ogous mechanistic pathways. The preference for internal *vs.* peripheral cleavage in the 2,5-disubstituted bicyclo[4.4.0] systems may stem from intrinsic differences in the strengths of the two carbon–carbon bonds involved in the two pathways.[7] Accordingly, a reactantlike transition state would adequately accommodate these observations. Additional work on this point is in progress.

Experimental Section[8]

N-**Benzyl-*trans*-decahydroquinol-4-one (1a)**.—A solution containing 10.3 g (86.6 mmol) of the formaldehyde–benzylamine adduct,[6] 8.55 g (68.8 mmol) of 1-acetylcyclohexene,[9] 40 ml of absolute ethanol, and 7.1 ml of concentrated hydrochloric acid was heated at reflux for 15 hr.[8a] The cooled solution was diluted with water and extracted with ether to remove unreacted acetylcyclohexene (*ca.* 3.8 g, 44%) and a small amount of benzaldehyde. The aqueous layer was made basic with potassium hydroxide and the product was isolated with ether[8b] affording 13.0 g of material that appeared to contain some uncyclized amino ketone. Accordingly, this material was heated at reflux in 140 ml of 95% ethanol for 18 hr. The product was isolated with ether[8b] and distilled affording 7.05 g (76% yield based on recovered acetylcyclohexene) of amino ketone **1a**: bp 132° (0.02 mm); λ_{max}^{film} 5.83 (CO), 8.12, 8.52, 8.72, 8.90, 9.13, 9.29, 9.68, 13.51, and 14.28 μ; $\delta_{TMS}^{CCl_4}$ 7.22 (C_6H_5) and 3.63 ppm (CH_2, AB quartet, J = 14 Hz, $\Delta\nu_{AB}$ = 51 Hz).

The analytical sample was secured *via* chromatography on Florisil and redistillation.

Anal. Calcd for $C_{16}H_{21}NO$: C, 79.0; H, 8.72; N, 5.76. Found: C, 79.2; H, 8.8; N, 5.7.

N-**Benzyl-*trans*-decahydroquinol-4-ol (2a)**.—A mixture of 3.28 g (13.5 mmol) of ketone **1a**, 6.77 g (33.2 mmol) of aluminum isopropoxide, and 13.0 ml of acetone in 130 ml of isopropyl alcohol was heated at reflux for 20 hr.[8a] An additional 65 ml of isopropyl alcohol was added and the acetone was removed by slow distillation. After an additional hour at reflux, the mixture was allowed to cool and then carefully poured into cold dilute aqueous sulfuric acid. The solution was washed thoroughly with ether, made basic with aqueous potassium hydroxide, and saturated with NaCl, and the product was isolated with hexane[8b] affording 2.71 g (82%) of viscous oil: bp 125–140° (0.2 mm); λ_{max}^{film} 2.97 (OH), 7.30, 8.08, 8.59, 8.92, 9.15, 9.50, 9.67, 10.00, 13.49, and 14.29 μ.

Anal. Calcd for $C_{16}H_{23}NO$: C, 78.5; H, 9.50; N, 5.73. Found: C, 78.5; H, 9.6; N, 5.7.

N-**Benzyl-*trans*-decahydroquinol-4-ol Methanesulfonate (3a)**.—A solution of 0.64 g (2.6 mmol) of alcohol **2a** and 0.50 g (4.4 mmol) of methanesulfonyl chloride in 14 ml of pyridine was stirred at 0° for 0.5 hr and at room temperature for 2 hr.[8a] Ice was added, the solution was poured into a mixture of saturated aqueous sodium chloride and 10% potassium hydroxide solution (10 ml), and the product was isolated with ether.[8b] Toluene was added to azeotrope the last traces of pyridine. The resulting mesylate (0.85 g) crystallized upon refrigeration. Recrystallization from ether–hexane afforded white crystals: mp 94–96°; λ_{max}^{KBr} 7.42, 8.51, 10.27, 10.71, 11.06, 12.05, 13.14, 13.32, and 14.23 μ.

N-**Methyl-*trans*-decahydroquinol-4-ol Methanesulfonate (3b)**.—The above procedure was applied to alcohol **2b**,[4] whereupon the oily mesylate derivative **3b** was obtained in 60% yield: λ_{max}^{film} 7.39, 8.49, 10.28, 10.77, and 11.06 μ.

Solvolysis of Mesylate 3a.—In a typical experiment, 623 mg (1.93 mmol) of mesylate **3a** in 80 ml of absolute ethanol containing 19.2 ml of water, 2.55 ml of 2 *N* sodium hydroxide, and 7.70 g (203 mmol) of sodium borohydride was stirred at room temperature for 20 hr.[8a] The mixture was diluted with water, extracted with methylene chloride,[8b] and distilled (80–85° at 0.02 mm). The following components were isolated by preparative gas chromatography.

N-**Benzyl-Δ$^{4(10)}$-octahydroquinoline (4a)**: λ_{max}^{film} 7.32, 8.75, 8.95, 9.55, 9.69, 11.98, 13.58, and 14.32 μ; $\delta_{TMS}^{CCl_4}$ 7.15 (C_6H_5), 5.35 (vinyl H, broad), and 3.57 ppm (CH_2, AB quartet, J = 14 Hz, $\Delta\nu_{AB}$ = 41 Hz).

