nm) was employed, the results were the same as in the previous irradiation of **1b** in methanol; however, with a Corex filter (λ <300 nm), substantial amounts of benzhydryl methyl ether and less oxirane were produced.

The irradiation of **1b** in benzene–2-propanol was carried out as follows. A solution of **1b** (0.74 g, 0.002 mol) in 190 ml of dry benzene and 10 ml of 2-propanol was irradiated for 45 min with a 450-W Hanovia (Type L, Model 679A-36) high-pressure quartz mercury-vapor lamp. After the removal of solvent, crystals of tetraphenylethylene oxide formed, mp 194–195.5°.

Anal. Calcd for $C_{26}H_{20}O$: C, 89.62; H, 5.79. Found: C, 89.37; H, 5.70.

The physical properties of this product were identical in every respect with those of an authentic sample prepared by the method of Mosher, Steffgen, and Lansbury.[17] Benzophenone (**3**), isopropyl diphenylacetate (**5**), and 2,2,4,4-tetraphenyloxetan-3-ol (**6**) were identified by comparing their NMR and ir spectra and their VPC retention times with those of authentic samples.

Acknowledgment. Acknowledgment (U.M., I.F., G.W.G.) is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research and to the Army Research Office, Durham (ARO-D-31-124-73-G4). These authors also wish to thank Dr. K. Ishikawa for technical assistance and to acknowledge the assistance of Dr. E. Elder and Mrs. J. Thompson in the preparation of the manuscript.

Registry No.—**1b**, 40112-59-2; **2b**, 470-35-9.

References and Notes

(1) Taken in part from the dissertation presented by J. P. Wasacz in partial fulfillment of the requirements of the Ph.D. degree at the University of Pennsylvania, 1969.
(2) R. S. Becker, J. Kolc, R. O. Bost, H. Dietrich, P. Petrellis, and G. W. Griffin, *J. Am. Chem. Soc.*, **90**, 3292 (1968); R. S. Becker, R. O. Bost, J. Kolc, N. R. Bertoniere, R. L. Smith, and G. W. Griffin, *ibid.*, **92**, 1302 (1970).
(3) P. Petrellis and G. W. Griffin, *Chem. Commun.*, 691 (1967); G. W. Griffin, *Angew. Chem., Int. Ed. Engl.*, **10**, 537 (1971).
(4) A. Trozzolo, T. Do-Minh, and G. W. Griffin, *J. Am. Chem. Soc.*, **92**, 1402 (1970).
(5) (a) P. J. Wagner, C. A. Stout, S. Searles, Jr., and G. S. Hammond, *J. Am. Chem. Soc.*, **88**, 1242 (1966); (b) J. L. Harper and C. T. Lester, *J. Org. Chem.*, **26**, 1294 (1961), and references cited therein.
(6) N. J. Turro and S. S. Edelson, personal communication.
(7) (a) H. Staudinger, *Chem. Ber.*, **44**, 521, 543 (1911). See L. A. Mileshina, R. N. Nurmukhameto, D. N. Shigorin, and Sh. Nadzhimuldinov, *Dokl. Akad. Nauk SSSR*, **182**, 684 (1968), for a discussion of the uv spectroscopy of diphenylketene. (b) H. Nozaki, M. Nakano, and K, Kondo [*Tetrahedron*, **22**, 477 (1966)] have studied the solution photochemistry of diphenylketene. Diphenylcarbene appears to be among the products when a high-pressure mercury lamp (200 W) is used as a source and either cyclohexene, tetrahydrofuran, or ether is employed as a solvent. (c) H. E. Zimmerman and D. H. Paskovich [*J. Am. Chem. Soc.*, **86**, 2149 (1964)] observed that irradiation of dimesitylketene with a low-pressure mercury lamp gives tetramesitylethylene (19%) and dimesityl ketone. Tetraphenylethylene is not reported to be a photoproduct of diphenylketene photolysis.
(8) Alcohols previously have been used to trap the nucleophilic arylcarbenes as ethers. See W. Kirmse, L. Horner, and H. Hoffmann, *Justus Liebigs Ann. Chem.*, **614**, 19 (1958); W. Kirmse, *ibid.*, **666**, 9 (1963).
(9) (a) H. Kristinsson and G. W. Griffin, *J. Am. Chem. Soc.*, **88**, 1579 (1966); (b) A. M. Trozzolo, W. A. Yager, G. W. Griffin, H. Kristinsson, and I. Sarkar, *ibid.*, **89**, 3357 (1967).
(10) (a) P. Yates and L. Kilmurry, *Tetrahedron Lett.*, 1739 (1964); P. Yates and L. Kilmurry, *J. Am. Chem. Soc.*, **88**, 1563 (1966); (b) H. U. Hostettler, *Tetrahedron Lett.*, 687 (1965); H. U. Hostettler, *Helv. Chim. Acta*, **49**, 2417 (1966); (c) N. J. Turro and R. M. Southam, *Tetrahedron Lett.*, 545 (1967); D. R. Morton, E. Lee-Ruff, R. M. Southam, and N. J. Turro, *J. Am. Chem. Soc.*, **92**, 4349 (1970); (d) P. Yates and R. O. Loutfy, *Acc. Chem. Res.*, **8**, 209 (1975).
(11) N. J. Turro, "Molecular Photochemistry", R. Breslow and M. Karplus, Ed., W. A. Benjamin, New York, N.Y., 1967, p 137.
(12) H. Zimmerman and J. Hull, *J. Am. Chem. Soc.*, **92**, 6515 (1970).
(13) R. Srinivasan, *Adv. Photochem.*, **1**, 83 (1963).
(14) J. H. Hall and R. Huisgen, *Chem. Commun.*, 1187 (1971); J. H. Hall, R. Huisgen, C. H. Ross, and W. Scheer, *ibid.*, 1188 (1971); H. Hamberger and R. Huisgen, *ibid.*, 1190 (1971); A. Dahman, H. Hamberger, R. Huisgen, and V. Markowski, *ibid.*, 1192 (1971).
(15) G. W. Griffin, N. E. Brightwell, K. Ishikawa, I. Lev, and S. Satra, presented at VIII International Conference on Photochemistry, Edmonton, Alberta, Canada, August 7–15, 1975, Abstract I-1.
(16) G. B. Hoey, D. O. Dean, and C. T. Lester, *J. Am. Chem. Soc.*, **77**, 391 (1955).
(17) W. A. Mosher, F. W. Steffgen, and P. T. Lansbury, *J. Org. Chem.*, **26**, 670 (1961).

