Preparation of 4a.—A solution of 2-cyclohexen-1-one (**2**, 4.90 g, 51 mmol), benzyl vinyl sulfide[6] (**3a**, 51.00 g, 340 mmol), and hexane was irradiated for 8 hr. Solvent was removed and the unreacted **3a** (37 g) was recovered by distillation. The light yellow viscous residue was then distilled through a short-path still to give a light yellow forerun (0.85 g), bp 30–157° (0.03 mm), and a yellow main distillation fraction, **4a** (8.05 g, 64%), bp 157–162° (0.03 mm). The residue was a viscous orange oil (2.85 g). Adduct **4a** had ir (CCl_4) 5.81 and 5.86 μ; mass spectrum (70 eV) m/e 247 (strongest high mass peak due to a M + 1 species);[18] nmr (CCl_4) δ 7.18 (5 H, single aromatic proton peak), 3.20–3.80 (3 H, —CH_2SCH—), 2.50–3.20 (2 H, aliphatic CH at ring juncture), and 1.20–2.40 (8 H, aliphatic CH_2, complex multiplet).

Anal. Calcd for $C_{15}H_{18}OS$ (mol wt, 246.3): C, 73.13; H, 7.36; S, 13.01. Found: C, 72.93; H, 7.54; S, 13.21.

Preparation of 4b.—Adduct **4b** was made in the same way from 2 (4.90 g, 51 mmol) and *n*-butyl vinyl sulfide[6] (**3b**, 39.34 g, 339 mmol). Irradiation time was 5.5 hr. After recovery of **3b** (24 g), the yellow residue was distilled to give a forerun (0.96 g), bp 97–104° (0.01 mm), and a yellow main distillation fraction, **4b** (6.69 g, 62%), bp 104–107° (0.01 mm). The residue was a red oil (2.75 g). Adduct **4b** had ir (CCl_4) 5.81 and 5.86 μ; mass spectrum (70 eV) m/e 212 (M^+); nmr (CCl_4) δ 0.91 (CH_3, center of poorly resolved triplet), 2.46 (—CH_2S—, center of poorly resolved triplet), 1.18–2.30 (12 H, aliphatic CH_2), 2.50–3.20 (2 H, aliphatic CH at ring juncture), and 3.20–3.80 (—SC**H**<).

Anal. Calcd for $C_{12}H_{20}OS$ (mol wt, 212.3): C, 67.87; H, 9.49; S, 15.10. Found: C, 68.03; H, 9.75; S, 15.27.

Preparation of 4c.—Adduct **4c** was prepared in a similar fashion from 2 (4.91 g, 51 mmol) and phenyl vinyl sulfide[7] (**3c**, 46.24 g, 340 mmol). Irradiation time was 14.5 hr (see Table I, footnote *b*). After recovery of **3c** (36.5 g), the yellow residue was distilled to yield a forerun (0.61 g), bp 30–141° (0.02 mm), and a yellow main distillation fraction, **4c** (5.87 g, 62%, see Table I, footnote *c*), bp 141–147° (0.02 mm). The residue was a red oil (2.01 g). Adduct **4c** had ir (CCl_4) 5.81 and 5.86 μ; mass spectrum (70 eV) m/e 232 (M^+); nmr (CCl_4) δ 7.18 (5 H, complex multiplet, aryl CH), 3.20–4.15 (—SC**H**<, complex multiplet), 2.30–3.15 (2 H, aliphatic CH at ring juncture), and 1.30–2.30 (8 H, aliphatic CH_2).

Anal. Calcd for $C_{14}H_{16}OS$ (mol wt, 232.3): C, 72.38; H, 6.94; S, 13.80. Found: C, 72.37; H, 7.05; S, 14.06.

