Reaction with 1d gave products with retention times at 180 °C of 2.0 (2-bromo-4,6-dimethylphenyl isopropyl ether), 2.7 (2-bromo-4,6-dimethylphenol),[10b] and 4.8 min (2-bromo-4,6-dimethyl-3-isopropylphenol).

Reaction with 1e gave components with retention times at 180 °C of 1.8 (2,4-dichloro-6-methylphenyl isopropyl ether), 3.6 (2,4-dichloro-6-methylphenol),[12] and 5.0 min (2,4-dichloro-3-isopropyl-6-methylphenol).

Reaction with 1f gave products with retention times at 180 °C of 4.8 (2,4-dibromo-6-methylphenyl isopropyl ether), 8.7 (2,4-dibromo-6-methylphenol),[11] and 11.5 min (2,4-dibromo-3-isopropyl-6-methylphenol).

Reaction with 1g gave products with retention times at 200 °C of 3.1 (3,5-dibromo-2,4,6-trimethylphenyl isopropyl ether), and 17.0 min (3,5-dibromo-2,4,6-trimethylphenol).

Properties of *m*-Isopropylphenols. 4-Chloro-2,6-dimethyl-3-isopropylphenol was obtained as a pale yellow oil. Anal. Calcd for $C_{11}H_{15}OCl$: C, 66.50; H, 7.61. Found: C, 66.71; H, 7.59. ^1H NMR δ 1.36 (d, J = 8 Hz, 6 H), 2.15 (br s, 3 H), 2.23 (s, 3 H), 3.75 (m, 1 H), 6.92 (br s, 1 H).

4-Bromo-2,6-dimethyl-3-isopropylphenol was obtained as a yellow oil. Anal. Calcd for $C_{11}H_{15}OBr$: C, 54.34; H, 6.22; Br, 32.86. Found: C, 54.51; H, 6.29; Br, 32.58. ^1H NMR δ 1.37 (d, J = 8 Hz, 6 H), 2.09 (s, 3 H), 2.23 (s, 3 H), 3.65 (sept, 1 H), 4.50 (br s, 1 H), 7.06 (s, 1 H).

2-Bromo-4,6-dimethyl-3-isopropylphenol. Anal. Calcd for $C_{11}H_{15}OBr$: C, 54.34; H, 6.22. Found: C, 54.31; H, 6.50. ^1H NMR δ 1.33 (d, J = 8 Hz, 6 H), 2.16 (s, 3 H), 2.27 (s, 3 H), 4.58 (sept, J = 8 Hz, 1 H), 5.60 (br s, 1 H), 6.74 (s, 1 H).

2,4-Dichloro-3-isopropyl-6-methylphenol was a pale yellow oil. Anal. Calcd for $C_{10}H_{12}OCl_2$: C, 54.82; H, 5.52. Found: C, 54.81; H, 5.71. ^1H NMR δ 1.37 (d, J = 8 Hz, 6 H), 2.19 (s, 3 H), 3.78 (sept, 1 H), 5.83 (br s, 1 H), 7.05 (br s, 1 H).

2,4-Dibromo-3-isopropyl-6-methylphenol was obtained as a yellow oil. Anal. Calcd for $C_{10}H_{12}OBr_2$: C, 38.99; H, 3.93. Found: C, 39.09; H, 3.81. ^1H NMR δ 1.41 (d, J = 8 Hz, 6 H), 2.22 (s, 3 H), 3.80 (m, 1 H), 5.75 (br s, 1 H), 7.26 (br s, 1 H).

Synthesis of Aryl Isopropyl Ethers. In a typical reaction, 0.02 mol of the phenol was added to a solution of potassium *tert*-butoxide (2.4 g, 0.021 mol) in 20 mL of Me_2SO. The resulting solution was stirred at room temperature for 1 h, and a solution of 2-bromopropane (2.7 g, 0.022 mol) in 10 mL of Me_2SO was added slowly. After 1 h the solution was diluted with 100 mL of water and extracted twice with mixed hexanes. The combined organic layers were washed with water and extracted with Claisen's alkali, until the alkaline layer was colorless. The organic layer was washed with water, dried over magnesium sulfate, and filtered and the solvent evaporated under vacuum to give the nearly pure ether, which was chromatographed on activity III alumina, eluting with mixed hexanes.

4-Chloro-2,6-dimethylphenyl isopropyl ether (28% yield) was a colorless oil. Anal. Calcd for $C_{11}H_{15}OCl$: C, 66.50; H, 7.61. Found: C, 66.28; H, 7.51. ^1H NMR δ 1.23 (d, J = 7 Hz, 6 H), 2.21 (d, J = 1 Hz, 6 H), 4.13 (m, J = 7 Hz), 6.95 (m, 2 H).

4-Bromo-2,6-dimethylphenyl isopropyl ether (31% yield) was a colorless oil. Anal. Calcd for $C_{11}H_{15}OBr$: C, 54.34; H, 6.22. Found: C, 54.18; H, 5.84. ^1H NMR δ 1.25 (d, J = 8 Hz, 6 H), 2.20 (s, 6 H), 4.10 (sept, J = 8 Hz, 1 H), 7.07 (br s, 2 H).

2-Bromo-4,6-dimethylphenyl isopropyl ether (22% yield) was a pale yellow oil. Anal. Calcd for $C_{11}H_{15}OBr$: C, 54.34; H, 6.22. Found: C, 54.39; H, 5.96. ^1H NMR δ 1.26 (d, J = 8 Hz, 6 H), 2.20 (s, 3 H), 4.42 (sept, J = 8 Hz), 6.84 (m, 1 H), 7.13 (m, 1 H).

2,4-Dichloro-6-methylphenyl isopropyl ether was a pale yellow oil. Anal. Calcd for $C_{10}H_{12}OCl_2$: C, 54.82; H, 5.52. Found: C, 54.79; H, 5.27. ^1H NMR δ 1.22 (d, J = 8 Hz, 6 H), 2.15 (s, 3 H), 4.37 (sept, J = 8 Hz, 1 H), 6.95 (d, J = 2 Hz, 1 H), 7.13 (d, J = 2 Hz, 1 H).

