mmol) of *N*-chlorosuccinimide and 1.36 g (18 mmol) of dimethyl sulfide at −30 °C was added dropwise 1.5 g (10 mmol) of 3,3-dideuterio-3-hydroxy-2-methyl-1-phenylpropene. The solution was stirred until clear (1 h). It was then poured onto an ice–NaCl solution mixture, and the organic layer was washed twice with saturated NaCl solution and dried over Na_2CO_3. The solvent was removed by rotary evaporation to yield 1.6 g (9 mmol) of the allylic chloride: ^{1}H NMR δ 1.93 (d, J = 1.5 Hz, CH_3), 6.58 (d, broad, =CH), 7.38 (s, C_6H_5).

3,3,3-Trideuterio-2-methyl-1-phenylpropene (Entry 4, Table I). The styryl chloride from above (0.7 g (4 mmol)), dissolved in THF, was added dropwise to 5 mL (5 mmol) of 1 M Super D in THF. The solution was stirred for several hours, washed with saturated NaCl, and dried over Na_2CO_3. Olefin remaining after solvent removal amounted to 0.46 g (3.4 mmol): ^{1}H NMR δ 1.82 (d, J = 1 Hz, CH_3), 6.25 (s, broad, =CH), 7.2 (s, C_6H_5).

(*Z*)-1,3-Dichloro-2-butene (Entry 10, Table I). Dimethyl sulfide (5.3 mL (72 mmol)) was added dropwise to a stirred mixture of 8 g (60 mmol) of *N*-chlorosuccinimide in dichloromethane at 0 °C. The mixture turned milky and was cooled to −30 °C. A dichloromethane solution of 1.76 g (20 mmol) of 2-butene-1,4-diol (91% cis) was added dropwise to the milky suspension. The solution was stirred and maintained at temperatures below 0 °C until it became clear. It was then poured onto a mixture of ice and NaCl solution. The organic layer was washed twice with saturated NaCl and then dried over Na_2CO_3, and the solvent was removed by rotary evaporation yielding 1.75 g (14 mmol of the dichloride: ^{1}H NMR δ 4.05 (m, CH_2), 5.93 (m, =CH) (this spectrum matched Sadtler 9282M).

(*Z*)-2-Butene (Entry 10). A diglyme solution of 1.35 g (11 mmol) of the *cis*-1,4-dichloro-2-butene was added dropwise to a suspension of 2.05 g (54 mmol) of lithium aluminum hydride in 50 mL of diglyme at −50 °C. After the addition, the reaction mixture was brought slowly to room temperature. The *cis*-2-butene was distilled out of the diglyme into a flask cooled to −78 °C. Approximately 0.5 g of olefin was isolated. The identity (isomeric purity) was confirmed by VPC comparison with commerical cis and trans isomers: ^{1}H NMR δ 1.6 (m, CH_3), 5.45 (m, =CH).

Spectral Data for Other Olefins. Olefins from Table I were purified by preparative gas chromatography, in a few cases removing slight quantities of allylic rearrangement isomers (<10%). These spectral data confirm the absence of significant cis–trans isomerization.

(*E*)-1-Deuterio-2-methyl-2-butene (entry 2): ^{1}H NMR δ 1.57 (d, broad, CH_3), 1.63 (s, broad, CH_3 + CH_2D), 5.32 (q, broad, =CH).

(*E*)-3,3-Dideuterio-2-methyl-1-phenylpropene (entry 3): ^{1}H NMR δ 1.82 (d, J = 1 Hz, CH_3 + CHD_2), 6.25 (s, broad, =CH), 7.2 (s, C_6H_5).

2-Deuterio-2-methyl-2-pentene (entry 5): ^{1}H NMR δ 0.91 (dt, J_d = 7.5 Hz, J_t = 1 Hz, CH_3), 1.60 (s, broad, CH_3), 1.68 (s, broad, CH_3), 1.92 (m, CHD), 5.13 (d, broad, =CH).

2,2-Dideuterio-2-methyl-2-pentene (entry 6): ^{1}H NMR δ 0.90 (s, broad, $-CH_3$), 1.57 (d, J = 1.5 Hz, CH_3), 1.65 (d, J = 1.5 Hz, CH_3), 5.12 (s, broad, =CH).

(*Z*)-4-Deuterio-3-methyl-2-pentene (entry 7): ^{1}H NMR δ 0.95 (d, broad, CH_3), 1.55 (d, broad, CH_3), 1.60 (s, broad, CH_3), 2.0 (m, broad, CHD), 5.16 (q, broad, =CH).