Bicyclo[4.2.0]octan-2-one (1). A. By Desulfurization of Adduct 4a with Raney Nickel Catalyst.—A solution of adduct **4a** (4.000 g, 16.26 mmol) in absolute ethanol (20 ml) was added to a suspension of W-2 Raney nickel catalyst[10] (20 g, decanted weight) in absolute ethanol (100 ml). The mixture was placed in an oil bath preheated to 65° and maintained at 62–67°, with stirring, for 0.5 hr. After cooling, the catalyst was removed by filtration and washed with an additional 50 ml of ethanol. The filtrates were combined and concentrated on a steam bath in order to remove the ethanol. Ether (100 ml) was added to the residue and the ethereal solution was washed with water (25 ml) and saturated NaCl solution (25 ml). After drying (Na_2SO_4), the ethereal solution was concentrated and the residue was distilled to give 630 mg of a colorless liquid, bp 67–71° (6 mm). The yellow residue (960 mg, 3.90 mmol) consisted entirely of recovered **4a**. The product exhibited four peaks on gas chromatography, one major (75%, area per cent) and three minor ones, and showed a single C=O band at 5.85 μ in the infrared spectrum. The major component (99.9% purity) was collected by preparative vpc (recovery yield was 86%) and its spectral characteristics were identical with those of an authentic sample of **1**.[12]

B. By Desulfurization of Adducts 4b and 4c with Raney Nickel Catalyst.—Adducts **4b** and **4c** were treated in the same way as **4a**. The results are tabulated in Table II.

Registry No.—**1**, 21813-31-0; **4a**, 21779-15-7; **4b**, 21779-16-8; **4c**, 21779-17-9.

Acknowledgment.—The author wishes to thank Dr. Donald H. Wheeler for his helpful comments during the course of this work.

(18) This is not an uncommon occurrence. Cases have been reported where the M + 1 peak is stronger than the molecular ion peak (*e.g.*, oxonium ions). See K. Biemann, "Mass Spectrometry, Organic Chemical Applications," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, pp 55–56.

Heterolytic Fragmentation of 4-Substituted Decahydroquinolines

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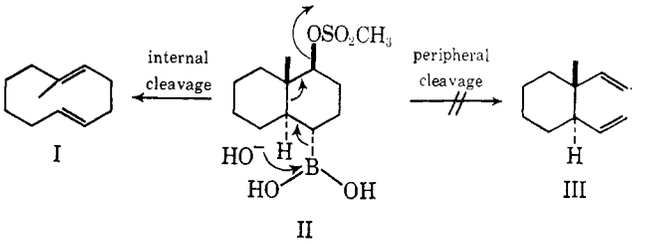
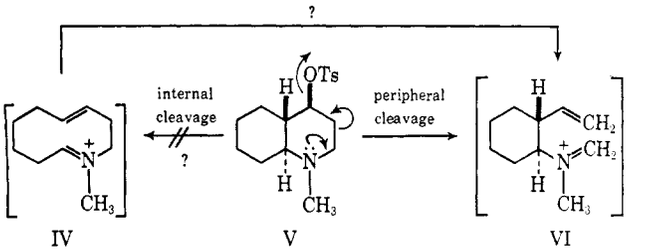
In the course of studies aimed at the development of new synthetic routes to medium ring compounds, we found that the boronate II underwent heterolytic fragmentation into 1-methyl-*trans,trans*-1,5-cyclodecadiene (I), the product of internal cleavage. None of the alternative (peripheral) cleavage product III could be detected.[1]



These findings contrast sharply with those of Grob and coworkers[2] who studied the seemingly analogous fragmentation reaction of the decahydroquinolyl tosylate V and concluded that the peripheral cleavage constituted the exclusive reaction pathway.

