Of greater significance was the finding that the reaction of triethyl phosphite with **4** also gave a by-product, mp 218–220°, *that did not contain phosphorus*.[2b] Suspecting that this by-product might be an impure dimer resulting from phosphite-catalyzed condensation of the quinone methide, we felt that a brief reinvestigation of this reaction would be of special interest in connection with our related studies on **1**. The present paper is concerned with the identification and mechanism of formation of a dimeric species derived from **4** and triethyl phosphite and with the production of analogous dimers in certain related reactions.



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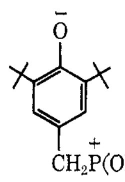

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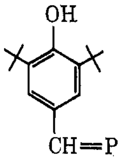

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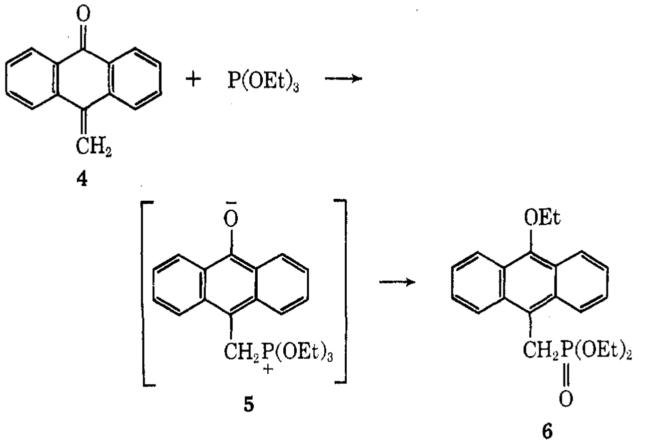
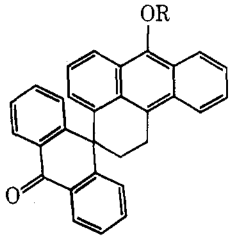
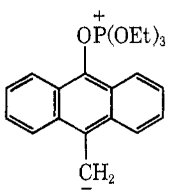


Results and Discussion

Reaction of 10-Methyleneanthrone (4) with Triethyl Phosphite.—This reaction was carried out under conditions very similar to those employed by Arbuzov, *et al.*[2b] Work-up[2b] afforded a yellow solid that did not contain phosphorus and was conclusively identified as 1,2-dihydro-7-ethoxy-3H-benz[*de*]anthracene-3-spiro-10′-anthrone (**7a**, 14% yield) by various spectrometric measurements (Experimental Section). The pure spiroanthrone melts at 236–237.5°, and its elemental composition is similar to that of the Russian workers' product;[2b] whether the two substances are, in fact, the same cannot be ascertained at present.



7a, R = Et
b, R = Me



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A plausible mechanism for the formation of **7a** is shown in Scheme I. Reaction 1 is consistent with the well-established behavior of **4** as a Diels–Alder diene.[4] Additions of **4** to other diene systems have apparently not been observed previously, although the ability of quinone methide **1** to function as a dienophile has been adequately demonstrated.[5] It might be supposed that reaction 1 is actually *catalyzed* by triethyl phosphite in a process involving three steps: formation of betaine **8** from the phosphite and **4**, addition of the carbanion

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[1] (a) Paper VI of a series on oxidation inhibitors. (b) Paper V: W. H. Starnes, Jr., J. A. Myers, and J. J. Lauff, *J. Org. Chem.*, **34**, 3404 (1969). (c) Presented at the 25th Southwest Regional Meeting of the American Chemical Society, Tulsa, Okla., Dec 4–6, 1969.

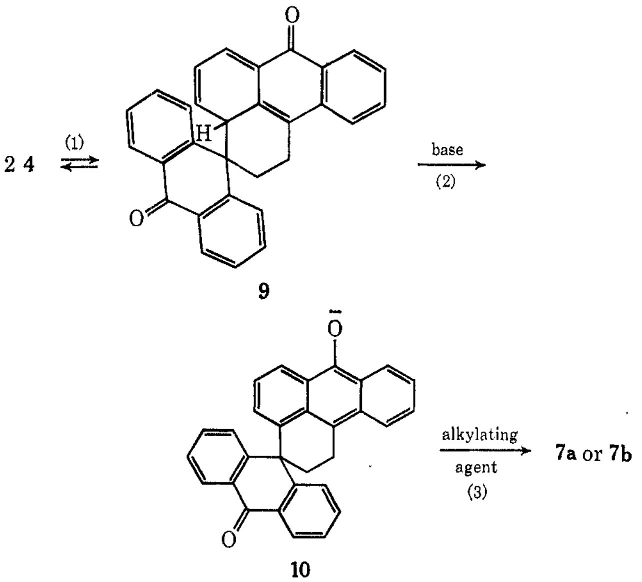
[2] (a) A. N. Al-Khafaji, Ph.D. Dissertation, University of Texas, Austin, Texas, 1966; (b) B. A. Arbuzov, V. M. Zoroastrova, and N. D. Ibragimova, *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 687 (1967).

