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.

Acknowledgment. We wish to thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the Robert A. Welch Foundation for their generous support of this research.

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.

References and Notes

(1) S. F. Martin and S. R. Desai, *J. Org. Chem.*, **42,** 1664 (1977).
(2) S. F. Martin and P. J. Garrison, *Tetrahedron Lett.*, 3875 (1977).
(3) (a) G. Büchi and M. Pawlak, *J. Org. Chem.*, **40,** 100 (1975); (b) P. L. Fuchs, *Tetrahedron Lett.*, 4055 (1974).
(4) (a) S. D. Darling and N. Subramanian, *J. Org. Chem.*, **40,** 2851 (1975); (b) S. D. Darling and V. B. Muralidharan, Abstracts, 172nd National Meeting of the American Chemical Society, San Francisco, Calif., August 1976, No. ORGN-13.
(5) For a comprehensive review of annelation, see (a) M. E. Jung, *Tetrahedron*, **32,** 3 (1976); and (b) R. E. Gawley, *Synthesis*, 777 (1976).
(6) The preparation of diethyl 1-dimethylamino-1,3-butadienylphosphonate has, however, been recently reported: H. Ahlbrecht and W. Farnung, *Synthesis*, 336 (1977).
(7) Cf. (a) S. Trippett and D. M. Walker, *J. Chem. Soc.*, 1266 (1961); (b) H. J. Bestman and B. Arnason, *Chem. Ber.*, **95,** 1513 (1962); (c) S. T. D. Gough and S. Tripett, *Proc. Chem. Soc., London*, 302 (1961).
(8) E. Zbiral and L. Fenz, *Monatsh. Chem.*, **96,** 1983 (1965).
(9) P. L. Fuchs, personal communication.
(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.
(12) J. V. Scanio and R. M. Starrett, *J. Am. Chem. Soc.*, **93,** 1539 (1971).
(13) K. W. Bowers, R. W. Giese, J. Grimshaw, H. O. House, N. H. Kolodny, K. Kronberger, and D. K. Roe, *J. Am. Chem. Soc.*, **92,** 2783 (1970).

Δ^3-Isopentenyl Methyl Sulfide. A New Terpenoid in the Scent Mark of the Red Fox (*Vulpes vulpes*)

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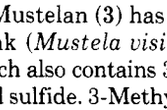
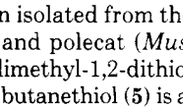
The red fox (*Vulpes vulpes*) uses a chemical communication system[2] based on the supracaudal gland,[3] the anal sac,[4] and the urine.[5] The major scent constituents of male and female red fox urine were identified by GC/MS[5] (Table I). A synthetic mixture of these compounds has been shown to induce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



1



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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

Table I. Volatile Constituents of Red Fox Urine

entry	compd	ca. concn, mg/L
1	4-heptanone	10
2	Δ^3-isopentenyl methyl sulfide (1)	50
3	6-methyl-5-hepten-2-one	2
4	benzaldehyde	1
5	acetophenone	50
6	2-phenylethyl methyl sulfide (2)	2
7	2-methylquinoline[a]	7
8	geranylacetone	7

[a] Male only.

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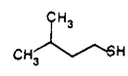
4



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also be of isoprenoid origin. These new terpenoid sulfur compounds suggest a broader significance of terpenes in mammalian olfaction.[17] We report herein the synthesis and spectral properties of compound **1**.

