under an atmosphere of nitrogen. The precipitate was washed at −78 °C with 200 mL of pentane. The combined pentane solutions were washed twice with 100-mL portions of propylene carbonate, which removed phosphate and diphenyl disulfide.[4b] The pentane was removed in vacuo to afford 59.6 g (57% yield) of **1**. The ^1H and ^{31}P NMR spectra showed that the yellow oil contained pentane, diphenyl disulfide, and methyl phenyl sulfide.

In another experiment of about the same size, the product was distilled, bp 37 °C (0.07 mm), to give 34 g (57% yield) of **1** contaminated with 6% of thioanisole. More careful distillation afforded **1** essentially free of thioanisole. There was of course a diminution in yield. For the experiments being reported, **1** contaminated with thioanisole was used.

Reaction of 1 with Benzoic Acid. To a solution of 2.44 g (0.02 mol) of benzoic acid in methylene chloride (20 mL) was added 4.0 g (0.0215 mol) of **1** dropwise over a period of 10 min under an atmosphere of nitrogen. After the addition, the methylene chloride solution was washed with water to remove trimethyl phosphate. The methylene chloride solution was evaporated to give 2.48 g (90%) of essentially pure methyl benzoate. The ^1H NMR spectrum was identical with that of authentic material.

Reaction of 1 with Phenol. To a solution of 1.88 g (0.02 mol) of phenol in 20 mL of methylene chloride was added dropwise 4.0 g (0.0215 mol) of **1** under an atmosphere of nitrogen with stirring at room temperature. The ^1H NMR spectrum of the reaction mixture after the addition showed that all of **1** had reacted. The methylene chloride solution was washed with water and concentrated to give 2.0 g (90%) of anisole whose ^1H NMR spectrum was identical with that of authentic material.

Reaction of 1 with Hydroquinone. Hydroquinone (0.55 g, 0.0048 mol) was treated with 2.0 g (0.01 mol) of **1** at 5–10 °C with stirring. The reaction mixture was treated with 5 mL of water, and the crystalline product was isolated by filtration and dried to give 0.475 g (69% yield) of 1,4-dimethoxybenzene, mp 55–56 °C (lit.[6] mp 56 °C).

Reaction of 1 with Salicylic Acid. Salicylic acid (0.414 g, 0.003 mol) and 1.2 g (0.0064 mol) of **1** were mixed at room temperature and then heated at 70–75 °C for 1.5 hr. Distillation yielded 0.44 g (85%) of methyl *o*-methoxybenzoate, bp 245 °C (lit.[7] bp 228 °C). The ^1H NMR spectrum had absorptions for aromatic hydrogens (4 H) and overlapping singlets for the hydrogens of methoxy groups at δ 3.9 (6 H).

Reaction of 2,4-Dimethylphenol with 1. To 1.2 g (0.009 mol) of 2,4-dimethylphenol was added 2.1 g (0.0112 mol) of **1** at 5 °C. The reaction mixture was stirred at room temperature for 30 min and then washed with three 8-mL portions of water. The product was distilled, bp 192 °C, to give 1.0 g (77%) of 2,4-dimethylanisole. The ^1H NMR spectrum was identical with that reported.[8]

Reaction of 2,6-Di-*tert*-butylphenol with 1. Several reactions were conducted using 0.27 g (0.00131 mol) of 2,6-di-*tert*-butylphenol and 0.30 g (0.00161 mol) of **1** in deuterated benzene. The course of the reactions was followed by ^1H NMR spectroscopy and GLC. A sample of product was isolated, and its ^1H NMR spectrum was identical with that reported.[9]

Reaction of Thiophenol and 1. To 0.30 g (0.00161 mol) of **1** in an NMR tube at −78 °C was added 0.177 g (0.00161 mol) of thiophenol in methylene chloride. The reaction mixture was allowed to warm to room temperature slowly. The methylene chloride solution was washed with water and concentrated under vacuum. The ^1H NMR spectrum in benzene-d_6 was identical with that of a known sample of thioanisole. The yield was 87%.

