All of the above observations are readily accommodated by invoking *reversible* addition of LAH to the phosphine oxide. Similar addition products have been described and have been assigned a structure, $Li[Al(OPHR_3)_4]$, in which a pentacoordinate phosphorus atom is linked to hydrogen.[7] We suggest that pseudorotation of the phosphorane, followed by dissociation into phosphine oxide and LAH, leads to the observed stereomutation.[8–11]

Reduction of optically active benzylphosphonium salts with LAH also gives racemic phosphines under conditions where such phosphines are optically stable.[12] However, we have found that while reduction of (+)-benzylmethylphenyl-*n*-propylphosphonium bromide with LAH in THF at room temperature gives racemic methylphenyl-*n*-propylphosphine, the recovered salt has suffered no change in optical purity. It is therefore likely, as has been suggested,[13] that racemization here occurs by pseudorotation of the *irreversibly* formed phosphorane (R_4PH) intermediate prior to loss of the benzyl anion.

(7) K. Issleib and G. Grams, *Z. Anorg. Allg. Chem.*, **299**, 58 (1959).

(8) Pseudorotation in phosphoranes containing a P–H bond is not without precedent: R. R. Holmes and R. N. Storey, *Inorg. Chem.*, **5**, 2146 (1966); D. Houalla, R. Wolf, D. Gagnaire, and J. B. Robert, *Chem. Commun.*, 443 (1969).

(9) The small amount of phosphine produced in the reduction of (+)-**5** is 80–90% racemized after 4–5 hr, even though the phosphine is optically stable under conditions which cause complete racemization of **5** by LAH (control experiment). An additional racemization mechanism must therefore play a minor role. The residual activity indicates net retention of configuration in the reduction, similar to the retention observed[2] in the reduction of **2**.

$$(+)\text{-}\mathbf{2} \xrightarrow{\text{LAH}} (-)\text{-}\mathbf{1} \xrightarrow{H_2O_2} (+)\text{-}\mathbf{2}$$

(10) The rapidity of the stereomutation of phosphetane 1-oxides by LAH is a useful diagnostic, since an enhancement in reaction rate, relative to the acyclic analogs, characterizes intermediate phosphorane formation in reactions of closely related phosphetane P(IV) derivatives: K. Bergesen, *Acta Chem. Scand.*, **21**, 1587 (1967); W. Hawes and S. Trippett, *Chem. Commun.*, 577 (1968); P. Haake, R. D. Cook, W. Schwarz, and D. R. McCoy, *Tetrahedron Lett.*, 5251 (1968); S. E. Cremer, R. J. Chorvat, and B. C. Trivedi, *Chem. Commun.*, 769 (1969); K. E. DeBruin, G. Zon, K. Naumann, and K. Mislow, *J. Amer. Chem. Soc.*, in press.

(11) (a) In the light of these results, the *absence* of racemization in the LAH reduction of **1** represents an anomaly, the source of which is likely to be the presence of the neighboring NH group. (b) Retention of configuration in the reduction of phosphine oxides with trichlorosilane (L. Horner and W. D. Balzer, *Tetrahedron Lett.*, 1157 (1965)) implies that the rate of loss of trichlorosiloxide ion from the intermediate $Cl_3SiOPHR_3$ is faster than the rate of pseudorotation (K. Naumann, G. Zon, and K. Mislow, *J. Amer. Chem. Soc.*, in press).

(12) W. E. McEwen, K. F. Kumli, A. Bladé-Font, M. Zanger, and C. A. VanderWerf, *J. Amer. Chem. Soc.*, **86**, 2378 (1964).

(13) T. J. Katz, C. R. Nicholson, and C. A. Reilly, *ibid.*, **88**, 3832 (1966); M. J. Gallagher and I. D. Jenkins in "Topics in Stereochemistry," Vol. 3, N. L. Allinger and E. L. Eliel, Ed., John Wiley & Sons, Inc., New York, N. Y., 1968, pp 29 and 74.