[3] These yields are recalculated values based on the actual numerical data of ref 2a and b.

[4] See, *inter alia*, (a) J. A. Norton, *Chem. Rev.*, **31**, 319 (1942), and references therein; (b) I. T. Millar and K. E. Richards, *J. Chem. Soc., C*, 855 (1967).

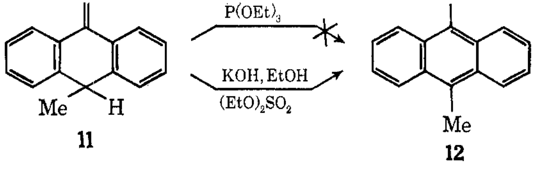
[5] J. D. McClure, *J. Org. Chem.*, **27**, 2365 (1962).

SCHEME I



moiety of **8** to the methylene group of a second quinone methide molecule, and internal cyclization of the newly formed betaine to form **9** and regenerate the phosphite. Although this sequence cannot be rigorously excluded, it seems rather unlikely in view of the phosphite's apparent preference for addition to the methylene group of **4** (as demonstrated by the isolation of **6**).[2] Also applicable here are some of our previous arguments against the addition of triethyl phosphite to the carbonyl group of **1**.[1b] Furthermore, postulation of a catalyzed dimerization of **4** actually seems unnecessary, since spontaneous dimerization apparently does occur in a closely related reaction. First described by Al-Khafaji,[2a] the reaction in question ensues when **4** and an alkyl iodide are heated together in methanolic sodium methoxide. If ethyl iodide is employed, the product is spiroanthrone **7a**.[2a] This result is clearly best accounted for by the mechanism of Scheme I (alkylating agent = EtI),[2a] with reaction 1 occurring in a spontaneous manner. In the present work Al-Khafaji's preparation of **7a** was repeated and found to give a product identical with that obtained from **4** and triethyl phosphite. Moreover, we also found that **4** was not converted to **9** (or other dimeric products) by refluxing in methanol alone. These observations indicate that reaction 1 is reversible and that the equilibrium lies far to the left under the conditions employed.

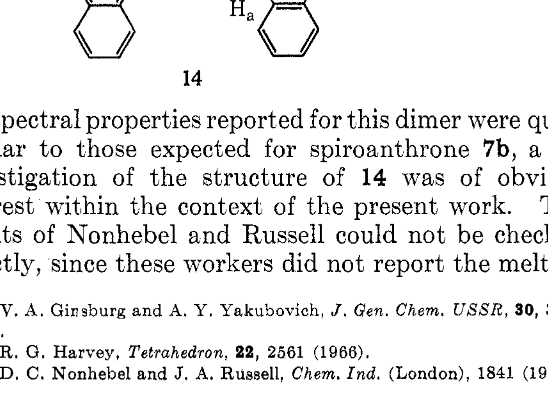
In the reaction of **4** with triethyl phosphite, conversion of **9** to **7a** might be considered to involve abstraction of the labile proton of **9** by the phosphite (reaction 2), followed by reaction of the protonated phosphite with anion **10** to form diethyl phosphite and **7a** (reaction 3). The feasibility of this sequence was tested by examining the behavior of triethyl phosphite toward two model compounds, 10-methylanthrone (**11**) and phenol, under conditions identical with those employed for reaction of the phosphite with **4**. An nmr spectral comparison *vs.* authentic 9-ethoxy-10-methylanthracene (**12**, prepared by alkylation of **11** with diethyl sulfate in ethanolic potassium hydroxide) showed that this ether was not formed in the reaction with **11**. Furthermore, no phenetole was formed in the reaction with phenol, a result consistent with the phosphite's failure to alkylate hydroquinone under more vigorous conditions.[6] In view of these facts, an Arbuzov-type reaction between anion **10** and protonated triethyl phosphite seems highly unlikely. On the other hand, alkylation of **10** by betaine **5** (or this betaine's conjugate acid) is a very reasonable possibility. The apparent conversion of **5** to **6** constitutes a very close analogy for such a reaction, and another analogy is provided by the well-documented formation of phenetole from phenol and various alkyltriethoxyphosphonium betaines.[7]