Experimental Section

Δ^3-Isopentenyl Methyl Sulfide (1). *p*-Toluenesulfonyl chloride (10.1 g, 53 mmol) and 4.23 g (47.7 mmol) 3-methyl-3-butenol (Aldrich) in pyridine/CH_2Cl_2 gave 11.13 g (97%) of tosylate which was used without further purification. Tosylate (4.8 g, 20 mmol) in 20 mL of HMPA was cooled to 0 °C and 2.4 g (44 mmol) of CH_3SLi[18] was added portionwise. After warming to 25 °C, the mixture was stirred overnight. The solution was then poured into 150 mL of water and extracted with 100 mL of petroleum ether. The petroleum ether was washed with 1 N NaOH, water, and brine. After drying over $MgSO_4$ the material was distilled to yield 1.77 g (76%) of compound **1**: bp 75 °C (85 mm); VPC (¼ in. × 10 ft Apiezon L at 110 °C; R_T = 5.5 min); IR (neat) 3.32, 6.03, 6.98, 7.30, 11.2 μm; NMR (220 mHz, $CDCl_3$) δ 1.74 (s, 3 H, C=CCH_3), 2.11 (s, 3 H, SCH_3), 2.27 (t, 2 H, J = 4.2 Hz, C=CCH_2), 2.57 (t, 2 H, J = 4.2 Hz, $-CH_2S-$), 4.73 (m, 2 H, CH_2=C); MS [*m/e* (% base)] 116 (26), 69 (4), 68 (17), 67 (17), 63 (5), 61 (100), 41 (20). Anal. Calcd for $C_6H_{12}S$: mol wt 116.0660. Found: mol wt 116.0662.

Registry No.—**1**, 5952-75-0; 3-methyl-3-butenol tosylate, 781-03-3; *p*-toluenesulfonyl chloride, 98-59-9; 3-methyl-3-butenol, 763-32-6; lithium methanethiolate, 35638-70-1.

References and Notes

(1) The Jackson Laboratory, Bar Harbor, Me. 04609.
(2) (a) M. W. Fox, Ed., "The Wild Canids: Their Systematics, Behavioral Ecology and Evolution," Van Nostrand-Reinhold, New York 1975; (b) G. Tembrock, *Handbuch Zool.*, **8(9)**, 3, 4, 10, 11 (1957).
(3) (a) E. S. Albone, *Nature (London)*, **256**, 575 (1975); (b) E. S. Albone and P. F. Flood, *J. Chem. Ecol.*, **2**, 167 (1976).
(4) E. S. Albone, G. Eglinton, J. M. Walker, and G. C. Ware, *Life Sci.*, **14**, 387 (1974).
(5) For a more detailed description of the collection analysis of fox urine see: J. W. Jorgenson, M. Novotny, M. Carmack, G. B. Copland, S. R. Wilson, S. Katona, and W. K. Whitten, *Science*, **199**, 796 (1978).
(6) W. K. Whitten, M. Wilson, S. R. Wilson, J. W. Jorgenson, M. Novotny, and M. Carmack, unpublished results.
(7) J. von Braun, W. Teufert, and K. Weissbach *Justus Liebigs Ann. Chem.*, **472**, 124 (1929).
(8) Compound **1** was considered as a possible product in the radical-catalyzed addition of CH_3SH to isoprene but was not detected: A. A. Oswald, K. Griesbaum, W. A. Thaler, and B. E. Hudson, Jr., *J. Am. Chem. Soc.*, **84**, 3897 (1962).
(9) The double-bond isomer 3,3-dimethylallyl methyl sulfide is well known and has been used as a terpene building block: A. F. Thomas, *Chimia*, **25**, 453 (1970); A. F. Thomas, *Helv. Chim. Acta*, **54** 1822 (1971); D. Michelot et al., *Syn. Comm.*, 95 (1977).
(10) Other sulfur-containing scent components are 5-thiomethylpentane-2,3-dione from the striped hyena[11] and dimethyl disulfide and dimethyl trisulfide from the golden hamster.[12] Skunk scent[13] has been shown to contain crotyl mercaptan, isopentyl mercaptan, and methyl crotyl sulfide but *no n*-butyl mercaptan as reported earlier.[14]
(11) J. W. Wheeler, D. W. von Endt, and C. Wemmer, *J. Am. Chem. Soc.*, **97**, 441 (1975).
(12) A. G. Singer, W. C. Agosta, R. J. O'Connell, C. Pfaffman, D. V. Bowen, and R. H. Field, *Science*, **191**, 948 (1976).
(13) K. K. Andersen and D. T. Bernstein, *J. Chem. Ecol.*, **1**, 493 (1975).
(14) (a) P. G. Stevens, *J. Am. Chem. Soc.*, **67**, 407 (1945); (b) G. A. Fester and F. A. Bertuzzi, *Rev. Fac. Quim. Ind. Agric., Univ. Nac. Litoral*, **5**, 85 (1937) [*Chem. Abstr.*, **31**, 7966 (1937)].
(15) Volatile sulfur constituents of plants and animals are the subject of a recent review: A. Kjaer, *Pure Appl. Chem.*, **49**, 137 (1977).
(16) H. Schildknecht, I. Wilz, F. Ensmann, N. Grund, and M. Ziegler, *Angew. Chem., Int. Ed. Engl.*, **15**, 242 (1976).
(17) E. S. Albone, *Chem. Br.* **13**, 92 (1977).
(18) T. R. Kelly, H. M. Dali, and W. G. Tsang, *Tetrahedron Lett.*, 3859 (1977).