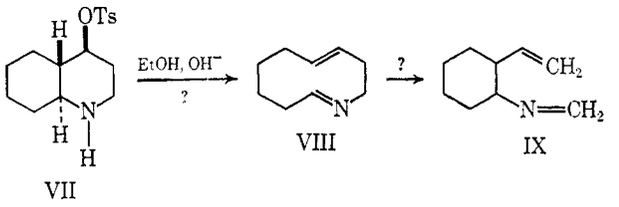


Since we could see no obvious basis for the divergent behavior of the two systems, we decided to explore fragmentations related to the amine system further. In particular, we wished to examine the possible isomerization of the medium-ring iminium salt IV into its cyclohexane counterpart VI, a reaction known to proceed with relative ease in related carbon systems.[3] Our findings, which we present at this time, show that the isomerization IV → VI is indeed facile, even at room temperature, and that the predominant, if not exclusive, fragmentation pathway of amine V must proceed by internal cleavage.

As our first objective we planned to study the solvolysis of the amine VII. We selected this amine in the hope that, if the medium-ring imine VIII was in fact a solvolysis product, it would show less tendency to rearrange to its isomer IX than the corresponding im-

(1) J. A. Marshall and G. L. Bundy, *Chem. Commun.*, 855 (1967).
(2) C. A. Grob, H. R. Kiefer, H. J. Lutz, and H. J. Wilkens, *Helv. Chim. Acta*, **50**, 416 (1967).
(3) *Cf.* C. A. Grob, H. Link, and P. W. Schiess, *ibid.*, **46**, 483 (1963).

inium salt IV. If so, then N methylation of the imine VII would presumably promote the rearrangement and this phase of the reaction could then be studied inde-



VII VIII IX

pendently. With this plan in mind, we undertook a synthesis of the *N*-benzyldecahydroquinolyl mesylate **3a** along the lines of Grob and Lutz.[4] Accordingly, 1-acetylcyclohexene was subjected to a Mannich reaction[5] with formaldehyde and benzylamine to give the ketone **1a**, but only in low yield. A substantial improvement (76% yield) was realized when the preformed condensation product of benzylamine and formaldehyde[6] was employed for this reaction. Reduction of ketone **1a** with aluminum isopropoxide afforded the alcohol **2a** which smoothly yielded the corresponding mesylate **3a** upon treatment with methanesulfonyl chloride in pyridine. We experienced experimental difficulties in attempted conversions of the *N*-benzyl compound **3a** into the corresponding N–H derivative and therefore decided to initially examine the solvolysis of the *N*-benzyl mesylate **3a**.

Grob and coworkers[2] solvolyzed the *N*-methyl derivative V in the presence of palladium on carbon under a hydrogen atmosphere in order to hydrogenate the initial fragmentation products and thereby prevent rearrangement of the medium-ring iminium salt IV into the cyclohexane derivative VI. For the same reason, we carried out the solvolysis of mesylate **3a** in the presence of sodium borohydride, a technique also employed by Grob, *et al.*,[2] to reduce the iminium double bond in related systems. Our findings, summarized in Table I,

TABLE I

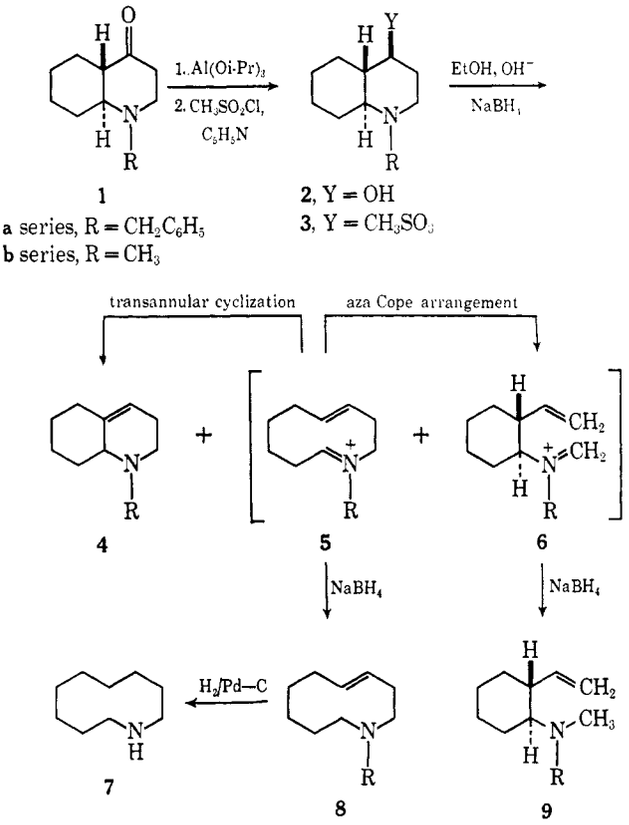
FRAGMENTATION OF THE DEHYDROQUINOLYL MESYLATE **3a**[a]

