similar treatment of Q-9 were separated, no monomethoxyquinone was observed. Heating of H_2Q-9 at 170° for 12 hr failed to yield a monomethoxy product.

The process which takes place in the mass spectrometer inlet system is visualized as occurring as depicted in I → IV. Peaks due to hydroquinone species have been observed in all spectra of ubiquinones[2] and the related multiprenylquinones.[6] The suggestion has been made[7] that the reduction of quinone to hydroquinone is brought about by residual material on the surface of the spectrometer inlet system. While the presence of peaks due to quinone, observed in the spectra of hydroquinone samples, may, in some instances, be due to air oxidation occurring during sample introduction, the present data suggest that in this case the process hydroquinone → quinone occurs in the inlet system.[7]

The monomethoxyquinone hydroquinones obtained thermally in the mass spectrometer inlet system are undoubtedly mixtures of the two possible isomers (III and IV). It has been previously demonstrated that ultraviolet irradiation of ubiquinone produced a "monomethoxyhydroxybenzoquinone"[8-10] which has more recently been shown to be a 50:50 mixture of the two possible isomers.[11] Nucleophilic displacement of methoxy groups of ubiquinone with ethanol in base[12,13] and with ammonia[14] have been shown to yield mixtures of both possible monomethoxy isomers.

Recently, 2-decaprenyl-3-methyl-6-methoxy-1,4-benzoquinone (V, n = 10) isolated[4] from *Rhodospirillum rubrum* has been implicated as a biosynthetic precursor to ubiquinone-10 in this organism.[4] Similarly, 2-nonaprenyl-3-methyl-6-methoxy-1,4-benzoquinone (V, n = 9) has since been isolated from *Pseudomonas ovalis*.[15] Prominent peaks in the mass spectrum of 2-decaprenyl-3-methyl-6-methoxy-1,4-benzoquinone (V, n = 10) at m/e 205 and 167 are characteristic[2,4] of the pyrilium (VI) and benzylium (VII) ions, respectively. It is important to recognize that the appearance of these prominent peaks coupled with corresponding parent ion peaks on mass spectra of ubiquinones-9 and -10 is artifactual and should not be mistaken for the presence of a naturally occurring monomethoxyquinone.

Experimental Section

Mass Spectrometric Determinations.—The mass spectra were determined using a modified CEC-103 spectrometer[2] at an ionizing voltage of 70 ev and probe temperatures as listed in Table I. It is pertinent to note that this instrument is equipped with a stainless steel inlet system, since thermal reactions at high temperatures are known to be promoted by metal surfaces.[16]

Pyrolysis of Ubiquinol-9 (II, n = 9). A.—Highly purified synthetic ubiquinone-9 (I, n = 9; 50 mg) was reduced with sodium hydrosulfite as previously described.[2] The resulting colorless ubiquinol-9 (II, n = 9) was heated at 285° under reduced pressure (<1 mm) for 20 min. The sample was then separated by thin-layer chromatography using silica gel G plates (1.0 mm) developed in hexane–ether (3:2). During this procedure the hydroquinones present were air-oxidized to the corresponding quinones which appeared as yellow-to-orange bands on the thin layer plates. The adsorbent was removed from the area of the plate below the Q-9 band (identified by use of a reference). This material was eluted and subjected to a second thin layer chromatographic separation using silica gel G plates (1.0 mm) developed five times using hexane–ether (9:1). Three distinct bands were apparent. The two more polar bands (R_{Q-9} 0.0, 0.4) showed uv absorption, λ_{max}^{hexane} 272 mμ, similar to Q-9.[17] The third quinone band (R_{Q-9} 0.65) was at λ_{max}^{hexane} 265 and 272 mμ (sh), characteristic of a monomethoxymethylmultiprenyl-1,4-benzoquinone;[4,15] V (n = 9) showed λ_{max}^{hexane} 265 and 272 mμ; and 2-phytyl-3-methyl-5-methoxy-1,4-benzoquinone exhibited λ_{max}^{hexane} 266 and 273 mμ.[18]

B.—When 40 mg of ubiquinol-9 was heated at 170° for 12 hr at 1-mm pressure, no monomethoxymethylmultiprenylbenzoquinone was detected.

