4 H); nmr (CF_3COOD) 4.42 (s, 4 H), 7.35 (AB, J = 9 Hz, 4 H), 11.4 ppm (s, 2 H).

Anal. Calcd for $C_{12}H_{10}ClNO_2S$: C, 53.84; H, 3.76; N, 5.23. Found: C, 53.52; H, 3.97; N, 5.25.

1-(*p*-Chlorophenyl)-3,4-dimethylenepyrrolidine (5).—The sulfone **2a** (500 mg) was left under vacuum (0.1 mm) and 135–138° overnight. The diene sublimed and was collected (300 mg, 79%). The crystalline residue (dimer) amounted to 80 mg (21%). The sublimed diene was virtually pure, the only impurities being traces of dimeric and polymeric material. The 300 mg were recrystallized from ether–hexane (without excessive heating) to give a first crop of 110 mg (melting point not detectable due to dimerization upon heating): ν_{max}^{Nujol} 1600, 1500, 1100, 900, 890, 810 cm^{-1}; $\lambda_{max}^{CH_3OH}$ 253 mμ (ε 25,780), 306 (4420); nmr ($CDCl_3$) δ 4.05 (~t, J = 2 Hz, 4 H), 5.05 (~t, J = 2 Hz, 2 H), 5.52 (t, J = 2 Hz, 2 H), 6.5 and 7.18 (AB, J = 9 Hz, 4 H); nmr (CF_3COOD) 4.7 (m, broad, 4 H), 5.43 (m, broad, 2 H), 5.93 (m, broad, 2 H), 7.55 ppm (s, 4 H); mass spectrum (50°) M^+ 205, *m/e* 190, 168, 154, 138, 111.

Anal. Calcd for $C_{12}H_{12}ClN$: C, 70.08; H, 5.88; N, 6.81. Found: C, 70.18; H, 5.94; N, 6.57.

Dimer of 1-(*p*-Chlorophenyl)-3,4-dimethylenepyrrolidine 6.—The dimer of **5** was obtained as a side product in the preparation of **5** (see above). By heating the sulfolene **2a** for 5 min in an oil bath of 170°, a complete conversion into crude **6** is observed (dec 220°). Owing to very poor solubility, purification of the dimer **6** was not feasible: nmr (CF_3COOD) δ 2–2.8 (m, 6 H), 4.1 (m, 2 H), 4.6–4.9 (m, 6 H), 5.5 (m, 2 H), 7.6 (m, 8 H); mass spectrum (205°) M^+ 410, *m/e* 204, 140, 138, 111; mass spectrum (300°) M^+ 613, 410, 205, *m/e* 270, 242, 218, 204, 190, 140, 138, 125, 111.

Diels–Alder Adduct with Dimethyl Acetylenedicarboxylate (7).—A solution of 860 mg (4.2 mmol) sublimed diene **5** and 1.5 ml (12 mmol) of dimethyl acetylenedicarboxylate in 10 ml of dry toluene was refluxed for 20 hr. After evaporation of the solvent the residue is crystallized from ether to give 720 mg of diester (mp 189–191°) (50%). Recrystallization of 500 mg thereof from CH_2Cl_2–ether gave 350 mg (mp 189–191°): ν_{max}^{Nujol} 1740, 1720, 1705, 1650, 1500, 1280, 1060, 810 cm^{-1}; $\lambda_{max}^{CH_3OH}$ 260 mμ (ε 24,890), 315 (2490); nmr ($CDCl_3$) δ 3.05 (s, 4 H), 3.76 (s, 6 H), 3.94 (s, 4 H), 6.35 and 7.13 (AB, J = 9 Hz, 4 H).

Anal. Calcd for $C_{18}H_{18}ClNO_4$: C, 62.21; H, 5.22; N, 4.04. Found: C, 62.54; H, 5.35; N, 4.08.

Diels–Alder Adduct with *N*-Phenylmaleimide (8).—A solution of 269 mg (1 mmol) of sulfone **2a** and 173 mg (1 mmol) of *N*-phenylmaleimide in 2.5 ml of xylene was refluxed under nitrogen for 3 hr. The mixture was then cooled and diluted with some benzene, and the product crystallized out: 250 mg; mp 204–206° (66%); ν_{max}^{Nujol} 1708, 1390, 795 cm^{-1}; nmr ($CDCl_3$) δ 2.7 (broad s, 4 H), 3.4 (m, 2 H), 4.04 (s, 4 H), 6.4 and 7.2 (AB, J = 9 Hz, 4 H), 7.4 (m, 5 H); mass spectrum 378 (M^+), 230, 204, 190, 138, 111.