11 **12**

In summary, it appears that the mechanism of Scheme I adequately accounts for spiroanthrone formation in the reactions of **4** discussed above. In both cases the Diels–Alder dimerization of **4** (reaction 1) probably occurs spontaneously and reversibly. In the reaction with triethyl phosphite, either betaine **5** or the phosphite itself could serve as the requisite base (reaction 2), and in this system anion **10** is probably alkylated (reaction 3) by betaine **5** and/or this betaine's conjugate acid. Reaction 2 might also be significantly reversible under certain conditions; however, protonation of **10** on C-3a (the labile proton's original point of attachment) seems much less likely than protonation of **10** on anionic oxygen or on C-11b.

Spiroanthrone 7b from Oxidation of 9-Methoxy-10-methylanthracene (13) with Anhydrous Cupric Chloride.—While the present investigation was in progress, Nonhebel and Russell[8] reported the formation of a novel dimeric product in oxidations of anthracene **13** with cupric chloride or cupric bromide. Obtained in 65–77% yield, the dimer was considered to be **14**, even though its nmr spectrum failed to show coupling of H_a with protons of the adjacent methylene group.[8] Since the spectral properties reported for this dimer were quite similar to those expected for spiroanthrone **7b**, a reinvestigation of the structure of **14** was of obvious interest within the context of the present work. The results of Nonhebel and Russell could not be checked directly, since these workers did not report the melting



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[6] V. A. Ginsburg and A. Y. Yakubovich, *J. Gen. Chem. USSR*, **30**, 3944 (1960).

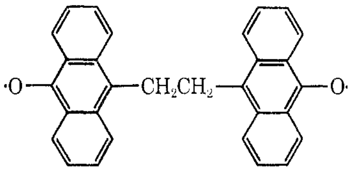
[7] R. G. Harvey, *Tetrahedron*, **22**, 2561 (1966).

[8] D. C. Nonhebel and J. A. Russell, *Chem. Ind.* (London), 1841 (1968).

point of their product or give details for its preparation. However, Nonhebel had previously described a general procedure for oxidation of aromatics with cupric halides.[9] Using this procedure, we oxidized **13** with anhydrous cupric chloride in benzene and obtained a product (approximate yield, 60–70%) that was conclusively identified as spiroanthrone **7b** by appropriate spectral measurements (Experimental Section). An oxidation in carbon tetrachloride gave a similar result, and no evidence could be obtained for the presence of **14** in either of the product mixtures. Compound **7b** prepared in this way had mp 221–222°, whereas mp 237–239° was observed for a reference sample prepared from **4** by the method of Al-Khafaji.[2a] However, the ir spectra of the two samples were identical in every respect, and their nmr spectra were also superimposable. The materials were therefore considered to be different crystalline modifications of **7b**, a conclusion that was further substantiated by conversion of the high-melting form to the low-melting form upon recrystallization, using the low-melting form for seeding. Structures **7b** and **14** have similar elemental compositions, and the spectral properties reported for **14** differ from those of **7b** in only one significant respect: the integrated intensities for the aromatic and methoxyl protons, as determined by nmr.[8] It therefore appears that the compound thought[8] to be **14** may actually have been **7b**, although this conclusion cannot be drawn with certainty in the absence of additional information relating to the results of Nonhebel and Russell.[8]

The mechanism for conversion of **13** to **7b** is obscure. A possible path (not necessarily the preferred one) would involve oxidative cyclization of **14**.

Oxidation of 10-Methyleneanthrone (4) with Molecular Oxygen.—The spontaneous dimerization–disproportionation of quinone methide **1** proceeds *via* a bisphenoxy radical intermediate.[10] This observation suggests the possible intermediacy of an analogous diradical (**15**) in the spontaneous conversion of **4** to **9**. Reaction of **15** with molecular oxygen might be expected to yield peroxide **16**, a substance which, in fact, has been reported to result from the photooxidation of **4**.[11] In view of these considerations, it appeared that an oxygen trapping experiment might provide evidence for the spontaneous (nonphotochemical) formation of **15**. Accordingly, a suspension of **4** in benzene was stirred for several days in the dark at room temperature under an atmosphere of pure oxygen. A considerable amount of oxygen (0.45 mol/mol of **4**) was absorbed, and the product mixture was found to contain appreciable quantities of anthraquinone (**17**) and spiro[anthracene-9(10H),2′-oxiran]-10-one (**18**). The presence of its characteristic odor indicated that formaldehyde was also a product, and the formation of **16** was suggested by a positive peroxide test and the presence of a sharp nmr singlet whose chemical shift (δ 2.14 ppm) fell within the range expected for resonance by the methylene protons of the cyclic peroxide. On the assumption that **16** was actually present, the yields of **16**, **17**, **18**, and recovered **4** were estimated from nmr measurements as 17, 34, 35, and 23%, respectively. Although these results cannot be regarded as conclusive evidence for the spontaneous formation of **15**, they do demonstrate the occurrence of an interesting autoxidation[12] which was apparently not detected by previous workers.