2,4-Dibromo-6-methylphenyl isopropyl ether was a yellow oil. Anal. Calcd for $C_{10}H_{12}OBr_2$: C, 38.99; H, 3.93. Found: C, 39.20; H, 3.98. ^1H NMR δ 1.20 (d, J = 7.5 Hz, 6 H), 2.14 (s, 3 H), 4.07 (sept, J = 7.5 Hz, 1 H), 7.05 (m, 2 H).

3,5-Dibromo-2,4,6-trimethylphenyl isopropyl ether was a yellow oil. Anal. Calcd for $C_{12}H_{16}OBr_2$: C, 42.89; H, 4.80. Found: C, 42.97; H, 5.01. ^1H NMR δ 1.39 (d, J = 8 Hz, 6 H), 2.41 (s, 6 H), 2.71 (s, 3 H), 4.16 (m, J = 8 Hz, 1 H).

Acknowledgment. We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, for a grant in support of this work.

Metalation-Induced Double Migration of Phosphorus from O→C. Convenient Preparation of Bis(2-hydroxyaryl)phosphinic Acids

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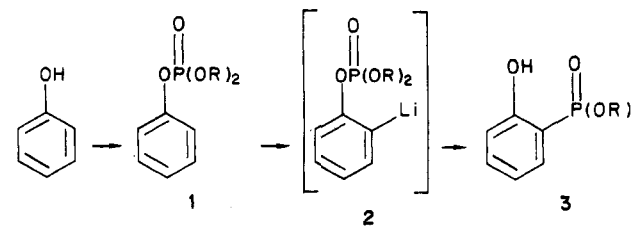
Received June 25, 1985

Treatment of diaryl ethyl phosphates **8** with lithium diisopropylamide in tetrahydrofuran yields ethyl bis(2-hydroxyaryl)phosphinates **9**. The reaction involves the double migration of phosphorus from O→C and is probably intramolecular. These phosphinate esters **9** on treatment with trimethylsilyl chloride and sodium iodide in acetonitrile undergo transesterification to give trimethylsilyl esters that yield the corresponding phosphinic acids **15** on treatment with water.

Treatment of dialkyl aryl phosphates **1** with lithium diisopropylamide results in a rearrangement that involves the fission of an oxygen–phosphorus bond and formation of a carbon–phosphorus bond, yielding dialkyl (2-hydroxyaryl)phosphonates **3**.[1-4] Since **1** can be easily obtained from phenols, the net result of the sequence of reactions shown in Scheme I is the introduction of a dialkyl phosphonyl group $-P(=O)(OR)_2$ group ortho to the phenolic OH group. We are interested in exploring the synthetic potential of this rearrangement and have previously shown[5] that (a) the above sequence of reactions can be

Scheme I



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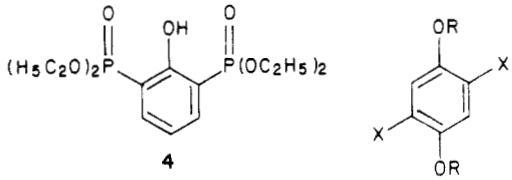
repeated with **3** to give tetraalkyl (2-hydroxy-1,3-arenediyl)diphosphonates **4** and (b) diphosphates, namely tetraethyl 1,4-phenylenediphosphate (**5a**) and tetraethyl 1,2-phenylenediphosphate (**6a**), on treatment with excess base undergo a double migration to yield tetraethyl (2,5-dihydroxy-1,4-phenylene)diphosphonate (**5b**) and tetraethyl (2,3-dihydroxy-1,4-phenylene)diphosphonate (**6b**), respectively.



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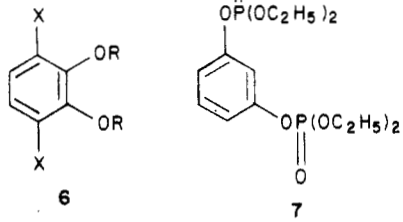

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7

	X	R
a	H	$-P(=O)(OC_2H_5)_2$
b	$-P(=O)(OC_2H_5)_2$	H
c	Li	$-P(=O)(OC_2H_5)_2$
d	Li	CH_3
e	H	$-C(=O)N(C_2H_5)_2$
f	$-C(=O)N(C_2H_5)_2$	H

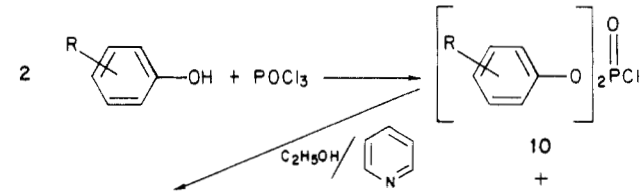
The rearrangement of **1** to **3** involves the ortho lithiation of the phosphate ester **1** followed by collapse of the lithiated species **2** with the migration of phosphorus from O→C (Scheme I).[6] The rearrangement of **5a** and **6a** may involve the dilithiation intermediates **5c** and **6c**, respectively. It is interesting to note in this context that a recent study[7] has shown that 1,4-dimethoxybenzene and 1,2-dimethoxybenzene form 2,5-dilithio **5d** and 1,4-dilithio **6d** intermediates, respectively, when treated with excess of lithiating reagent. Further, 1,3-dimethoxybenzene fails to undergo dilithiation and gives a complex mixture. This is in agreement with our observation that tetraethyl 1,3-phenylenediphoshate (**7**) yields a complex mixture when treated with excess base.[8] Recently **5e** has been shown to undergo dilithiation and double O–C 1,3-migration of carbamoyl group to yield **5f**.[9]

In this paper we report the preparation of ethyl bis(2-hydroxyaryl)phosphinates **9** from diaryl ethyl phosphates **8** by making use of this methodology. This involves another kind of ortho anion induced double 1,3-migration of phosphorus.

In addition, the conversion of the phosphinates to the corresponding phosphinic acids is reported.