(*E*)- and (*Z*)-1,1,1,4,4,4-hexadeuterio-2,3-dimethyl-2-butene (entries 8 and 9): ^{1}H NMR δ 1.63 (s, CH_3).

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Registry No. 1,1-Dideuterio-3-methyl-2-buten-1-ol, 6158-92-5; 1-bromo-1,1-dideuterio-3-methyl-2-butene, 70576-39-5; 1,1,1-trideuterio-3-methyl-2-butene, 1560-58-3; (*E*)-2-methyl-2-buten-1-ol, 497-02-9; (*E*)-1-bromo-2-methyl-2-butene, 57253-30-2; (*E*)-1-deuterio-2-methyl-2-butene, 70576-40-8; (*E*)-1,1-dideuterio-2-methyl-3-phenyl-2-propen-1-ol, 70576-41-9; (*E*)-1-chloro-1,1-dideuterio-2-methyl-3-phenyl-2-propene, 70576-42-0; (*E*)-3,3-dideuterio-2-methyl-1-phenylpropene, 70576-43-1; (*E*)-3,3,3-trideuterio-2-methyl-1-phenylpropene, 70576-44-2; 4-methyl-3-penten-2-ol, 4325-82-0; 2-methyl-4-chloro-2-pentene, 21971-94-8; 2-methyl-4-deuterio-2-pentene, 70576-45-3; 2-deuterio-4-methyl-3-penten-2-ol, 70576-46-4; 2-methyl-4-chloro-4-deuterio-2-pentene, 70576-47-5; 2-methyl-4,4-dideuterio-2-pentene, 70576-48-6; (*Z*)-3-methyl-3-penten-2-ol, 64683-06-3; (*Z*)-3-methyl-4-chloro-2-pentene, 70576-49-7; (*Z*)-4-deuterio-3-methyl-2-pentene, 70576-50-0; (*Z*)-1,1,4,4-tetradeuterio-2,3-dimethyl-2-buten-1,4-diol, 70576-51-1; (*Z*)-1,1,4,4-tetradeuterio-1,1-dichloro-2,3-dimethyl-2-butene, 70576-52-2; (*Z*)-1,1,1,4,4,4-hexadeuterio-2,3-dimethyl-2-butene, 38132-19-3; (*E*)-1,1,4,4-tetradeuterio-2,3-dimethyl-2-buten-1,4-diol, 70576-53-3; (*E*)-1,1,4,4-tetradeuterio-1,4-dichloro-2,3-dimethyl-2-butene, 70576-54-4; (*E*)-1,1,1,4,4,4-hexadeuterio-2,3-dimethyl-2-butene, 38132-24-0; (*Z*)-2-butene-1,4-diol, 6117-80-2; (*Z*)-1,4-dichloro-2-butene, 1476-11-5; (*Z*)-2-butene, 590-18-1.

Electrosynthesis of Heteroatom–Heteroatom Bonds. 4. Direct Cross-Coupling of Dialkyl (or Diaryl) Phosphites with Disulfides by a Sodium Bromide Promoted Electrolytic Procedure

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Homologues of *S*-alkyl (or -aryl) *O,O*-dialkyl (or -diaryl) phosphorothiolates (**1**) are of interest as effective pesti-

$$\underset{\mathbf{2}}{(RO)_2P(O)H} + \underset{\mathbf{3}}{R'\text{-}S\text{-}S\text{-}R'} \xrightarrow[NaBr]{-e} \underset{\mathbf{1}}{(RO)_2P(O)\text{-}S\text{-}R'}$$

cides,[1] and a variety of synthetic procedures for **1** have been investigated.[2-8] As a result, the formation of the S–P bond of **1** has been achieved by the reaction of dialkyl (or diaryl) phosphites (**2**) with sulfenyl chlorides,[2] sulfenyl cyanides,[3] thiosulfonates,[4] disulfides,[5] and sulfur,[6] by the condensation of phosphorochloridate with thiols,[7] and by other reactions.[8]

In our preceding papers,[9a] we reported the electrolytic S–N bond-making reaction, yielding various sulfenamides from disulfides and amines. These results prompted us to extend the electrochemical procedure to making the S–P bond of **1** and we found that the direct cross-coupling of dialkyl (or diaryl) phosphites (**2**) with disulfides (**3**) proceeds smoothly by sodium bromide assisted electrolysis.