Anal. Calcd for $C_{16}H_{21}N$: C, 84.5; H, 9.32; N, 6.16. Found: C, 84.3; H, 9.4; N, 6.0.

N-**Benzyl-*trans*-4-azacyclodecene (8a)**: λ_{max}^{film} 7.30, 7.40, 7.94, 8.85, 9.13, 9.33, 9.51, 9.69, 10.27, 13.52, and 14.33 μ; $\delta_{TMS}^{CCl_4}$ 7.15 (C_6H_5), 5.35 (vinyl H, six lines), and 3.46 ppm (CH_2).

Anal. Calcd for $C_{16}H_{23}N$: C, 83.9; H, 10.0; N, 6.12. Found: C, 84.0; H, 10.2; N, 6.3.

A 176-mg sample of this amine in 14 ml of methanol containing 0.2 ml of concentrated $HClO_4$ was hydrogenated over 225 mg of 5% Pd–C. The uptake of hydrogen ceased after 4 hr whereupon the mixture was filtered. The filtrate was first washed with pentane, then made basic with aqueous potassium hydroxide, and the product was isolated with methylene chloride[8b] affording 79 mg (74%) of **azacyclodecane (7)**: λ_{max}^{film} 2.98 (NH), 6.75, 6.89, 7.39, and 8.76 μ.

The picrate derivative was obtained as yellow needles, mp 192–193° (lit.[10] mp 191–192°).

***trans*-1-Methylbenzylamino-2-vinylcyclohexane (9a)**: λ_{max}^{film} 6.08, 6.67, 6.87, 7.02, 9.68, 9.99, 10.92, 13.56, and 14.31 μ; $\delta_{TMS}^{CCl_4}$ 7.13 (C_6H_5).

Anal. Calcd for $C_{16}H_{23}N$: C, 83.9; H, 10.0; N, 6.12. Found: C, 83.7; H, 9.8; N, 6.3.

Solvolysis of Mesylate 3b.—The procedure described above for mesylate **3a** was employed. Distillation of the crude material afforded a mixture of amines, bp 73–85° (3.5 mm), in 60–70% yield. The following components were isolated by preparative gas chromatography.

N-**Methyl-Δ$^{4(10)}$-octahydroquinoline (4b)**: λ_{max}^{film} 7.23, 7.79, 8.58, 8.91, 9.28, 9.48, 9.73, and 11.95 μ.

Anal. Calcd for $C_{10}H_{17}N$: C, 79.4; H, 11.3; N, 9.3. Found: C, 79.2; H, 11.45; N, 9.1.

N-**Methyl-*trans*-4-azacyclodecene (8b)**: λ_{max}^{film} 7.28, 7.80, 9.07, 9.27, 9.46, 9.54, and 10.27 μ; $\delta_{TMS}^{CCl_4}$ 5.31 (vinyl H multiplet) and 2.24 ppm (NCH_3).

Anal. Calcd for $C_{10}H_{19}N$: C, 78.4; H, 12.5; N, 9.1. Found: C, 78.6; H, 12.5; N, 8.9.

***trans*-1-Dimethylamino-2-vinylcyclohexane (9b)**: λ_{max}^{film} 3.26 (vinyl CH), 6.09 (C=C), 7.37, 8.74, 9.01, 10.02, and 10.91 μ.

The picrate derivative had mp 117–118° (lit.[11] mp 117–119°).

Registry No.—**1a**, 21779-38-4; **2a**, 21779-39-5; **3a**, 21779-40-8; **3b**, 21779-41-9; **4a**, 21779-42-0; **4b**, 21779-43-1; **7**, 4396-27-4; **8a**, 21779-44-2; **8b**, 21779-45-3; **9a**, 21779-46-4; **9b**, 21779-47-5.

Acknowledgment.—We are greatly indebted to the National Science Foundation for their support of this work. J. H. B. greatfully acknowledges support from a Public Health Service Predoctoral Research Fellowship (5 F01 GM 37934, Division of General Medical Sciences).

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(7) J. A. Marshall, *Rec. Chem. Progr.*, **30**, 3 (1969).

(8) (a) The apparatus described by W. S. Johnson and W. P. Schneider [*Org. Syn.*, **30**, 18 (1950)] was used to maintain a nitrogen atmosphere over reaction mixtures. (b) The isolation procedure consisted of thoroughly extracting the reaction mixture with the specified solvent, washing the combined extracts with saturated brine, and drying the extracts over anhydrous magnesium sulfate. (c) Melting points were determined on a Fisher-Johns hot stage. (d) Microanalyses were done by Micro-Tech Laboratories, Inc., Skokie, Ill.

(9) Aldrich Chemical Co., Inc., Milwaukee, Wis.

(10) N. J. Leonard, S. Swann, Jr., and J. Figueras, Jr., *J. Amer. Chem. Soc.*, **74**, 4620 (1952).

(11) H. Booth and F. E. King, *J. Chem. Soc.*, 2688 (1958).