Results and Discussion

Diaryl chlorophosphates **10** are generally prepared by refluxing 2 mol of phenol with 1 mol of phosphorus oxychloride with or without a catalyst. In this study the



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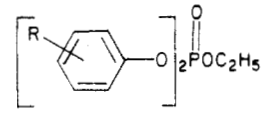

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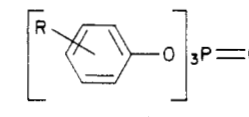

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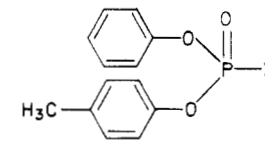

12, X = Cl
13, X = OC_2H_5

a, R = H
b, R = 3-CH_3-
c, R = 4-CH_3
d, R = 4-OCH_3

method of Kuzmenko and Rapp[10] using anhydrous aluminum chloride as a catalyst was used. It was found that the major product **10** was always accompanied by significant amounts of triaryl phosphate **11**. The two products were however readily separated by fractional distillation under reduced pressure. 4-Methylphenyl phenyl phosphorochloridate (**12**) was prepared by the reaction of 1 mol of phenyl dichlorophosphate with 1 mol of 4-methylphenol in presence of anhydrous $AlCl_3$. Treatment of diaryl chlorophosphates **10** (and **12**) with ethanol[11] gave diaryl ethyl phosphates **8** (and **13**) in fair to good yields. All these compounds except ethyl bis(3-methylphenyl) phosphate (**8b**) and ethyl 4-methylphenyl phenyl phosphate (**13**) were previously known.

Rearrangement of Diaryl Ethyl Phosphates 8 to Ethyl Bis(2-hydroxyaryl)phosphinates 9. Diaryl ethyl phosphates **8** on treatment with excess of lithium diisopropyl amide at −78 °C in tetrahydrofuran (THF) followed by warming to room temperature underwent clean rearrangement to give ethyl bis(2-hydroxyaryl)phosphinates **9**. The crude products **9** obtained as thick pastes exhibited a single signal at ca. 42–44 ppm in their ^{31}P NMR spectra. Pure products **9** were obtained after flash column chromatography as white crystalline solids in 63–73% yields. In the ^{13}C NMR spectra of ethyl bis(2-hydroxyaryl)phosphinates **9**, the one-bond C–P coupling constant[12] was found to be in the range 135–140 Hz. The two-bond coupling of phosphorus to C-6 carbon (7.81–9.76 Hz) was found to be larger than the two-bond coupling of phosphorus to C-2 carbon (3.91–5.86 Hz). The three-bond coupling of phosphorus to C-5 carbon (11.72–13.67 Hz) was larger than the three-bond coupling of phosphorus to C-3 carbon (7.81–11.72 Hz). All compounds were fully characterized by ^1H, ^{13}C, and ^{31}P NMR spectra and elemental analysis.

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(6) Other examples of ortho anion induced O→C 1,3-migrations are the following. Silicon: Habich, D.; Effenberger, F. *Synthesis* **1979**, 841. Carbamoyl group: Sibi, M. P.; Snieckus, V. *J. Org. Chem.* **1983**, *48*, 1935.
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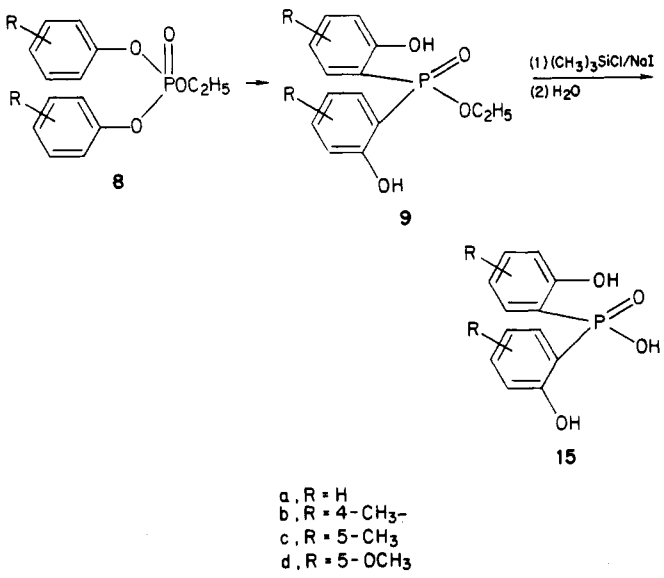
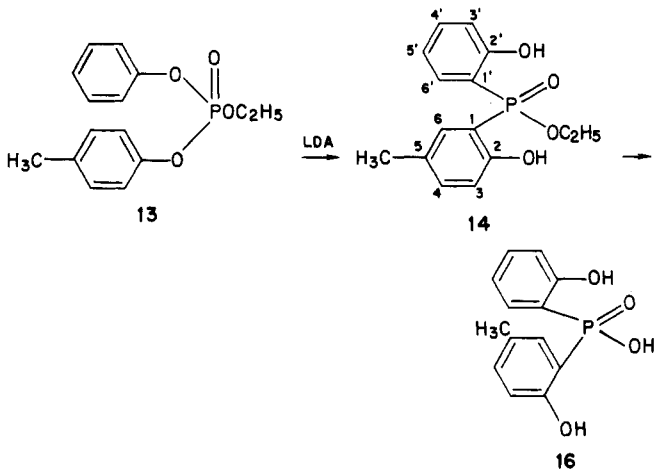
(12) For comparison, ethyl diphenylphosphinate was prepared by the reaction of diphenyl phosphinyl chloride with ethanol in presence of triethylamine: Berlin, K. D.; Austin, T. H.; Nagabhushanam, M. *J. Org. Chem.* **1965**, 30, 1267. ^{13}C NMR of ethyl diphenylphosphinate: δ 131.84 (C_4), 131.68 (d, 136.72 Hz, C_1), 131.48 (d, 9.78 Hz, C_2, C_6), 128.37 (d, 13.67 Hz, C_3, C_5), 60.97 (d, 5.86 Hz, CH_2), 16.43 (d, 5.86 Hz, CH_3).



