

Figure 1. ^1H NMR spectra of the olefinic region of **2**: (a) width $\times 1$; (b) width $\times 2$; (c) width $\times 4$. (d) The decoupled spectrum of **2**.

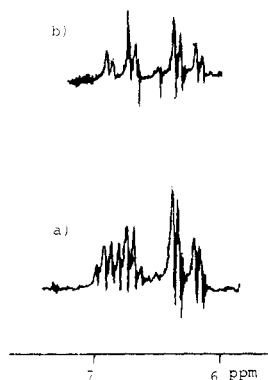


Figure 2. (a) ^1H NMR spectrum of the olefinic region of **1**. (b) The decoupled spectrum of **1**.

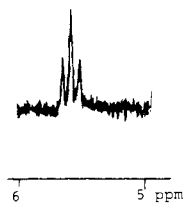


Figure 3. ^1H NMR spectrum of the olefinic region of **3**.

Experimental Section

Most of the boranes were prepared according to the standard procedure.³ (5-Decenyl)dimethylborane,⁴ (5-decenyl)dichloroborane,⁵ bis(5-decenyl)chloroborane,⁶ and bis(1-hexenyl)chloroborane⁶ were prepared as previously described. Some of the boranes were distilled under reduced pressure, and others were used after evaporation of the solvent. Boiling ranges at reduced pressures are as follows: 5-decenyl-9-BBN, 152–154 °C (0.02 mmHg); bis(5-decenyl)chloroborane, 110–115 °C (0.005 mmHg); (5-decenyl)dimethylborane, 43–45 °C (1 mmHg); (5-decenyl)dichloroborane, 64–70 °C (2 mmHg); bis(1-hexenyl)chloroborane, 70–72 °C (0.05 mmHg); (1-hexenyl)(1,2-phenylenedioxy)borane,

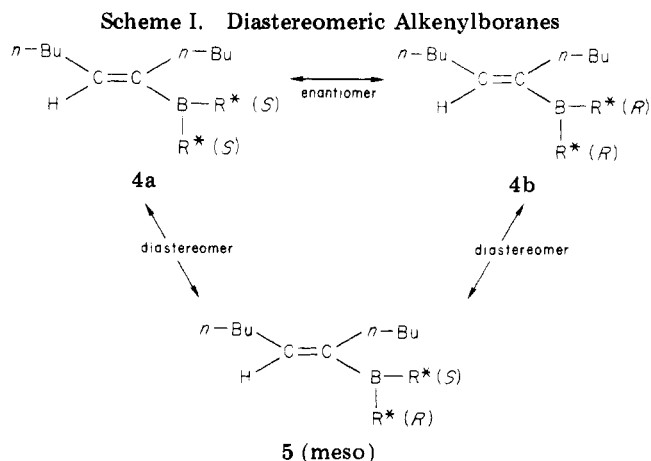
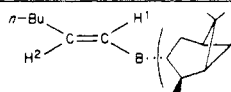


Table III. ^1H NMR Spectra of (1-Hexenyl)diisopinocampheylboranes^a

borane	chemical shift (δ in THF)			
	H ¹	H ²	ΔH^1	ΔH^2
	6.64	6.28		
6a from (+)- α -pinene				
6b from (\pm)- α -pinene	6.64	6.28	0.04	0.04
	6.60	6.24		

^a See footnote *a* to Table I. The NMR spectra were recorded in THF.

60–70 °C (0.01 mmHg); 1-hexenyl-9-BBN, 52–55 °C (0.01 mmHg). ^1H NMR spectra were measured on a JEOL PS-100 spectrometer. Chemical shifts are in parts per million, referenced to Me_4Si .

Acknowledgments. Financial support from the Ministry of Education, Science and Culture (Grants 247020, 321709, and 334029) and from JSPS (Basic Chemical Research Foundation) is gratefully acknowledged.

Registry No. **1**, 55168-92-8; **2**, 69082-89-9; **3**, 69082-90-2; **6a**, 70179-28-1; (\pm)-**6b**, 70223-51-7; *meso*-**6**, 70223-52-8; (*E*)-(1-hexenyl)bis(*trans*-2-methylcyclohexyl)borane, 70223-53-9; (*Z*)-(5-decenyl)(1,2-phenylenedioxy)borane, 70179-29-2; (*Z*)-(5-decenyl)-9-borabicyclo[3.3.1]nonane, 69322-52-7; (*Z*)-(5-decenyl)dimethylborane, 64285-24-1; (*Z*)-(5-decenyl)dichloroborane, 64285-25-2; bis[(*Z*)-(5-decenyl)]chloroborane, 64323-54-2; tris[(*Z*)-(5-decenyl)]borane, 70179-30-5; (*E*)-(1-hexenyl)dicyclohexylborane, 37609-12-4; (*E*)-(2-hexenyl)(1,2-phenylenedioxy)borane, 37490-22-5; (*E*)-(1-hexenyl)-9-borabicyclo[3.3.1]nonane, 69322-45-8; bis[(*E*)-(1-hexenyl)]chloroborane, 41929-38-8.