A Nonoxidative Method for Ketone Transposition

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In the course of studies directed toward the synthesis of eremophilane sesquiterpenes,[1] we required a route for

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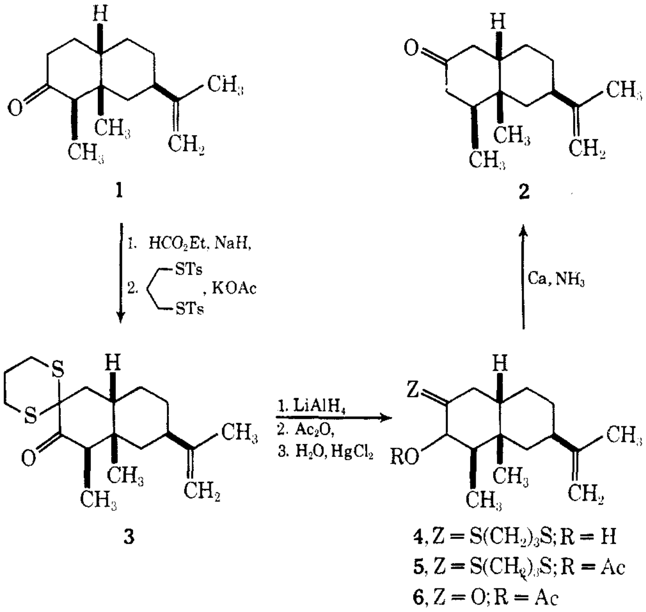
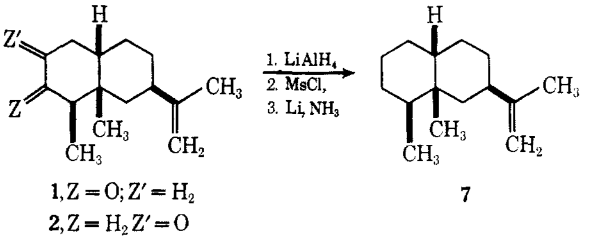
(1) *Cf.* L. H. Zalkow, F. X. Markley, and C. Djerassi, *J. Amer. Chem. Soc.*, **82**, 6354 (1960).

the conversion of ketone 1[2] into the isomeric ketone 2. Existing methods for such ketone transpositions appeared unpromising, since they either require reagents such as ozone,[3] bromine,[4] or strong acids[5] that would react with the isopropenyl grouping present in these ketones, or they proceed *via* intermediates that could afford mixtures of products.[6] In the hopes of circumventing the potential hazards inherent in the aforementioned methods, we examined the mild nonoxidative scheme outlined in Chart I. Our success with this new scheme suggests that it may find more general applications and we therefore report our experimental findings at this time.

CHART I



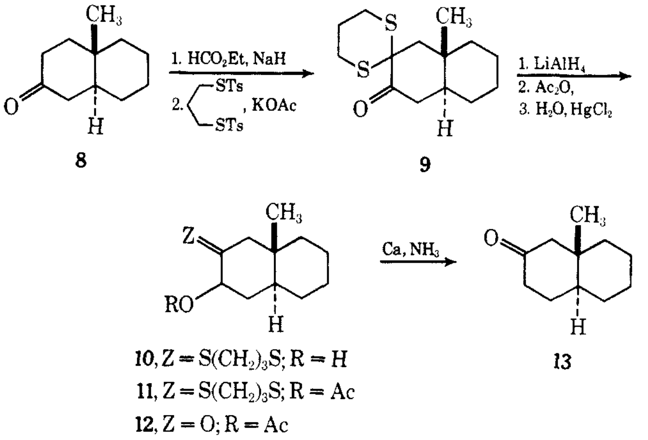
The hydroxymethylene derivative of ketone 1 afforded the thioketal ketone 3 in 85% yield upon treatment with 1,3-propanedithiol di-*p*-toluenesulfonate and potassium acetate in ethanol.[7] Reduction with lithium aluminum hydride gave the alcohol 4 which was converted to the acetate 5 in high overall yield. Hydrolysis of the thioketal grouping of acetate 5 was effected in 82% yield following the procedure of Corey and Crouse.[8] Reduction of the resulting keto acetate 6 with calcium in ammonia afforded the desired ketone 2 in 78% yield. The stereochemical integrity of ketone 2 was demonstrated through its conversion into the hydrocarbon 7 *via* the sequence outlined below.



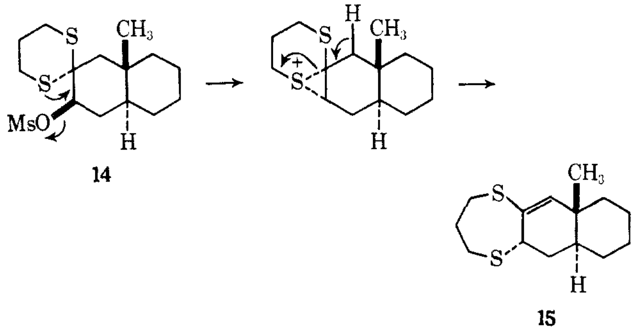
Application of the same (nonepimerizing) sequence to ketone 1 likewise afforded hydrocarbon 7.

As a further extension of these studies we have examined the ketone transposition outlined in Chart II. This conversion proceeded in 53–58% yield, depending upon the extent to which the intermediates were purified.

CHART II



Several alternative methods for removing the ketonic function of the keto thioketal 9 have been briefly explored without success. Attempted Wolff–Kischner reduction,[9] even under mild conditions,[10] afforded mainly polymeric material. Attempted conversion of the alcohol 10 into the mesylate derivative 14 afforded a crystalline product in nearly quantitative yield with spectral properties compatible with structure 15. This material presumably arises *via* the indicated pathway.[11]



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[2] An efficient synthesis of this ketone is described in the Ph.D. dissertation of H. Roebke ("Addition of Organocopper Reagents to Conjugated Ketones," Northwestern University, 1969). An alternative synthesis has recently been described by E. Piers and J. Keziere [*Tetrahedron Lett.*, 583 (1968); *Can. J. Chem.*, **47**, 137 (1969)].

