Preparation of Diester Dienone 12. A mixture of 235 mg (0.883 mmol) of diester **9** and 2.5 mL of mesitylene was refluxed for 42 h under N_2. The solvent was removed at 20 torr with a Kugelrohr apparatus and the residue was purified by preparative TLC with the solvent system 60% ether/30-60 °C petroleum ether (R_f 0.40) to yield 119 mg (51%) of crystalline diene **12**: mp 67-69 °C; IR (CCl_4) 1721, 1702 (sh), 1685, 1634 cm^{-1}; NMR ($CDCl_3$) 1.60-3.00 (10 H, m), 3.66 (3 H, s), 3.75 (3 H, s), 5.68 (1 H, t, J = 9 Hz), 7.07 (1 H, s); UV (ethanol) λ_{max} 219 nm (ϵ 11 400); mass spectrum, m/e (relative intensity) 266 (M^+, 1), 234 (75), 207 (32), 175 (100), 147 (96), 91 (38).

Anal. Calcd for $C_{14}H_{18}O_5$: C, 63.15; H, 6.81. Found: C, 63.04; H, 6.95.

Acknowledgment. We acknowledge the financial assistance of the Natural Sciences and Engineering Research Council of Canada.

Registry No. **3**, 98-89-5; **4**, 3196-23-4; **5**, 18448-47-0; **6**, 54396-74-6; **7**, 23519-90-6; **8**, 83605-36-1; **9**, 83605-37-2; **10**, 83605-38-3; **11**, 83605-39-4; **12**, 83605-40-7; diazomethane, 334-88-3.

Novel Synthesis of 5,5-Dimethyl-1-octalin Derivatives

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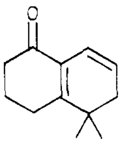
Pyrolysis of 3-isopropenyl-2-allylcyclohex-2-en-1-one (**4**) at ca. 275 °C yielded 3,4,5,6-tetrahydro-5,5-dimethyl-1(2*H*)-naphthalenone (**1**) as the chief product. Higher pyrolysis temperatures also yielded methyl substituted α-tetralones derived from **1**. Reductive methylation of **1** gave the trans-angularly methylated derivative **9** as the only product. The dienolate intermediate in this transformation was also trapped as a trimethylsilyl ether, **8**. Mechanisms for the pyrolytic rearrangement and the reductive alkylation are discussed.

Many terpenoid natural products incorporate fused six-membered rings bearing a *gem*-dimethyl grouping adjacent to the ring fusion. These include sesquiterpenes of the bicyclofarnesol class (e.g., drimenol), many diterpenes (labdanes, abietanes, and beyeranes among others), and virtually all triterpenes having two or more carbocyclic rings. Synthesis of this structural feature has generally been accomplished either by methylation of appropriate cyclic enones, derived in some cases from aromatic precursors[1] and in others by Robinson annulation,[2] or by acid-induced cyclization of a polyolefinic epoxide derivative.[3]