Reaction of ethyl 4-methylphenyl phenyl phosphate (**13**) with lithium diisopropylamide gave a crude product that exhibited a single ^{31}P signal at 42.1 ppm in its ^{31}P NMR spectrum. The pure product **14**, isolated in 63% yield



after flash column chromatography, exhibited two different hydroxy protons at δ 9.75 and 10.05 in its ^1H NMR spectrum. In addition, it exhibited a singlet for Ar-CH_3 (2.28, s, 3 H), a triplet for CH_3 (1.40 3 H, J_{H-H} = 7 Hz), a doublet of quartet for CH_2 (4.18, $J_{H-H} \approx J_{P-H} \approx 7$ Hz, 2 H), and a multiplet for aromatic protons (6.75–7.62). These data are compatible with ethyl (2-hydroxy-5-methylphenyl)-(2′-hydroxyphenyl)phosphinate structure for **14**. The structure was further confirmed by ^{13}C NMR spectrum that contained two different hydroxyl bearing carbons [δ 159.73 (3.9 Hz, C_2) and 161.94 (3.91 Hz, C_2')] and two different aromatic carbons linked to phosphorus [110.84 (138.67 Hz, C_1) and 111.42 (136.72 Hz, C_1')]. The formation of a single phosphorus-containing product is indicative of the intramolecular nature of the reaction. If the reaction was intermolecular, several phosphorus-containing products including **9a** and **9c** would be possible.

We have previously reported[5] the hydrolysis of diethyl (2-hydroxyaryl)phosphonates via transesterification with trimethylsilyl chloride and sodium iodide followed by treatment with water to yield (2-hydroxyaryl)phosphonic acids. It was found that the hydrolysis of **9** to **15** could be achieved in a similar manner. The transesterification was performed at room temperature and required 20 h. The silyl esters on treatment with water gave good yields of bis(2-hydroxyaryl)phosphinic acids **15**. Phosphinate ester **14** was similarly converted to phosphinic acid **16**. All of the phosphinic acids prepared were characterized by ^1H, ^{13}C, and ^{31}P NMR spectra and elemental analysis.

Experimental Section

Melting points were obtained on a Mel-Temp melting point apparatus and are uncorrected. ^{31}P and ^{13}C spectra were obtained in $CDCl_3$ (unless otherwise stated) at 24.15 and 15.04 MHz, respectively. The chemical shift (+δ) values are downfield from H_3PO_4 (cap) for ^{31}P spectra and from Me_4Si for ^{13}C spectra. ^1H NMR spectra were obtained in $CDCl_3$ (unless otherwise stated) with Me_4Si as internal standard.

Diphenyl chlorophosphate and phenyl dichlorophosphate were purchased from Aldrich Chemical Co. Other diaryl chlorophosphates were prepared as described below.

Diaryl Chlorophosphates 10. A phenol (0.4 mol) was carefully added to a stirred mixture of phosphorus oxychloride (0.2 mol) and anhydrous $AlCl_3$ (0.56 g). The reaction mixture was first held at 110–125 °C for 3 h and then at 160–170 °C for 3 h. The crude products were then fractionally distilled under reduced pressure.

Bis(3-methylphenyl) Chlorophosphate (10b). There were obtained double-distilled bis(3-methylphenyl) chlorophosphate (68%) [bp 153–155 °C (0.05 mmHg); lit.[13] bp 160–164 °C (1.0 mmHg); ^{31}P NMR δ −5.31] and tris(3-methylphenyl) phosphate (**11b**) (19.5%) [bp 204 °C (0.05 mmHg); lit.[14] bp 258–263 °C (4 mmHg); ^{31}P NMR δ −17.64].

Bis(4-methylphenyl) Chlorophosphate (10c). There was obtained double-distilled bis(4-methylphenyl) chlorophosphate (55%): bp 150 °C (0.02 mmHg); lit.[15] bp 160–165 °C (0.08 mmHg); ^{31}P NMR δ −4.85. Tris(4-methylphenyl) phosphate[14] (**11c**) (13%) was present in the crude product as estimated by ^{31}P NMR at δ −17.08.

Bis(4-methoxyphenyl) Chlorophosphate (10d). There were obtained double-distilled bis(4-methoxyphenyl) chlorophosphate (**10d**) (30%) [bp 180 °C (0.02 mmHg); lit.[10] bp 209–210 °C (5–6 mmHg); ^{31}P NMR δ −3.79] and tris(4-methoxyphenyl) phosphate (**11d**) (34%) [bp 242–244 °C (0.02 mmHg); lit.[16] bp 290–292 °C (2.0 mmHg); ^{31}P NMR δ −16.02].

4-Methylphenyl Phenyl Chlorophosphate (12). A mechanically stirred mixture of phenyl dichlorophosphate (0.1 mol) and anhydrous aluminum chloride (0.25 g) was heated to 80 °C, and then *p*-cresol (0.1 mol) was added dropwise. After the completion of addition, the mixture was held at 120–125 °C for 5 h. It was next distilled under reduced pressure: bp 140 °C (0.02 mmHg); lit.[10] bp 224–228 °C (35 mmHg); ^{31}P NMR δ −5.20; ^{13}C NMR δ 20.78 (CH_3), 119.99 (d, 3.91 Hz, C_2, C_6), 120.32 (d, 5.86 Hz, $C_{2'}$,$C_{6'}$), 126.35 ($C_{4'}$), 129.99 ($C_{3'}$, $C_{5'}$), 130.38 (C_3,C_5), 136.09 (C_4), 147.59 (d, 9.77 Hz, C_1), 149.80 (d, 9.77 Hz, $C_{1'}$).

Diaryl Ethyl Phosphates 8. To a stirred solution of absolute ethanol (0.125 mol) in pyridine (0.3 mol) was added slowly diaryl chlorophosphate (0.1 mol), keeping the temperature below 40 °C. The mixture was next stirred at room temperature for 2.5 h. Water (250 mL) and chloroform (120 mL) were next added. After stirring for 30 min, the organic layer was separated. It was washed with (2 × 50 mL) water, dried over anhydrous Na_2SO_4, and rotoevaporated to yield diaryl ethyl phosphate that was purified by distillation under reduced pressure.

Ethyl Diphenyl Phosphate (8a): yield 80%; bp 122–124 °C (0.05 mmHg); lit.[17] bp 130 °C (0.1 mmHg); ^1H NMR δ 1.30 (t, J_{H-H} = 7 Hz, 3 H, CH_3), 4.28 (m, 2 H, CH_2), 7.25 (apparent s, 10 H, Ar); ^{13}C NMR δ 15.99 (d, 7.32 Hz, CH_3), 65.38 (d, 6.10 Hz, CH_2), 119.96 (d, 4.88 Hz, C_2, C_6), 125.23 (C_4), 129.70 (C_3, C_5), 150.64 (d, 7.32 Hz, C_1); ^{31}P NMR δ −11.93.