Entry	$NaBH_4$, equiv	Temp., °C	Time, hr	Distilled yield, %	Composition, %[b] 4a	8a	9a
1	80	−5	186	65	18	58	24
2	80	50	20	77	18	44	39
3	105	20	110	76	19	46	35
4	105	25	13	93[c]	21	49	30
5	105[d]	40	86[d]	41	35	0	65

[a] In 80% aqueous ethanol, 0.05 *M* in NaOH and 0.02 *M* in mesylate **3a**. [b] Gas chromatographic analysis. [c] A crystalline sample of mesylate **3a** was employed. [d] The solution was stirred for 38 hr before addition of $NaBH_4$.

show that under these conditions internal cleavage constitutes the major reaction pathway with 44–58% of the distilled product consisting of the azacyclodecene **8a**. The structure of this component was confirmed through its reduction into azacyclodecane (**7**). The other products of the fragmentation reaction were identified as the octahydroquinoline **4a** and the vinylcyclohexane **9a** on the basis of their spectral properties. Significantly, when the solvolysis was allowed to proceed for a number of hours before the addition of sodium borohydride, none of the medium ring amine **8a** could be detected in the distilled product (Table I, entry 5). These findings indicate that the aza Cope rearrangement **5** → **6** must take place with comparative ease. See Scheme I. The relatively higher percentage of octahydroquinoline **4a** obtained in this experiment may stem from the transannular cyclization of the intermediate iminium salt **5**.

SCHEME I



The *N*-methyl counterpart **3b** of the mesylate **3a** exhibited analogous behavior upon solvolysis in aqueous ethanol (Table II). In this case, an even higher proportion of the medium ring amine **8b** resulted from solvolyses conducted in the presence of sodium borohydride. As before, the subsequent addition of sodium borohydride to reactions in progress resulted in a marked decrease in this product and a corresponding increase in the cyclohexane isomer **9b**. Owing to the apparent instability of the initially formed iminium salts, we were unable to define conditions whereby this latter isomer could be isolated as the major product and in high yield.

TABLE II

FRAGMENTATION OF THE DECAHYDROQUINOLYL MESYLATE **3b**[a]

Entry	Time, hr	Distilled yield, %	Product ratio[b] 4b	8b	9b
1	20	60–70[c]	3.3	10.5	1
2	43[d]	47	1.4	1	1

[a] At 25° in 80% aqueous ethanol, 0.05 *M* in NaOH, 0.02 *M* in mesylate **3b**, and containing 105 equiv of $NaBH_4$. [b] Gas chromatographic analysis. [c] Range for three runs. [d] The solution was stirred for 20 hr before addition of $NaBH_4$.

To summarize, our findings show that heterolytic fragmentations of γ-amino mesylates and the related boronates (*e.g.*, II and V) most likely proceed *via* anal-

(4) C. A. Grob and H. J. Lutz, *Helv. Chim. Acta*, **48**, 791 (1965).
(5) *Cf.* F. F. Blicke, *Org. Reactions*, **1**, 303 (1942).
(6) E. R. Braithwaite and J. Graymore, *J. Chem. Soc.*, 143 (1953).

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-$\Delta^{4(10)}$-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-$\Delta^{4(10)}$-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 FO1 GM 37934, Division of General Medical Sciences).

(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

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