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The Solvomercuration–Demercuration of Representative Olefins in the Presence of Alcohols. Convenient Procedures for the Synthesis of Ethers

Sir:

Recently a remarkably simple procedure was described for the synthesis of alcohols from representative olefins *via* a Markovnikov hydration.[1] The synthesis involves oxymercuration of the unsaturated compound with mercuric acetate in the presence of a 50:50 tetrahydrofuran–water medium, followed by *in situ* reduction of the oxymercurial with sodium borohydride in the presence of sodium hydroxide.

This combined solvomercuration–demercuration procedure is capable of considerable variation and may be widely utilized for the addition of various nucleophilic reagents to olefinic double bonds under very mild conditions. For optimum results it is necessary to vary the mercuric salt so as to avoid competition of the anion of the salt with the desired nucleophile for the mercuric intermediate.

Thus, mercuric acetate achieves a satisfactory synthesis of methyl, ethyl, and isopropyl ethers from the corresponding alcohols and representative olefins, utilizing essentially the original procedure.[1,2] However, the synthesis of more hindered derivatives, such as the *t*-butyl ethers, required a shift to a mercuric salt containing a less nucleophilic anion, such as mercuric trifluoroacetate. Finally, to achieve the synthesis of amines by adding acetonitrile as the nucleophilic reagent, it proved desirable to utilize a salt containing an even less nucleophilic anion, mercuric nitrate.[3]

Since the olefins are quite soluble in the pure alcohols, we utilized the latter for the reaction mixture in place of the 50:50 tetrahydrofuran–water mixture utilized in the hydration procedure. In the great majority of cases involving mercuric acetate, the alkoxymercuration stage proceeded quite rapidly, with a reaction time of 10 min being quite satisfactory. In a few cases involving relatively hindered reactants, longer reaction times were necessary.

For the most part the yields are quite satisfactory. Only in the case where *t*-butyl alcohol was utilized as the nucleophilic reagent were the yields relatively low.

The following procedure is representative. In the flask were placed 100 ml of anhydrous isopropyl alcohol and 100 mmol of mercuric acetate. Then, 100 mmol of 2-methyl-1-butene was introduced into the vigorously stirred suspension. Ten minutes after the addition of the olefin, the reduction of the mercurial intermediate was achieved by adding 100 ml of 3 *M* sodium hydroxide and 100 ml of 0.5 *M* sodium borohydride in 3 *M* sodium hydroxide, both in water. The mixture was allowed to stir for 2 hr, until the mercury had coagulated and settled. The product, *t*-amyl isopropyl ether, was extracted with pentane and isolated in 81% yield, bp 112–114°, $n^{20}D$ 1.3946.

In all cases involving mercuric acetate and methyl or ethyl alcohol the reaction mixture became homogeneous in 1 to 5 min following addition of the olefin, and high yields of the corresponding ethers were obtained. It was gratifying that even tertiary olefins, such as 2-methyl-1-butene and α-methylstyrene, reacted smoothly to produce the corresponding *t*-alkyl ethers. In the case of mercuric acetate and isopropyl alcohol, the rates were appreciably slower and these reactions

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(1) H. C. Brown and P. J. Geoghegan, Jr., *J. Amer. Chem. Soc.*, **89**, 1522 (1967).

(2) It should be pointed out that the synthesis of cyclohexyl methyl ether was achieved previously by treating cyclohexene in methanol with mercuric acetate, precipitation of the mercurial as the chloride, and reduction of the chloride with sodium borohydride (F. G. Bordwell and M. L. Douglass, *ibid.*, **88**, 993 (1966)). The present procedure is not only more convenient in allowing the reaction to be carried out in a single vessel, but it possesses the enormous advantage of making unnecessary the isolation and handling of the toxic intermediate.

(3) H. C. Brown and J. T. Kurek, *ibid.*, **91**, 5647 (1969).