Ethyl Bis(3-methylphenyl) Phosphate (8b): yield 78%; bp 145 °C (0.02 mmHg); ^1H NMR δ 1.32 (t, J_{H-H} = 7 Hz, 3 H, CH_3), 2.30 (s, 6 H, CH_3), 4.30 (dq, J_{H-H} = 7 Hz, J_{P-H} = 9 Hz, 2 H, CH_2),

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6.88–7.30 (m, 8 H, Ar); ^{13}C NMR δ 16.04 (d, 5.86 Hz, CH_3), 21.30 (CH_3), 65.25 (d, 5.86 Hz, CH_2), 116.94 (d, 5.86 Hz, C_6), 120.58 (d, 5.86 Hz, C_2), 125.97 (C_4), 129.34 (C_5), 139.86 (C_3), 150.51 (d, 7.81 Hz, C_1); ^{31}P NMR δ −11.88. Anal. Calcd for $C_{16}H_{19}O_4P$: C, 62.74; H, 6.21; P, 10.13. Found: C, 62.38; H, 6.20; P, 9.99.

Ethyl Bis(4-methylphenyl) Phosphate[18] **(8c)**: yield 54%; bp 143–145 °C (0.01 mmHg); ^1H NMR δ 1.30 (t, J_{H-H} = 7 Hz, 3 H, CH_3), 2.26 (s, 6 H, CH_3), 4.26 (dq, $J_{H-H} = J_{P-H}$ = 7 Hz, 2 H, CH_2), 7.10 (s, 8 H, Ar); ^{13}C NMR δ 16.03 (d, 6.10 Hz, CH_3), 20.61 (CH_3), 65.21 (d, 6.10 Hz, CH_2), 119.67 (d, 3.66 Hz, C_2, C_6), 130.02 (C_3, C_5), 134.65 (C_4), 148.45 (d, 7.32 Hz, C_1); ^{31}P NMR δ −11.52.

Ethyl Bis(4-methoxyphenyl) Phosphate (8d): yield 61%; bp 195–196 °C (0.05 mmHg); lit.[19] bp 192–195 °C (0.005 mmHg); ^1H NMR δ 1.30 (t, J_{H-H} = 8 Hz, 3 H, CH_3), 3.72 (s, 6 H, OCH_3), 4.26 (m, 2 H, CH_2), 6.70–7.25 (apparent AB quartet, J_{H-H} = 9 Hz, 8 H, Ar); ^{13}C NMR δ 16.03 (d, 6.10 Hz, CH_3), 55.51 (OCH_3), 65.30 (d, 6.10 Hz, CH_2), 114.52 (C_3, C_5), 120.85 (d, 4.88 Hz, C_2, C_6), 144.06 (d, 7.32 Hz, C_1), 156.72 (C_4); ^{31}P NMR δ −10.82.

Ethyl 4-Methylphenyl Phenyl Phosphate (13): yield 52%; bp 150–152 °C (0.05 mmHg); ^1H NMR δ 1.30 (t, J_{H-H} = 8 Hz, CH_3), 2.26 (s, 3 H, CH_3), 4.28 (dq, J_{H-H} = 8 Hz, J_{P-H} = 9 Hz, 2 H, CH_2), 7.10 and 7.24 (two apparent s, 9 H, Ar); ^{13}C NMR δ 16.04 (d, 5.86 Hz, CH_3), 20.65 (CH_3), 65.38 (d, 5.86 Hz, CH_2), 119.67 (d, 5.86 Hz, C_2, C_6), 119.99 (d, 3.91 Hz, $C_{2'}$, $C_{6'}$), 125.19 ($C_{4'}$), 129.60 ($C_{3'}$, $C_{5'}$), 130.12 (C_3, C_5), 134.80 (C_4), 148.30 (d, 7.81 Hz, C_1), 150.57 (d, 5.86 Hz, $C_{1'}$); ^{31}P NMR δ −11.73. Anal. Calcd for $C_{15}H_{17}O_4P$: C, 61.64; H, 5.82; P, 10.62. Found: C, 61.39; H, 5.41; P, 10.58.

Ethyl Bis(2-hydroxyaryl)phosphinate (9). To 16.16 g (0.16 mol) of diisopropylamine in THF (50 mL) under nitrogen atmosphere at −78 °C was added *n*-butyllithium (100 mL of a 1.6 M solution). The mixture was stirred for 30 min, and then a solution of diaryl ethyl phosphate (8; 0.04 mol) in THF (50 mL) was syringed into the reaction mixture. After the reaction mixture was stirred at −78 °C for 1 h, the dry ice–acetone bath was removed and stirring was continued for an additional 3 h. It was next poured over a mixture of 300 mL of saturated aqueous ammonium chloride and 500 mL of CH_2Cl_2. The organic layer was separated, washed with water, and dried over anhydrous Na_2SO_4. Removal of solvents on a rotoevaporator left **9** as a thick reddish paste. The pure product was obtained as a white crystalline solid after flash column chromatography (silica gel 40 μm, Baker Chemical Co., chloroform–acetone (100:1) elutant) and was once crystallized from CH_2Cl_2–hexanes.

Ethyl Bis(2-hydroxyphenyl)phosphinate (9a): yield 72%; mp 129–130 °C; ^1H NMR δ 1.38 (t, J_{H-H} = 7 Hz, 3 H, CH_3), 4.18 (dq, $J_{H-H} \approx J_{P-H}$ = 7 Hz, 2 H, CH_2), 6.80–7.10 (m, 4 H, Ar), 7.25–7.60 (m, 4 H, Ar), 9.94 (br s, 2 H, OH); ^{13}C NMR δ 16.30 (d, 5.86 Hz, CH_3), 62.53 (d, 5.86 Hz, CH_2), 111.36 (d, 138.67 Hz, C_1), 118.30 (d, 7.81 Hz, C_3), 119.80 (d, 13.67 Hz, C_5), 131.42 (d, 7.81 Hz, C_6), 135.19 (C_4), 162.00 (d, 5.86 Hz, C_2); ^{31}P NMR δ +41.90. Anal. Calcd for $C_{14}H_{15}O_4P$: C, 60.43; H, 5.39; P, 11.15. Found: C, 60.48; H, 5.57; P, 11.17.

