mophilone in 5 ml of dry ether. The reaction mixture was stirred for 1 hr at room temperature, refluxed for 2 hr, then cooled in an ice bath and cold water was added until no further reaction occurred. After filtration, the solution was extracted with ether and the latter extract was washed with aqueous bicarbonate, then brine and finally dried and concentrated to give 0.179 g of a pale yellow, mobile liquid. Chromatography of the latter on 10 g of activity I neutral alumina gave 0.074 g of a hydrocarbon fraction in the petroleum ether eluent and 0.102 g of a ketone fraction in the ethyl ether eluent. GLC analysis (5% Carbowax column) of the hydrocarbon fraction showed two major components (50 and 30%, respectively), while GLC analysis of the ketone fraction (3% SE-30) showed one major component (70%). Preparative GLC (5% Ucon polar) gave 7$\alpha(H)$-eremophila-9,11-diene (**4**) as the major component (>98% purity by GLC): ν_{max} (CCl_4) 1640, 882 cm^{-1}; δ (CCl_4) 0.94 (3 H, d, J = 6 Hz), 1.03 (3 H, s), 1.82 (3 H, s), 4.78 (2 H, br s), 5.40 (1 H, m); ORD (c 0.06, CH_3OH), plain negative curve $[\phi]_{589}$ −80.2°; mol wt by mass spectrometry (peak-to-peak distance measurement using 1,2-dichlorooctafluorocyclohexene-1 as reference) 204.186 (calcd for $C_{15}H_{24}$, 204.188).

Anal. Calcd for $C_{15}H_{24}$: C, 88.16; H, 11.84. Found: C, 88.00; H, 11.90.

A comparison of the ir and NMR spectra of 7$\alpha(H)$-eremophila-9-11-diene (**4**) with those of eremophilene (**3**) showed that they were not identical and a direct comparison with an authentic sample of eremophilene by GLC showed their nonidentity (5% Carbowax column).[6] However, hydrogenation (Pt, EtOH) of both dienes gave the same saturated hydrocarbon as determined by GLC (5% Carbowax column) and mass spectral analysis. The major component of the ketone fraction was collected by preparative GLC (3% SE-30 column) and was identified as *cis*-dihydroeremophilone[7] by GLC, ir, ORD, and NMR: δ (CCl_4) 0.93 (d, J = 5 Hz), 1.15 (3 H, s), 1.87 (3 H, s), 4.85 (2 H, br s).

7$\alpha(H)$-Eremophil-9-en-11-ol (7). To 0.436 g of eremophilone (containing ~15% isoeremophilone) in 15 ml of anhydrous ether, 0.406 g of *m*-chloroperbenzoic acid (85% active) was added and the solution was stirred at room temperature for 24 hr. After addition of water, the solution was extracted with ether and the combined ether extracts were washed with aqueous sodium bicarbonate, then brine and finally concentrated to give 0.45 g of a colorless liquid. GLC analysis (3% SE-30 column) showed one major peak (80%). No starting material remained. Chromatography on neutral alumina (activity II–III) gave eremophilone 11-oxide (95% purity by GLC) in the benzene eluent: δ (CCl_4) 0.97 (3 H, s), 0.99 (3 H, d, J = 5.5 Hz), 1.27 (3 H, s), 6.46 (1 H, t, J = 3.8 Hz); complete disappearance of band at 896 cm^{-1} in ir.

To 50 mg of lithium aluminum hydride in 20 ml of anhydrous ether was added a solution of 400 mg of eremophilone 11-oxide in 5 ml of dry ether and the solution was stirred at room temperature for 1 hr and then refluxed for 2 hr. The solution was then cooled, moist ether was added, and, after filtration, the ether layer was dried and concentrated to give 0.375 g of a colorless, viscous liquid, the GLC (3% SE-30) of which showed a complex mixture containing two major components (50:30). This crude product (0.242 g) was dissolved in 10 ml of anhydrous ether containing 0.133 g of anhydrous aluminum chloride and this was added to a solution of 0.076 g of lithium aluminum hydride and 0.399 g of anhydrous aluminum chloride in 15 ml of anhydrous ether. The reaction mixture was stirred at room temperature for 1 hr and then refluxed for 2 hr. After the usual work-up, 0.201 g of a viscous liquid was obtained, the GLC (3% SE-30) of which showed a complex mixture with one component (51%). Chromatography on 10 g of neutral alumina (activity II–III) gave in the benzene–ether (96:4) eluent 16 mg of 7$\alpha(H)$-eremophil-9-en-11-ol (**7**, 97% by GLC on 3% SE-30 and 15% Carbowax 2014 columns). This product was not identical, by ir and NMR comparisons, with eremoligenol (**6**):[10] ν_{max} (CCl_4) 3600, 3460, 1665 cm^{-1}; δ (CCl_4) 0.93 (unresolved doublet, $J \simeq 6$ Hz), 1.04 (3 H, s), 1.22 (3 H, s), 1.27 (3 H, s), 5.40 (1 H, m); mol wt by mass spectrometry (peak-to-peak distance measurement using 1,2-dichlorooctafluorocyclohexene-1) 222.187 (calcd for $C_{15}H_{26}O$, 222.198).

