method failed with ethyl heptafluorobutyrate; instead, the free acid, heptafluorobutyric acid, was distilled from the reaction mixture.

This new method to prepare acyl chlorides from their corresponding esters by heating the esters with a mixture of chlorosulfonic acid and phthaloyl chloride is believed to have wide generality and could be particularly useful when the ester is more accessible than the acid. However, the yields may not be satisfactory when the product is somewhat unstable to the reaction conditions. The reaction apparently fails when the acidity of the parent acid approaches that of chlorosulfonic acid.

Experimental Section

Chlorofluoroacetyl Chloride. A mixture of 140.5 g (1 mol) of ethyl chlorofluoroacetate,[1] 203 g (1 mol) of phthaloyl chloride, and 116.5 g (1 mol) of chlorosulfonic acid was heated at total reflux in a still connected to an ice-cooled receiver backed up by a dry ice cooled trap. When the pot temperature reached 120 °C, distillation was started, and the volatile material was distilled from the reaction mixture until the pot temperature rose to 200 °C. The condensates in the receiver and the dry ice cooled trap were combined and distilled through a spinning-band column to give 129.3 g (88%) of chlorofluoroacetyl chloride[2,3] as a colorless liquid: bp 69–70 °C; ^{1}H NMR (neat) δ 6.41 (d, J = 51 Hz); ^{19}F NMR (neat) δ −137.7 (d, J = 51 Hz).

Bromofluoroacetyl Chloride. Ethyl bromofluoroacetate was treated in a similar manner with phthaloyl chloride and chlorosulfonic acid to give bromofluoroacetyl chloride in 62% yield as a colorless liquid: bp 90–91 °C; ^{1}H NMR ($CFCl_3$) δ 6.65 (d, J = 51 Hz); ^{19}F NMR ($CFCl_3$) δ −141.7 (d, J = 51 Hz).

Anal. Calcd for $C_2HBrClFO$: C, 13.70; H, 0.58; F, 10.83. Found: C, 13.85; H, 0.71; F, 10.71.

Registry No.—Chlorofluoroacetyl chloride, 359-32-0; bromofluoroacetyl chloride, 359-23-9; phthaloyl chloride, 88-95-9; chlorosulfonic acid, 7790-94-5; ethyl bromofluoroacetate, 401-55-8; ethyl chlorofluoroacetate, 401-56-9; chloroacetyl chloride, 79-04-9; ethyl chloracetate, 105-39-5; acetyl chloride, 75-36-5; ethyl acetate, 141-78-6.

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Synthesis of β-Damascenone from Prenyl Phenyl Sulfone. A (C_5 + C_5 + C_3) Procedure[1]

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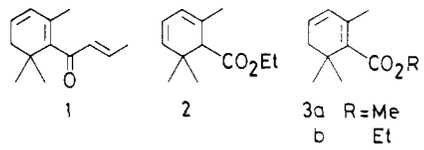
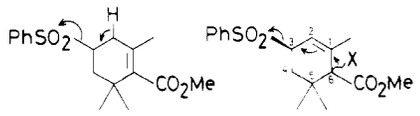
Damascenone (**1**), a significant constituent of Bulgarian rose oil (*Rosa damascena* Mil), has a characteristic odor useful for the creation of modern fragrances.[2,3] Several attempts for obtaining **1** involve (a) coupling of C_9 and C_4 units starting from 2,2,6-trimethylcyclohexanone derivatives,[4] (b) C_3 unit extention of cyclocitral and its related compounds,[5] (c) combination of C_{11} and C_2 units,[6] and others.[7] Especially, *N*-bromosuccinimide oxidation–dehydrobromination,[8] epoxidation followed by acid-catalyzed ring opening,[5g] mercuric acetate oxidation–deacetoxylation,[9] and selenious acid oxidation[10] have been extensively examined for the construction of a conjugated double bond in the cyclohexene ring of cyclocitral and cyclogeranic acid. However, these methods resulted in poor product selectivity and low total yield.