We have devised a synthesis of bicyclic ketone **1** by a novel rearrangement involving a [1, 5] sigmatropic shift of hydrogen followed by an electrocyclic ring closure. Subsequent conversion of **1** to the useful *trans*-3,4,4a,5,6,8a-hexahydro-5,5,8a-trimethyl-1(2*H*)-naphthalenone (**2**) was then achieved by a reductive alkylation sequence.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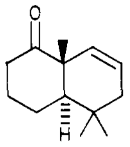
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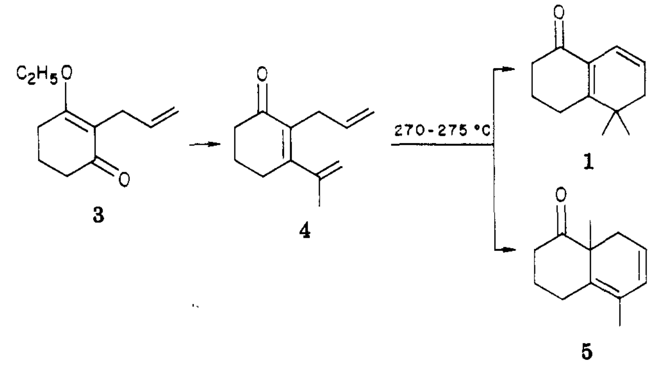
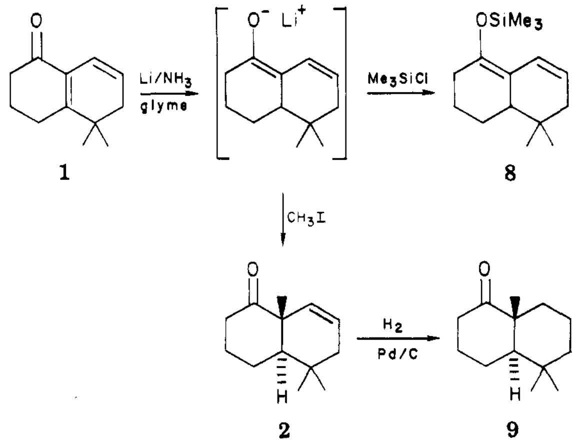
We begin with an enol ether derivative, **3**, of 2-allylcyclohexan-1,3-dione.[4] Reaction of **3** with isopropenyllithium, followed by acid hydrolysis, gave the rearrangement precursor **4** (Scheme I). Controlled pyrolysis of **4** at 270-275 °C generated **1** in 65-70% isolated yield, together with a small amount (ca. 8%) of an isomer, tentatively identified as **5**, and <2% of an unidentified contaminant which accompanies **1**. No unreacted **4** remained in the pyrolysate.

Scheme I



Scheme II



A similar pyrolysis of **4** at 290-300 °C gave a lower yield of **1** together with rearranged and demethylated products believed to be aryl ketones **6** and **7**. That the latter are

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[1] Ireland, R. E.; Dawson, M. I.; Welch, S. C.; Hagenbach, A.; Bordner, J.; Trus, B. *J. Am. Chem. Soc.* **1973**, *95*, 7829 and other papers.

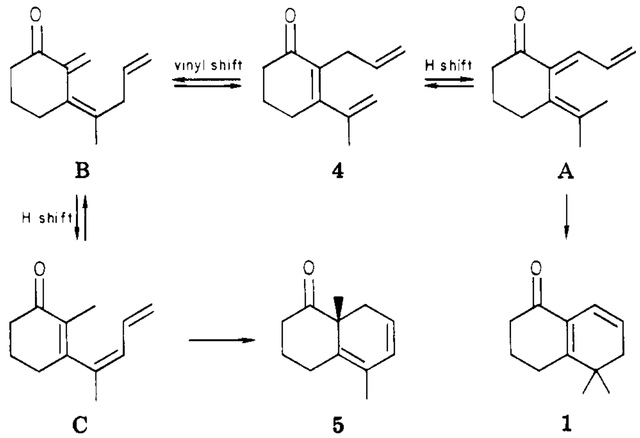
[2] Stork, G.; Uyeo, S.; Wakamatsu, T.; Grieco, P.; Labovitz, J. *J. Am. Chem. Soc.* **1971**, *93*, 4945 and other papers.

[3] (a) van Tamelen, E. E.; Seiler, M. P.; Wierenga, W. *J. Am. Chem. Soc.* **1972**, *94*, 8229. (b) van Tamelen, E. E.; Anderson, R. J. *Ibid.* **1972**, *94*, 8225 and other papers.

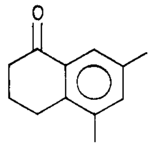
[4] Verhe, R.; Schamp, N.; DeBuyck, L.; DeKimpe, N.; sadones, M. *Bull. Soc. Chim. Belg.* **1975**, *84*, 747.