Anal. Calcd for $C_{22}H_{19}ClN_2O_2$: C, 69.76; H, 5.05; N, 7.34. Found: C, 70.10; H, 5.13; N, 7.29.

Registry No.—**2a**, 32515-66-5; **3**, 32515-67-6; **4**, 32515-68-7; **5**, 32515-69-8; **6**, 32515-70-1; **7**, 32515-71-2; **8**, 32515-72-3.

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Allenes from Fragmentation of Tosylhydrazones

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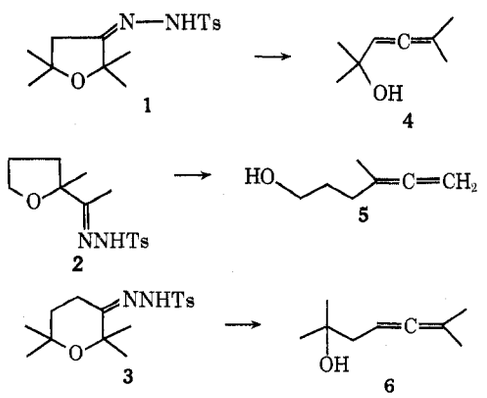
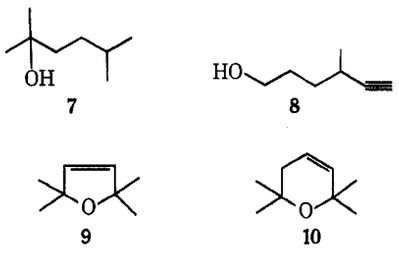
Tosylhydrazones **1**, **2**, and **3** undergo fragmentation on treatment with 2 equiv of butyllithium to form allenic alcohols **4**, **5**, and **6**. Mechanistic pathways and structural restrictions on the reaction are discussed.

We describe here the fragmentation of three α-alkoxytosylhydrazones to form the related allenes. In each case the tosylhydrazone reacted with 2 equiv of butyllithium in ether–hexane to give an allenic alcohol in 48–58% yield, **1**, **2**, and **3** leading to **4**, **5**, and **6** as indicated. These products were characterized by ir



and nmr spectroscopy; in addition, **4** was reduced over platinum to the saturated alcohol **7**, which was identical with an authentic sample.[2] Excess base favored partial isomerization of **5** to the terminal acetylene **8**, and both **1** and **3** yielded a small amount of olefinic ether (**9** and **10**, respectively) in addition to allenes.



Closely related transformations suggest two possible pathways for these fragmentations. A mechanism considered[3] for the base-catalyzed decomposition of α,β-epoxytosylhydrazones is reproduced in eq 1 and involves carbon–oxygen bond cleavage in the first step. The reaction of simple tosylhydrazones with butyl-

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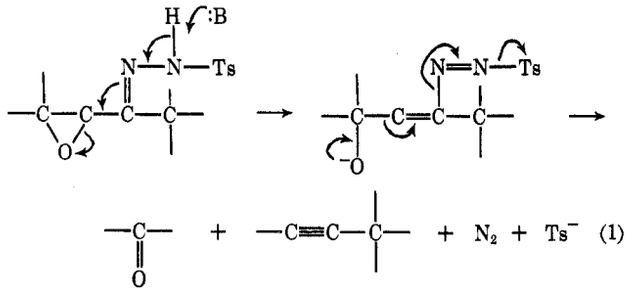
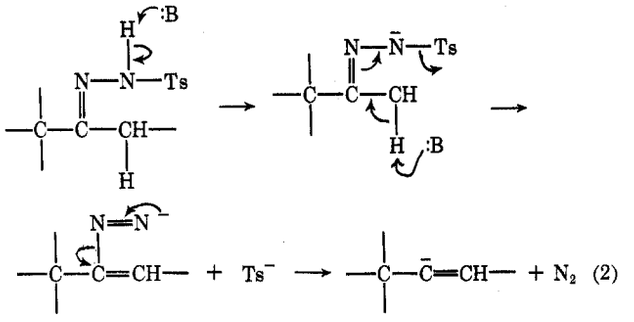
(2) Authentic **7** was prepared by reaction of isopentylmagnesium bromide with acetone: L. R. C. Barclay and J. W. Hilchie, *J. Org. Chem.*, **22**, 633 (1957).