Simple and Mild Dehalogenation Reactions Effected by Molybdenum Hexacarbonyl on Alumina

Howard Alper* and Lance Pattee

Department of Chemistry, University of Ottawa,
Ottawa, Ontario, Canada K1N 9B4

Received January 22, 1979

One of the most active areas of research in organic chemistry involves the use of reagents supported on porous solids to effect various synthetic transformations. Such reactions often occur under gentle conditions, are simple to work up, and can be selective as well. Recent studies,

(3) For the preparation of alkenylboranes, see H. C. Brown, "Organic Syntheses via Boranes", Wiley, New York, N.Y., 1975.

(4) Y. Yamamoto, H. Yatagai, K. Maruyama, A. Sonoda, and S.-I. Murahashi, *J. Am. Chem. Soc.*, **99**, 5652 (1977).

(5) H. C. Brown and N. Ravindran, *J. Am. Chem. Soc.*, **98**, 1798 (1976).

(6) H. C. Brown and N. Ravindran, *J. Am. Chem. Soc.*, **98**, 1785 (1976).

Table I. Yields of Products Obtained from Reaction of 1 with Mo(CO)₆/Al₂O₃

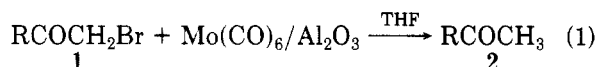
R	yield of 2, ^a %	R	yield of 2, ^a %
<i>p</i> -CH ₃ OC ₆ H ₄	60	<i>p</i> -C ₆ H ₅ C ₆ H ₄	73
<i>p</i> -ClC ₆ H ₄	83	1-adamantyl	88
<i>p</i> -BrC ₆ H ₄	71	2-naphthyl	80

^a Yields are of pure materials. Products were identified by comparison of melting or boiling points and spectral data (IR, NMR) with authentic samples.⁴

particularly by Posner and co-workers,¹ have clearly demonstrated the utility of alumina as a support.

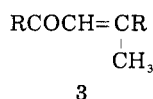
Comparatively little work has been done in the area of organic reactions effected by organometallic compounds supported on alumina. Molybdenum hexacarbonyl on alumina can catalyze olefin disproportionation and isomerization reactions.² The nature of the molybdenum species adsorbed on alumina (at different temperatures) is a subject of some controversy.³ We now report a simple and mild dehalogenation reaction effected by Mo(CO)₆ on alumina.

Treatment of molybdenum hexacarbonyl, adsorbed on alumina, with an α -halo ketone (1) in tetrahydrofuran at room temperature for 18 h gives the monoketone (2) in 60–88% yield (eq 1). Product yields for several R groups



are listed in Table I. Bromides are more reactive than chlorides. 2-Bromo-4'-phenylacetophenone (1, R = *p*-C₆H₅C₆H₄) was recovered unchanged when exposed to alumina in the absence of the metal carbonyl.

There are genuine advantages of this method when compared with conditions needed for the homogeneous reaction previously described by Alper and DesRoches.⁴ Reaction of an α -halo ketone with Mo(CO)₆ in refluxing 1,2-dimethoxyethane (~82 °C), for 48 h, afforded the α,β -unsaturated ketone 3 in addition to 2. Using Mo-



(CO)₆/Al₂O₃ enables one to effect the dehalogenation under very gentle conditions, avoiding the formation of the condensation byproduct 3. Furthermore, the reaction is faster than that using homogeneous conditions, and the yields of 2 are consistently higher (e.g., 2, R = 1-adamantyl, is formed in 88% yield by Mo(CO)₆/Al₂O₃ but in only 14% yield by Mo(CO)₆ under homogeneous conditions).

Experimental Section

Spectral data were recorded with a Unicam SP-1100 infrared spectrometer and Varian T-60 or HA-100 proton magnetic resonance spectrometers. Solvents were dried by standard methods. Molybdenum hexacarbonyl and all α -halo ketones were commercial products. All reactions were run under a dry nitrogen atmosphere.