Meanwhile, Büchi reported a simple preparation of α-ethyl safranate (**2**) via intramolecular Wittig reaction from ethyl α-isopropylideneacetylacetate.[5c] However, **2** cannot be transformed completely to the corresponding β isomer (**3b**) since **2** is equilibrated in acidic media with the corresponding β and γ isomers. This result suggests that the desired β-diene system should be constructed by a kinetically controlled reaction in basic media.

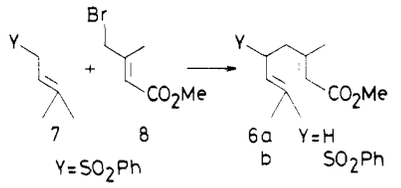


1 2 3a R=Me b Et

On the basis of the above consideration we have developed a base-catalyzed desulfination of **4** and **5** in the expectation that the phenylsulfonyl group would be eliminated as shown in the arrows. The sulfones **4** and **5** were prepared by the acid-catalyzed cyclization of methyl 5-(phenylsulfonyl)geranate (**6b**), which could be obtained by coupling of prenyl phenyl sulfone (**7**) with (2*E*)-4-bromo-3-methyl-2-butenoate (**8**). Stork reported stannic chloride and boron trifluoride



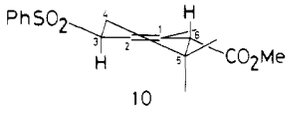
4 5a X=α-H b β-H



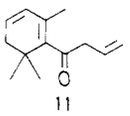
7 8 6a Y=H b SO_2Ph

catalyzed cyclization of methyl geranate (**6a**) into methyl cyclogeranate in benzene.[11] Smit also obtained methyl cyclogeranate in 92% yield with sulfuric acid in nitromethane.[12] Although geranyl[13] and farnesyl phenyl sulfones[14] can be cyclized to the corresponding alicyclic sulfones, reports on attempts to cyclize other functionalized polyene sulfones have not yet appeared in the literature.

Sulfone **7** was treated with lithium diisopropylamide in THF and allowed to react with **8** at −78 °C, affording **6b** in 91% yield. The C_{10} ester **6b** was cyclized successfully with sulfuric acid in nitromethane at −10 ~ 25 °C for 13 h to give a mixture of **4** and **5b** (95:5) in 90% yield. The lower reaction temperature and the shorter reaction time (Table I, entry 2) seem to facilitate the formation of the α-isomer **5a** along with **4** and **5b** in 90% yield. Although carrying out a cyclization with highly diluted sulfuric acid in nitromethane (entry 3) failed to give **6b**, cyclization with sulfuric acid in acetic acid at 25 °C for 44 h provided a mixture of **4**, **5a**, and **5b** in 84% yield. As shown in Table I, the stronger acidic media would promote the isomerization of **5a** into the more thermodynamically stable isomers **4** and **5b**.



10



11

Contrary to the successful cyclization with protonic acid, conversion of **6b** into **4** and **5** did not take place on treatment with stannic chloride and boron trifluoride,[15] although both

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Table I. Cyclization of 6b with Sulfuric Acid

entry	acid–solvent	v/v	time, h	temp, °C	yield, %	product ratio 4	5a	5b
1	H_2SO_4–CH_3NO_2	1:2	13	−10 ~ 25	90	95	0	5
2		1:1	2.5	−10 ~ 0	90	76	20	4
3		1:5	18	25	0[a]			
4	H_2SO_4–AcOH	1:1	17	25	70	87	2	11
5		1:2	44	25	84	60	30	10
6		1:5	120	25	0[a]			

[a] Starting material **6b** was recovered.

acids resulted in the cyclization of methyl geranate[11] and polyisoprenyl sulfones.[13,14]