(3) A. Eschenmoser, D. Felix, and G. Ohloff, *Helv. Chim. Acta*, **50**, 708 (1967); M. Tanabe, D. F. Crowe, R. L. Dehn, and G. Detre, *Tetrahedron Lett.*, 3739 (1967).



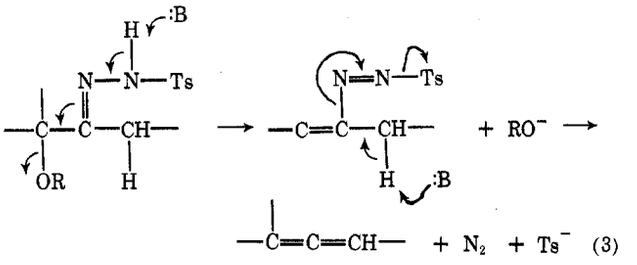
(1)

lithium, however, requires 2 equiv of base, as shown in eq 2, and leads to a vinyl anion which is subsequently

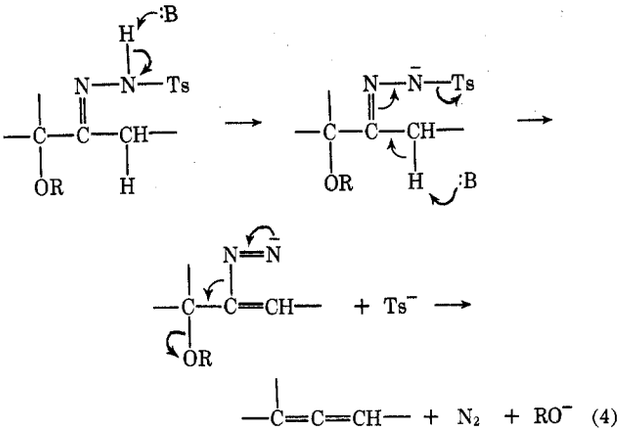


(2)

protonated to furnish the product olefin.[4] The two analogous sequences for formation of allenes are given in eq 3 and 4; the key difference is scission of the carbon–oxygen bond upon reaction of 1 (eq 3) or 2 (eq 4)



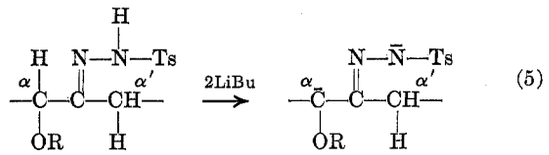
(3)



(4)

equiv of butyllithium. Since treatment of **1** with a single equivalent of base and subsequent work-up leads only to recovered starting material, it is clear that 2 equiv of base are needed for ether cleavage and that the pathway of eq 3 is not operative here. Without the ring strain of an epoxide there is insufficient driving force for immediate elimination of alkoxide ion, and these α-alkoxy derivatives apparently react according to eq 4.

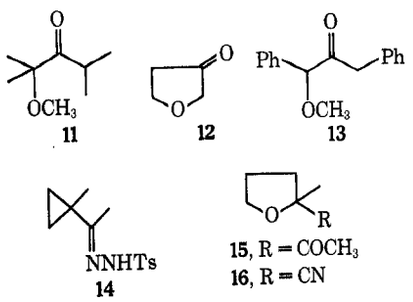
It is known[4,5] that simple tosylhydrazones fragment according to eq 2 only when the second mole of base can attack the hydrogen of a methyl or methylene group. The same restriction appears applicable here, for the tosylhydrazone of α-methoxydiisopropyl ketone (**11**) gave no allene upon exposure to butyllithium. A further structural restriction is that there can be no hydrogen on the carbon bearing the α-alkoxy group; the tosylhydrazones of dihydro-3(2*H*)-furanone (**12**) and α-methoxydibenzyl ketone (**13**), for example, did not yield allenes. This behavior probably results from preferential removal of the more acidic α proton on the carbon bearing oxygen (eq 5)[6] rather than the less



(5)

acidic α' proton necessary for allene formation. Within these restrictions this fragmentation reaction should provide a convenient route to allenes structurally related to **4**, **5**, and **6**.