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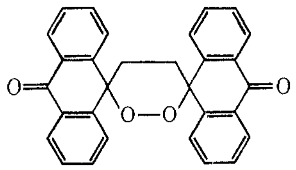

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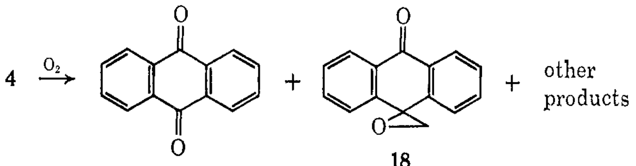

17 **18**

10-Methyleneanthrone (**4**) has been frequently referred to in the literature as being the only extant example of a stable (isolable) quinone methide containing an unsubstituted *exo*-methylene moiety.[13] It now appears that the Diels–Alder dimerization of **4** is actually quite facile (though highly reversible), and that this quinone methide is more susceptible to autoxidation than has been realized heretofore.[14]

Experimental Section[15]

Materials.—Triethyl phosphite was distilled *in vacuo* under nitrogen and stored under nitrogen at $-15°$; it contained no impurities detectable by nmr or vpc analysis. Benzene was dried over sodium ribbon. Anhydrous cupric chloride was prepared by heating the dihydrate under vacuum at 110°. The other chemicals used were either highly purified articles of commerce or materials prepared by standard literature procedures, as indicated below. Purities were verified by spectral measurements, vpc analyses, and the determination of appropriate physical constants.

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(9) D. C. Nonhebel, *J. Chem. Soc.*, 1216 (1963).

(10) R. H. Bauer and G. M. Coppinger, *Tetrahedron*, **19**, 1201 (1963); N. P. Neureiter, *J. Org. Chem.*, **28**, 3486 (1963); B. R. Loy, *ibid.*, **31**, 2386 (1966).

(11) A. Mustafa and A. M. Islam, *J. Chem. Soc.*, S81 (1949).

(12) Noteworthy features of this oxidation are the relatively high yield of **18** and the apparent absence of 10-methyleneanthrone polyperoxide from the products. Possible routes to the autoxidation products of **4** are suggested by Mayo's work on the autoxidation of styrene [F. R. Mayo, *J. Amer. Chem. Soc.*, **80**, 2465 (1958), and references therein], but firm mechanistic conclusions are obviously unwarranted in the absence of additional information.

(13) See, *inter alia*, ref 2a and 4b, and A. B. Turner, *Quart. Rev.* (London), **18**, 347 (1964).

(14) For an earlier comment on the autoxidative stability of **4**, see P. L. Julian, W. Cole, and T. F. Wood, *J. Amer. Chem. Soc.*, **57**, 2508 (1935).

(15) Melting points were determined with a Fisher-Johns apparatus and are uncorrected. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn. Drierite was used as the drying agent for organic solutions. Evaporations were done on rotary evaporators at room temperature under 5–10-mm pressure. Infrared, 100-MHz nmr, and high resolution mass spectra were obtained with Perkin-Elmer Model 21, Varian Model HA-100, and AEI MS-9 spectrometers, respectively. The nmr measurements were made at ambient temperature on dilute solutions containing TMS for internal standardization. Abbreviations used for nmr peak multiplicities are s (singlet), t (triplet), q (quartet), and m (multiplet). Exact mass measurements are referred to C = 12 amu. A major part of the instrumental analytical work was done by the Analytical Division of this laboratory.

10-Methyleneanthrone (4).—The standard method of synthesis for 4 involves the condensation of anthrone with formaldehyde.[16] Despite various attempts to improve this preparation,[17,18] it is still reported to give inconsistent results.[4b] In our hands the method of Barnett and Matthews[17] afforded a product containing anthraquinone as a major impurity (analysis by nmr and high resolution mass spectrometry). Recognition of this difficulty led to development of the following procedure, which consistently gave 4 containing no impurities detectable by nmr analysis.