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Table I
Conditions[a] and Results of Electrosynthesis of *O,O*-Diethyl *S*-Phenyl Phosphorothiolates 1

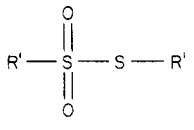
entry	halide salt (amt, mg)	electrodes	amt of electricity, F/mol (mA cm^{-2})	time, h	product yield,[b] %
1	none	Pt	3.5 (2.8-0.1	60.3	23
2	NaBr (3)	Pt	2.6 (1.2-0.1)	73	72
3	NaBr (10)	Pt	3.0 (3.7-0.1)	15.3	84
4	NaBr (50)	Pt	3.5 (5.0-2.0)	5	91
5	NaBr (50)	Pt	2.0 (2.7-0.8)	5.5	81
6	NaBr (100)	Pt	3.5 (4.3-0.9)	8	87
7	NaI (50)	Pt	3.5 (11.0-1.4)	4.4	73
8	NaCl (50)	Pt	3.5 (1.4-0.2)	28	59
9	KBr (50)	Pt	3.5 (6.7-1.2)	7.5	76
10	LiBr (50)	Pt	3.5 (4.2-1.5)	5.5	69
11	Et_4NBr (50)	Pt	3.5 (10.3-2.8)	3.8	46
12	NaBr (50)	C	3.5 (2.6-0.7)	14.5	41
13	NaBr (50)	Sus	3.5 (4.3-0.5)	19.1	57

[a] Electrolyses were carried out in MeCN (20 mL) containing Et_4NClO_4 (100 mg) at a constant applied voltage of 3 V at 20-25 °C. [b] Isolated yields based on 3.

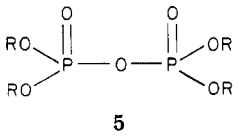
Table II
Electrosynthesis of *S*-Alkyl (or Aryl) *O,O*-Dialkyl (or Diaryl) Phosphorothiolates 1

entry	phosphite 2 R	disulfide 3 R′	current density, mA/cm^2 (F/mol)	time, h	product convrsn, %	product selectivity, %
1	methyl	phenyl	4.0-1.6 (3.5)	8	89	67
2	methyl	benzyl	5.3-0.3 (3.5)	27.5	95	71
3	methyl	butyl	5.7-0.8 (3.5)	12	81	88
4	methyl	cyclohexyl	5.0-2.5 (3.5)	5.2	83	57
5	methyl	$(CH_2)_2COOMe$	3.3-1.0 (2.8)	9	69	57
6	methyl	CH_2COOEt	2.2-0.9 (3.5)	12	100	75
7	ethyl	phenyl	5.0-2.0 (3.5)	5	91	100
8	ethyl	benzyl	3.0-1.8 (3.5)	10	91	98
9	ethyl	butyl	5.0-1.7 (3.5)	7.4	96	72
10	ethyl	cyclohexyl	2.4-0.9 (3.5)	11.2	97	79
11	ethyl	$(CH_2)_2COOMe$	4.8-1.2 (2.5)	5.8	97	58
12	ethyl	CH_2COOEt	3.1-0.8 (2.0)	7	89	78
13	isopropyl	phenyl	5.0-2.2 (4.0)	7	92	80
14	isopropyl	benzyl	3.3-0.5 (3.5)	8.3	100	97
15	isopropyl	cyclohexyl	7.7-2.0 (3.5)	5.6	82	78
16	phenyl	phenyl	6.0-0.5 (3.5)	6.8	57	89
17	phenyl	benzyl	5.0-0.1 (3.0)	12.6	68	75
18	phenyl	cyclohexyl	6.1-0.1 (3.5)	13	49	92

Electrolysis of a suspension of diethyl phosphite (**2**, R = Et), diphenyl disulfide (**3**, R′ = phenyl), and sodium bromide in acetonitrile containing Et_4NClO_4 as a supporting electrolyte was carried out at a constant voltage of 3 V, at 20–25 °C in a cell fitted with two platinum-foil electrodes. The anode potential varied between 0.1 and 0.9 V vs. $Ag/AgClO_4$. During the electrolysis the current density varied from 5 to 1 mA/cm^2. After passage of 2.0–3.5 F/mol (based on **3**) of electricity, the desired **1** (R = Et, R′ = phenyl) was obtained in 72–91% yields, depending upon the amount of bromide salt present (Table I, entries 2–6). A similar electrolysis without sodium bromide (entry 1) gave only a 23% yield of **1** along with thiosulfonate **4** (R′ = phenyl, 22%) and a small amount of tetraethyl pyrophosphate **5** (R = Et).[10] These results suggest that sodium bromide plays a significant role in the S–P bond formation.