[3] *Cf.* J. E. Bridgeman, E. R. H. Jones, G. D. Meakins, and J. Wicha, *Chem. Commun.*, 898 (1967).

[4] *Cf.* J. E. Gurst and C. Djerassi, *J. Amer. Chem. Soc.*, **86**, 5542 (1964); R. L. Clarke, *J. Org. Chem.*, **28**, 2626 (1963); E. J. Corey, *J. Amer. Chem. Soc.*, **75**, 4832 (1953).

[5] *Cf.* W. Reusch and R. Le Mahieu, *ibid.*, **86**, 3068 (1964); A. Hassner, J. M. Larkin, and J. E. Dowd, *J. Org. Chem.*, **33**, 1733 (1968).

[6] *Cf.* M. N. Huffman, M. H. Lott, and A. Tillotson, *J. Biol. Chem.*, **218**, 565 (1956).

[7] R. B. Woodward, A. A. Patchett, D. H. R. Barton, D. A. Ives, and R. B. Kelly, *J. Chem. Soc.*, 1131 (1957).

[8] E. J. Corey and D. Crouse, *J. Org. Chem.*, **33**, 298 (1968).

[9] Huang-Minlon, *J. Amer. Chem. Soc.*, **68**, 2487 (1946).

[10] D. J. Cram, M. R. V. Sahyun, and G. R. Knox, *ibid.*, **84**, 1734 (1962).

[11] *Cf.* G. Stork and H. T. Cheung, *ibid.*, **87**, 3783 (1965).

Experimental Section[12]

3,3-(Propane-1,3-dithio)-1*c*,9*c*-dimethyl-7*c*-isopropenyl-(10H*r*)-decal-2-one (3).[12f]—The procedure of Turner, *et al.*,[13] was employed for the hydroxymethylation of ketone **1**.[2] Thus, from 340 mg of ketone **1** was obtained 382 mg of the hydroxymethylene derivative: $\lambda_{\max}^{\text{film}}$ 3.24 (vinyl H), 6.08 (C=C), 6.28, 8.43, 8.67, 9.73, 11.23, and 13.20 μ.

A solution of the above derivative (382 mg, 1.54 mmol), 975 mg (2.37 mmol) of propane-1,3-dithiol di-*p*-toluenesulfonate,[14] and 1.27 g of potassium acetate in 17 ml of absolute ethanol was heated at reflux for 11 hr according to the procedure of Woodward.[7] The cooled mixture was poured into brine and the products were isolated with ether.[12b] The crude product was filtered through 40 ml of Fisher alumina with 300 ml of benzene. Removal of the solvent afforded crystalline material which was recrystallized from ethanol, affording 425 mg (85%) of thioketal ketone **3**: mp 98–99.5°; $\lambda_{\max}^{\text{KBr}}$ 5.89, 6.07, 8.81, 9.57, 11.01, 11.15, and 12.52 μ; $\delta_{\text{TMS}}^{\text{CCl}_4}$ 4.63 (C=CH$_2$), 1.69 [C=C(CH$_3$)], 0.94 (C-1 CH$_3$, doublet, J = 6.5 Hz), and 0.79 ppm (C-9 CH$_3$).

The analytical sample was obtained by recrystallization from hexane and sublimation at 100° (0.05 mm), mp 99.5–101°.

Anal. Calcd for $C_{18}H_{28}OS_2$: C, 66.63; H, 8.70; S, 19.76. Found: C, 66.66; H, 8.85; S, 19.57.

3,3-(Propane-1,3-dithio)-1*c*,9*c*-dimethyl-7*c*-isopropenyl-(10-H*r*)-decal-2*c*-ol (4).[12f]—A solution of 350 mg (1.08 mmol) of thioketal ketone **3** in 20 ml of ether was added dropwise to 40 mg (1.05 mmol) of lithium aluminum hydride in 10 ml of ether. The mixture was stirred for 15 hr, treated with water and base,[12e] stirred for 1 hr, and then dried over anhydrous magnesium sulfate. The salts were removed by filtration and washed well with ether. Removal of the solvent afforded 345 mg (98%) of crystalline alcohol **4**, which was recrystallized from hexane to give 294 mg (84%) of white crystals: $\lambda_{\max}^{\text{KBr}}$ 2.91 (OH), 3.24 (vinyl H) 6.06, 7.20, 7.27, 7.92, 8.16, 10.17, and 11.28 μ; $\delta_{\text{TMS}}^{\text{CCl}_4}$ 4.62 (C=CH$_2$), 3.89 (CHOH, $W_{1/2}$ = 5 Hz), 1.68 [C=C(CH$_3$)], 1.06 (C-1 CH$_3$, doublet, J = 7 Hz), and 1.04 ppm (C-9 CH$_3$).

The analytical sample was obtained by recrystallization from hexane and sublimation at 80° (0.05 mm), mp 97–104°.

Anal. Calcd for $C_{18}H_{30}OS_2$: C, 66.20; H, 9.26; S, 19.64. Found: C, 66.25; H, 9.27; S, 19.88.