Deoxygenation of α,β-Unsaturated Aldehydes and Ketones via the Catecholborane Reduction of the Corresponding Tosylhydrazones

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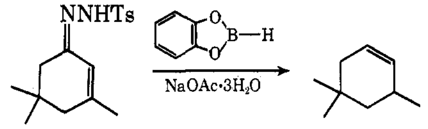
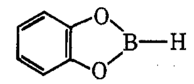
The reduction of tosylhydrazones with boron hydrides offers a mild and convenient alternative to the Wolff–Kishner and Clemmensen reductions.[2–4] In the initial reports, it was observed that α,β-unsaturated systems were reduced with migration of the double bond.[2,5]



This migration offers exciting synthetic possibilities such as the formation of less stable positional isomers (exocyclic double bonds vs. endocyclic double bonds) and deconjugation of conjugated double bonds. Indeed these synthetic manipulations have been recently reported to occur (except in cyclohexenone derivatives) using sodium cyanoborohydride as the reducing agent.[6] This report[6] has prompted us to report our studies utilizing catecholborane (I) for the reductions of α,β-unsaturated tosylhydrazones.



I

We find that catecholborane (I) cleanly reduces the tosylhydrazones of α,β-unsaturated carbonyl compounds, including the cyclohexenone derivatives, in high yields. The catecholborane procedure offers a number of advantages over the current procedures in that (1) the reaction requires only 1 equiv of hydride (as opposed to 12 equiv in the $NaBH_3CN$ procedure); (2) it is carried out under mild conditions (temperature below 62°, pH near neutral); (3) common organic solvents are employed such as chloroform (as opposed to the DMF–sulfolane system utilized in the $NaBH_3CN$ procedure); and (4) clean isomerizations are obtained with no alkane formation. The reductions are practical for sensitive systems since the necessary tosylhydrazones are prepared at neutral pH in ethanol.