4



5

Next, we examined the effect of halide ions by using sodium halides. Entries 7 and 8 reveal that both sodium iodide and sodium chloride were less effective than sodium bromide. Furthermore, variation of the cation yielded percentages of **1** in the following order (yield (percent) for entries 4, 9, 10, and 11): Na^+ (91) > K^+ (76) > Li^+ (69) > Et_4N^+ (46). The product yields also seem to depend, in part, upon the electrodes employed since carbon or stainless steel (SUS 27) electrodes provided **1** (R = Et, R′ = Ph) in 41 or 57% yield, respectively (entries 12 and 13).

A number of select dialkyl (or diaryl) phosphites **2** were allowed to react with disulfides **3**. The results of the electrosyntheses of phosphorothiolates **1** are summarized in Table II.

Mechanistic Consideration. A plausible mechanism for the S–P bond-making reaction is illustrated in Scheme I. The current–potential curves of various electrolysis

Scheme I

$$2Br^- \xrightarrow{\text{at the anode}} Br_2 + 2e^- \quad (1)$$

$$\underset{\mathbf{2}}{(RO)_2P(O)H} + Br_2 \rightarrow \underset{\mathbf{a}}{(RO)_2P(O)Br} + HBr \quad (2)$$

$$\underset{\mathbf{a}}{(RO)_2P(O)Br} + \underset{\mathbf{3}}{R'SSR'} \rightarrow \underset{\mathbf{1}}{(RO)_2P(O)SR'} + \underset{\mathbf{b}}{R'SBr} \quad (3)$$

$$\underset{\mathbf{2}}{(RO)_2P(O)H} + \underset{\mathbf{b}}{R'SBr} \rightarrow \underset{\mathbf{1}}{(RO)_2P(O)SR'} + HBr \quad (4)$$

$$2\underset{\mathbf{2}}{(RO)_2P(O)H} + \underset{\mathbf{3}}{R'SSR'} \xrightarrow{2 \text{ faradays/mol}} 2\underset{\mathbf{1}}{(RO)_2P(O)SR'} + H_2 \quad (5)$$

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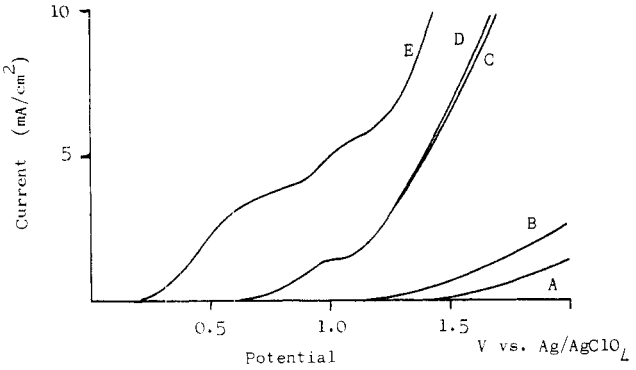


Figure 1. Current–potential curves: (A) 100 mg of Et_4NClO_4 in 20 mL of MeCN; (B) 2 mmol of **2** (R = Et) in system A; (C) 1 mmol of **3** (R′ = phenyl) in system A; (D) 2 mmol of **2** (R = Et) and 1 mmol of **3** (R′ = phenyl) in system A; (E) 50 mg of NaBr in system D.

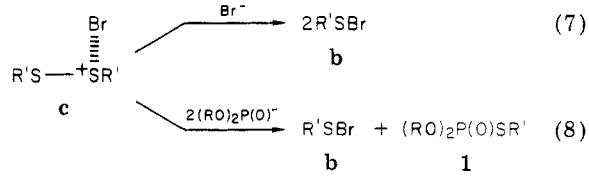
systems are shown in Figure 1. Curve E reveals that the current begins to pass at 0.4–0.5 V vs. $Ag/AgClO_4$, closely related to the discharge potential of bromide ion (0.6 V vs. SCE).[9b] Therefore, under the employed conditions (0.7–0.9 V vs. $Ag/AgClO_4$), the bromide ion would be oxidized to bromine and/or bromonium ion by loss of two electrons at the anode (eq 1). The reaction of phosphite **2** with bromine would produce the corresponding phosphorobromidates[12] (**a**, eq 2), which can react with disulfides **3** to give the desired products **1** as well as sulfenyl bromides (**b**, eq 3). The reaction of **2** with **b** would also occur to provide **1** (eq 4).[13] The electrochemical S–P bond-making process involves a two-electron oxidation of bromide, producing 2 mol of **1** from 2 mol of **2** and 1 mol of **3** (summary eq 5). Actually, the passage of 2 F/mol of electricity can provide **1** in 81% yield (Table I, entry 5). Apparently, bromide ion can be regenerated in the electrolysis solution as an oxidation catalyst. The presence of the reaction intermediate **a** could not be ascertained, but the similar electrolysis of a mixture of **2** (R = Et) and NaBr in acetonitrile without adding **3** gave pyrophosphate **5** in 22% yield, which would be derived from the condensation of **a** and **2** in the presence of a trace of water (eq 6). Indeed, addition of water to the electrolysis solution readily provided **5** together with polymers of **2**.