Alkyl Nitrate Nitration of Active Methylene Compounds. Nitration of Alkylphosphonate Esters[1]

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In continuation[2] of our studies of the alkyl nitrate nitration, we are now reporting on its application, with some success, to the preparation of 1-nitroalkylphosphonates **1** directly from the corresponding alkylphosphonate esters **2** (eq 1).

$$\underset{\mathbf{2}}{RCH_2P(O)(OR')_2} \xrightarrow[(2)\ H^+]{(1)\ (i\text{-}C_3H_7)_2NLi\text{–}THF\text{–}n\text{-}C_3H_7ONO_2} \underset{\mathbf{1}}{RCHP(O)(OR')_2}(NO_2) + RCH_2PNO_2 + n\text{-}C_3H_7OP(O)(OR')_2 \quad (1)$$

Recently, Petrov and co-workers[3] reported several methods for preparing compounds **1** which essentially involved the nitration of 2-oxoalkyl-, 2-alkoxyvinyl-, and 2-alkoxy-1-alkylvinylphosphonate esters with nitric acid in acetic anhydride. These methods suffer from the lack of readily available starting materials. Another procedure[4] which affords exclusively tertiary nitroalkylphosphonates consisted of oxidizing the corresponding 1-aminoalkylphosphonate esters.

In the present study, the alkyl nitration of esters **2** was investigated in such systems as potassium amide–liquid ammonia (A), butyllithium–THF (B), and lithium diisopropylamide–THF (C). Of these, system A was found to be unsuitable. For example, in a control test diethyl ethylphosphonate (**3**) was converted in a 60% yield to ethyl *P*-ethylphosphoramidate (eq 2). Moreover, treatment of dibutyl

$$\underset{\mathbf{3}}{C_2H_5P(O)(OC_2H_5)_2} \xrightarrow[(2)\ NH_4Cl]{(1)\ KNH_2\text{–liquid } NH_3} C_2H_5P(O)(NH_2)OC_2H_5 \quad (2)$$

butylphosphonate (**4**) with *n*-propyl nitrate in system A resulted in a 50% recovery of ester **4**. The remaining material constituted a mixture which could not be resolved.

Nitrations of **4** were successful in systems B and C, affording dibutyl 1-nitrobutylphosphonate (**5**) in yields of 27 and 41%, respectively. Similarly, dibutyl pentylphosphonate was converted in system C in 47% yield to dibutyl 1-nitropentylphosphonate (**6**). However, nitration of ester **3** in this system gave a mixture from which the nitro compound could not be separated.

As in the case of carboxylic esters,[5] the nitration reaction of **2** gave, in addition to **1**, cleavage products, namely, nitroalkanes and trialkyl phosphates (eq 1). It was ascertained that the cleavage occurred during the nitration and not in the acidification step as shown by the fact that trialkyl phosphates were isolated prior to acidification. Moreover, compound **6** was quantitatively regenerated from its sodium or lithium salt on acidification with acetic acid. It is very likely that the cleavage reaction occurs by the reaction pathway proposed for the nitration of carboxylic esters.[5]

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