An attempt to generate an allene through ring opening of a cyclopropyl ketone derivative failed. Fragmentation of **14** gave only 1-methyl-1-vinylcyclopropane, the product expected from a simple tosylhydrazone.



11 **12** **13**

14 **15**, R = $COCH_3$; **16**, R = CN

The ketones used in this work were all previously known with the exception of **15**, which was prepared by addition of methylmagnesium bromide to 2-methyltetrahydro-2-furonitrile (**16**)[7] and subsequent hydrolysis. We assume that the tosylhydrazones derived from these ketones are mixtures of syn and anti isomers, since they melted over rather wide ranges even when analytically pure.

Experimental Section

Materials and Equipment.—Unless otherwise noted, both ir and nmr spectra were obtained for carbon tetrachloride solutions, the former on a Perkin-Elmer 237B spectrophotometer and the latter on a Varian A-60 (60 MHz) nmr spectrometer. Vpc was carried out using a Varian Aerograph Model 700 Autoprep equipped with a 10 ft × 0.375 in. aluminum column packed with 30% SE-30 on Chromosorb W and operated at 110–135° with a helium carrier gas flow rate of 120 ml/min. Melting points are corrected.

(4) R. H. Shapiro and M. J. Heath, *J. Amer. Chem. Soc.*, **89**, 5734 (1967); G. Kaufman, F. Cook, H. Shechter, J. Bayless, and L. Friedman, *ibid.*, **89**, 5736 (1967).

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(6) For an investigation of such systems, see J. H. Robson and H. Shechter, *ibid.*, **89**, 7112 (1967).

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Preparation of Tosylhydrazones. A. General Procedure.—A solution containing equimolar quantities of ketone and *p*-toluenesulfonyl hydrazine in anhydrous methanol or ethanol was heated at reflux for 1–2 hr. The corresponding tosylhydrazone, which crystallized from solution on cooling, was isolated by filtration, dried *in vacuo*, and used in the next step without further purification. An analytical sample was prepared by recrystallization from methanol or ethanol. These derivatives all showed ir absorption ($CHCl_3$) at approximately 3200, 1600, and 1160 cm^{-1}.

B. 2,2,5,5-Tetramethyltetrahydrofuran-3-one Tosylhydrazone (1).—2,2,5,5-Tetramethyltetrahydrofuran-3-one[8] gave a 94% yield of **1**: mp 169–171°; nmr ($CDCl_3$) δ 1.23 (s), 1.25 (s) (12 H), 2.44 (s, 5 H), 7.30 (d, J = 8 Hz, 2 H), 7.5 (br, 1 H), 7.83 (d, J = 8 Hz, 2 H).

Anal. Calcd for $C_{15}H_{22}N_2O_3S$: C, 58.03; H, 7.15; N, 9.03. Found: C, 58.14; H, 7.18; N, 9.10.

C. Methyl 2-(2-Methyltetrahydrofuryl) Ketone Tosylhydrazone (2).—Methyl 2-(2-methyltetrahydrofuryl) ketone (**15**) gave 70% of **2**: mp 128–130°; nmr ($CDCl_3$) δ 1.25 (s), 1.78 (s), 1.4–2.2 (m), 2.43 (s), 3.8 (m), 7.41 (d, J = 8 Hz), 7.6 (br, 1 H), 7.86 (d, J = 8 Hz).

Anal. Calcd for $C_{14}H_{26}N_2O_3S$: C, 56.73; H, 6.80; N, 9.45. Found: C, 56.78; H, 6.80; N, 9.54.

D. Dihydro-2,2,6,6-tetramethyl-2*H*-pyran-3(4*H*)-one Tosylhydrazone (3).—Dihydro-2,2,6,6-tetramethyl-2*H*-pyran-3(4*H*)-one[9] gave 82% of **3**: mp 151–154°; nmr ($CDCl_3$) δ 1.13 (s, 6 H), 1.27 (s, 6 H), 1.6–2.4 (m, 4 H), 2.44 (s, 3 H), 7.28 (d, J = 8 Hz, 2 H), 7.6 (br, 1 H), 7.83 (d, J = 8 Hz, 2 H).