0022-3263/82/1947-5096$01.25/0

Scheme III



derived from 1 was indicated by complete conversion of 1 to 6 and 7, accompanied by tars, when the pyrolysis temperature was raised to 330–340 °C.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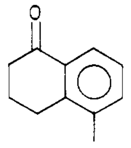
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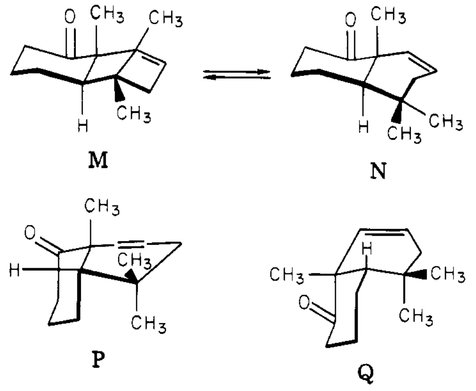
Spectroscopic evidence supporting the assignment of structures 1, 4, and 5 is presented in the Experimental Section. Compound 6 was identified by comparison with an authentic sample (Aldrich) and 7 by the correspondence of the ^{1}H NMR and mass spectra with literature values.[5]

Further support for the structure of 1 derives from its conversion to the angularly methylated products 2 and 9. As shown in Scheme II, 1 was reduced by lithium in ammonia to a dienolate intermediate which could be trapped as a silyl ether (8) or methylated in a nearly quantitative conversion to 2. Reduction of 2 gave 9, which was assigned the trans configuration on the strength of the ^{1}H NMR line width ($w_{1/2}$) of the angular methyl group relative to that of Me_4Si[6] ($\Delta w_{1/2}$ = 0.8 ± 0.1 Hz), methyl chemical shift values,[7] the EI mass spectrum,[7c] and a 2,4-DNP melting point.[8b]

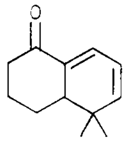
Discussion

The different migratory aptitudes of various atoms and groups in [1,5] sigmatropic rearrangements have been examined by several research groups. In particular, the facility of vinyl shifts[9] relative to alkyl shifts and the qualitative migrational order CHO > COR > H > $CH{=}CH_2$ > $CONH_2$ > CO_2Ph > CO_2CH_3 > CN ≈ $C{\equiv}CH$ > alkyl were reported.[10] These facts suggest that the pyrolytic conversion of 4 to 1 and 5 involves competing sigmatropic shifts, as shown in Scheme III.

Scheme IV



A suprafacial [1,5] hydrogen shift converts 4 to the fully conjugated triene A, which then undergoes a facile electrocyclic ring closure to 1. Alternatively, a vinyl shift in 4 generates triene B, which can rearrange to the fully conjugated isomer C by a [1,5] hydrogen shift. Electrocyclic closure of C yields product 5. Since 5 is not produced by pyrolysis of 1, its possible genesis via methyl shifts in 1 seems to be ruled out. It is curious, however, that the isomeric trienes 10 and 11, derived respectively from 1 and 5 by [1,5] hydrogen shifts, are not among our pyrolysis products (detection limit ca. 2%). Thus the fully conjugated dienone 10 is expected to show a stronger and longer wavelength ultraviolet absorption ($\lambda_{max} \approx 314$ nm, $\epsilon \approx 7700$)[11] than that of cross-conjugated 1 ($\lambda_{max} = 290$ nm, $\epsilon = 4063$). Furthermore, 10 and 11 have three olefinic protons, whereas 1 and 5 have only two.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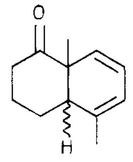
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Alkylation of the dienolate ion obtained by dissolving-metal reduction of 1 (Scheme II) appears to give the trans product exclusively. A conformational analysis of this reaction suggests that this selectivity is due to stereoelectronic control.

The all-chair conformer M (Scheme IV) of the trans isomer suffers a 1,3-diaxial methyl crowding that can be relieved by twisting the unsaturated ring into a half-boat (conformer N). In both of these conformers the bond to the angular methyl group is roughly perpendicular to the planes of the carbonyl and olefinic functional groups. Consequently, the transition state leading to this isomer should have a very favorable orbital overlap. Conformers of the cis isomer (inter alia P and Q) may have somewhat less severe nonbonded interactions, but the transition states that lead to this isomer are destabilized by the poorer orbital overlap evident in these configurations.