Our results are summarized in Table I.

The reaction most likely proceeds via the formation of an unstable diazene intermediate.[7] A reasonable mechanism is outlined in Scheme I which is based on analogy to known

Scheme I

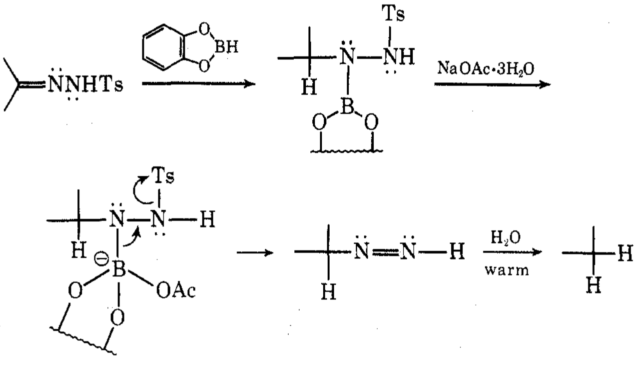
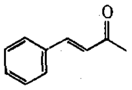
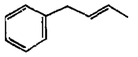
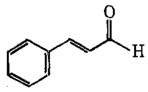
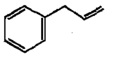
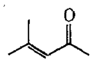
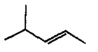
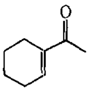
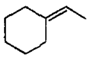
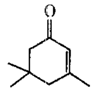
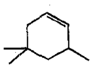
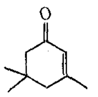
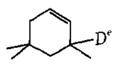


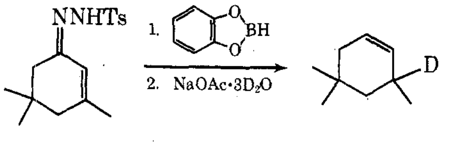
Table I
Conversion of Carbonyl Reagents to the Corresponding Methylene Derivatives[a]

Carbonyl reagent[a]	Registry no.	Product[b]	Registry no.	Yield, %
	122-57-6		1560-06-1	72[c]
	104-55-2		300-57-2	53[c]
	141-79-7		4461-48-7	65[c]
	932-66-1		1003-64-1	77[c] (61)[f]
	78-59-1		933-12-0	66[d] (48)[f]
			57325-57-2	66[d]

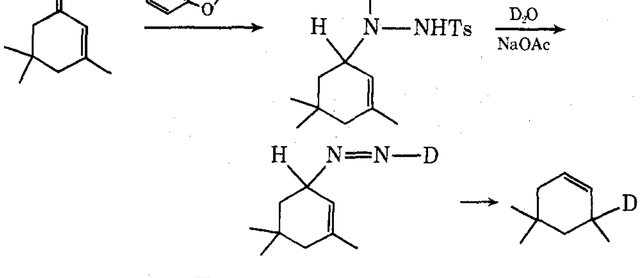
[a] The carbonyl reagents were first converted to the corresponding tosylhydrazone derivatives. [b] Products exhibited physical and spectral parameters in agreement with those of authentic samples and literature reports. [c] GLC analysis. [d] NMR analysis. [e] NaOAc·3D_2O utilized rather than NaOAc·3H_2O. [f] Isolated yield.

borane reactions such as the elimination of a borane derivative when the boron is β to an electronegative substituent.[8]

The reduction of the tosylhydrazone of isophorone followed by decomposition with NaOAc·3D_2O led to the formation of 3,5,5-trimethylclohexene-*3-d*. This result, and



the observation that the least stable alkene is formed exclusively in a number of instances, strongly support a concerted decomposition of the diazene intermediate.[9] The available data do not differentiate between an intermolecular and an intramolecular decomposition however. Control experiments clearly demonstrate that deuterium–hydrogen exchange occurs rapidly in both the tosylhydrazones and the reduced intermediate.[10] Consequently it is likely that deuterium is incorporated prior to diazene decomposition.