3,3-(Propane-1,3-dithio)-1*c*,9*c*-dimethyl-7*c*-isopropenyl-(10-H*r*)-decal-2*c*-yl Acetate (5).[12f]—A solution of 250 mg (0.767 mmol) of thioketal alcohol **4** and 162 mg of sodium acetate in 2 ml of acetic anhydride was heated at reflux for 7 hr.[12a] The cooled mixture was poured into aqueous sodium bicarbonate and stirred to hydrolyze the acetic anhydride and the product was isolated with ether.[12b] Removal of the solvent afforded 310 mg (>100%) of crystalline material which was chromatographed on 60 ml of Fisher alumina. Elution with benzene gave 253 mg (90%) of thioketal acetate **5** which exhibited mp 97–98.5° after three recrystallizations from hexane; $\lambda_{\max}^{\text{KBr}}$ 3.24 (vinyl H), 5.77, (CO), 6.08, 7.30, 8.07, 9.80, 10.12, and 11.21 μ; $\delta_{\text{TMS}}^{\text{CCl}_4}$ 5.34 (CHOAc, $W_{1/2}$ = 6 Hz), 4.62 (C=CH$_2$), 2.07 (CH$_3$CO), 1.65 [C=C(CH$_3$)], 1.01 (C-9 CH$_3$), and 0.87 ppm (C-1 CH$_3$, doublet, J = 7.5 Hz).

Anal. Calcd for $C_{20}H_{32}O_2S_2$: C, 65.16; H, 8.75; S, 17.40. Found: C, 65.10; H, 8.90; S, 17.43.

1*c*,9*c*-Dimethyl-7*c*-isopropenyl-2*t*-acetoxy-10H*r*)-decal-2-one (6).[12f]—The procedure of Corey[8] was employed. A mixture of 3.0 g (8.15 mmol) of thioketal acetate **5**, 4.56 g of mercuric chloride, 2.75 g of cadmium carbonate, 4.1 ml of water, and 77.5 ml of acetonitrile was heated at 50° for 7 hr.[12a] The cooled solution was filtered to remove the cadmium carbonate. The filtrate was washed two times with brine, the aqueous washes were back-extracted with ether, and the combined organic extracts were dried over anhydrous magnesium sulfate. Short-path distillation of the product at 85° (0.05 mm) afforded 1.85 g (82%) of keto acetate **6**: $\lambda_{\max}^{\text{film}}$ 3.25 (vinyl H), 5.82 (CO), 5.88 (CO), 8.10, 9.36, 9.51, and 11.22 μ; $\delta_{\text{TMS}}^{\text{CCl}_4}$ 4.91 (CHOAc, doublet, J = 12 Hz), 4.65 (C=CH$_2$), 2.09 (CH$_3$CO), 1.68 [C=C(CH$_3$)], 1.09 (C-9 CH$_3$), and 0.92 ppm (C-1 CH$_3$, doublet, J = 7 Hz).

The 2,4-dinitrophenylhydrazone derivative exhibited mp 183.5–184.5° after four recrystallizations from ethanol.

Anal. Calcd for $C_{23}H_{30}N_4O_6$: C, 60.25; H, 6.59; N, 12.22. Found: C, 60.24; H, 6.59; N, 12.41.

In another experiment, using the same conditions as above, the other epimer of keto acetate **6** was obtained in 70% yield after distillation: $\lambda_{\max}^{\text{film}}$ 3.25 (vinyl H), 5.77 (broad, CO), 6.07, 8.20, 9.81, 10.19, and 11.17 μ; $\delta_{\text{TMS}}^{\text{CCl}_4}$ 4.94 (CHOAc, doublet, J = 3.5 Hz), 4.65 (C=CH$_2$), 2.06 (CH$_3$CO), 1.68 [C=C(CH$_3$)], 1.19 (C-9 CH$_3$), and 0.91 ppm (C-1 CH$_3$, doublet, J = 7 Hz).

1*c*,9*c*-Dimethyl-7*c*-isopropenyl-(10H*r*)-decal-3-one (2).[12f]—A solution of 2.00 g (7.2 mmol) of keto acetate **6** in 250 ml of ether was added over 10 min to a solution of 1.73 g (43.2 mg-atoms) of calcium in 1 l. of distilled ammonia. The mixture was stirred an additional 5 min and was then quenched with solid ammonium chloride. Brine was added to the residue which remained after evaporation of the ammonia, and the product was isolated with ether[12b] affording 1.89 g of material which was chromatographed on 190 ml of silica gel. The material eluted with 3% ether in benzene was distilled at 60° (0.05 mm) affording 1.24 g (78%) of ketone **2** which was 98% pure by gas chromotographic analysis:[12d] $\lambda_{\max}^{\text{film}}$ 3.24 (vinyl H), 5.84 (CO), 6.07, 7.80, 7.93, 8.06, 8.68, and 11.26 μ; $\delta_{\text{TMS}}^{\text{CCl}_4}$ 4.63 (C=CH$_2$), 1.68 [C=C(CH$_3$)], 1.07 (C-9 CH$_3$), and 0.88 ppm (C-1 CH$_3$, doublet, J = 6 Hz).

The 2,4-dinitrophenylhydrazone derivative exhibited mp 167.5–168° after three recrystallizations from ethanol.