We believe this is a rare example of stereoelectronic control in α-alkylation of a dienolate anion. The interesting steric approach control observed in methylation of 3β,20β-bis(benzoyloxy)-7-oxo-5α,$\Delta^{9(11)}$-pregnene[12] does not contradict the importance of the stereoelectronic effect,

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(5) Burnham, J. W.; Duncan, W. P.; Eisenbraun, E. J.; keen, G. W.; Hemming, M. C. *J. Org. Chem.* **1974**, *39*, 1416.

(6) Williamson, K. L.; Howell, T.; Spencer, T. A. *J. Am. Chem. Soc.* **1966**, *88*, 325.

(7) (a) Wenkert, E.; Strike, D. *J. Am. Chem. Soc.* **1964**, *86*, 2044. (b) Smitman, D.; Tsai, M.-Y.; Watt, D.; Edwards, C.; Stotter, P. *J. Org. Chem.* **1979**, *44*, 2838. (c) Ohloff, G.; Giersch, W.; Schulte-Elte, K.; Vial, C. *Helv. Chim. Acta* **1976**, *59*, 1140.

(8) (a) Cocker, J. D.; Halsall, T. G. *J. Chem. Soc.* **1957**, 3441. (b) Sondheimer, F.; Elad, D. *J. Am. Chem. Soc.* **1957**, *79*, 5542.

(9) (a) Paquette, L. A.; Carmody, M. J. *J. Am. Chem. Soc.* **1975**, *97*, 5841. (b) Semmelhack, M. F.; Weller, H. N.; Foos, J. S. *Ibid.* **1977**, *99*, 292. (c) Semmelhack, M. F.; Weller, H. N.; Clardy, J. *J. Org. Chem.* **1978**, *43*, 3791. (d) Bushby, R. J.; Jones, D. W. *J. Chem. Soc., Chem. Commun.* **1979**, 188. (e) Alder, R.; Grimme, W. *Tetrahedron* **1981**, *37*, 1809.

(10) (a) Field, D. J.; Jones, D. W.; Kneen, G. *J. Chem. Soc., Perkin Trans. 1* **1978**, 1050. (b) Field, D. J.; Jones, D. W. *Ibid.* **1980**, 714.

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since overlap is preserved in the boatlike transition state leading to the 8α-methylated product. An all-boat transition state is of course possible for the cis methylation of 1, but this introduces additional unfavorable interactions.

Experimental Section

Infrared spectra were recorded on a Perkin-Elmer 237B grating spectrophotometer. Proton magnetic resonance spectra were taken in deuteriochloroform solution by using either a Varian T-60 or a Bruker WM 250 250-MHz spectrometer and are calibrated in parts per million (δ) downfield from tetramethylsilane as an internal standard. Carbon-13 NMR spectra were obtained with a Varian CFT-20 spectrometer or with the Bruker 250-MHz instrument. Mass spectra were taken with a Finnigan 4000 GC/MS spectromer or, in the case of high-resolution measurements, with a Varian MAT CH-5DF spectrometer. Ultraviolet spectra were recorded on a Unicam SP-800 spectrophotometer. Melting points were measured on either a Hoover-Thomas apparatus (capillary tube) or on a Reichert hot-stage microscope and are uncorrected.

All reactions in which strongly basic reagents were used were conducted under nitrogen or argon with solvents purified by distillation from suitable drying agents in the absence of oxygen.

3-Ethoxy-2-allylcyclohex-2-en-1-one (3). A solution of 2-allylcyclohexane-1,3-dione[4] (1.0 g) in benzene (40 mL) containing 6 mL of ethanol and 40 mg of *p*-toluenesulfonic acid was refluxed through a Dean–Stark trap filled with 4A molecular sieves. After 24 h this solution was cooled, washed with 10% sodium hydroxide solution, and worked up in the usual fashion. Distillation (Kugelrohr) of the resulting yellow oil gave 0.95 g (80%) of 3: IR (neat) $\tilde{\nu}_{max}$ 1640 (s), 1610 (s), 1230 (s), 1125 (s), 1030 (m), 995 (w), 925 (m), 910 (m) cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 1.35 (3 H, t, J = 6 Hz), 1.7–2.8 (6 H), 3.0 (2 H, br d, J = 6 Hz), 4.05 (2 H, q, J = 6 Hz), 4.6–6.0(3 H); mass spectrum (70 eV), *m/ e* (relative intensity) 180 (55), 165 (20), 151 (100), 137 (40), 123 (20), 103 (25), 95 (40); molecular ion mass 180.11473, calcd for $C_{11}H_{16}O_2$ 180.11503.