Reaction of Succinimide with 1. To a solution of 0.46 g (0.00465 mol) of succinimide in 5 mL of methylene chloride at 5 °C was added 1.01 g (0.00567 mol) of **1** over 10 min. The trimethyl phosphate and methanol were distilled at 40–65 °C (0.15 mm), and the residue was recrystallized from methanol to give 0.405 g (76%) of *N*-methylsuccinimide, mp 66–68 °C (lit.[10] mp 71 °C).

Reaction of Phthalimide with 1. Phthalimide (0.10 g, 0.00068 mol) and 0.235 g (0.0012 mol) of **1** were mixed at −78 °C. After standing at room temperature overnight, a solid formed which was separated by centrifugation, washed with water, and dried to give 0.70 g (64%) of *N*-methylphthalimide, mp 132–134 °C (lit.[11] mp 134 °C).

Reaction of Uracil with 1. Uracil (0.064 g, 0.00057 mol) and 0.230 g (0.0012 mol) of **1** were mixed at 0 °C. A solid formed on standing. Trimethyl phosphate was removed at 80 °C (0.1 mm) to give 0.65 g (88%) of 1,3-dimethyluracil, mp 120–121 °C (lit.[12] mp 120–121 °C).

Acknowledgment. This research has been supported by the National Science Foundation and by the National Cancer Institute, Grant No. CA-10737. R.M. wishes to acknowledge support from the National Science Foundation Undergraduate Research Program.

Registry No.—**1**, 1455-07-8; **2**, 121-45-9; **3**, 28715-70-0; **8**, 100-68-5; anisole, 100-66-3; 1,4-dimethoxybenzene, 150-78-7; methyl *o*-methoxybenzoate, 606-45-1; 2,4-dimethylanisole, 6738-23-4; methyl benzoate, 93-58-3; *N*-methylsuccinimide, 1121-07-9; *N*-methylphthalimide, 550-44-7; 1,3-dimethyluracil, 874-14-6; benzoic acid, 65-85-0; phenol, 108-95-2; hydroquinone, 123-31-9; salicylic acid, 69-72-7; 2,4-dimethylphenol, 105-67-9; 2,6-di-*tert*-butylphenol, 128-39-2; thiophenol, 108-98-5; succinimide, 110-14-5; phthalimide, 85-41-6; uracil, 66-22-8; 2,6-di-*tert*-butylanisole, 1516-95-6.

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Heteroatom-Substituted Butadienylphosphonium Salts as Reagents. A New Synthesis of 2-Ethoxycyclohexadienes and Cyclohexenones

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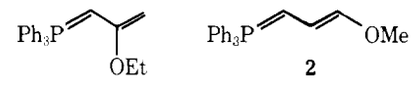
In connection with a general research program designed to discover and develop new methodology for annelation and homologation operations, we have examined the synthetic utility of several functionalized allylidenetriphenylphosphoranes, and some of our efforts have been duly rewarded. For example, (2-ethoxyallylidene)triphenylphosphorane (**1**)



1 **2**

was found to react smoothly with α,β-unsaturated ketones to produce 2-ethoxy-1,3-cyclohexadienes which could be converted to substituted cyclohexenones by subsequent acid-catalyzed hydrolysis.[1] In another investigation, (3-methoxyallylidene)triphenylphosphorane (**2**) was found to be a highly effective reagent for the facile three-carbon homologation of aldehydes and ketones to α,β-unsaturated aldehydes via intermediate 1-methoxy-1,3-butadienes.[2] These results have naturally stimulated further studies to ascertain whether other unsaturated, heteroatom-substituted phosphoranes or phosphonium salts might also be useful as synthetic reagents.

The important discovery that butadienyltriphenylphosphonium salts[3] **3** (X = H) and diethyl butadienylphosphonates[4] **4** (X = H) undergo reactions with the enolates of carbonyl compounds **5** to produce cyclohexadienes **6** (X = H) suggested to us that the placement of a heteroatom group onto

