preparation of many new anions other than **1**–**3** from conjugated dienes. We are investigating this and also further reactions of new dianion **1**.

Experimental Section

Melting points were determined on a Kofler hot-stage and are uncorrected. NMR spectra were recorded on a Varian T-60 spectrometer. Chemical shifts are expressed in parts per million downfield from tetramethylsilane. Gas chromatography (GC) was performed with a Varian Aerograph, Model 700, equipped with a 6 ft × 0.25 in. column packed with 10% UCON LB550X on Chromosorb W.

Dianion 1. To a mixture of 2.24 g (20 mmol) of KO-t-Bu, 20 mL of pentane, and 9.6 mL (20 mmol) of 2.2 M n-BuLi in hexane (ALFA Division, Ventron Corp.) in an argon-filled round-bottom flask was added dropwise via dropping funnel over 5 min with stirring 1.15 mL of 2,3-dimethyl-1,3-butadiene in 20 mL of pentane. After being stirred 10 min more, the orange dianion **1** salt was allowed to settle, the supernatant was removed via syringe, and the solid was blown dry with argon. For reactions, it was suspended in 20 mL of dry THF; a saturated solution in THF-d_8 gave a ^{1}H NMR spectrum consisting of a single broad peak at δ 1.05. This dianion preparation proceeds in 70–80% yield as judged by the yields of quench products given below.

Anion 2. The same metalation procedure quantitatively converted a mixture of (Z)- and (E)-piperylenes to pentadienyl anion, as indicated by its ^{1}H NMR spectrum.[6] The outer C–C rotation barriers in the carbanion prepared in this way are noticeably higher than those of the earlier preparation.

Anion 3. To a mixture of 0.58 g (5.1 mmol) of KO-t-Bu, 15 mL of pentane and 0.57 g (5.1 mmol) of 1,3-cycloheptadiene in an argon-filled round-bottom flask was added dropwise via syringe 2.0 mL (5.2 mmol) of 2.6 M n-BuLi in hexane over 5 min with stirring. After being stirred for 10 min more, the green monoanion **3** salt was allowed to settle, the supernatant was removed via syringe, and the solid was blown dry with argon. For reactions, it was dissolved in 20 mL of ether. This anion preparation proceeds in 50–60% yield.

Reaction of Dianion 1 with D_2O and Diethyl Sulfate. To an argon-filled, septum-capped, 250-mL, round-bottom flask equipped with magnetic stirring bar at −78 °C were added 30 mL of dry THF and 2 equiv of D_2O or diethyl sulfate. The reaction was conducted with rapid stirring by dropwise addition of dianion suspension via syringe through the septum cap. After being stirred for 30 min, the reaction mixture was quenched with 1 mL of H_2O. For the D_2O quench, 20 mL of pentane was added, and the solution was extracted 5× with water to remove THF and inorganic salts. The pentane solution was dried over magnesium sulfate, and the product was purified by distillation. For the diethyl sulfate quench, 20 mL of 10% KOH in 80% ethanol was added to the THF solution to hydrolyze any remaining diethyl sulfate. After 3 h of reflux, the solution was extracted with pentane and dried over magnesium sulfate, and the pentane was removed by rotary evaporation. The product was purified by GC at 90 °C. The yield of dideuterio-2,3-dimethylbutadiene (MS, m/e 84; ^{1}H NMR (4H) δ 1.7) was 73%. The yield of 2,3-dipropyl-1,3-butadiene was 71%.

Reaction of Anion 3 with D_2O. One equivalent of D_2O was added quickly to the ether solution of **3**. The solution was extracted with saturated ammonium chloride, and the ether was removed by distillation. A Kugelrohr distillation was performed at 130 °C, and the distillate was purified by preparative GC. The yield of 5-deuterio-1,3-heptadiene (MS, m/e 95; ^{1}H NMR (3 H) δ 2.0) was 52%.

Acknowledgment. We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, for the support of this research.

Registry No.—**1,** 69780-62-7; **2,** 35731-42-1; **3,** 35731-46-5; 2,3-dimethyl-1,3-butadiene, 513-81-5; (Z)-piperylene, 1574-41-0; (E)-piperylene, 2004-70-8; 1,3-cycloheptadiene, 4054-38-0; dideuterio-2,3-dimethylbutadiene, 52221-66-6; 2,3-dipropyl-1,3-butadiene, 16356-06-2; 5-deuterio-1,3-heptadiene, 69780-63-8; D_2O, 7789-20-0; diethyl sulfate, 64-67-5.

References and Notes

(1) R. Ben-Shoshan and R. Pettit, *J. Chem. Soc., Chem. Commun.*, 247 (1968), and references therein. The compound was formed from iron polycarbonyls and allene.

(2) R. B. Bates, D. W. Gosselink, and J. A. Kaczynski, *Tetrahedron Lett.*, 199 (1967).

(3) S. W. Staley and F. L. Wiseman, Jr., *J. Org. Chem.*, **35,** 3868 (1970).