3-Isopropenyl-2-allylcyclohex-2-en-1-one (4). A solution of isopropenyllithium in ether was prepared by slow addition of 2.0 g (17 mmol) of 2-bromopropene in 30 mL of ether to a stirred suspension of 0.5 g of lithium metal (alloyed with 4% sodium) in 30 mL of ether, maintained at 0 °C under an argon atmosphere. Following this addition, the mixture was warmed to reflux for a few minutes, at which point lithium bromide precipitated. The resulting clear solution of isopropenyllithium was slowly added to a cold (−78 °C) solution of enol ether 3 (1.0 g) in 40 mL of ether under argon. This reaction mixture was then warmed to room temperature, stirred for 2 h, and quenched with cold ammonium chloride solution. The ether phase was separated, washed with 5% aqueous hydrochloric acid and brine, dried with magnesium sulfate, and evaporated. Distillation (Kugelrohr) of the resulting yellow oil gave 0.82 g (85%) of 4: IR (neat) $\tilde{\nu}_{max}$ 1670 (s), 1640 (w), 1610 (w), 905 (m) cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 1.8 (3 H, m), 1.8–2.6 (6 H, m), 3.0(2 H, br d, J = 6 Hz), 4.7 (2 H, m), 4.9 (2 H, m), 5.3–6.0 (1 H, m); mass spectrum (70 eV),*m/e* (relative intensity) 176 (63), 161 (85), 148 (75), 133 (60), 119 (50), 105 (100), 91 (40); molecular ion mass 176.11982, calcd for $C_{12}H_{16}O$ 176.12012.

Pyrolytic Rearrangement of Trienone 4. A solution of trienone 4 (5.9 g) in 75 mL of benzene was added slowly (1 h) at the top of a heated column (30 cm long, 12 mm in diameter) packed with Pyrex beads and swept (top to bottom) with dry nitrogen. The temperature of this pyrolysis column was held between 270 and 280 °C, and the effluent was condensed in a trap cooled to −78 °C by dry ice. Purification of the crude product by chromatography (silica gel, hexane–ethyl acetate) gave 5 (0.47 g, 8%) followed by 1 (3.8 g, 65%).

3,4,5,6-Tetrahydro-5,5-dimethyl-1(2*H*)-naphthalenone (1) was characterized by the following: IR carbonyl absorption at 1690 cm^{-1}; UV (alcohol solution) λ_{max} 290 nm (ϵ 4065); ^{1}H NMR δ 1.05 (6 H, s), 1.7–2.5 (8 H, m), 5.5–5.8 (1 H, m), 6.4 (1 H, br d, J = 10 Hz); mass spectrum (70 eV), *m/e* (relative intensity) 176 (38), 161 (63), 143 (16), 133 (15), 119 (20), 105 (100), 91 (22), 77 (13); molecular ion mass 176.11984, calcd for $C_{12}H_{16}O$ 176.12012.

3,4,8,8a-Tetrahydro-5,8a-dimethyl-1(2*H*)-naphthalenone 5 was charcterized by the following: IR carbonyl absorption at 1705 cm^{-1}; UV (alcohol solution) λ_{max} 276 nm (ϵ 4250); ^{1}H NMR δ 1.10 (3 H, s), 1.73 (3 H, s), 1.5–2.6 (8 H, m), 5.60 (2 H, br s); mass spectrum (70 eV), *m/e* (relative intensity) 176 (2), 161 (47), 133 (30), 119 (40), 105 (100), 91 (23), 77 (13); molecular ion mass 176.11982, calcd for $C_{12}H_{16}O$ 176.12012.