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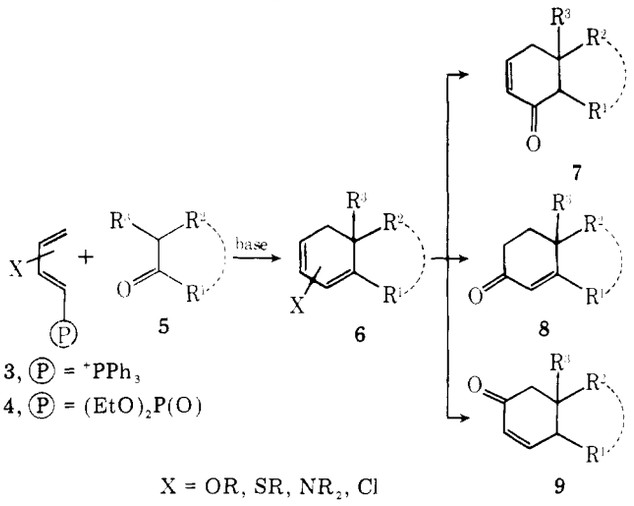
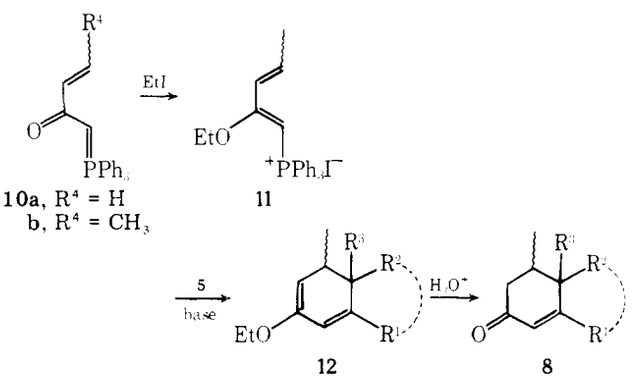
Scheme I



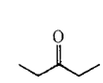
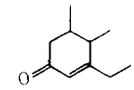
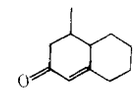
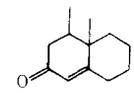
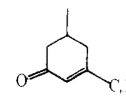
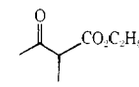
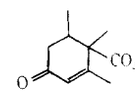
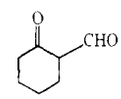
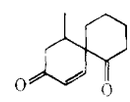
the dienes **3** and **4** (X = OR, SR, NR_2, Cl) would allow the construction of the functionalized cyclohexadienes **6** (X = OR, SR, NR_2, Cl), which may serve as useful intermediates in a number of synthetic sequences. Within the context of devising new strategies for annelation, it is crucial to recognize that the heteroatom-substituted dienes **6** possess the enone moiety as a latent functionality which may be conveniently unmasked by a variety of hydrolytic procedures (Scheme I). Thus, by varying the specific orientation of the heteroatom substituent X on the diene unit of either **3** or **4**, each of the cyclohexenones **7–9** might then be prepared. Although the overall reaction sequence **5** → **8** is synthetically equivalent to the normal Robinson annelation reaction and related processes,[5] the conversion of the ketones **5** into the cyclohexenones **7** and **9** via the dienes **6** would constitute a useful and novel approach for the construction of substituted cyclohexenones that are not readily accessible by classical annelation methods. As the first application of this general strategy, we now wish to report the successful utilization of a functionalized butadienylphosphonium salt as a reagent for the annelation operation **5** → **8**.

Since an examination of the literature produced no information relevant to the preparation of the requisite heteroatom-substituted butadienyltriphenylphosphonium salts,[6] the synthesis of various members of this unusual class of reagents was undertaken. Based upon our previous experience in the preparation of (2-ethoxy-1-propenyl)triphenylphosphonium iodide, the immediate precursor of **1**,[1] we anticipated that one particularly facile route to (2-alkoxy-1,3-butadienyl)triphenylphosphonium salts such as **11** would involve the O-alkylation of the acylmethylenetriphenylphosphoranes **10**.