Anal. Calcd for $C_{21}H_{28}N_4O_4$: C, 62.98; H, 7.05; N, 13.99. Found: C, 63.09; H, 6.99; N, 14.04.

1*c*,9*c*-Dimethyl-7*c*-isopropenyl-(10H*r*)-decalin (7).[12f] **A. From 1*c*,9*c*-Dimethyl-7*c*-isopropenyl-(10H*r*)-decal-2-one (1)**.—A solution of 0.229 g (1.04 mmol) of ketone **1** in 10 ml of ether was added dropwise to 40 mg (1.04 mmol) of lithium aluminum hydride in 10 ml of ether. The mixture was stirred for 15 hr, treated with water and base,[12e] stirred for 1 hr, and then dried over anhydrous magnesium sulfate. The salts were removed by filtration and washed well with ether. Removal of the solvent from the filtrate afforded 0.23 g of alcohol, mp 78–83°, which was recrystallized from hexane: $\lambda_{\max}^{\text{KBr}}$ 2.99 (OH), 3.23 (vinyl H), 6.06, 9.64, 9.75, 10.29, 10.45, 11.05, and 11.25 μ; $\delta_{\text{TMS}}^{\text{CCl}_4}$ 4.63 (C=CH$_2$), 3.79 (CHOH, doublet, J = 3 Hz), 1.66 [C=C(CH$_3$)], 1.06 (C-9 CH$_3$), and 0.92 ppm (C-1 CH$_3$, doublet, J = 7.5 Hz).

A solution of 230 mg (1.04 mmol) of the above alcohol in 0.5 ml of pyridine was cooled to 0° and treated with 0.09 ml of methanesulfonyl chloride.[12a] The mixture was stirred for 3.5 hr at room temperature, ice was added, and stirring was continued for an additional 5 min. The mixture was poured into ether, washed with 4% sulfuric acid until acidic, with aqueous sodium bicarbonate solution until neutral, and with brine, and dried over anhydrous magnesium sulfate. Removal of the solvent from the filtered solution afforded the oily methanesulfonate derivative.

A solution of this material in 1.24 ml of ethanol was added dropwise to a solution of 0.27 g (38.5 mg-atoms) of lithium wire in 14 ml of distilled ammonia at −70°. The mixture was stirred at −70° for 1 hr, then at room temperature with a Dry Ice acetone condenser for 0.5 hr. Sufficient ethanol was added to discharge the blue color; then solid ammonium chloride and brine were added. The product was isolated with hexane,[12b] filtered through 20 ml of Woelm neutral alumina (activity grade I) with 300 ml of pentane, and distilled at 60° (0.05 mm) affording 162 mg (76%) of decalin **7**[2] which was 98% pure by gas chromatographic analysis:[12d] $\lambda_{\max}^{\text{film}}$ 3.24 (vinyl H), 6.06, 6.88, 7.26, 8.31, 8.47, 9.95, 10.63, 10.74, 11.25, and 11.50 μ; $\delta_{\text{TMS}}^{\text{CCl}_4}$ 4.63 (C=CH$_2$), 1.68 [C=C(CH$_3$)], 0.96 (C-9 CH$_3$), and 0.68 ppm (C-1 CH$_3$, doublet, J = 6.5 Hz).

Anal. Calcd for $C_{15}H_{26}$: C, 87.30; H, 12.70. Found: C, 87.42; H, 12.48.

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(12) (a) The apparatus described by W. S. Johnson and W. P. Schneider ["Organic Syntheses," Coll. Vol. IV, John Wiley & Sons, Inc., New York, N. Y. 1963, p 132] was used to maintain a nitrogen atmosphere. (b) The isolation procedure consisted of thorough extractions with the specified solvent, washing the combined extracts with saturated brine solution, and drying the extracts over anhydrous magnesium sulfate. The solvent was removed from the filtered extracts under reduced pressure on a rotary evaporator. (c) Microanalyses were performed by Micro-Tech Laboratories, Inc., Skokie, Ill. (d) Gas chromatographic analyses were performed on an F & M Model 720 instrument employing helium as the carrier gas. (e) Lithium aluminum hydride reactions were decomposed by cautiously adding 1 ml of water, 1 ml of 15% sodium hydroxide solution, and then 3 ml of water for each 1 g of lithium aluminum hydride used. (f) The nomenclature employed in this manuscript is based on the trivial name "decalin" for decahydronaphthalene. Relative stereochemistry is designated by "*c*" and "*t*" to denote a *cis* or *trans* relationship to some reference (*r*) substituent according to Beilstein ("Handbuch Der Organischen Chemie," E III, Vol. VI, part 7, p x).

(13) R. B. Turner, K. H. Gänshirt, P. E. Shaw, and J. D. Tauber, *J. Amer. Chem. Soc.*, **88**, 1776 (1966).

(14) We are indebted to Dr. M. Scheinbaum for a detailed procedure and seed crystals.

B. From 1*c*,9*c*-Dimethyl-7*c*-isopropenyl-10H*r*)-decal-3-one (2).[12f]—A solution of 100 mg (0.455 mmol) of ketone **2** in 10 ml of ether was reduced as outlined above to give 100 mg (98%) of alcohols (a 50:50 mixture of epimers by gas chromatographic analysis):[12d] $\lambda_{\max}^{\text{film}}$ 3.00 (OH), 3.25 (vinyl H), 6.07, 8.91, 9.57, 9.73, 10.14, and 11.26 μ.