Formation of Tetralones 6 and 7. By use of the pyrolysis apparatus described in the previous section, a solution of trienone 4 (8.7 g) in 100 mL of benzene was pyrolyzed at 295–305 °C. Removal of polar tarry products by a preliminary chromatography on silica gel gave 7.1 g of crude product, which was then rechromatographed (silica gel, hexane–ethyl acetate). Most of the eluted material (5.6 g) proved to be a mixture of 1 and smaller amounts of aromatic ketones (IR and ^{1}H NMR analysis). This mixture was repyrolyzed at 330–340 °C, and the product was chromatographed and rechromatographed to purify the chief aromatic products; dienone 1 was completely transformed by the last pyrolysis. The final purification of the major products was achieved by preparative gas chromatography on an SE-30 column.

5,7-Dimethyl-1-tetralone (6) was identified by a characteristic carbonyl stretching absorption at 1690 cm^{-1}, a ^{1}H NMR spectrum displaying signals at δ 2.2 (3 H, s), 2.3 (3 H, s), 1.7–3.0 (6 H, m), 7.05 (1 H, br s), and 7.6 (1 H, br s), and a mass spectrum (70 eV) with ions at *m/e* (relative intensity) 174 (93), 159 (31), 146 (100), 132 (42), 118 (95), and 91 (32). The ^{1}H NMR and mass spectra were identical with those obtained from an authentic sample of 6, purchased from Aldrich Chemical Co., Milwaukee, WI.

5-Methyl-1-tetralone (7) was identified by a carbonyl stretching absorption at 1690 cm^{-1}, its ^{1}H NMR spectrum [δ 2.25 (3 H, s), 1.7–3.0 (6 H, m), 6.95–7.25 (2 H, m), 7.78 (1 H, dd, J = 8, 2 Hz)], and its mass spectrum (70 eV): *m/e* (relative intensity) 160 (78), 145 (28), 132 (100), 104 (90), 103 (26), 78 (25), 77 (24). This data agrees well with those reported by Burnham et al.[5] for 7.

Preparation of Silyl Enol Ether 8. To a solution of Li metal (0.024 g, 3.4 mmol) in 50 mL of ammonia, containing 5 mL of dry glyme and maintained at reflux, was added over 15 min a solution of dienone 1 (0.20 g, 1.14 mmol) in 10 mL of glyme. The resulting mixture was stirred for 10 min, the ammonia was evaporated, and the residue taken to dryness. The enolate salt was redissolved in 15 mL of fresh glyme, cooled to 0 °C, and quenched with a solution of trimethylsilyl chloride (0.21 g, 1.9 mmol) in 5 mL of glyme containing triethylamine (0.08 mL, 0.57 mmol). This reaction mixture was warmed to room temperature and poured into a mixture of 50 mL of pentane and 20 mL of 5% $NaHCO_3$. The organic layer was wahsed with brine, dried ($MgSO_4$), and evaporated to give 0.2 g (70%) of 8: IR (neat) $\tilde{\nu}_{max}$ 3040 (w), 2950 (s), 1640 (m), 1360 (m), 1250 (2), 1200 (s), 1140 (m), 940 (s), 790 (s) cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 0.17 (9 H, s), 0.70 (3 H, s), 0.91 (3 H, s), 1.0–2.4 (9 H), 5.2–5.7 (1 H, m), 6.27 (1 H, br d, J = 9 Hz) ; mass spectrum (70 eV), *m/e* (relative intensity) 250 (100), 235 (21), 207 (19), 145 (17), 73 (37); molecular ion mass 250.17534, calcd for $C_{15}H_{26}OSi$ 250.17530.