Although our initial attempts to acylate[7] methylenetriphenylphosphorane with acryloyl chloride to give **10a** were unsatisfactory, the reaction of methylenetriphenylphosphorane with crotonyl chloride proceeded smoothly according to the literature[8] to give crotonylmethylenetriphenylphosphorane (**10b**). Alkylation of **10b** with ethyl iodide in refluxing acetonitrile produced (2-ethoxy-1,3-pentadienyl)triphenylphosphonium iodide (**11**) in 73% yield. The subsequent reaction of the ethoxydienylphosphonium salt **11** with lithium or sodium enolates of various carbonyl compounds proceeded as expected to give the 2-ethoxy-1,3-cyclohexadienes **12** via an initial 1,4 addition followed by an intramolecular Wittig reaction.[3] When subjected to treatment with dilute aqueous acid, the ethoxydienes **12** suffered facile hydrolysis to provide the desired cyclohexenones **8** in fair to moderate overall yields (Table I).

Table I. Annelation of Cyclohexenones 8

entry	starting carbonyl compound 5	product cyclohexenone 8	% yield
a			33
b			64
c			22
d			56
e			40
f			25

As is evident from Table I, this new procedure for annelation may be employed for the preparation of a number of monocyclic and bicyclic cyclohexenone derivatives, but there have been several apparent limitations which should be mentioned. For example, the lithium enolates of β-disubstituted aldehydes such as cyclohexanecarboxaldehyde and diphenylacetaldehyde as well as the lithium enolates of hindered ketones such as diisopropyl ketone failed to react appreciably with the phosphonium salt **11** to give cyclohexadienes of type **12**.

Initial efforts to extend this new synthetic strategy for annelation to the construction of cyclohexenones of types **7** and **9** using functionalized butadienylphosphonium salts have been unrewarding. Preliminary results seem to indicate that neither (3-chloro-1,3-butadienyl)triphenylphosphonium salts[9] nor (3-methoxy-1,3-butadienyl)triphenylphosphonium salts react with enolates in a fashion analogous to that observed for **11**. Furthermore, several attempts to prepare 1-heteroatom-substituted butadienylphosphonium salts have been uniformly unsuccessful. The principal focus of present and future studies is, therefore, an investigation of the related heteroatom-substituted butadienylphosphonates **4**, and these results will be reported independently.

Experimental Section[10]

(2-Ethoxy-1,3-pentadienyl)triphenylphosphonium Iodide (11). A solution containing crotonylmethylenetriphenylphosphorane (**10b**;[8] 26.0 g, 0.075 mol) and ethyl iodide (23.5 g, 0.15 mol) in anhydrous acetonitrile (75 mL) was heated at reflux for 18 h. The excess aceto-

nitrile was completely removed in vacuo, and the residue was triturated with anhydrous ether at −50 °C, whereupon the crude phosphonium salt 11 (34.5 g) crystallized. The phosphonium salt thus obtained was sufficiently pure for use in subsequent annelation reactions. Recrystallization from methylene chloride/ether afforded 27.3 g (73%) of **11**: mp 161–162 °C; NMR ($CDCl_3$) δ 7.78 (m, 15 H), 7.15 (dq, 1 H, J = 7 and 16 Hz), 6.52 (dq, 1 H, J = 1.5 and 16 Hz), 5.67 (d, 1 H, J = 17 Hz), 4.04 (q, 2 H, J = 7 Hz), 1.05 (dd, 3 H, J = 1.5 and 7 Hz), 0.70 (t, 3 H, J = 7 Hz).

Anal. Calcd for $C_{25}H_{26}IOP$: C, 60.00; H, 5.29. Found: C, 60.28; H, 5.35.

General Procedure for the Conversion of Carbonyl Compounds 5a–d into Cyclohexenones 8a–d. To a well-stirred solution of lithium diisopropylamide [prepared from diisopropylamine (0.49 g, 4.9 mmol) and *n*-butyllithium (4.8 mmol, 2.32 N in hexane) in anhydrous tetrahydrofuran (THF) (25 mL)] at −25 °C under dry nitrogen was slowly added a solution of the appropriate ketone **5a–d** (4.8 mmol) in anhydrous THF. After 1 h, unrecrystallized (2-ethoxy-1,3-pentadienyl)triphenylphosphonium iodide (**11**) (3.60 g, 7.2 mmol) was added. The resulting orange mixture was stirred at room temperature for 1 h, heated at reflux for 18 h, and then allowed to cool to room temperature. Aqueous 1 N HCl (50 mL) was added and the heterogeneous mixture stirred vigorously at room temperature for an additional 3 h. The layers were then separated, and the aqueous layer was extracted with ether (3 × 50 mL). The combined organic layers were washed with saturated $NaHCO_3$ and dried ($MgSO_4$), and the excess solvents were removed under reduced pressure. The crude cyclohexenones **8a–d** thus obtained were purified by either vacuum distillation or by bulb to bulb distillation (Kügelrohr).