(4) L. Lochmann, J. Popišil, and D. Lim, *Tetrahedron Lett.*, 257 (1966); M. Schlosser and G. Rauchschwalbe, *J. Am. Chem. Soc.*, **100,** 3258 (1978), and references therein. Schlosser and co-workers have used this system for a variety of metalations, including one of a conjugated diene (2,4-dimethyl-1,3-pentadiene).

(5) A reaction occurs, but quenching of the products with water failed to give 2,3-dimethylbutadiene.

(6) R. B. Bates, D. W. Gosselink, and J. A. Kaczynski, *Tetrahedron Lett.*, 205 (1967).

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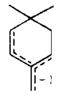
(8) R. B. Bates and D. A. McCombs, *Tetrahedron Lett.*, 977 (1969); H. Kloosterziel and J. A. A. van Drunen, *Recl. Trav. Chim. Pays-Bas*, **88,** 1084 (1969).

(9) 2-Vinylallyl anion i is an unisolated intermediate in the KO-t-Bu–t-BuOH catalyzed isomerization of ii to iii (Allen S. Roth, M.S. Thesis, University of Arizona, 1972); however, all of our efforts to produce **5** or a simple derivative in high concentration have failed.



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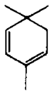

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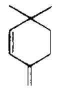

iii

One-Step Method for Converting Esters to Acyl Chlorides

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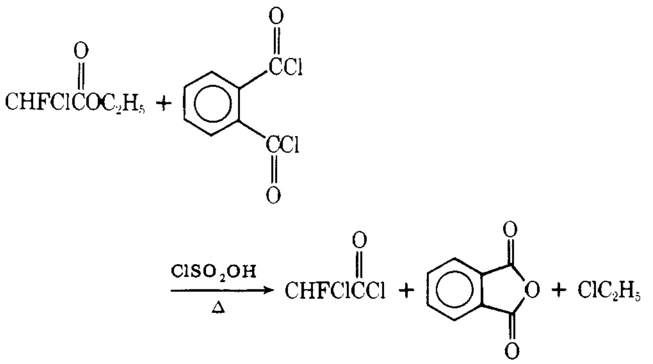
Acyl chlorides are usually prepared from the parent carboxylic acids or their salts. This is true even when the corresponding ester is more accessible because there is no general method for a one-step conversion of esters to acyl chlorides.

Our research required a large sample of chlorofluoroacetyl chloride. The ethyl ester of chlorofluoroacetic acid is readily available,[1] but the free acid is difficult to prepare in good yield because of its volatility and extreme water solubility.[2] The sodium salt also presents difficulties because it is thermally unstable. To overcome these problems, we developed a one-step method for the conversion of esters to the corresponding acyl chlorides by using a mixture of phthaloyl chloride and chlorosulfonic acid.

Chlorofluoroacetyl chloride was prepared in 50% yield by heating an equimolar mixture of ethyl chlorofluoroacetate and chlorosulfonic acid and distilling out the chloride as it was formed. The yield was improved to 88% when an equimolar amount of phthaloyl chloride was added to the reaction mixture. Some gases, particularly ethyl chloride, were also formed, so the product was collected in an efficiently cooled receiver.



Bromofluoroacetyl chloride and chloroacetyl chloride were also prepared in good yields by this same method from their corresponding esters. In addition, acetyl chloride was formed from ethyl acetate, but in this case the yield was only 52%. The 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.

References and Notes

(1) B. Englund in "Organic Syntheses", Collect. Vol. 4, N. Rabjohn, Ed., Wiley, New York, 1963, pp 184–186.
(2) J. A. Young and P. Tarrant, *J. Am. Chem. Soc.*, **71**, 2432 (1949).
(3) W. J. Middleton, U.S. Patent 4 122 115, 1978.

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

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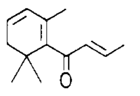
Damascenone (1), a significant constituent of Bulgarian rose oil (*Rosa damascena* Mil), has a characteristic odor useful for the creation of modern fragrances.[2,3] Several attempts for obtaining 1 involve (a) coupling of C_9 and C_4 units starting from 2,2,6-trimethylcyclohexanone derivatives,[4] (b) 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.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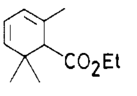
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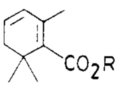
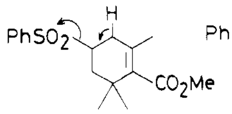

3a R = Me
b Et

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.

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 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.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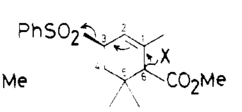
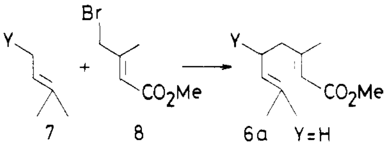
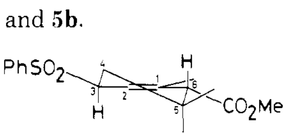

5a X = α-H
b β-H



7 8 Y = SO2Ph
6a Y = H
b SO2Ph

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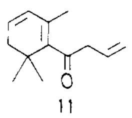
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Contrary to the successful cyclization with protonic acid, conversion of 6b into 4 and 5 did not take place on treatment with stannic chloride and boron trifluoride,[15] although both

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