A mixture of anthrone (25.00 g, 0.129 mol) and methanol (125 ml) was thoroughly degassed by bubbling with nitrogen and then heated to reflux, with stirring. After addition of piperidine (0.75 ml), a 37% solution of formaldehyde (35 ml, 0.47 mol) was introduced during 5 min while refluxing and nitrogen bubbling were continued. The well-stirred mixture was refluxed under nitrogen for an additional 10 min, cooled to room temperature, and allowed to stand under nitrogen until precipitation appeared complete. The crude solid was then recovered by filtration and washed several times with cold (−56°) methanol; in typical runs this solid weighed 12–15 g. Recrystallization from cyclohexane, with filtering of the hot solution to remove a small amount of an insoluble impurity, gave 8.3–10.5 g (31–39%) of pure **4** as pale golden platelets: mp 147–148° (lit.[16] mp 148°); nmr ($CDCl_3$) δ 6.22 (s, 2, $=CH_2$) and 7.3–8.4 ppm (m, 8, aromatic H).

Reaction of 4 with Triethyl Phosphite.—Triethyl phosphite (1.61 g, 9.69 mmol) was added to a slurry of finely powdered **4** (2.00 g, 9.70 mmol) in methylene chloride (2.0 ml), and the stirred mixture was gradually heated to 95° during 10 min. After an additional hour of heating (95 ± 1°) and stirring, the hot mixture was filtered. The filtrate solidified on cooling and yielded 0.30 g (14%) of 1,2-dihydro-7-ethoxy-3H-benz[*de*]anthracene-3-spiro-10′-anthrone (**7a**), mp 231.5–234°, upon recrystallization from aqueous ethanol. A further recrystallization (methanol-benzene) gave bright yellow microcrystals, mp 235–236°, which were shown to be identical with an authentic sample of **7a** (*vide infra*) by nmr and ir spectral comparisons and a mixture melting point determination.

Reaction of 4 with Ethyl Iodide and Sodium Methoxide in Methanol.—This experiment was performed under nitrogen, using a procedure very similar to that described by Al-Khafaji.[2a] Sodium methoxide (1.60 g, 29.6 mmol) was added with stirring to a gently refluxing solution of **4** (2.00 g, 9.70 mmol) in methanol (100 ml). Ethyl iodide (30 ml, 58.5 g, 0.375 mol) was then introduced dropwise into the dark red-brown mixture during 20 min while stirring and refluxing were continued. After an additional 35 min of refluxing and stirring, the mixture (now a pale yellow solution) was concentrated at the boiling point until precipitation occurred, cooled to room temperature, and filtered. The recovered solid was washed with several small portions of cold methanol; it then weighed 1.08 g (51%) and melted at 235–238°. Two recrystallizations of the product from methanol–benzene gave pure **7a** as bright yellow microcrystals: mp 236–237.5° (lit.[2a] mp 237–238°); ir (CS_2) 1668 cm^{-1} (anthrone $C{=}O$), no OH; nmr (CCl_4) δ 7.8–8.5 (m, 5; 6-, 8-, 11-, 1′-, and 8′-H), 6.6–7.5 (m, 10; 4-, 5-, 9-, 10-, 2′-, 3′-, 4′-, 5′-, 6′-, and 7′-H), 4.28 (q, 2, J = 7 Hz, OCH_2), 3.31 (poorly resolved t, 2, J = 6 Hz, CH_2Ar), 2.22 (poorly resolved t, 2, J = 6 Hz, $C\mathbf{H}_2CH_2Ar$), and 1.66 ppm (t, 3, J = 7 Hz, CH_3); mass spectrum (70 eV) *m/e* 440 (too weak for accurate high resolution mass measurement, presumably $C_{32}H_{24}O_2$), 438.1600 (medium; calcd for $C_{32}H_{22}O_2$, 438.1620), and 410.1309 (strong; calcd for $C_{30}H_{18}O_2$, 410.1307).

Anal. Calcd for $C_{32}H_{24}O_2$: C, 87.24; H, 5.49. Found: C, 87.51; H, 5.60.

In a parallel experiment, a solution of **4** (1.00 g) in pure methanol (50 ml) was refluxed with stirring under nitrogen for 1.0 hr and then allowed to stand at room temperature under nitrogen overnight. The precipitated solid (0.70 g) and the methanol-soluble material (0.30 g) were recovered and examined separately by nmr. Both fractions were found to be essentially pure **4**, and their spectra showed no aliphatic peaks assignable to dimeric structures.