$$\underset{\mathbf{a}}{(RO)_2P(O)Br} \xrightarrow[-HBr]{H_2O} (RO)_2P(O)OH \xrightarrow[-HBr]{\mathbf{a}} \mathbf{5} \qquad (6)$$

As another plausible intermediate for the S–P bond formation, one should consider the formation of the bromonium ion adduct **c** derived from direct attack of bromine on **3**, since intermediate **c** would react with **2** or bromide ion to give **1** or **b** (Scheme II). However, the electrolysis of a mixture of disulfide **3** (R′ = phenyl) and sodium bromide in acetonitrile gave no detectable amount of **b** but only the recovered **3** (89%) and the thiosulfonate **4** (R′ = phenyl, 4%),[14] indicating that the reaction (eq 7) may be ruled out from the hypothesis of the S–P bond-making reaction. However, the pathway shown in eq 8 cannot be excluded completely.

The similar current–potential curves of the systems C and D reveal that the reaction of **2** with **3** does not take place under these reaction conditions. If an equilibrium reaction between **2** and **3** did occur, one would observe

Scheme II



another oxidation peak due to R′SH at a lower potential.[15] Judging from the current–potential curve of the system C, it is unlikely that such an equilibrium reaction between **2** and **3** occurs.

Experimental Section

All melting points and boiling points are uncorrected. ^1H NMR spectra were obtained at 60 MHz with a Hitachi R-24 spectrometer. Chemical shifts (δ) are expressed in parts per million downfield from internal Me_4Si. IR spectra were determined with a JASCO Model IRA-I grating spectrometer. Current–potential measurements were carried out by using a Kowa Electronics Model PGS-1550 potentiogalvanostat and an FG-102A function generator. Elemental analyses were performed in our laboratory.

Materials. Commercially available chemicals were used unless otherwise noted. Disulfides **3** (R = cyclohexyl, CH_2COOEt,[16] and CH_2CH_2COOH)[17] were prepared by electrolytic coupling of corresponding thiols according to the reported procedure.[9a] Disulfide **3** (R = CH_2CH_2COOMe)[17] was obtained on treatment of **3** (R = CH_2CH_2COOH) with an excess amount of diazomethane.

General Procedure. A mixture of phosphite **2** (2.3 mmol), disulfide **3** (1 mmol), and halide salts in MeCN (20 mL) containing Et_4NClO_4 (100 mg) was placed in a cell (3.5-cm diameter, 10-cm high) fitted with a gas exit pipe, a thermometer, a magnetic stirrer, and two platinum-foil electrodes (3 × 2 cm^2) being placed parallel, 5 mm apart. The regulated dc power was supplied by a Metronix Model 543B instrument. The reaction conditions and results are summarized in Tables I and II. A typical experimental procedure is given below.

Electrosynthesis of *O,O*-Diethyl *S*-Phenyl Phosphorothiolate (1, R = Ethyl, R′ = Phenyl) (Table II, Entry 7). A mixture of **3** (R′ = phenyl, 218 mg, 1 mmol), **2** (R = Et, 320 mg, 2.3 mmol), and NaBr (50 mg) in MeCN (20 mL) containing Et_4NClO_4 (100 mg) was electrolyzed with vigorous stirring at 3 V of constant applied voltage (anode potential 0.7–0.9 V vs. $Ag/AgClO_4$, in MeCN) at 22–24 °C. During the course of the electrolysis the initial current density of 5 mA/cm^2 dropped to 2 mA/cm^2. After passage of 3.5 × 10^{-3} faradays of electricity the mixture was concentrated in vacuo and the residue was chromatographed (SiO_2, hexane/benzene/AcOEt) to give **1** (R = Et, R′ = phenyl, 454 mg, 91%) along with the recovered **2** (72 mg) and **3** (19 mg). **1** (R = Et, R′ = phenyl): bp 84–88 °C (0.02 torr) (lit.[18] bp 85 °C (0.02 torr)); IR (neat) 3062 (HAr), 1259 (P=O), 1160 (PO) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.30 (t, 6, CH_3), 4.11 (q, 2, CH_2), 4.26 (q, 2, CH_2), 7.03–7.73 (m, 5, HAr).