Ethyl Bis(2-hydroxy-4-methylphenyl)phosphinate (9b): yield 63%; mp 156–158 °C; ^1H NMR δ 1.35 (t, J_{H-H} = 7 Hz, 3 H, CH_3), 2.28 (s, 6 H, CH_3), 4.12 (dq, $J_{H-H} = J_{P-H}$ = 7 Hz), 6.60–6.88 (m, 4 H, Ar), 7.28 (q, J_{H-H} = 7 Hz, J_{P-H} = 11 Hz, 2 H, Ar), 9.88 (s, 2 H, OH); ^{13}C NMR δ 16.30 (d, 5.86 Hz, CH_3), 21.56 (CH_3), 62.27 (d, 5.86 Hz, CH_2), 108.43 (d, 140.62 Hz, C_1), 118.37 (d, 9.77 Hz, C_3), 121.03 (d, 11.72 Hz, C_5), 131.16 (d, 7.81 Hz, C_6), 146.35 (C_4), 161.87 (d, 5.86 Hz, C_2); ^{31}P NMR δ +44.73. Anal. Calcd for $C_{16}H_{19}O_4P$: C, 62.74; H, 6.21; P, 10.13. Found: C, 62.16; H, 6.38; P, 9.86.

Ethyl Bis(2-hydroxy-5-methylphenyl)phosphinate (9c): yield 73%; mp 134–135 °C; ^1H NMR δ 1.38 (t, J_{H-H} = 7 Hz, 3 H, CH_3), 2.25 (s, 6 H, CH_3), 4.15 (dq, $J_{H-H} \approx J_{P-H} \approx$ 7 Hz, 2 H, CH_2), 6.75–6.96 (m, 2 H, Ar), 7.05–7.32 (m, 4 H, Ar), 9.74 (s, 2 H, OH, exchanges with D_2O); ^{13}C NMRδ 16.36 (d, 7.81 Hz, CH_3), 20.52 (CH_3), 62.40 (d, 5.86 Hz, CH_2), 111.10 (d, 138.67 Hz, C_1), 118.17 (d, 11.72 Hz, C_3), 129.02 (d, 13.67 Hz, C_5) 131.03 (d, 7.81 Hz, C_6), 136.22 (C_4), 159.86 (d, 3.90 Hz, C_2); ^{31}P NMR δ +44.28. Anal. Calcd for $C_{16}H_{19}O_4P$: C, 62.74; H, 6.21; P, 10.13. Found: C, 62.50; H, 6.22; P, 10.21.

Ethyl Bis(2-hydroxy-5-methoxyphenyl)phosphinate (9d): yield 63%; mp 107 °C; ^1H NMR δ 1.40 (t, J_{H-H} = 8 Hz, 3 H, CH_3), 3.75 (s, 6 H, OCH_3), 4.18 (dq, $J_{H-H} \approx J_{P-H} \approx$ 8 Hz, 2 H, CH_2), 6.78–7.15 (m, 6 H, Ar), 9.42 (s, 2 H, OH, exchangeable with D_2O); ^{13}C NMR δ 16.30 (d, 5.86 Hz, CH_3), 55.84 (OCH_3), 62.59 (d, 7.81 Hz, CH_2), 111.22 (d, 138.67 Hz, C_1), 114.86 (d, 9.76 Hz, C_6), 119.34 (d, 11.72 Hz, C_3), 122.20 (C_4), 152.65 (d, 13.67 Hz, C_5), 155.96 (d, 3.91 Hz, C_2); ^{31}P NMR δ +42.71. Anal. Calcd for $C_{16}H_{19}O_6P$: C, 56.80; H, 5.62; P, 9.17. Found: C, 56.42; H, 5.62; P, 9.18.

Ethyl (2-Hydroxy-5-methylphenyl)(2′-hydroxyphenyl)phosphinate (14): yield 63%; mp 110–111 °C; ^1H NMR δ 1.40 (t, J_{H-H} = 7 Hz, 3 H, CH_3), 2.28 (s, 3 H, CH_3), 4.18 (dq, $J_{H-H} \approx J_{P-H} \approx$ 7 Hz, 2 H, CH_2), 6.75–7.62 (m, 7 H, Ar) 9.75 (s, 1 H, OH), 10.05 (s, 1 H, OH); ^{13}C NMR δ 16.30 (d, 5.86 Hz), 20.39 (CH_3), 62.40 (d, 5.86 Hz), 110.84 (d, 138.67 Hz, C_1), 111.42 (d, 136.72 Hz, $C_{1'}$), 118.17 (d, 11.72 Hz, C_3, $C_{3'}$), 119.80 (d, 13.67 Hz, $C_{5'}$), 129.02 (d, 13.67 Hz, C_5), 130.90 (d, 7.81 Hz, C_6), 131.42 (d, 7.81 Hz, $C_{6'}$), 135.19 ($C_{4'}$), 136.22 (C_4), 159.73 (d, 3.91 Hz, C_2), 161.94 (d, 3.91 Hz, $C_{2'}$); ^{31}P NMR δ +44.18. Anal. Calcd for $C_{15}H_{17}O_4P$: C, 61.64; H, 5.82; P, 10.62. Found: C, 61.52; H, 5.67; P, 10.57.

Bis(2-hydroxyaryl)phosphinic Acid (15). To a stirred solution of an ethyl bis(2-hydroxyaryl)phosphinate **9** (0.0075 mol) and sodium iodide (0.0225 mol) in acetonitrile (25 mL) under nitrogen was added trimethylsilyl chloride (0.0225 mol). The mixture was stirred at room temperature for 20–24 h. It was next filtered to remove NaCl, and volatiles were removed on a rotary evaporator. $CHCl_3$ (30–40 mL) was added to the residue when some more sodium chloride precipitated out. After filtration, $CHCl_3$ was removed on a rotary evaporator. Water (35 mL) was added to the crude silyl ester. On stirring, a yellowish solid precipitated out and was collected by filtration. The yellow solid was dissolved in acetonitrile (10 mL), and water (15 mL) was added. Removal of solvents on rotary evaporator now gave a white solid (removal of iodine). The crude products were purified by crystallization from appropriate solvents.