Reaction of 10-Methylanthrone (11) with Triethyl Phosphite.—A stirred solution of 10-methylanthrone[19] (0.50 g, 2.4 mmol) and triethyl phosphite (0.41 g, 2.5 mmol) in methylene chloride (0.50 ml) was slowly heated to 95° during 8 min, kept at 95 ± 1° for 1.0 hr, cooled to room temperature, and then evaporated under vacuum. The semisolid residue (0.70 g) was not subjected to purification. However, the absence of 9-ethoxy-10-methylanthracene (**12**) and other 10-methylanthracene derivatives was conclusively shown by nmr analysis (C_6D_6) of the total product mixture, using a pure sample of **12** (*vide infra*) for comparison.

9-Ethoxy-10-methylanthracene (12).—This preparation was carried out under nitrogen. A 10-ml portion of a solution of potassium hydroxide (5.6 g, 0.10 mol) in absolute ethanol (100 ml) was added to 2.00 g (9.60 mmol) of **11** dissolved in absolute ethanol (20 ml), and the resulting dark red-brown solution was heated to 50°, with stirring. Diethyl sulfate (2 ml) was then added, and stirring was continued at 50° until the color of the mixture changed to pale yellow (5–10 min required). Increments of potassium hydroxide solution and diethyl sulfate were added alternately at 50° in a similar manner until all of the base and 20 ml (23 g, 0.15 mol) of the sulfate had been introduced. The last portion of base caused very little color change, an observation indicating that essentially all of **11** had reacted. After cooling to room temperature, the mixture was filtered, and the recovered solid (largely inorganic) was washed several times with fresh portions of absolute ethanol. The filtrate and washings were combined, concentrated by boiling, and diluted with water until the boiling solution exhibited a slight turbidity. Cooling yielded a precipitate, which was recovered in the usual way. This material weighed 1.80 g (79%), melted at 88.5–91.5°, and was shown to be essentially pure **12** by nmr analysis. Recrystallization of the product from aqueous methanol, followed by two recrystallizations from methanol alone, gave pale golden flakes of analytically pure material: mp 94–94.5°; ir (CS_2) no OH or $C{=}O$; nmr (CCl_4) δ 8.03–8.36 (m, 4; 1-, 4-, 5-, and 8-H), 7.24–7.49 (m, 4; 2-, 3-, 6-, and 7-H), 4.17 (q, 2, J = 7 Hz, CH_2), 2.96 (s, 3, $C\mathbf{H}_3Ar$), and 1.59 ppm (t, 3, J = 7 Hz, $C\mathbf{H}_3CH_2$); mass spectrum (64 eV) *m/e* 236.1202 (medium; calcd for $C_{17}H_{16}O$, 236.1201), 234.1024 (medium; calcd for $C_{17}H_{14}O$, 234.1045), and 206.0741 (strong; calcd for $C_{15}H_{10}O$, 206.0732).

Anal. Calcd for $C_{17}H_{16}O$: C, 86.40; H, 6.83. Found: C, 86.78; H, 6.81.

Reaction of Phenol with Triethyl Phosphite.—Triethyl phosphite (0.80 g, 4.8 mmol) was added to a solution of phenol (0.45 g, 4.8 mmol) in methylene chloride (1.0 ml). The well-stirred mixture was slowly warmed to 95° during 4 min and then kept at 95 ± 1° for 1.0 hr. Examination of the total product by nmr (C_6D_6) showed that a reaction (transesterification?) had occurred to some extent. However, no trace of phenetole could be detected. The absence of phenetole was confirmed by rerunning the spectrum after adding an authentic sample of the pure ether.