The stereochemistry of **4** and **5** was elucidated spectroscopically. If the phenylsulfonyl group on C-3 is assumed to be in the equatorial conformation because of steric requirements, the compounds **5** can be represented by **10** and its C-6 epimer. The *gem*-methyl groups of **5b** are bisected by the carbomethoxyl group and are influenced by a similar shielding effect (δ 0.90 and 0.93), while those of **5a** are located in different stereotopic positions relative to the carbomethoxyl group, resulting in a pair of signals (δ 0.88 and 1.07). Furthermore, the stereochemistry is also supported by the fact that an equatorial proton on C-6 of **5a** absorbs at a lower field (δ 2.86) than that of **5b** (δ 2.53).

Both **4** and **5** were subjected independently to potassium *tert*-butoxide catalyzed elimination in *t*-BuOH-THF at 5–10 °C, providing methyl safranate (**3a**) in 85% yield, respectively. The spectra of **3a** were consistent with the reported data,[16] and VPC analysis indicated that **3a** was 99% pure. Therefore, without separation of **4** and **5**, the mixture can be used for the preparation of **3a.** The higher reaction temperature prompted the formation of the γ isomer, resulting in low product selectivity.

Büchi reported a conversion of **3b** into **11** by the action of allyllithium[17] in ether at −60 °C.[5c] We modified the method and realized one-step conversion of **3a** into **1.** Thus, **3a** was treated with an excess amount of allyllithium in dry THF at −20 °C for 5 h, affording **1** in 85% yield. VPC analysis revealed that the product contains 99.5% of **1.** Presumably, the enolate of **11** isomerizes preferentially to the more stable **1** under the workup conditions. ^1H NMR and IR spectra of synthetic **1** were superimposable on those of authentic material.[18]

Experimental Section

Melting points are uncorrected. IR spectra were determined with a JASCO IRA-1 grating spectrometer. ^1H NMR spectra were determined at 100 MHz with a JEOL FX-100 spectrometer. Samples were dissolved in $CDCl_3$, and the chemical shift values are expressed in δ values (ppm) relative to Me_4Si as an internal standard.

Methyl 3,7-Dimethyl-5-(phenylsulfonyl)-2,6-octadienoate (6b). Ethereal BuLi (0.9 mL, 1.5 mmol) was added dropwise to a solution of **7** (266 mg, 1.26 mmol) in dry THF (5 mL) and diisopropylamine (0.2 mL, 1.5 mmol) at −78 °C under Ar. After being stirred at −78 °C for 20 min, **8** (296 mg, 1.53 mmol) in dry THF (5 mL) was added dropwise to the solution in a period of 10 min and the mixture was stirred for 5 min. After being quenched with saturated NH_4Cl (1 mL), the organic substances were extracted with ether. The combined extracts were washed with brine, dried (Na_2SO_4), and concentrated in vacuo. The residue was chromatographed (SiO_2, 3:1 hexane–AcOEt) to give **6b** (370 mg, 91%) as colorless crystals: mp 85.8–86.3 °C (10:1 hexane–ether); IR ($CDCl_3$) 1711 (C=O), 1647 (C=C), 1593 (Ph), 1445, 1435, 1302, 1143 (SO_2), 775, 681 cm^{-1}; ^1H NMR δ 1.13 (s, 3, CH_3), 1.64 (s, 3, CH_3), 2.08 (s, 3, CH_3), 2.42 (dd, J = 14 and 11 Hz, 1, CH), 3.03 (dd, J = 14 and 4 Hz, 1, CH), 3.65 (s, 3, CH_3O), 3.94 (m, 1, $CHSO_2$), 4.90 (d, J = 11 Hz, 1, CH=), 5.65 (br s, 1, CH=), 7.40–7.96 (m, 5, Ar). Anal. Calcd for $C_{11}H_{22}O_4S$: C, 63.34; H, 6.88. Found: C, 63.22; H, 6.62.