***O,O*-Dimethyl *S*-Phenyl Phosphorothiolate (1,[19] R = Methyl, R′ = Phenyl, Entry 1):** bp 70–75 °C (0.005 torr); IR (neat) 3060 (HAr), 1261 (P=O), 1189 (PO) cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.71, 3.93 (s, 6, CH_3), 7.23–7.75 (m, 5, HAr).

***S*-Benzyl *O,O*-Dimethyl Phosphorothiolate (1, R = Methyl, R′ = Benzyl, Entry 2):** bp 90–95 °C (0.005 torr) (lit.[6e] pb 98 °C (0.01 torr)); IR (neat) 3060 (HAr), 1260 (P=O), 1185 (PO) cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.56, 3.77 (s, 6, CH_3), 3.88, 4.13 (s, 2, CH_2), 7.11–7.51 (m, 5, HAr).

***S*-Butyl *O,O*-Dimethyl Phosphorothiolate (1,[20] R = Methyl, R′ = Butyl, Entry 3):** bp 45–50 °C (0.01 torr); IR (neat) 1260 (P=O), 1189 (PO) cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.73–1.12 (m, 3, CH_3), 1.12–1.97 (m, 4, CH_2), 2.57–3.12 (m, 2, CH_2), 3.69, 3.90 (s, 6, CH_3).

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S-Cyclohexyl O,O-Dimethyl Phosphorothiolate (1, R = Methyl, R′ = Cyclohexyl, Entry 4): bp 64–68 °C (0.02 torr); IR (neat) 1258 (P=O), 1188 (PO) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.04–2.51 (br, 10, CH_2), 2.98–3.56 (br, 1, CHS), 3.66, 3.88 (s, 6, CH_3).

Anal. Calcd for $C_8H_{17}O_3PS$: C, 42.85; H, 7.64. Found: C, 42.67; H, 8.03.

O,O-Dimethyl S-[2-(Methoxycarbonyl)ethyl] Phosphorothiolate (1, R = Me, R′ = CH_2CH_2COOMe, Entry 5): bp 57–62 °C (0.02 torr); IR (neat) 1740 (C=O), 1250 (P=O), 1180 (PO) cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.50–3.50 (m, 4, CH_2), 3.72 (s, 6, CH_3), 3.92 (s, 3, CH_3).

Anal. Calcd for $C_6H_{13}O_5PS$: C, 31.58; H, 5.74. Found: C, 31.11; H, 6.04.

O,O-Dimethyl S-(Ethoxycarbonyl)methyl Phosphorothiolate (1, R = Me, R′ = CH_2COOEt, Entry 6): bp 76–80 °C (0.01 torr) (lit.[21] bp 86 °C (0.05 torr)); IR (neat) 1740 (C=O), 1260 (P=O), 1185 (PO) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.28 (t, 3, CH_3), 3.45, 3.72 (s, 2 CH_2), 3.72, 3.93 (s, 6, CH_3), 4.31 (q, 2, CH_2S).

S-Benzyl O,O-Diethyl Phosphorothiolate (1, R = Ethyl, R′ = Benzyl, Entry 8): bp 110–114 °C (0.02 torr) (lit.[2] bp 129–131.5 °C (0.15 torr)); IR (neat) 3055 (HAr), 1260 (P=O), 1162 (PO) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.30 (t, 6, CH_3), 3.81–4.40 (m, 6, CH_2), 7.11–7.53 (m, 5, HAr).

S-Butyl O,O-Diethyl Phosphorothiolate (1, R = Ethyl, R′ = Butyl, Entry 9): bp 35–40 °C (0.01 torr) (lit.[22] bp 131–133 °C (10 torr)); IR (neat) 1464 (CH_2), 1258 (P=O), 1162 (PO) cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.70–1.10 (m, 3, CH_3), 1.10–1.93 (m, 4, CH_2), 1.33 (t, 6, CH_3), 2.53–3.10 (m, 2, CH_2S), 4.07 (q, 2, CH_2), 4.21 (q, 2, CH_2).