Anal. Calcd for $C_{16}H_{24}N_2O_3S$: C, 59.24; H, 7.46; N, 8.64. Found: C, 59.38; H, 7.52; N, 8.52.

E. Tosylhydrazone of α-Methoxydiisopropyl Ketone (11).—This derivative was obtained from **11**[10] in 83% yield, mp 111–124°.

Anal. Calcd for $C_{15}H_{24}N_2O_3S$: C, 57.66; H, 7.74; N, 8.97. Found: C, 57.75; H, 7.66; N, 9.14.

F. Tosylhydrazone of Dihydro-3(2*H*)-furanone (12).—This derivative was obtained from **12**[11] in 88% yield, mp 139–147° dec.

Anal. Calcd for $C_{11}H_{14}N_2O_3S$: C, 51.95; H, 5.55; N, 11.02. Found: C, 52.01; H, 5.55; N, 11.13.

G. Tosylhydrazone of α-Methoxydibenzyl Ketone (13).—This derivative was prepared from **13**,[12] mp 100–104°.

Anal. Calcd for $C_{23}H_{24}N_2O_3S$: C, 67.63; H, 5.92; N, 6.86. Found: C, 67.63; H, 5.90; N, 6.88.

H. Methyl 1-(1-Methylcyclopropyl) Ketone Tosylhydrazone (14).—This derivative was obtained from the commercially available ketone in 76% yield, mp 138–141°.

Anal. Calcd for $C_{13}H_{18}N_2O_3S$: C, 58.62; H, 6.81; N, 10.52. Found: C, 58.88; H, 6.80; N, 10.54.

Reaction of Tosylhydrazones with *n*-Butyllithium. A. General Procedure.—A slurry of tosylhydrazone in ether (10 ml/g) was stirred at 25° under nitrogen and 2.5–3.0 equiv of a 2.55 *M* solution of *n*-butyllithium in hexane was added dropwise during a period of 30 min. After an additional 10 min water was added and the mixture was extracted with ether. The resulting ethereal solution was dried (Na_2SO_4) and concentrated, and the residue was distilled at reduced pressure. When more than one product was present the ratio of components was determined from their relative vpc peak areas. Analytical samples were obtained by preparative vpc.

B. Reaction of 2,2,5,5-Tetramethyltetrahydrofuran-3-one Tosylhydrazone (1) with *n*-Butyllithium.—Tosylhydrazone **1** gave a 58% yield of 2,5-dimethyl-3,4-hexadien-2-ol (**4**): bp 57° (12 Torr); ir 3600, 3500–3100, 1950 cm^{-1}; nmr δ 1.27 (s, 6 H), 1.71 (d, J = 3 Hz, 6 H), 2.2 (br, 1 H), 5.10 (m, 1 H). The spectral data for **1** are in agreement with published[13] values.

The distillation forerun contained a 3% yield of 2,2,5,5-tetramethyl-2,5-dihydrofuran (**9**):[14] ir 3050 cm^{-1}; nmr δ 1.23 (s, 12 H), 5.55 (s, 2 H).

C. Reaction of Methyl 2-(2-Methyltetrahydrofuryl) Ketone Tosylhydrazone (2) with *n*-Butyllithium.—Tosylhydrazone **2** gave a 53% yield of distillate (bp 45°, 1.0 Torr) containing two components in a 9:1 ratio. The major component was identified as 4-methyl-4,5-hexadien-1-ol (**5**): ir 3625, 3500–3100, 3020, 1940 cm^{-1}; nmr δ 1.68 (t, J = 3 Hz), 1.2–2.3 (m) (7 H), 3.26 (s, 1 H, exchanges with D_2O), 3.54 (t, J = 7 Hz, 2 H), 4.54 (m, 2 H).

Anal. Calcd for $C_7H_{12}O$: C, 74.95; H, 10.78. Found: C, 74.84; H, 10.84.

The minor component was identified as 4-methyl-5-hexyn-1-ol (**8**): ir 3625, 3500–3100, 3300, 2085 cm^{-1}; nmr δ 1.17 (d, J = 7 Hz, 3 H), 1.4–1.8 (m, 4 H), 1.92 (d, J = 2.5 Hz, 1 H), 2.38 (m, 1 H), 3.06 (br s, 1 H, exchanges with D_2O), 3.55 (t, J = 6 Hz, 2 H).