2,6,6-Trimethyl-1-(methoxycarbonyl)-4-(phenylsulfonyl)cyclohexene (4) and 1,5,5-Trimethyl-6-(methoxycarbonyl)-3-(phenylsulfonyl)cyclohexene (5). An ice-cooled mixture of AcOH (6 mL) and H_2SO_4 (3 mL) was added dropwise to an ice-cooled solution of **6b** (104 mg, 0.32 mmol) in CH_2Cl_2 (0.5 mL) under vigorous stirring. After being stirred at 25 °C for 44 h, ice water was added to the mixture and the organic substances were extracted with benzene. The combined extracts were washed with brine, dried (Na_2SO_4), and concentrated in vacuo. The residue was treated with CH_2N_2 and chromatographed (SiO_2, 3:1 hexane–AcOEt) to give **4** and **5** as a yellow oil. The isomers **4** and **5** were separated by crystallization from hexane–ether (10:1). **5a** and **5b** were separated by repeated chromatography (SiO_2, 4:1 hexane–AcOEt).

4: mp 156–156.8 °C; IR ($CDCl_3$) 1716 (C=O), 1656 (C=C), 1586 (Ph), 1304, 1146 (SO_2), 777, 679 cm^{-1}; ^1H NMR δ 1.05 (s, 3, CH_3), 1.16 (s, 3, CH_3), 1.67 (s, 3, CH_3), 1.47 (d, J = 10 Hz, 1, CH), 1.92 (dd, J = 12 and 4 Hz, 1, CH), 2.10–2.36 (m, 2, CH_2), 3.21–3.60 (m, 1, CH), 3.75 (s, 3, CH_3O), 7.51–8.12 (m, 5, Ar). Anal. Calcd for $C_{17}H_{22}O_4S$: C, 63.34; H, 6.88. Found: C, 63.34; H, 7.09.

5a: IR ($CDCl_3$) 1736 (C=O), 1646 (C=C), 1311, 1149 (SO_2) cm^{-1}; ^1H NMR δ 0.88 (s, 3, CH_3), 1.07 (s, 3, CH_3), 1.72 (s, 3, CH_3), 1.40–2.00 (m, 2, CH_2), 2.86 (br s, 1, CHCO), 3.40–4.00 (m, 1, CHSO), 3.68 (s, 3, CH_3O), 5.71 (br s, 1, CH=), 7.48–8.04 (m, 5, Ar). Anal. Calcd for $C_{17}H_{22}O_4S$: C, 63.34; H, 6.88. Found: C, 63.41; H, 7.06.

5b: IR ($CDCl_3$) 1726 (C=O), 1649 (C=C), 1307, 1137 (SO_2) cm^{-1}; ^1H NMR δ 0.90 (s, 3, CH_3), 0.93 (s, 3, CH_3), 1.69 (s, 3, CH_3), 1.60–1.96 (m, 2, CH_2), 2.53 (br s, 1, CHCO), 3.41 (s, 3, CH_3O), 3.62–3.88 (m, 1, CHSO), 5.82 (br s, 1, CH=), 7.40–7.92 (m, 5, Ar). Anal. Calcd for $C_{17}H_{22}O_4S$: C, 63.34; H, 6.88. Found: C, 63.07; H, 6.62.

Cyclization of 6b in Nitromethane. A solution of **6b** (29 mg, 0.09 mmol) in CH_2Cl_2 (0.5 mL) was added dropwise to an ice-cooled mixture of H_2SO_4 (0.5 mL) and CH_3NO_2 (1 mL), and the reaction mixture was stirred at −10 °C for 5 h and at 25 °C for 8 h. After the addition of ice water to the mixture, the organic substances were extracted with benzene. The usual workup and chromatography (SiO_2, 3:1 hexane–AcOEt) gave **4** and **5b** (26 mg, 90%, **4**/**5b** = 95:5 from ^1H NMR) as yellow crytals.