The above mixture of alcohols was converted into the mesylate derivative as outlined above: $\lambda_{\max}^{\text{film}}$ 3.24, 6.08, 7.39, 8.50, 10.24, 10.6–11.2 (broad), 11.61, 12.80 and 13.7 μ.

A solution of this material in 0.7 ml of ethanol was reduced as outlined above affording, after chromatography and distillation, 61 mg (66%) of decalin **7**.[2]

3,3-(Propane-1,3-dithio)-10*r*-methyl-(9H*t*)-decal-2-one (9).[12f]—The procedure outlined above for the preparation of thioketal ketone **3** was followed using 265 mg of the hydroxymethylene ketone obtained (95% yield) from decalone **8**[15] by the procedure of Turner.[13] The crude product was filtered through 40 ml of Fisher alumina with 300 ml of benzene. Removal of the solvent afforded crystalline material which was recrystallized from ethanol affording 332 mg (90%) of thioketal ketone **9**. Recrystallization from hexane and sublimation at 80° (0.05 mm) afforded material of mp 133.5–135°; $\lambda_{\max}^{\text{KBr}}$ 5.92 (CO), 8.07, 8.46, 8.59, 8.94, 9.13, 9.33, 9.89, 10.88, 11.00, 11.41, 11.56, 12.20, 13.54, and 14.43 μ; $\delta_{\text{TMS}}^{\text{CDCl}_3}$ 1.07 ppm (C-10 CH_3).

Anal. Calcd for $C_{14}H_{22}OS_2$: C, 62.16; H, 8.20; S, 23.71. Found: C, 62.44; H, 8.26; S, 23.65.

3,3-(Propane-1,3-dithio)-10*r*-methyl(9H*t*)-decal-3*c*-ol (10).[12f]—A solution of 798 mg (2.95 mmol) of thioketal ketone **9** in 30 ml of ether was added dropwise to 114 mg (3.0 mmol) of lithium aluminum hydride in 30 ml of ether. The mixture was stirred for 15 hr, treated with water and base,[12e] stirred for 1 hr, and then dried over anhydrous magnesium sulfate. The salts were removed by filtration and washed well with ether and chloroform. Removal of the solvent afforded 800 mg (100%) of crystalline alcohol **10**. Two recrystallizations from hexane and sublimation at 80° (0.07 mm) afforded 536 mg of material with mp 105.5–107.5°; $\lambda_{\max}^{\text{KBr}}$ 2.85 (OH), 9.12, 9.29, 9.74, 9.93, 10.55, 10.91, 11.39, and 13.14 μ; $\delta_{\text{TMS}}^{\text{CDCl}_3}$ 3.83 (CHOH, X of ABX, $J_{\text{AX}} + J_{\text{BX}} = 15$ Hz) and 1.11 ppm (C-10 CH_3).

Anal. Calcd for $C_{14}H_{24}OS_2$: C, 61.70; H, 8.88; S, 23.53. Found: C, 61.97; H, 8.96; S, 23.56.

3,3-Propane-1,3-dithio)-10*r*-methyl-(9H*t*)-decal-2*c*-yl Acetate (11).[12f]—A solution of 247 mg (0.945 mmol) of thioketal alcohol **10** and 200 mg of sodium acetate in 2.5 ml of acetic anhydride was heated at reflux for 4 hr.[12a] The cooled mixture was poured into aqueous sodium bicarbonate and stirred to hydrolyze the acetic anhydride. The aqueous layer was extracted with ether and the combined organic extracts were washed with aqueous sodium bicarbonate and brine and dried over anhydrous magnesium sulfate. Removal of the solvent afforded 300 mg (100%) of crystalline acetate **11**. Two recrystallizations from hexane and sublimation at 90° (0.07 mm) afforded 260 mg of material with mp 137.5–138.5°; $\lambda_{\max}^{\text{KBr}}$ 5.75 (CO), 8.09, 9.35, 9.69, 10.94, 11.15, 13.01, and 15.00 μ; $\delta_{\text{TMS}}^{\text{CDCl}_3}$ 5.16 (CHOAc, X of ABX, $J_{\text{AX}} + J_{\text{BX}} = 15$ Hz), 2.14 (CH_3CO), and 1.14 ppm (C-10 CH_3).

Anal. Calcd for $C_{16}H_{26}O_2S_2$: C, 61.10; H, 8.33; S, 20.39. Found: C, 61.12; H, 8.27; S, 20.42.

2-Acetoxy-10*r*-methyl-(9H*t*)-decal-3-one (12).[12f]—Application of the hydrolysis procedure outlined above for thioketal **6** using 188 mg (0.60 mmol) of thioketal **11** afforded 139 mg (100%) of crystalline keto acetate **12** as a mixture of epimers. Two recrystallizations from hexane and sublimation at 80° (0.05 mm) afforded 113 mg (84%) of material with mp 137–148°; $\lambda_{\max}^{\text{KBr}}$ 5.71 (CO), 5.82 (CO), 7.97, 9.16, 9.49, 9.60, 9.97, 9.65, 11.13, and 15.15 μ; $\delta_{\text{TMS}}^{1:1\ \text{CDCl}_3-\text{CCl}_4}$ 5.4–5.0 (CHOAc, multiplet), 2.23 and 2.17 (CH_3CO), and 0.80 ppm (C-10 CH_3).