***trans*-3,4,4a,5,6,8a-Hexahydro-5,5,8a-trimethyl-1(2*H*)-naphthalenone (2).** A solution of water in glyme was prepared by dissolving 0.10 mL of water in 50.0 mL of dry glyme. Dienone 1 (0.20 g, 1.14 mmol) was then dissolved in 10 mL of the above solution and added dropwise to a refluxing solution of 0.024 g (3.4 mmol) of Li metal in 50 mL of ammonia. Stirring was continued for a few minutes after the addition was completed, the ammonia was evaporated, and the residue was taken to dryness under vacuum (0.2 torr). This residue was dissolved in 40 mL of glyme and cooled to 0 °C, and to it was added 2 mL of methyl iodide in 5 mL of glyme. The solution was warmed to room temperature, stirred for 1 h, quenched with water, and evaporated to dryness, and the residue was dissolved in methylene chloride. The washed and dried organic solution yielded 0.15 g (65%) of 2: IR (neat) $\tilde{\nu}_{max}$ 3050 (w), 2950 (s), 1700 (s); ^{1}H NMR (CDCl$_3$) δ 0.90 (3 H, s), 1.00 (3 H, s), 1.32 (3 H, s), 1.8–2.5 (9 H), 5.6 (2 H, br s); mass spectrum (70 eV), *m/e* (relative intensity) 192 (11), 177 (2), 159 (31), 121 (100), 170 (68), 93 (59), 91 (37), 82 (26), 79 (36); molecular ion mass 192.15143, calcd for $C_{13}H_{20}O$ 192.15142.

5,5,8a-Trimethyloctahydro-1(2*H*)-naphthalenone (9). A solution of 50 mg of 2 in ethanol containing 20 mg of 10% palladium on charcoal was shaken in a hydrogen atmosphere (40 psi) for 7 h. The workup yielded 45 mg of 9: IR (neat) $\tilde{\nu}_{max}$ 1700 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 0.85 (3 H, s), 0.95 (3 H, s), 1.24 (3 H, s), 1.2–2.6 (13 H); mass spectrum (70 eV), *m/e* (relative intensity) 194 (3), 179 (10), 161 (7), 123 (17), 111 (100), 95 (29), 82 (26), 81 (26), 69

(25), 67 (22), 55 (26). A 2,4-DNP derivative was obtained; mp 166–168 °C (lit.[8b] mp 168.5–170 °C).

Acknowledgment. We thank Ernest Oliver and Brian Musselman for their assistance in obtaining mass spectra, Jo Kotarski for her graphics work, and Don Farnum for many helpful discussions.

Registry No. 1, 83587-88-6; 2, 83587-89-7; 3, 82976-52-1; 4, 83587-90-0; 5, 83587-91-1; 6, 13621-25-5; 7, 6939-35-1; 8, 83587-92-2; 9, 16776-05-9; 2-allylcyclohexane-1,3-dione, 42738-68-1; ethanol, 64-17-5; 2-bromopropene, 557-93-7.

Acylation of Ketone Silyl Enol Ethers with Acid Chlorides. Synthesis of 1,3-Diketones

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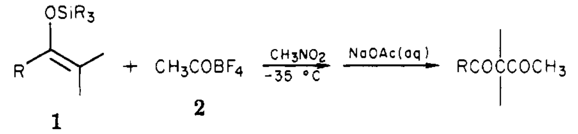
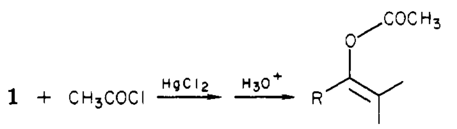
Trimethylsilyl enol ethers of ketones are acylated by a variety of acid chlorides in the presence of zinc chloride or antimony trichloride. The major product of this reaction is the 1,3-diketone resulting from C-acylation. Some O-acylation is observed in most cases. Yields of 1,3-diketones varied but were usually good to excellent.