2,6,6-Trimethyl-1-(methoxycarbonyl)cyclohexa-1,3-diene (Methyl β-Safranate) (3a). The ester **4** (180 mg, 0.56 mmol) in dry THF (1 mL) was added to a solution of *t*-BuOK (271 mg, 2.2 mmol) dissolved in dry *t*-BuOH (4 mL) at 25 °C, and the mixture was stirred at 10 °C for 24 h. After most of the solvent was removed in vacuo, 0.5 mL of water was added to the residue which was subsequently acidified with 5% HCl. The ether extracts were washed with brine, dried (Na_2SO_4), and concentrated in vacuo. The residues was treated with CH_2N_2 and chromatographed (SiO_2, 10:1 hexane–ether) to give **3a** (86 mg, 85%) as a colorless oil. VPC (SE-30, 5m-4φ, 138 °C) revealed that the oil contained more than 99% of **3a** and less than 1% of its γ isomer: IR ($CDCl_3$) 1706 (C=O), 1431, 1360, 1289, 1250, 1219, 1066 cm^{-1}; ^1H NMR δ 1.11 (s, 6 CH_3), 1.80 (s, 3, CH_3), 2.10 (d, J = 3.4 Hz, 2, CH_2), 3.76 (s, 3, CH_3O), 5.77 (d, J = 9.5 Hz, 1, CH=), 5.90 (dd, J = 9.5 and 3.4 Hz, 1, CH=). The ester **5** was treated in a similar manner to give **3a** in 85% yield.

1-(2,6,6-Trimethylcyclohexa-1,3-dienyl)-(2*E*)-buten-1-one (β-Damascenone) (1). The ester **3a** (33 mg, 0.18 mmol) in dry THF (3 mL) was added to allyllithium, which was prepared from allyl phenyl ether (96 mg, 0.72 mmol) and lithium wire (3 mm, 1.8 mmol) in dry THF (2 mL) under Ar at −20 °C.[17] After being stirred at −20 °C for 5 h, the mixture was quenched with 0.1 mL of saturated NH_4Cl and the organic substances were extracted with ether. The usual workup and chromatography (SiO_2, 10:1 hexane–ether) gave **1** (29.3 mg, 85%) as a colorless oil. VPC (SE-30, 4m-4φ, 179 °C) indicated that the product contained 99.5% of **1**: IR ($CDCl_3$) 1632 (C=O), 1438, 1294, 1252, 1222, 973 cm^{-1}; ^1H NMR δ 1.07 (s, 6, CH_3), 1.65 (s, 3, CH_3), 1.94 (dd, J = 6.8 and 1.5 Hz, 3, CH_3), 2.12 (d, J = 2.7 Hz, 2, CH_2), 5.77 (d, J = 13 Hz, 1, CH=), 5.91 (dd, J = 4.0 and 13.0 Hz, 1, CH=), 6.17 (dq, J = 15.6 and 1.5 Hz, 1, CH=), 6.84 (dq, J = 15.6 and 6.8 Hz, 1, CH=).

Registry No.—1, 23726-93-4; **3a**, 10063-97-5; **4**, 69795-74-0; **5a**, 69795-75-1; **5b**, 69795-76-2; **6b**, 69795-77-3; **7**, 15874-80-3; **8**, 19041-17-9; allyllithium, 3052-45-7; allyl phenyl ether, 1746-13-0.

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(18) We are grateful to Professor S. Isoe, Department of Chemistry, Faculty of Science, Osaka City University, for his generous gift of the ^1H NMR and IR spectral data of an authentic sample of **1.**