C.—A sample (30 mg) of ubiquinol-9 in a nitrogen-flushed sealed ampoule was pyrolized by heating to 320° in a Wood's metal bath during ~30 min and then allowed to cool. Separation of the reaction mixture as described above yielded a purified product with λ_{max}^{hexane} 266 and 273 mμ (sh) identifying it as a monomethoxymethylmultiprenylbenzoquinone (IV).[4,15,18]

Pyrolysis of Ubiquinone-9 (I, n = 9).—Samples of ubiquinone-9 (I, n = 9) were pyrolized using each of the procedures (A, B, and C) described above for ubiquinol-9. Under none of these conditions was a product corresponding to the monomethoxymethylmultiprenylbenzoquinone detected.

Registry No.—I (n = 9), 15393-57-4; II (n = 9), 5677-54-3; III (n = 9),[19a] 15393-55-2; III (n = 9),[19b] 15393-56-3; IV (n = 9),[19a] 15350-50-2; IV (n = 9),[19b] 7200-28-4.

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Synthesis of O,O-Dialkyl S-Aryl Phosphorothiolates

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The dialkyl S-aryl phosphorothiolates are isomeric with important phosphorothionate insecticides but only the dimethyl and diethyl S-(4-nitrophenyl) derivatives have been examined for toxicological and other bio-

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TABLE I

O,O-DIALKYL S-ARYL PHOSPHOROTHIOLATES

Substituents[d] Alkyl	Substituents[d] Phenyl	Yield, %	Calcd, % C	Calcd, % H	Found, % C	Found, % H	Characteristic ir bands, cm^{-1}
Methyl	H	19	44.00	5.08	43.94	5.17	1260 (P=O), 1180 (P-OCH_3), 3060 (aromatic H)
Methyl	4-Cl	69	38.00	3.99	38.19	4.14	1263 (P=O), 1180 (P-OCH_3), 3070 (aromatic H)
Ethyl	H	69	48.74	6.14	49.00	6.24	1255 (P=O), 1160 (P-OC_2H_5), 3060 (aromatic H)
Ethyl	4-Cl	68	42.80	5.01[a]	43.01	5.21	1256 (P=O), 1160 (P-OC_2H_5), 815 (*para*-substituted phenyl)
Ethyl	2-Cl	66	42.80	5.01	42.59	5.19	1258 (P=O), 1160 (P-OC_2H_5), 745 (*ortho*-substituted phenyl)
Ethyl	2,4,5-Cl_3	65	34.43	3.47	34.58	3.48	1262 (P=O), 1160 (P-OC_2H_5), 880 (1,2,4,5-substituted phenyl)
Ethyl	4-Br	60	36.91	4.34	36.70	4.50	1255 (P=O), 1158 (P-OC_2H_5), 810 (*para*-substituted phenyl)
Ethyl	4-F[b]	68	45.45	5.30	45.40	5.51	1256 (P=O), 1152 (P-OC_2H_5), 822 (*para*-substituted phenyl)
Ethyl	4-CH_3[b]	75	50.72	6.59	50.54	6.67	1253 (P=O), 1158 (P-OC_2H_5), 802 (*para*-substituted phenyl)
Ethyl	4-NO_2[c]		41.23	4.81	38.46	5.38	1260 (P=O), 1160 (P-OC_2H_5), 1523 and 1342 (NO_2-phenyl)
Isopropyl	H	75	52.51	6.98	52.31	7.17	1258 (P=O), 1385 ($CH(CH_3)_2$), 742 and 690 (monosubstituted phenyl)
Isopropyl	4-Cl	73	46.65	5.88	46.85	6.00	1258 (P=O), 1385 and 1375 ($CH(CH_3)_2$), 818 (*para*-substituted phenyl)
Isopropyl	2,4,5-Cl_3	87	38.13	4.27	38.40	4.40	1263 (P=O), 1385 and 1365 ($CH(CH_3)_2$), 880 (1,2,4,5-substituted phenyl)

[a] Additional analysis. Calcd: Cl, 12.61; S, 11.41; P, 11.01. Found: Cl, 12.51; S, 11.23; P, 11.11. [b] A 1:1:1 molar ratio of reactants was used in these syntheses. [c] The yellow crystals, mp 41.5–41.7°, collected during attempted purifications of the S-(4-nitrophenyl) derivative had an infrared spectrum consistent with the proposed ethyl S-(4-nitrophenyl) sulfide structure, including bands at 2980, 2920, and 2870 ($-C_2H_5$) and at 1520 and 1320 cm^{-1} (NO_2-phenyl). [d] Respective registry no.: 4237-00-7; 3309-87-3; 1889-58-3; 4524-70-3; 15224-41-6; 15224-42-7; 15224-36-9; 333-42-6; 4143-38-8; 3270-86-8; 15267-38-6; 15267-39-7; 15267-40-0.