4,5-Dimethyl-3-ethyl-2-cyclohexen-1-one (8a): 33% as a 63:37 mixture of diastereomers; bp 80–82 °C (2.5 mm); IR (film) 1670 cm^{-1} (C=O); NMR ($CDCl_3$) δ 5.83 (m, 1 H), 1.90–2.70 (complex, 6 H), 0.90–1.35 (complex, 9 H); mass spectrum, *m/e* 152, 110 (base), 81. Exact mass: calcd for $C_{10}H_{16}O$, 152.1201; found, 152.1198.

4-Methyl-4,4a,5,6,7,8-hexahydro-2(3*H*)-naphthalenone (8b): 64%; bp 101–103 °C (1.2 mm); IR (film) 1670 cm^{-1} (C=O); NMR ($CDCl_3$) δ 5.83 (br s, 1 H), 0.90–2.60 (complex, 11 H), 1.09 (d, 3 H, J = 6 Hz); mass spectrum, *m/e* 164, 122 (base), 94, 79. This material was identical with an authentic sample prepared independently.[1]

4,4a-Dimethyl-3,4,5,6,7,8-hexahydro-2(3*H*)-naphthalenone (8c): 20% as a 65:35 mixture of diastereomers;[11] purified by bulb to bulb distillation (1.0 mm) (oven 100 °C); IR (film) 1665 cm^{-1} (C=O); NMR ($CDCl_3$) δ 5.89 (br s, 0.35 H), 5.80 (br s, 0.65 H), 1.28 (s, 1.95 H), 1.05 (s, 1.05 H), 0.90–2.6 (complex, 14 H); mass spectrum, *m/e* 178, 136 (base), 121.

5-Methyl-3-phenyl-2-cyclohexen-1-one (8d): 56%; bp 113–115 °C (0.05 mm); mp 34–36 °C (lit.[13] mp 34–36 °C); IR (film) 1660 cm^{-1} (C=O); NMR ($CDCl_3$) δ 7.30–7.6 (m, 5 H), 6.38 (br s, 1 H), 1.95–2.90 (complex, 5 H), 1.11 (d, 3 H, J = 6 Hz); mass spectrum, *m/e* 186, 144 (base), 116, 115.

General Procedure for the Conversion of 1,3-Dicarbonyl Compounds 5e and 5f into Cyclohexenones 8e and 8f. To a stirred suspension of sodium hydride (0.24 g of a 50% dispersion in mineral oil, 5.1 mmol) in anhydrous THF (25 mL) at 0 °C under nitrogen was slowly added a solution of the appropriate 1,3-dicarbonyl compound **5e,f** (4.6 mmol). After the evolution of hydrogen ceased (ca. 30 min), the butadienylphosphonium salt 11 (3.50 g, 7.0 mmol) was added and the resulting reddish-brown mixture was heated at reflux for 18 h. Workup as previously described produced the cyclohexenones **8e,f.**

Ethyl 1,2,6-Trimethyl-4-oxo-2-cyclohexenecarboxylate (8e): 40% as an 85:15 mixture of diastereomers; bp 80–82 °C (0.05 mm); IR (film) 1670 and 1735 (C=O) cm^{-1}; NMR ($CDCl_3$) δ 5.96 (br s, 0.15 H), 5.90 (br s, 0.85 H), 4.25 (q, 1.70 H, J = 7 Hz), 4.22 (q, 0.30 H, J = 7 Hz), 2.10–2.95 (complex, 3 H), 1.90 (d, 2.55 H, J = 1.5 Hz), 1.10–1.50 (complex, 6 H), 0.94 (d, 2.55 H, J = 6 Hz); mass spectrum, *m/e* 210, 168, 137, 109, 82 (base). Exact mass: calcd for $C_{12}H_{18}O_3$, 210.1256; found, 210.1258.