Recent work in our laboratory has shown that a variety of trialkylsilyl enol ethers 1 are readily acylated with acetyl tetrafluoroborate 2.[1] This method gives 1,3-diketones in reasonable yields (eq 1). Other methods for the acylation

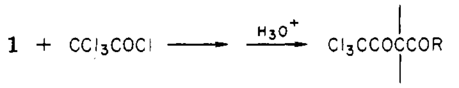


(1)

of trialkylsilyl enol ethers give exclusive O-acylation (eq 2)[2] or are restricted to polyhalogenated acid chlorides (eq 3).[3]

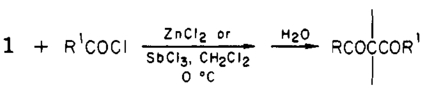


(2)



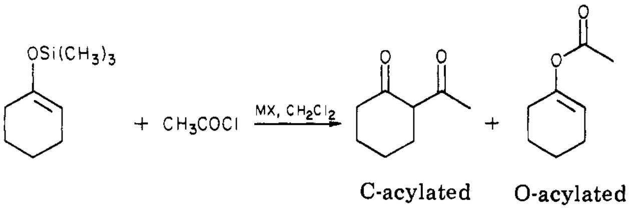
$$1 + CCl_3COCl \longrightarrow \xrightarrow{H_3O^+} Cl_3CCOCCOR \quad (3)$$

Further investigation of the acylation of ketone silyl enol ethers has led us to what we believe are more general and convenient methods to accomplish this transformation. Reaction of trialkylsilyl enol ethers with acid chlorides in the presence of zinc chloride or antimony trichloride (Table I) results in good to excellent yields of 1,3-diketones (eq 4). We report here some of the results obtained in our study of this acylation reaction.



$$1 + R^1COCl \xrightarrow[\text{0 °C}]{\text{ZnCl}_2\text{ or SbCl}_3,\ \text{CH}_2\text{Cl}_2} \xrightarrow{H_2O} RCOCCOR^1 \quad (4)$$

Table I. Reaction of MX with Cyclohexanone Trimethylsilyl Enol Ether and Acetyl Chloride

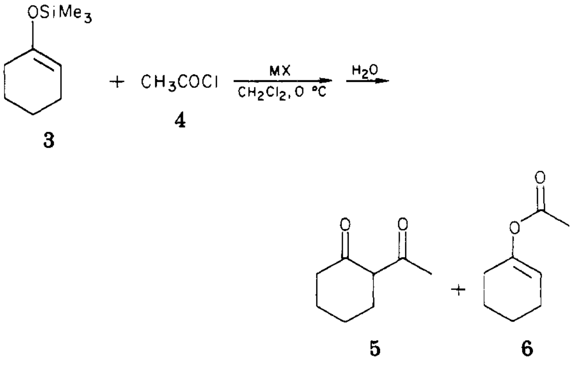


entry	MX	% yield[a] C-acylated	% yield[a] O-acylated
I	ZnCl$_2$	63	3
II	SbCl$_3$	65	15
III	TiCl$_4$	48	trace
IV	SbCl$_5$	35	7
V	SnCl$_4$	34	0
VI	BCl$_3$	27	0
VII	FeCl$_3$	23	0
VIII	AlCl$_3$	22	1
IX	NiBr$_2$	8	0
X	CoBr$_2$	3	trace
XI	SiCl$_4$	trace	0
XII	CuCl$_2$	trace	6
XIII	n-Bu$_3$SnCl	0	0
XIV	CuCl	0	0

[a] Yields determined by GC analysis.

Results and Discussion

Initial experiments involved the survey of a variety of Lewis acids as promoters for the reaction of acetyl chloride, 4, with cyclohexanone trimethylsilyl enol ether, 3, in methylene chloride at 0 °C (eq 5).



(5)

Zinc chloride gave a 63% yield of C-acylated product 5 with 3% O-acylated product 6 and approximately 20% recovered cyclohexanone. Antimony trichloride also gave satisfactory

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[1] Kopka, I; Rathke, M. W. *J. Org. Chem.* 1981, *46*, 3771.

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[3] (a) Murai, S.; Kuraki, Y.; Hasegawa, K.; Tsutsumi, S. *J. Chem. Soc., Chem. Commun.* 1972, 946. (b) Kramarova, E. P.; Baukov, Y. I.; Lutsenko, I. F. *Zh. Obshch. Khim.* 1975, 45, 478. (c) For reaction with oxaloyl chloride see: Murai, S.; Hasegawa, K.; Sonodu, N. *Angew. Chem., Int. Engl. Ed.* 1975, *14*, 636.

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