logical properties. These two compounds appear to have a relatively high mammalian toxicity compared with the corresponding phosphorothionate isomers, but their toxicity to insects is relatively low.[2-5]

To further investigate the toxic properties of this class of compounds, we sought a synthetic method generally applicable to them. Several published methods suggest routes to S-aryl phosphorothiolates but each is subject to particular limitations which restrict its general usefulness.[6-9]

The reaction of bromotrichloromethane, triethyl phosphite, and butane-1-thiol, which reportedly involves a radical-chain transfer mechanism (eq 1–3) has been

$$RS\cdot + (C_2H_5O)_3P \longrightarrow (C_2H_5O)_3P(SR)\cdot \quad (1)$$

$$(C_2H_5O)_3P(SR)\cdot + BrCCl_3 \longrightarrow ((C_2H_5O)_3P\cdot SR)^+Br^- + CCl_3\cdot \quad (2)$$

$$((C_2H_5O)_3P\cdot SR)^+Br^- \longrightarrow (C_2H_5O)_2P(O)SR + C_2H_5Br \quad (3)$$

shown to produce O,O-diethyl S-butyl phosphorothiolate in high yield and has indicated a possible route of general utility in phosphorothiolate synthesis.[10] We have found this reaction very useful in the synthesis of O,O-dialkyl S-aryl phosphorothiolates in which the alkyl group is methyl, ethyl, or *i*-propyl and the aryl group is substituted phenyl. Highest yields of the S-butyl phosphorothiolate resulted when the molar ratio of triethyl phosphite–bromotrichloromethane–butane-1-thiol was 1:2:4, respectively,[10] so this was the molar ratio we used in most syntheses. However, the diethyl S-(4-methylphenyl) and S-(4-fluorophenyl) derivatives were obtained in high yields beginning with equimolar quantities of reactants.

Trimethyl phosphite was the least reactive of the three trialkyl phosphites used. After the reactants were mixed, the reaction mixture warmed slightly but no spontaneous boiling or color change was observed as in some of the triethyl and tri-*i*-propyl syntheses. O,O-dimethyl S-(2,4,5-trichlorophenyl) phosphorothiolate could not be prepared by the method. Heating and exposing the reaction mixture to uv light did not initiate the reaction.

Multimolecular column adsorption chromatography[11] enabled purification of all products with the exception of O,O-diethyl S-(4-nitrophenyl) phosphorothiolate. Repeated attempts to purify this product by this technique consistently resulted in the isolation of ethyl 4-nitrophenyl sulfide. Thermal decomposition of O,O-diethyl S-aryl phosphorothiolates to form ethyl S-aryl sulfides and alkyl polyphosphates has been reported.[8] Evidently this phosphorothiolate is sufficiently unstable to be degraded by activated Florisil.

Experimental Section

The trialkyl phosphite, bromotrichloromethane, and aromatic thiol, in 1:2:4 molar ratio to give a 1-g theoretical yield, were mixed in 2.5 × 20 cm borosilicate tubes. Reaction occurred spontaneously with heat evolution after an incubation period of one to several minutes. When the reaction mixture had cooled to room temperature, it was dissolved in 25 ml of hexane and rinsed onto the Florisil column.[11] Each fraction was collected in a tared beaker. In initial purifications thin layer chromatography[12] was used to monitor column fractions. Unreacted aromatic thiol was predominantly eluted in the first three fractions. Most of the phosphorothiolates, with the exception of the diethyl S-(4-nitrophenyl) compound, came off the column in fractions 9, 10, and 11. Tlc showed the product to be homogenous in all cases examined. After evaporation of solvents the beakers containing the product were reweighed and the yield calculated.

All ir spectra were obtained on a Beckman IR-10 spectrophotometer using a KBr sealed cell, 0.1-mm path length. Scans were made in CCl_4 from 4000 to 1320 cm^{-1} and in CS_2 from 1320 to 400 cm^{-1}.

The phosphorothioates synthesized, yields, elemental analyses, and some characteristic ir absorption bands are found in Table I.

Registry No.—Ethyl S-(4-nitrophenyl)sulfide, 7025-60-9.

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