A 30-mg sample of this material was chromatographed on 10 ml of Fisher alumina. Elution with 10% ether in benzene afforded material, mp 145–149°, after recrystallization from hexane and sublimation at 90° (0.05 mm).

Anal. Calcd for $C_{13}H_{20}O_3$: C, 69.61; H, 8.99. Found: C, 69.65; H, 8.91.

10*r*-Methyl-(9H*t*)-decal-2-one (13).[12f]—A solution of 85 mg (0.38 mmol) of keto acetate **12** (a mixture of epimers) in 15 ml of ether was added over 10 min to a solution of 200 mg of calcium in 75 ml of distilled ammonia. The addition funnel was rinsed with 5 ml of ether. The mixture was stirred an additional 5 min and was then quenched with solid ammonium chloride. Brine was added to the residue which remained after evaporation of the ammonia, and the product was isolated with ether.[12d] Removal of the solvent afforded a mixture of alcohol and ketone **13**, $\lambda_{\max}^{\text{film}}$ 2.91 and 5.85 μ.

This mixture was dissolved in 5 ml of acetone and cooled to 0°. Jones reagent[16] (~10 drops) was added with rapid stirring until the red color remained. After stirring for 3 min, the mixture was treated with isopropyl alcohol to destroy the excess oxidizing agent and the product was isolated with ether.[12d] Short-path distillation at 70° (0.05 mm) afforded 51 mg (80%) of ketone **13** which was pure by gas chromatographic analysis:[12d] $\lambda_{\max}^{\text{film}}$ 5.82 (CO), 8.11, 8.40, 10.09, and 11.13 μ; $\delta_{\text{TMS}}^{\text{CCl}_4}$ 0.79 ppm (C-9 CH_3). The infrared and nmr spectra and the gas chromatographic retention time, by peak enhancement, were identical with those of an authentic sample of ketone **11**.[17]

Attempted Formation of Mesylate 14.—A solution of 90 mg (0.33 mmol) of thioketal alcohol **10** in 0.2 ml of pyridine was cooled to 0° and treated with 0.03 ml of methanesulfonyl chloride.[12a] The mixture was stirred for 2 hr at room temperature, ice was added, and stirring was continued for an additional 5 min. The mixture was poured into ether, washed with 4% sulfuric acid until acidic and with aqueous sodium bicarbonate until neutral, and dried over anhydrous magnesium sulfate. Removal of the solvent afforded 90 mg of a crystalline product: $\lambda_{\max}^{\text{KBr}}$ 6.19, 6.91, 7.03, 7.67, 7.92, 8.11, 10.05, 11.54, 11.44, 11.71, 13.31, and 14.20 μ; $\delta_{\text{TMS}}^{\text{CDCl}_3}$ 5.80 (C=CH, $W_{1/2} = 1.5$ Hz), 3.88 (CHS, poorly resolved doublet, $J = 4$ Hz), and 0.96 ppm (C-10 CH_3).

Registry No.—**2**, 21736-21-0; 2,4-dinitrophenylhydrazone derivative of **2**, 21736-22-1; **3**, 21779-09-9; **4**, 21736-23-2; **5**, 21779-10-2; **6**, 21736-24-3; 2,4-dinitrophenylhydrazone of **6**, 21779-58-8; epimer of **6**, 21740-16-9; **7**, 21740-17-0; **9**, 21740-18-1; **10**, 21740-19-2; **11**, 21740-20-5; **12**, 21740-21-6; **13**, 21740-22-7.

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[15] *Cf.* M. Yanagita and K. Yamakawa, *J. Org. Chem.*, **21**, 500 (1956).

[16] K. Bowden, I. M. Heilbron, E. R. H. Jones, and B. C. L. Weedon, *J. Chem. Soc.*, **39** (1946).

[17] J. A. Marshall and R. D. Carroll, *J. Org. Chem.* **30**, 2748 (1965).

Enolene Rearrangements. II. Rearrangement of 3-Ethyl-4-pentenophenone to 3-Methyl-4-hexenophenone[1]

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The parent example of the "abnormal Claisen rearrangement" is now known to involve the isomerization of an *o*-(α-ethylallyl)phenol (**1a**, **1b**, or **1c**) to an *o*-(α,γ-dimethylallyl)phenol (**3a**, **3b**, or **3c**) by sigmatropic [1,5] hydrogen shifts, *via* a spirodienone intermediate (**2a**, **2b**, or **2c**), as shown in Scheme I.[2-6] In support of this mechanism, when the lower homologs **1d**

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[2] (a) W. M. Lauer and W. F. Filbert, *J. Amer. Chem. Soc.*, **58**, 1388 (1936); (b) C. D. Hurd and M. A. Pollack, *J. Org. Chem.*, **3**, 550 (1939); (c) E. N. Marvell, D. R. Anderson, and J. Ong, *ibid.*, **27**, 1109 (1962).

[3] W. M. Lauer and H. E. Ungenade, *J. Amer. Chem. Soc.*, **61**, 3047 (1939).

[4] R. M. Roberts and R. G. Landolt, *J. Org. Chem.*, **31**, 2699 (1966).

[5] A. Habich, R. Barner, R. M. Roberts, and H. Schmid, *Helv. Chim. Acta*, **45**, 1943 (1962).

[6] W. M. Lauer and T. A. Johnson, *J. Org. Chem.*, **28**, 2913 (1963).