Bis(2-hydroxyphenyl)phosphinic Acid (15a). The yield was 48% of white granular crystals crystallized from boiling water to which a few drops of ethanol were added: mp 171–172 °C; ^1H NMR (CD_3OD/Me_4Si) δ 6.70–7.00 (m, 4 H, Ar), 7.22–7.75 (m, 4 H, Ar); ^{13}C NMR (CD_3OD/Me_4Si) δ 117.33 (d, 9.77 Hz, C_3), 117.78 (d, 140.62 Hz, C_1), 119.99 (d, 11.72 Hz, C_5), 133.50 (d, 7.81 Hz, C_6), 135.06 (C_4), 161.81 (d, 3.81 Hz, C_2); ^{31}P NMR (CD_3OD/H_3PO_4) δ +32.90. Anal. Calcd for $C_{12}H_{11}O_4P$: C, 57.60; H, 4.40; P, 12.40. Found: C, 57.61; H, 4.52; P, 12.38.

Bis(2-hydroxy-4-methylphenyl)phosphinic Acid (15b): yield 77%; mp 138 °C (from water); ^1H NMR (CD_3OD/Me_4Si) δ 2.28 (s, 6 H, CH_3), 6.60–6.82 (m, 4 H, Ar), 7.46 (dd, J_{H-H} = 7 Hz, J_{P-H} = 15 Hz, 2 H, Ar H at C_6); ^{13}C NMR (CD_3OD/Me_4Si) δ 21.56 (CH_3), 114.86 (d, 142.58 Hz, C_1), 117.65 (d, 7.81 Hz, C_3), 121.03 (d, 11.72 Hz, C_5), 133.36 (d, 7.81 Hz, C_6), 145.96 (s, C_4), 161.74 (d, 5.86 Hz, C_2); ^{31}P NMR (CD_3OD/H_3PO_4Cap) δ +33.76. Anal. Calcd for $C_{14}H_{15}O_4$ P 0.5 H_2O: C, 58.53; H, 5.57; P, 10.80. Found: C, 58.47; H, 5.49; P, 10.71.

Bis(2-hydroxy-5-methylphenyl)phosphinic Acid (15c): yield 79%; mp 173–173.5 °C (from ethanol–water); ^1H NMR (CD_3OD/Me_4Si) δ 2.24 (s, 6 H, CH_3), 6.77 (dd, J_{H-H} = 8 Hz, J_{P-H} = 5 Hz, 2 H, H at C_3), 7.10–7.55 (m, 4 H, Ar); ^{13}C NMR (CD_3OD/Me_4Si) δ 20.45 (CH_3), 117.33 (d, 9.77 Hz, C_3), 117.49 (d, 139.65 Hz, C_1), 129.31 (d, 12.70 Hz, C_5), 133.33 (d, 8.79 Hz, C_6), 135.83 (C_4), 159.63 (d, 4.88 Hz, C_2); ^{31}P NMR (CD_3OD/H_3PO_4Cap) δ +33.21. Anal. Calcd for $C_{14}H_{15}O_4P \cdot {}^1/_8H_2O$: C, 59.94; H, 5.44; P, 11.06; H_2O, 0.80. Found: C, 59.61; H, 5.43; P, 11.20; H_2O, 0.83. Anal. (after further drying). Calcd for $C_{14}H_{15}O_4P$: C, 60.43; H, 5.40. Found: C, 60.37; H, 5.06.

Bis(2-hydroxy-5-methoxyphenyl)phosphinic Acid (15d): yield 65%; mp 169–170 °C (from ethanol–water); ^1H NMR (CD_3OD/Me_4Si) δ 3.74 (s, 6 H, OCH_3), 6.68–7.10 (m, 4 H, Ar), 7.23 (dd, J_{H-H} = 3 Hz, J_{P-H} = 13 Hz, 2 H, H at C_6); ^{13}C NMR (CD_3OD/Me_4Si) δ 56.25 (OCH_3), 117.28 (d, 9.76 Hz, C_6), 117.93 (d, 139.16 Hz, C_1) 118.46 (d, 10.99 Hz, C_3), 121.99 (d, 2.44 Hz, C_4), 153.68 (d, 15.87 Hz, C_5), 155.63 (d, 3.66 Hz, C_2); ^{31}P NMR (CD_3OD/H_3PO_4Cap) δ +31.59. Anal. Calcd for $C_{14}H_{15}O_6P \cdot 0.1H_2O$: C, 53.88; H, 4.87; P, 9.94; H_2O, 0.58. Found: C, 53.60; H, 4.96; P, 10.04; H_2O, 0.58.

(18) Known compound: Helgstrandt, A. J. E.; Johansson, K. N. G.; Misiorny, A.; Noren, J. O.; Stenning, G. B. *Chem. Abstr.* **1980**, *93*, 46825*W*.

(19) Finnegan, R. A.; Matson, J. A. *J. Chem. Soc., Chem. Commun.* **1975**, *23*, 928.

(2-Hydroxy-5-methylphenyl)(2'-hydroxyphenyl)phosphinic Acid (16): yield 80%; mp 164 °C (from water); ^{1}H NMR (CD_3OD/Me_4Si) δ 2.25 (s, 3 H, CH_3), 6.62–7.78 (m, 7 H, Ar); ^{13}C NMR (CD_3OD/Me_4Si) δ 20.39 (CH_3), 117.33 (d, 9.77 Hz, C_3,$C_{3'}$), 117.33 (d, 138.67 Hz, C_1), 117.91 (d, 140.62 Hz, $C_{1'}$), 119.99 (d, 11.72 Hz, $C_{5'}$), 129.21 (d, 11.72 Hz, C_5), 133.43 (d, 5.86 Hz, C_6, $C_{6'}$), 135.06 ($C_{4'}$), 135.83 (C_4), 159.66 (d, 5.86 Hz, C_2), 161.81 (d, 3.91 Hz, $C_{2'}$); ^{31}P NMR (CD_3OD/H_3PO_4Cap) δ +33.00. Anal. Calcd for $C_{13}H_{13}O_4P$: C, 59.09; H, 4.92; P, 11.74. Found: C, 59.02; H, 5.09; P, 11.64.