Solvolytic Rearrangement Route to *D*-Homosteroids

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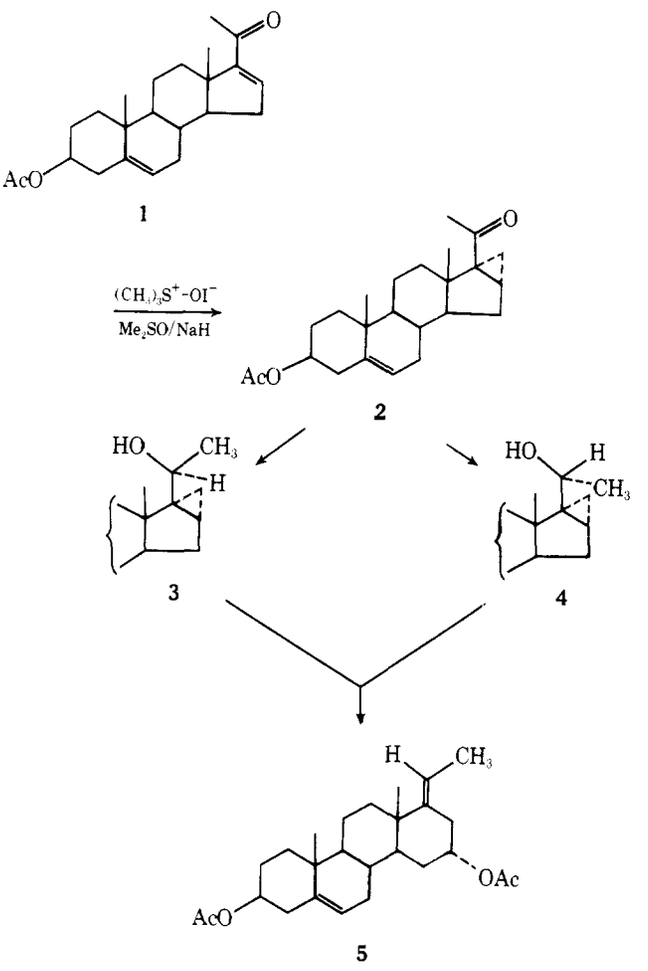
In connection with previous studies aimed at modifying the ring system of steroids,[2,3] we have carried out an acid-promoted ring expansion on the *D* ring of 16α,17α-cyclopropano steroids **3** and **4.** This rearrangement has been previously observed in the simple 1-bicyclo[3.1.0]hexylethan-1-ol systems.[4]

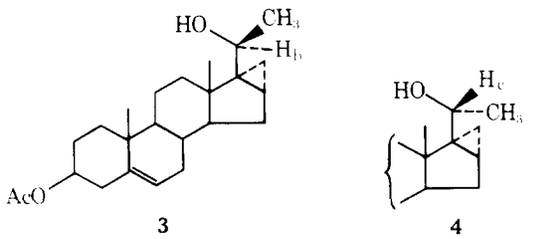
Scheme I



The synthesis of key intermediates **3** and **4** was accomplished by reaction of dimethylsulfoxonium methylide with **1** to form the cyclopropyl ketone **2** which was then reduced to a mixture of epimeric alcohols with sodium borohydride (Scheme I).

The stereochemistry of the introduced methylene group in **2** was assumed to be that which would result from the preferred α attack of the ylide on the least hindered side of the molecule. The orientation of addition to steroid cyclohexenones and cyclopentenones with dimethylsulfoxonium methylide generally corresponds to that of the Michael reaction and of the conjugate addition of organometallic reagents.[5-7]

Unambiguous evidence of the presence of a cyclopropyl methylene group in **2** was obtained from spectroscopic data. The chemical ionization mass spectrum (methane as carrier gas) shows *m/e* 371 $(M + H)^+$. The NMR spectrum clearly shows the cyclopropyl protons at δ 0.76–0.80 as well as the loss of the Δ^{16}-hydrogen. The IR spectrum exhibits a higher frequency absorption at 1677 cm^{-1} for the C-20 carbonyl as compared to that observed in the spectrum of the unsaturated ketone **1** (1663 cm^{-1}). The reduction of **2** afforded, after chromatographic separation, the two diastereoisomers **3** and **4** in a ratio of 1:1. The two isomers were readily distinguished



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