5-Methylspiro[5.5]undec-1-ene-3,7-dione (8f): 25% as a 57:43 mixture of diastereomers; purified by bulb to bulb distillation (0.1 mm) (oven 100 °C); IR (film) 1680 and 1705 (C=O) cm^{-1}; NMR ($CDCl_3$) δ 7.05 (dd, 0.43 H, J = 1.5 and 10 Hz), 6.80 (dd, 0.57 H, J = 1.5 and 10 Hz), 6.05 (d, 0.57 H, J = 10 Hz), 5.97 (d, 0.43 H, J = 10 Hz), 1.50–3.00 (complex, 11 H), 1.00 (d, 1.71 H, J = 7 Hz), 0.93 (d, 1.29 H, J = 7 Hz); mass spectrum, *m/e* 192, 148, 121, 106, 79. Exact mass: calcd for $C_{12}H_{16}O_2$, 192.1150; found, 192.1147.

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Registry No.—**5a,** 96-22-0; **5b,** 108-94-1; **5c,** 583-60-8; **5d,** 98-86-2; **5e,** 609-14-3; **5f,** 1193-63-1; *cis*-**8a,** 67688-31-7; *trans*-**8a,** 67688-32-8; **8b,** 17299-39-7; *cis*-**8c,** 22465-74-3; *trans*-**8c,** 17566-24-4; **8d,** 29490-59-3; *cis*-**8e,** 67688-33-9; *trans*-**8e,** 67688-34-0; *cis*-**8f,** 67688-35-1; *trans*-**8f,** 67688-36-2; **10b,** 67688-37-3; **11,** 67688-38-4.

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(10) Melting points were determined on a Thomas-Hoover capillary melting point apparatus and are uncorrected. ^1H NMR spectra were determined on a Varian HA-100 spectrometer using tetramethylsilane as a reference. The infrared spectra were recorded on a Beckman IR-5A spectrophotometer. Low-resolution mass spectra were obtained on a Du Pont (CEC) 21-491 instrument, and high-resolution mass spectra were obtained on a 21-110 instrument. GLC analyses were performed on a Varian Aerograph 2740 equipped with a flame ionization detector and a 6 ft × 0.125 in. 10% Carbowax, Chromasorb HP column. Microanalyses were performed by Chemalytics, Inc., Tempe, Ariz.
(11) Based upon the literature values[12] for the chemical shifts of the angular methyl group of the 4,4a-*cis*-dimethyl isomer and the 4,4a-*trans*-dimethyl isomer, the *trans*-dimethyl isomer (δ 1.28) appears to be the major product.
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Δ^3-Isopentenyl Methyl Sulfide. A New Terpenoid in the Scent Mark of the Red Fox (*Vulpes vulpes*)

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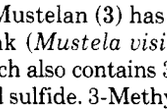
The red fox (*Vulpes vulpes*) uses a chemical communication system[2] based on the supracaudal gland,[3] the anal sac,[4] and the urine.[5] The major scent constituents of male and female red fox urine were identified by GC/MS[5] (Table I). A synthetic mixture of these compounds has been shown to induce characteristic marking behavior in wild red foxes.[6]

The characteristic "skunky odor" of fox urine is clearly due to the two sulfur compounds Δ^3-isopentenyl methyl sulfide (**1**) and 2-phenylethyl methyl sulfide (**2**). Compound **2** is



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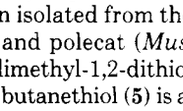

2

known[7] but, to our knowledge, Δ^3-isopentenyl methyl sulfide, a new terpenoid, has not been previously reported.[8,9] Δ^3-Isopentenyl pyrophosphate is probably the biological precurser of compound **1.** The terpenoid nature of this sulfide should be compared with other recently reported scent constituents.[10,15] Mustelan (**3**) has been isolated from the anal gland of the mink (*Mustela vision*) and polecat (*Mustela putorius*),[16] which also contains 3,3-dimethyl-1,2-dithiolane (**4**) and diisopentyl sulfide. 3-Methyl-1-butanethiol (**5**) is a component of the scent of striped skunk (*Mephitis mephitis*)[13] and may