Registry No. **8a**, 841-46-3; **8b**, 99706-37-3; **8c**, 74270-18-1; **8d**, 58544-30-2; **9a**, 99706-39-5; **9b**, 99706-40-8; **9c**, 99706-41-9; **9d**, 99725-84-5; **10a**, 770-12-7; **10b**, 6630-14-4; **10c**, 6630-15-5; **10d**, 20464-82-8; **12**, 891-63-4; **13**, 99706-38-4; **14**, 99706-42-0; **15a**, 99706-43-1; **15b**, 99706-44-2; **15c**, 99706-45-3; **15d**, 99706-46-4; **16**, 99706-47-5; $(PhO)_2P(O)Cl$, 2524-64-3; HO-*m*-$C_6H_4CH_3$, 108-39-4; HO-*p*-$C_6H_4CH_3$, 106-44-5; HO-*p*-$C_6H_4OCH_3$, 150-76-5.

Cope Rearrangements in the Thiophene Series

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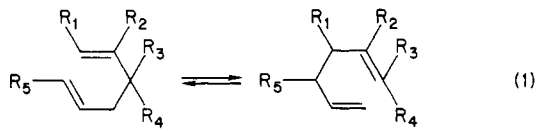
Received September 16, 1985

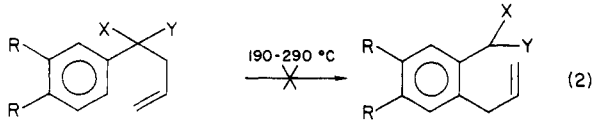
The inability to observe Cope rearrangment at elevated temperatures for diethyl α-allylphenylmalonate[3] does not extend to the analogous systems resulting from replacement of the benzene ring by 2- and 3-thiophene nuclei. Thermal rearrangement of diethyl α-allyl-2-thienylmalonate (**5**) at 250–260 °C for 12 h produces the expected Cope rearrangement product diethyl (3-allyl-2-thienyl)malonate (**6**) (49%) accompanied by ethyl 6-carboethoxy-5,6-dihydro-4*H*-5-cyclopenta[*b*]thiopheneacetate (**7**) (28%). The structural verification of **6** was obtained by degradation to 3-allyl-2-methylthiophene which was compared with an authentic sample obtained by synthesis. The structure of **7** was based on analogy.[3] Similar results were observed with the 3-substituted analogues of **5**, both diethyl (2-allyl-3-thienyl)malonate (**14**) and ethyl 4-carboethoxy-5,6-dihydro-4*H*-5-cyclopenta[*b*]-thiopheneacetate (**15**) being formed. In this case the structure of **14** was verified by synthesis. Speculative mechanistic considerations are offered regarding the mode of transformation of **6** to **7** and **14** to **15**. That the methine proton of the malonate substituent in **6** and **14** is involved in this transformation is seen by the inability of the appropriate methyl-substituted derivative of **6** to undergo thermal cyclization.

The thermal intramolecular rearrangement of 1,5-hexadiene systems discovered by Cope[1] has been the subject of many studies and is now classified as a [3.3] sigmatropic rearrangement[2] as shown in eq 1.



(1)

In the last of a series of papers published in 1956, Cope reported the study of several cases where the R_1R_2 portion of the hexadiene system shown in eq 2 was part of a benzene ring.[3,4]

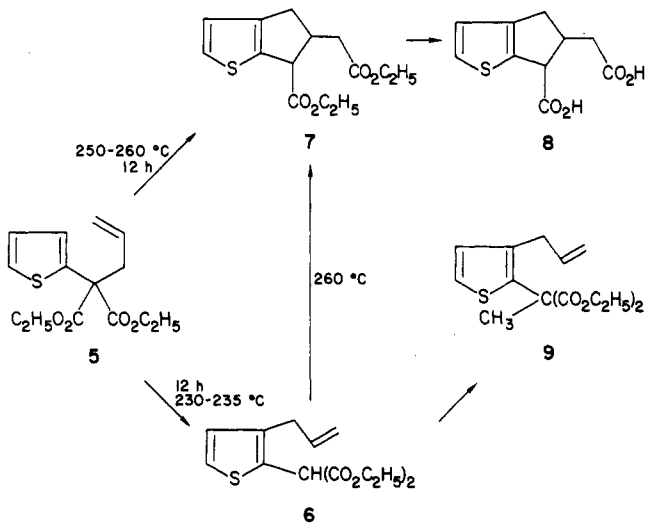


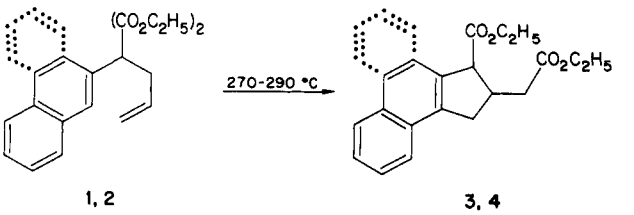
(2)

R=H or OCH_3
X, Y=CN, $CO_2C_2H_5$, C_6H_5

Failure to observe any change other than decomposition was attributed to lack of alkene character of the benzene bond. When the aromatic portion of the hexadiene system was phenanthrene (**1**) or naphthalene (**2**) as shown in eq 3, rearrangement was observed, but the products of rearrangement were not as anticipated, **1** giving rise to **3** and **2** to **4**.

Scheme I





(3)

The present paper reports the results obtained when the aromatic unit in the above system is a thiophene nucleus.

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(2) Rhoads, S. J.; Raulins, N. R. *Org. React. (N.Y.)* **1975**, *22*, 1.
(3) Cope, A. C.; Field, L.; MacDowell, D. W. H.; Wright, M. E.; *J. Am. Chem. Soc.* **1956**, *78*, 2547.
(4) Cope, A. C.; MacDowell, D. W. H.; Meili, J. E. *J. Am. Chem. Soc.* **1956**, *78*, 2551.

0022-3263/86/1951-0183$01.50/0