Registry No.—**1**, 562-23-2; **2**, 22489-11-8; **4**, 54868-40-5; **5**, 54814-46-9; **7**, 54832-19-8; eremophilone 11-oxide, 54814-47-0; $LiAlH_4$, 16853-85-3.

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(11) Ir spectra were recorded with a Perkin-Elmer 237B spectrophotometer, NMR spectra were obtained with a Varian A-60 spectrometer, and mass spectra were obtained using a Varian M-66 mass spectrometer. GLC analyses were performed using a F & M biomedical gas chromatograph, Model 400.
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A New Mild Conversion of Ketones to the Corresponding Methylene Derivatives

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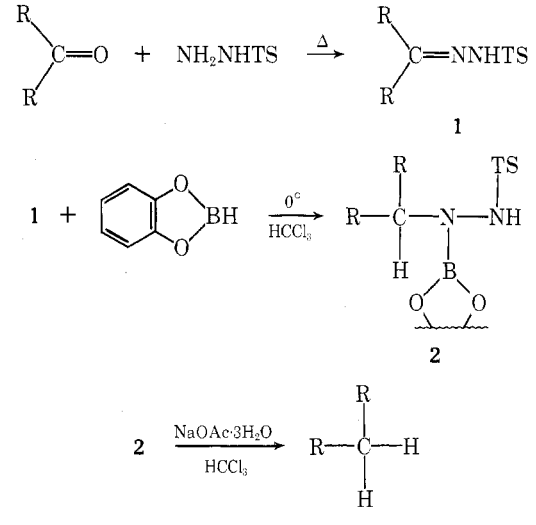
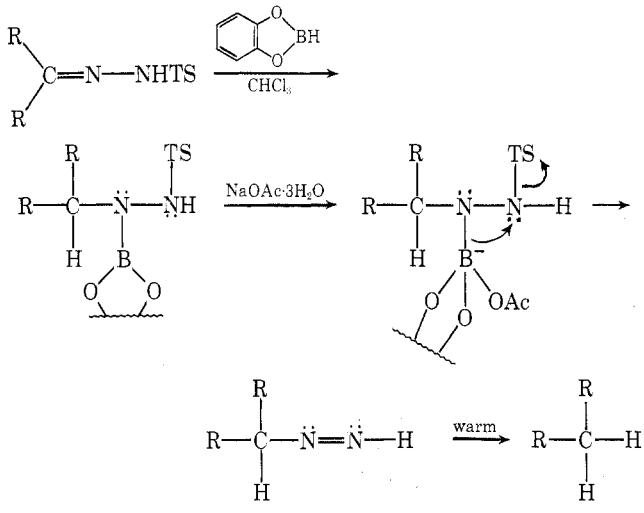
We wish to report a new, mild conversion of ketones to the corresponding methylene derivatives. The conversion involves the reduction of tosylhydrazones with catecholborane followed by decomposition of the reduction product (Scheme I).

Scheme I



The conversion of carbonyl compounds to their corresponding methylene derivatives is one of the key transformations in organic synthesis. Not surprisingly, a great deal of literature exists concerning this transformation.[1] The reduction procedures that are generally employed utilize strong acids or bases which preclude the presence of sensitive functional substituents.[2] The more recently reported reduction procedures involve the less reactive hydride reagents and carbonyl derivatives.[3,4] However, these new procedures involve the utilization of large excesses of hydride.[3] We felt that the reduction of tosylhydrazones with catecholborane would be an ideal way to achieve the reduction of carbonyl compounds. The tosylhydrazones are readily prepared, requiring no acid or base catalysis.[3a] Furthermore, the use of the mild, commercially available (Aldrich) catecholborane negates the need for excess hydride, which

Scheme II



should permit the reduction of functionally substituted carbonyl compounds.[5,6]

A reasonable mechanism for the reduction is outlined in Scheme II and is based on analogy to known reactions. Thus, it has long been recognized that organoboranes which contain an electronegative substituent β to the boron atom are prone to elimination, especially in the presence of nucleophiles.[7,8] Furthermore, diazenes are unstable and decompose to yield alkanes in the presence of proton sources.[9,10]

The reaction appears to be a general one, producing good yields of the reduction products. It depends only on the availability and stability of the tosylhydrazone derivative. Owing to the mildness of the reaction, we feel that it should be applicable to a variety of substituted ketones.[5]

Our results are summarized in Table I.