Oxidation of 9-Methoxy-10-methylanthracene (13) with Cupric Chloride.—A solution of the anthracene[19,20] (2.22 g, 10.0 mmol) in dry benzene (40 ml) was stirred and heated under reflux with anhydrous cupric chloride (2.69 g, 20.0 mmol) for 14.4 hr. At the end of this time HCl evolution was negligible. The hot mixture was filtered, and the recovered solid was washed several times with fresh portions of solvent. Evaporation *in vacuo* of the combined filtrate and washings left a gummy residue whose mass spectrum (70 eV) showed no peak at *m/e* 428 (parent ion for **14**) and displayed only a weak peak at *m/e* 412 (a likely fragment from **14**).[21] However, the spectrum did exhibit peaks assignable to 1,2-dihydro-7-methoxy-3H-benz[*de*]anthracene-3-spiro-10′-anthrone (**7b**, *vide infra*) at *m/e* 426.1607 (weak; calcd for $C_{31}H_{22}O_2$, 426.1620) and 410.1303 (strong; calcd for $C_{30}H_{18}O_2$, 410.1307). An nmr spectral comparison *vs.* authentic **7b** (*vide infra*) indicated that this substance was one of the residue's major constituents (yield estimated from spectrum, 60–70%). Crystallization of the residue from methanol–benzene gave a reddish gum containing considerable **7b** (analysis by nmr) and a second crop (0.50 g) consisting of **7b** in essentially pure form (analysis by nmr and ir), mp 209–214°. Three recrystallizations of the second crop from methanol–benzene afforded a very pure sample of a low-melting form of **7b** as flat orange needles, mp 221–222°. The ir and nmr spectra of this material were identical in every respect with the spectra of a higher melting form of the compound (mp 237–239°; *vide infra*).

A similar oxidation of **13** was carried out in refluxing carbon tetrachloride (reaction time, 23 hr). Product isolation was not

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[16] K. H. Meyer, *Ann.*, **420**, 134 (1920).

[17] E. de B. Barnett and M. A. Matthews, *Ber.*, **59**, 767 (1926).

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[21] The *m/e* 412 peak cannot be taken as evidence for the presence of a small amount of **14**, since the spectrum of authentic **7b** also exhibits a weak peak at *m/e* 412.

attempted; however, analysis of the crude mixture by nmr and mass spectrometry suggested that **14** was absent and that **7b** had again been formed in *ca.* 60–70% yield.

Reaction of 4 with Methyl Iodide and Sodium Methoxide in Methanol.—The procedure employed was similar to that of Al-Khafaji[2a] and essentially equivalent to that used for the analogous reaction with ethyl iodide (*vide supra*). Addition of methyl iodide (40 ml, 91 g, 0.64 mol) to a boiling solution of **4** (1.71 g, 8.29 mmol) and sodium methoxide (2.00 g, 37.0 mmol) in methanol (100 ml) required 50 min; stirring and refluxing were continued for 40 min after the addition was complete. Concentration of the pale yellow solution afforded 0.83 g (47%) of spiroanthrone **7b**, mp 229.5–232.5°. Two recrystallizations of the product from methanol–benzene gave pure **7b** as slender, bright yellow needles: mp 237–239° (lit.[2a] mp 227–228°); ir (CS_2) 1667 cm^{-1} (anthrone C=O), no OH; nmr (CCl_4) δ 7.9–8.5 (m, 5; 6-, 8-, 11-, 1′-, and 8′-H), 6.7–7.6 (m, 10; 4-, 5-, 9-, 10-, 2′-, 3′-, 4′-, 5′-, 6′-, and 7′-H), 4.14 (s, 3, CH_3), 3.33 (poorly resolved t, 2, J = 6 Hz, CH_2Ar), and 2.24 ppm (poorly resolved t, 2, J = 6 Hz, CH_2CH_2Ar); mass spectrum (70 eV) m/e 426.1607 (weak; calcd for $C_{31}H_{22}O_2$, 426.1620) and 410.1300 (strong; calcd for $C_{30}H_{18}O_2$, 410.1307).

Anal. Calcd for $C_{31}H_{22}O_2$: C, 87.30; H, 5.20. Found: C, 87.44; H, 5.26.

Recrystallization of 0.10 g of pure **7b** (mp 237–239°) from methanol–benzene, using the low-melting form of **7b** (*vide supra*) for seeding, gave 0.08 g of flat orange needles that melted sharply at the lower temperature.