S-Cyclohexyl O,O-Diethyl Phosphorothiolate (1, R = Ethyl, R′ = Cyclohexyl, Entry 10): bp 67–70 °C (0.01 torr) (lit.[23] bp 99–102 °C (0.2 torr)); IR (neat) 1249 (P=O), 1155 (PO) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.03–2.20 (br, 10, CH_2), 1.36 (t, 6, CH_3), 2.93–3.58 (br, 1, CHS), 4.09 (q, 2, CH_2), 4.23 (q, 2, CH_2).

O,O-Diethyl S-[2-(Methoxycarbonyl)ethyl] Phosphorothiolate (1, R = Et, R′ = CH_2CH_2COOMe, Entry 11): bp 67–70 °C (0.02 torr) (lit.[24] bp 137 °C (3.0 torr)); IR (neat) 1738 (C=O), 1248 (P=O), 1160 (PO) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.36 (t, 6, CH_3), 2.50–3.40 (m, 4, CH_2), 3.70 (s, 3, CH_3), 4.09 (q, 2, CH_2), 4.24 (q, 2, CH_2).

O,O-Diethyl S-(Ethoxycarbonyl)methyl Phosphorothiolate (1, R = Et, R′ = CH_2COOEt, Entry 12): bp 70–75 °C (0.005 torr) (lit.[25] bp 78–81 °C (0.01 torr)); IR (neat) 1738 (C=O), 1258 (P=O), 1160 (PO) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.12–1.58 (m, 9, CH_3), 3.45, 3.70 (s, 2, CH_2S), 3.92–4.49 (m, 6, CH_2).

O,O-Diisopropyl S-Phenyl Phosphorothiolate (1,[19] R = Isopropyl, R′ = Phenyl, Entry 13): bp 88–92 °C (0.02 torr); IR (neat) 3048 (HAr), 1388, 1378, 1256 (P=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.24, 1.34 (dd, 12, CH_3), 4.48–5.04 (m, 2, CH), 7.26–7.66 (m, 5, HAr).

S-Benzyl O,O-Diisopropyl Phosphorothiolate (1, R = Isopropyl, R′ = Benzyl, Entry 14): bp 90–95 °C (0.01 torr) (lit.[26] bp 126 °C (0.04 torr)); IR (neat) 3056 (HAr), 1390, 1380, 1258 (P=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.26, 1.36 (dd, 12, CH_3), 3.96, 4.17 (s, 2, CH_2), 4.41–4.97 (m, 2, CH_2), 7.10–7.50 (m, 5, HAr).

S-Cyclohexyl O,O-Diisopropyl Phosphorothiolate (1, R = Isopropyl, R′ = Cyclohexyl, Entry 15): bp 60–65 °C (0.005 torr); IR (neat) 1452 (CH_2), 1386, 1376, 1246 (P=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.95–2.35 (br, 10, CH_2), 1.28, 1.38 (dd, 12, CH_3), 2.95–3.53 (br, 1, CHS), 4.43–4.99 (m, 2, CH).

Anal. Calcd for $C_{12}H_{25}O_3PS$: C, 51.41; H, 8.99. Found: C, 51.12; H, 9.08.

O,O-Diphenyl S-Phenyl Phosphorothiolate (1, R = Phenyl, R′ = Phenyl, Entry 16): bp 106–110 °C (0.02 torr); IR (neat) 3048 (HAr), 1274 (P=O), 1190 (PO) cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.95–7.65 (m, 15, HAr).

Anal. Calcd for $C_{18}H_{15}O_3PS$: C, 63.15; H, 4.42. Found: C, 63.16; H, 4.49.

S-Benzyl O,O-Diphenyl Phosphorothiolate (1, R = Phenyl, R′ = Benzyl, Entry 17): mp 64–66 °C (lit. mp 65–67 °C); IR (Nujol) 3040 (HAr), 1278 (P=O), 1194 (PO) cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.03, 4.25 (s, 2, CH_2), 7.07–7.40 (m, 15, HAr).

S-Cyclohexyl O,O-Diphenyl Phosphorothiolate (1, R = Phenyl, R′ = Cyclohexyl, Entry 18): bp 102–105 °C (0.01 torr); IR (neat) 3050 (HAr), 1485 (CH_2), 1262 (P=O), 1190 (PO) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.00–1.40 (br, 10, CH_2), 3.10–3.80 (br, 1, CHS), 7.30 (br, s, 10, HAr).

Anal. Calcd for $C_{18}H_{21}O_3PS$: C, 62.06: H, 6.08. Found: C, 62.03; H, 6.36.