General Procedure for Reaction of α -Halo Ketones with Mo(CO)₆/Al₂O₃. Alumina (30 g, Fisher A-540) was dried overnight at 300 °C. After cooling to room temperature, it was suspended in hexane (180 mL) containing Mo(CO)₆ (2.64 g, 10.0 mmol). The hexane was removed by rotary evaporation, and

Mo(CO)₆/Al₂O₃ was then heated at 100 °C (oil-bath temperature) for 1 h. To the cooled solid was added the α -halo ketone (1, 3.0 mmol) in tetrahydrofuran (60 mL), and the reaction mixture was stirred at room temperature for 18 h. Workup, after filtration, was effected according to the procedures described for the homogeneous reaction.⁴

Acknowledgments. We are grateful to the National Research Council of Canada for support of this research.

Registry No. 1 (R = *p*-CH₃OC₆H₄), 2632-13-5; 1 (R = *p*-ClC₆H₄), 536-38-9; 1 (R = *p*-BrC₆H₄), 99-73-0; 1 (R = *p*-C₆H₅C₆H₄), 135-73-9; 1 (R = 1-adamantyl), 5122-82-7; 1 (R = 2-naphthyl), 613-54-7; 2 (R = *p*-CH₃OC₆H₄), 100-06-1; 2 (R = *p*-ClC₆H₄), 99-91-2; 2 (R = *p*-BrC₆H₄), 99-90-1; 2 (R = *p*-C₆H₅C₆H₄), 92-91-1; 2 (R = 1-adamantyl), 1660-04-4; 2 (R = 2-naphthyl), 93-08-3; Mo(CO)₆, 13939-06-5; Al₂O₃, 1344-28-1.

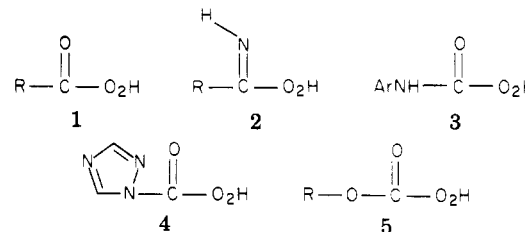
Epoxidation of Alkenes with O-Ethylperoxycarbonic Acid Generated in Situ in an Alkaline Biphasic Solvent System

Robert D. Bach,* Michael W. Klein, Rose A. Ryntz, and Joseph W. Holubka

Department of Chemistry, Wayne State University, Detroit, Michigan 48202

Received January 9, 1979

The direct oxidation of an alkene to its 1,2-epoxide is most typically accomplished by an organic peracid¹ (1)



such as *m*-chloroperbenzoic acid (MCPA).² Alternate procedures based upon the utilization of hydrogen peroxide as the oxidant have also been developed, most notably by Payne.³ Although hydrogen peroxide itself is not sufficiently reactive to epoxidize a nonconjugated carbon-carbon double bond, its reactivity can be markedly enhanced by placing the OOH moiety in conjugation with a multiple bond as exemplified by structures 1–5. A synthetically useful adaptation of this principle has been accomplished by the in situ formation of a peroxyimidic acid (2) by the addition of H₂O₂ to a nitrile.⁴ Both acetonitrile^{3a,5} and benzonitrile^{3b} have been employed as a coreactant in the epoxidation of a variety of alkenes. Peroxybenzimidic acid (2, R = C₆H₅) has been shown to be a more reactive but less discriminating epoxidizing reagent than MCPA in its reactions with polyunsaturated substrates.⁶ *N*-Arylperoxycarbonic acids (3), derived from the addition of H₂O₂ to aryl isocyanates, have also found

(1) G. H. Posner, *Angew. Chem., Int. Ed. Engl.*, **17**, 487 (1978), and references cited therein.

(2) A. Brenner and R. L. Burwell, Jr., *J. Catal.*, **52**, 364 (1978).

(3) A. Brenner and R. L. Burwell, Jr., *J. Catal.*, **52**, 353 (1978), and references cited therein.

(4) H. Alper and D. DesRoches, *J. Org. Chem.*, **41**, 806 (1976).

(1) (a) Swern, *D. Org. React.* **1953**, **7**, 378. (b) "Organic Peroxides", Wiley-Interscience: New York, N.Y., 1970; Vol. II, p 452.

(2) Fieser, M.; Fieser, L. F. "Reagents for Organic Synthesis"; Wiley-Interscience: New York, N.Y., 1967; Vol. I, p 135.

(3) (a) Payne, G. B.; Deming, P. H.; Williams, P. H. *J. Org. Chem.* **1961**, **26**, 659. (b) Payne, G. B. *Tetrahedron* **1962**, **18**, 763.

(4) Wilberg, K. B. *J. Am. Chem. Soc.* **1953**, **75**, 3961.

(5) Bach, R. D.; Knight, J. W. *Org. Synth.*, in press.

(6) Carlson, R. G.; Behn, N. S.; Cowles, C. *J. Org. Chem.* **1971**, **36**, 3832.