Experimental Section

Materials. The reagents, including catecholborane, were obtained from Aldrich Chemical Co. The tosylhydrazones were prepared according to the method of Hutchins[3,6] and exhibited melting points and spectral characteristics in accord with published values.[3,11]

General Procedure for Reductions. The reduction of isophorone is representative. The tosylhydrazone of isophorone, 2.5 mmol (0.768 g), was dissolved in 6 ml of chloroform at 0°C. Catecholborane (2.75 mmol, 0.31 ml) was added and the reduction allowed to proceed for 2 hr. Sodium acetate trihydrate (7.5 mmol, 1.02 g) was added and the reaction mixture was brought to a gentle reflux for 1 hr. NMR analysis indicated a 66% yield of 3,5,5-trimethylcyclohexene with no evidence of the corresponding alkane. The products were isolated via silica gel chromatography and preparative GLC. All exhibited physical and spectral characteristics in accord with published values.[3]

Preparation of 3,5,5-Trimethylcyclohexene-*3-d*. The reduction was carried out as described above except that NaOAc·3D_2O was employed:[12] NMR ($CDCl_3$) δ 5.47 (m, 2), 1.73 (m, 2), 1.47 (m, 1), 1.35 (m, 1), 0.92 (m, 9); mass spectrum (70 eV) *m/e* (rel intensity) 125 (48, M^+), 110 (100), 69 (74), 56 (33).

Acknowledgment. We wish to thank Research Corporation for support of this work. We also wish to thank Professor R. O. Hutchins for helpful discussions.

Registry No.—Catecholborane, 274-07-7; 4-phenyl-3-buten-2-one tosylhydrazone, 17336-65-1; cinnamaldehyde tosylhydrazone, 7318-33-4; 4-methyl-3-penten-2-one tosylhydrazone, 5362-76-5; 1-acetylcyclohexene tosylhydrazone, 41780-85-2; 3,5,5-trimethyl-2-cyclohexen-1-one tosylhydrazone, 21195-62-0.

References and Notes

(1) Visiting Professor, 1975, from the University of Arkansas at Little Rock.
(2) G. W. Kabalka and John D. Baker, *J. Org. Chem.*, **40**, 1834 (1975).
(3) R. O. Hutchins, C. A. Milewski, and B. E. Maryanoff, *J. Am. Chem. Soc.*, **95**, 3662 (1973).
(4) L. Caglioti, *Tetrahedron*, **22**, 487 (1966).
(5) It was originally reported (in ref 3) that this was the major reaction when sodium cyanoborohydride was used to reduce the tosylhydrazone. It has since been noted that reduction to the hydrocarbon is the major reaction when sodium cyanoborohydride is utilized (see ref 6).
(6) R. O. Hutchins, M. Kacher, and L. Rua, *J. Org. Chem.*, **40**, 923 (1975).
(7) A similar mechanism has been proposed for the sodium cyanoborohydride reduction of tosylhydrazones of α,β-unsaturated carbonyl reagents.
(8) (a) D. J. Pasto and R. Snyder, *J. Org. Chem.*, **31**, 2777 (1966); (b) H. C. Brown and R. M. Gallivan, *J. Am. Chem. Soc.*, **90**, 2906 (1968); (c) C. E. McKenna and T. G. Traylor, *ibid.*, **93**, 2313 (1971).
(9) The regiospecific incorporation of deuterium rules out a reduction-hydroboration-elimination sequence analogous to that observed in diborane reductions of α,β-unsaturated ketones. See L. Caglioti, G. Cainelia, G. Maina, and A. Selva, *Tetrahedron*, **20**, 957 (1964).
(10) In one experiment, the tosylhydrazone of isophorone was reduced with 1 equiv of catecholborane. Three equivalents of D_2O were added which resulted in the immediate disappearance of the NMR signal due to NH.
(11) G. L. Closs, L. E. Closs, and W. A. Boll, *J. Am. Chem. Soc.*, **85**, 3796 (1963).
(12) The NaOAc·3D_2O was prepared by dissolving anhydrous NaOAc in a slight excess of D_2O and allowing the "hydrate" to crystallize.