Electrolysis of 3 (R′ = Phenyl) and NaBr in MeCN. A mixture of **3** (R′ = phenyl, 218 mg, 1 mmol) and NaBr (129 mg, 1.25 mmol) in MeCN (20 mL) containing Et_4NClO_4 (100 mg) was electrolyzed at 3 V (applied voltage), 4–3 mA/cm^2, at 29–30 °C for 2.5 h. After 2×10^{-3} faraday of electricity was passed and the solvent was removed, chromatography (SiO_2, hexane/benzene) gave **4** (R′ = phenyl, 11 mg, 4%) and recovered **3** (195 mg, 89%).

Electrolysis of 2 (R = Et) and NaBr in MeCN. A mixture of **2** (R = Et, 141 mg, 1 mmol) and NaBr (129 mg, 1.25 mmol), in MeCN (20 mL), was electrolyzed at 3 V (applied voltage), 1.4–1 mA/cm^2, at 27–28 °C for 6 h. After 1×10^{-3} faraday of electricity was passed and the solvent was removed, chromatography (SiO_2, $CHCl_3$/AcOEt) gave **5** (R = Et, 63 mg) and recovered **2** (37 mg). IR and ^1H NMR spectra of **5** were identical with those of authentic sample.

Electrolysis of a Mixture of 2 and 3 without Using Halide Salts. A solution of **2** (R = Et, 320 mg, 2.3 mmol) and **3** (R′ = phenyl, 222 mg, 1 mmol) in MeCN (20 mL) containing Et_4NClO_4 (100 mg) was electrolyzed at a constant voltage of 3 V (anode potential 1.0–1.2 V vs. $Ag/AgClO_4$), giving 2.8–0.1 mA/cm^2, at 19–25 °C. After passage of 3.5×10^{-3} faraday of electricity during 60 h, the mixture was concentrated in vacuo and the residue was chromatographed (SiO_2, hexane/benzene/AcOEt) to give **1** (R = Et, R′ = phenyl, 117 mg, 23%), **2** (117 mg, 37%), **3** (19 mg, 9%), and **4** (R′ = phenyl, 54 mg, 22%).

Registry No. **1** (R = Me, R^1 = phenyl), 4237-00-7; **1** (R = Me, R^1 = benzyl), 7205-16-5; **1** (R = Me, R^1 = butyl), 26901-83-7; **1** (R = Me, R^1 = cyclohexyl), 70550-08-2; **1** (R = Me, R^1 = CH_2CH_2COOMe), 70550-09-3; **1** (R = Me, R^1 = CH_2COOEt), 2088-72-4; **1** (R = Et, R^1 = phenyl), 1889-58-3; **1** (R = Et, R^1 = benzyl), 13286-32-3; **1** (R = Et, R^1 = butyl), 20195-07-7; **1** (R = Et, R^1 = cyclohexyl), 26437-23-0; **1** (R = Et, R^1 = CH_2CH_2COOMe), 70550-10-6; **1** (R = Et, R^1 = CH_2COOEt), 2425-25-4; **1** (R = isopropyl, R^1 = phenyl), 15267-38-6; **1** (R = isopropyl, R^1 = benzyl), 26087-47-8; **1** (R = isopropyl, R^1 = cyclohexyl), 70550-11-7; **1** (R = phenyl, R^1 = phenyl), 70562-38-8; **1** (R = phenyl, R^1 = benzyl), 13879-47-5; **1** (R = phenyl, R^1 = cyclohexyl), 70550-12-8; **2** (R = Me), 868-85-9; **2** (R = Et), 762-04-9; **2** (R = isopropyl), 1809-20-7; **2** (R = phenyl), 4712-55-4; **3** (R^1 = phenyl), 882-33-7; **3** (R^1 = benzyl), 150-60-7; **3** (R^1 = butyl), 629-45-8; **3** (R^1 = cyclohexyl), 2550-40-5; **3** (R^1 = $(CH_2)_2COOMe$), 15441-06-2; **3** (R^1 = CH_2COOEt), 1665-65-2; **4** (R^1 = phenyl), 1212-08-4; **5** (R = Et), 107-49-3.

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Convenient Synthesis of 9-Methylbenzo[*a*]pyrene[1]

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In connection with some studies concerning the diol epoxide mechanism of carcinogenesis for polycyclic aromatic hydrocarbons, we required a convenient synthesis

(1) In the earlier literature, this is referred to as 2′-methyl-3,4-benzpyrene; see "The Ring Index", 2nd Ed.; The American Chemical Society: Washington D.C.; 1960, p 922, entry 6399 for the presently accepted numbering.

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