Anal. Calcd for $C_7H_{12}O$: C, 74.95; H, 10.78. Found: C, 75.10; H, 10.94.

D. Reaction of Dihydro-2,2,6,6-tetramethyl-2*H*-pyran-3(4*H*)-one Tosylhydrazone (3) with *n*-Butyllithium.—Tosylhydrazone **3** gave a 74% yield of distillate containing two components in a 2:1 ratio. The major component was identified as 2,6-dimethyl-4,5-heptadien-2-ol (**6**): ir 3600, 3560, 3500–3100, 1950 cm^{-1}; nmr 1.15 (s, 6 H), 1.34 (s, 1 H, exchanges with D_2O), 1.68 (d, J = 3 Hz, 6 H), 2.04 (d, J = 8 Hz, 2 H), 4.86 (m, 1 H).

Anal. Calcd for $C_9H_{16}O$: C, 77.09; H, 11.50. Found: C, 77.03; H, 11.47.

The minor component was identified as 2,2,6,6-tetramethyl-2,3-dihydropyran (**10**): ir 3025, 700 cm^{-1}; nmr δ 1.16 (s, 12 H), 1.87 (m, 2 H), 5.59 (br s, 2 H).

Anal. Calcd for $C_9H_{16}O$: C, 77.09; H, 11.50. Found: C, 77.06; H, 11.55.

E. Reaction of Methyl 1-(1-Methylcyclopropyl) Ketone Tosylhydrazone (14) with *n*-Butyllithium.—Tosylhydrazone **14** gave 1-methyl-1-vinylcyclopropane[15] which was isolated by vpc: ir 3065, 890 cm^{-1}, nmr 0.53 (s, 4 H), 1.16 (s, 3 H), 4.6–5.5 (m, 3 H). There was no evidence of formation of 3-methyl-1,2-pentadiene.

Methyl 2-(2-Methyltetrahydrofuryl) Ketone (15).—To 8.5 ml of *ca.* 3 *M* methylmagnesium bromide (*ca.* 1.4 equiv) in ether was added dropwise 2.0 g of nitrile **16**[7] in 20 ml of ether. The resulting mixture was heated at reflux for 1 hr and then treated with 2 *M* aqueous hydrochloric acid until acidic. After being stirred at room temperature for 15 min, the reaction mixture was worked up with ether and water to give 1.95 g (84%) of yellow oil. This showed a single peak on vpc analysis. A sample was purified by vpc: ir 2960 (m), 2750 (m), 1720 (s), 1350 (m), 1105 (m), 1038 cm^{-1} (m); nmr δ 1.23 (s, 3 H), 1.4–2.4 (m), 2.10 (s) (7 H), 3.85 (m, 2 H).

Anal. Calcd for $C_7H_{12}O_2$: C, 65.59; H, 9.44. Found: C, 65.45; H, 9.54.

Catalytic Hydrogenation of 2,5-Dimethyl-3,4-hexadien-2-ol (4).—A solution of 0.257 g of **4** in 2.0 ml of methanol was hydrogenated at 1 atm over 20 mg of platinum oxide. A hydrogen uptake of approximately 2 mol was observed, after which the solution was filtered and concentrated, and the residue was collected by preparative vpc. The major component, amounting to 60% of the volatile material was identified as 2,5-dimethyl-2-hexanol (**7**) by comparison of its ir and nmr spectra with those obtained from an authentic sample:[2] ir 3600, 3500–3100 cm^{-1}; nmr δ 0.88 (d, J = 5 Hz, 6 H), 1.13 (s, 6 H), 1.2–1.7 (m, 5 H), 2.47 (s, 1 H, exchanges with D_2O).

Registry No.—**1**, 32319-67-8; **2**, 32319-68-9; **3**, 32319-69-0; **4**, 2424-45-5; **5**, 32319-71-4; **6**, 32319-72-5; **7**, 3730-60-7; **8**, 32319-74-7; **9**, 32319-75-8; **10**, 32319-76-9; **11** tosylhydrazone, 32319-77-0; **12** tosylhydrazone, 1708-19-6; **13** tosylhydrazone, 32380-91-9; **14**, 22301-72-0; **15**, 32318-87-9; 1-methyl-1-vinylcyclopropane, 16906-27-7.

Acknowledgment.—We are grateful to the National Science Foundation for support of this investigation through Grant No. GP-17319.

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