Table I
Conversion of Ketones to the Corresponding Methylene Derivatives[a]

Ketone[a]	Registry no.	Product[b]	Registry no.	Yield, %[c]
2-Octanone	111-13-7	Octane	111-65-9	91 (81)[d]
Isophorone	78-59-1	3,5,5-Trimethylcyclohexene[e]	933-12-0	41
Cyclohexanone	108-94-1	Cyclohexane	110-82-7	92
2-Methylcyclohexanone	583-60-8	Methylcyclohexane	108-87-2	64
Norbornanone	497-38-1	Norbornane	279-23-2	63

[a] The ketones were first converted to the corresponding tosylhydrazones. [b] Products exhibited physical and spectral parameters in agreement with those of authentic samples. [c] GLC analysis. [d] Isolated yield. [e] Reduction occurs with migration of the double bond.

Experimental Section[11]

Materials. The tosylhydrazones (Table II) were prepared according to the method described by Hutchins et al.[3a]

General Procedure for Reductions. The reduction of 2-octanone is representative. The tosylhydrazone of 2-octanone (52.7 mmol, 15.64 g) was dissolved in 105 ml of chloroform at −10°.[12] Catecholborane (58 mmol, 6.31 ml) was added and the hydroboration was allowed to proceed for 20 min. Sodium acetate trihydrate[13] (155 mmol, 21.1 g) was then added and the reaction mixture was brought to a gentle reflux for 1 hr.[14] GLC analysis indicated a 90.8% yield of octane with no evidence for alkene formation. The product was distilled from the reaction mixture, bp 124–127°. The yield of octane was 4.78 g (81%).

Table II
Melting Points of the Tosylhydrazones Utilized

Ketone	Registry no.	Mp, °C
2-Octanone	54798-76-4	96.5–98
Isophorone	21195-62-0	142–144
Cyclohexanone	4545-18-0	155–158
2-Methylcyclohexanone	52826-41-2	112–114
Norbornanone	38397-34-1	194–196

Acknowledgment. We wish to thank the Research Corporation for support of this study.

References and Notes

(1) See, for example, (a) W. Reusch, "Reduction", R. L. Augustine, Ed., Marcel Dekker, New York, N.Y., 1968, pp 171–211; (b) H. O. House, "Modern Synthetic Reactions", 2nd ed, W. A. Benjamin, Menlo Park, Calif., 1972, Chapter 4.
(2) For example the strongly basic conditions required in the Wolff–Kishner reductions preclude the incorporation of functionality such as amide, ester, cyano, halogen, etc. A similar situation holds for the Clemmensen reduction.
(3) See, for example, (a) R. O. Hutchins, C. Milewski, and B. Maryanoff, *J. Am. Chem. Soc.*, **95,** 3662 (1973); (b) L. Caglioti, *Tetrahedron,* **22,** 487 (1966).
(4) Another useful route involves the reduction of the ketone to the corresponding alcohol, transformation of the alcohol to a suitable leaving group, and displacement of that group with hydride reagents: C. W. Jefford, D. Kirkpatrick, and F. Daley, *J. Am. Chem. Soc.*, **94,** 8905 (1972).
(5) Control experiments indicated that catecholborane did not react with *n*-octyl bromide and acetonitrile after 2 hr under the conditions reported. Even more surprising, 1-octene was not hydroborated after 4 hr by catecholborane at 0° in $CHCl_3$.
(6) Boron hydrides react extremely rapidly with carbonyl groups and their derivatives. See H. C. Brown, "Boranes in Organic Chemistry", Cornell University Press, Ithaca, N.Y., 1972, pp 227–251.
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(10) It should be noted that the reduction of isophorone occurs with migration of the double bond. This phenomenon has been cited as evidence against a mechanism involving carbanion formation. See, for example, ref 3a.
(11) Melting points and boiling points are uncorrected. NMR spectra were obtained using a Varian Associates A-60 instrument.
(12) Methylene chloride gives similar results.
(13) Sodium acetate induces the decomposition of the intermediate **2.** The product is obtained in lower yields if no acetate is added.
(14) The product may also be obtained in an identical yield by stirring the mixture at room temperature for 24 hr.

Reaction of *o*-Chlorotoluene with Alkali Amides. A Study of the Metal Effect in Benzyne Reactions

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Since the pioneering work by Wittig[1] and Roberts[2] on the chemistry of arynes, extensive research has been done in this area. A monograph which summarizes much of this work has appeared.[3] Roberts[4] and coworkers have observed that *the reaction of o-chlorotoluene with potassium amide yields o- and m-toluidine in approximately equal amounts.* This result is surprising, since one would expect the inductive effect of the methyl group to operate in such a way as to make the amount of the ortho isomer which is formed much greater than that of the meta isomer. For example, treatment of *p*-chlorotoluene with potassium amide in liquid ammonia yields *m*- and *p*-toluidine in a 3:2 ratio,