Oxidation of 4 with Molecular Oxygen.—A suspension of **4** (0.50 g, 2.4 mmol) in dry benzene (3.0 ml) was degassed by the freeze–thaw method and then stirred rapidly (magnetic bar) in the dark at 24–25° under an atmosphere of pure oxygen. After 122.4 hr the total absorbed oxygen amounted to 24.7 ml (volume corrected to 0° and 760 mm, 1.10 mmol), and at this point the rate of oxygen uptake had decreased to a negligibly small value. The final reaction mixture had a strong formaldehyde odor and contained a white solid, which was recovered by filtration and washed several times with fresh benzene. This solid (fraction A) weighed 0.07 g and gave a doubtful positive test for peroxide(s) with potassium iodide in acetic acid. Evaporation of the combined filtrate and washings yielded 0.50 g of pale yellow powder (fraction B), whose peroxide test was definitely positive. Analysis by nmr showed that fractions A and B contained anthraquinone (**17**), spiro[anthracene-9(10H),2′-oxiran]-10-one (**18**), and **4**; these identifications were confirmed by nmr peak enhancements resulting from addition of the pure substances. Fraction B also contained a material that exhibited a sharp singlet at δ 2.14 ppm ($CDCl_3$). Double verification was obtained for the presence of **18** by adding the authentic epoxide[22] to solutions of B in two different solvents ($CDCl_3$, C_6D_6). Enhancement of a singlet assigned to the methylene protons of **18** (δ 3.38 ppm in $CDCl_3$, 2.67 ppm in C_6D_6) occurred in both cases, and enhancement of several aromatic peaks was also observed. The mass spectrum (70 eV) of fraction A showed strong parent peaks for **17** and **4** at m/e 208.0534 (calcd for $C_{14}H_8O_2$, 208.0524) and 206.0734 (calcd for $C_{15}H_{10}O$, 206.0732), respectively. The mass spectrum (70 eV) of fraction B also contained intense parent peaks for **17** (m/e 208.0534) and **4** (m/e 206.0748), as well as a weak parent peak for **18** (m/e 222.0665; calcd for $C_{15}H_{10}O_2$, 222.0681. The parent peak of pure **18** was shown to be weak at 70 eV). Quantitative calculations based on the nmr spectrum showed that the composition of fraction A was **17**, 77%; **18**, 4%; **4**, 19%. On the assumption that the material resonating at 2.14 ppm was peroxide **16**, the composition of fraction B was estimated by nmr as **16**, 19%; **17**, 23%; **18**, 37%; **4**, 21%. Thus the total yields of **16**, **17**, **18**, and recovered **4** were estimated to be 17, 34, 35, and 23%, respectively.

An attempt to reproduce the published preparation[11] of **16** gave none of the desired product.

Registry No.—**4**, 4159-04-0; **7a**, 24165-82-0; **7b**, 24215-76-7; **12**, 24165-83-1.

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Reaction of a Quinone Methide with Tri-*n*-butylphosphine[1]

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Quinone methide **2** reacts with tri-*n*-butylphosphine in benzene or *n*-heptane solution to form an isolable inner salt, (3,5-di-*t*-butyl-4-oxybenzyl)tri-*n*-butylphosphonium betaine (**4**). Betaine **4** can also be prepared by dehydrochlorination of phosphonium chloride (**3**) with methanolic sodium methoxide. The betaine retains its structure in polar solvents (methanol, ethanol, dimethyl sulfoxide, or acetone), but, when warmed with relatively nonpolar solvents (benzene, toluene, *p*-dioxane, or cyclohexene), it decomposes to form bisphenol **9** and tri-*n*-butylphosphine as major products. Decomposition of **4** in the presence of benzaldehyde gives considerable amounts of stilbenol **8** and tri-*n*-butylphosphine oxide; decomposition in the presence of chloroprene gives, *inter alia*, spirotrienone **13**. These observations and the results of experiments with model compounds suggest that the decomposition of **4** probably produces ylide **5** and quinone methide **2**, *in situ*, and that bisphenol **9** then results from a sequence involving addition of **5** to **2**, followed by prototropic shifts and loss of tri-*n*-butylphosphine. The reactions of quinone methide **2** with triethyl phosphite and tri-*n*-butylphosphine are briefly compared.

Observations made during the course of previous work[3] suggested that quinone methides were involved as reactive intermediates during the inhibition of autoxidation by certain synergistic antioxidant systems containing hindered phenols and compounds of trivalent phosphorus. It appeared that separate investigations of quinone methide–phosphorus(III) nucleophile reactions might provide insight into the overall inhibition process, and this supposition prompted an examination of the reaction of triethyl phosphite with quinone methide **2**.[4] Since the results of that study were both interesting and unexpected,[4] we felt that information about the behavior of **2** toward other trivalent phosphorus nucleophiles would be desirable for purposes of comparison. The reaction of **2** with tri-*n*-butylphosphine was therefore investigated, and the present paper describes the results obtained. To our knowledge, no other reactions of quinone methides with phosphines have previously been described in the literature.

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[1] (a) Paper VII of a series on oxidation inhibitors. (b) Paper VI: W. H. Starnes, Jr., *J. Org. Chem.*, **35**, 1974 (1970). (c) Presented at the 159th National Meeting of the American Chemical Society, Houston, Texas, Feb 25, 1970.

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