Table I. Results Realized for the Conversion of Representative Olefins into Ethers by the Solvomercuration–Demercuration Procedure Utilizing Mercuric Acetate or Trifluoroacetate and Alcohols

Olefin	$Hg(O_2CCX_3)_2$ X	Ether, ROR′ R	Yield of ethers, %,[a–c] for R′ = Methoxy	Ethoxy	Isopropoxy	*t*-Butoxy
1-Hexene	H	2-Hexyl	90	98	91 (20)	27[d] (480)
	F		100	100	100	100
3,3-Dimethyl-1-butene	H	Pinacolyl	83[e]	72	12	4 (1400)
	F		100	100	99	85[f] (1100)
Styrene	H	α-Phenethyl	97			
	F					90 (20)
Cyclohexene	H	Cyclohexyl	100	100	73 (90)	18 (1440)
	F		100	100	98	90
Norbornene	H	*exo*-Norbornyl	89	60	15 (30)	1 (1200)
	F		100	100	95	90 (600)
2-Methyl-1-butene	H	*t*-Amyl	100	100	90	0 (1440)
	F		88	86	58 (1)	0
α-Methylstyrene	H	*t*-Cumyl	100			

[a] Yield by glpc analysis. [b] Reaction time was 10 min unless specified otherwise in parentheses (minutes). [c] All new compounds gave satisfactory elementary analyses and nmr spectra. [d] The product contained 12% of *n*-hexyl *t*-butyl ether. [e] The product contained 2% of 3,3-dimethyl-1-butyl methyl ether. [f] Product contains both the Markovnikov and anti-Markovnikov ethers.

were allowed to proceed for approximately 10 min after the solutions had become homogeneous. Finally, the reactions with mercuric acetate and *t*-butyl alcohol were very slow and the yields of the desired ethers were low.

The use of mercuric trifluoroacetate provides both a fast rate and a high yield of essentially all of the ethers, including the *t*-butyl ether derivatives. Only in the case of 2-methyl-1-butene were we unsuccessful in preparing the *t*-butyl ether. Evidently the formation of the di-*t*-alkyl ether involves such high steric strain[4] as to provide a major hurdle which the system fails to surmount. The results with mercuric acetate and trifluoroacetate are summarized in Table I.

Mercuric trifluoroacetate was readily prepared in molar quantities by the following simple procedure. One mole of mercuric oxide was dissolved in 300 ml of trifluoroacetic acid. Then 1 mol of trifluoroacetic anhydride was added at a rate sufficient to maintain a gentle reflux. The solvent was removed under vacuum[5] and 418 g (98% yield) of mercuric trifluoroacetate, mp 164–168°, was obtained (mp 167–169° after two recrystallizations from trifluoroacetic acid[6]). In contrast to mercuric acetate, the salt is easily soluble at 25° in a wide variety of organic solvents such as dimethylformamide, dimethyl sulfoxide, acetone, ethyl acetate, tetrahydrofuran, ethyl ether, and benzene.[7]

Both the high reactivity of the reagent and its high solubility in the alcohols used as reaction media result in very fast reactions. With two exceptions the reactions are essentially complete in 10 min or less to provide excellent yields of the desired ethers. In the case of norbornene[8] and 3,3-dimethyl-1-butene the initial product in *t*-butyl alcohol is not the *t*-butoxy derivative, but the corresponding trifluoroacetate. Reduction at this stage yields the ester or alcohol. However, on standing at room temperature, the initial products are converted into the *t*-butoxy derivatives and reduction then yields the desired *t*-butyl ethers. This is the reason for the relatively long reaction times utilized for these derivatives (Table I).

No rearrangements were observed. Even the labile olefin, 3,3-dimethyl-1-butene, was converted into pinacolyl methyl ether without change in the carbon skeleton. In almost all cases the reactions proceeded to give the Markovnikov product essentially exclusively. However, in the reaction of mercuric acetate with 3,3-dimethyl-1-butene and methanol the presence of 2% of the anti-Markovnikov methyl ether was observed in the product. In the related reaction of 1-hexene and *t*-butyl alcohol the product contained 12% of the anti-Markovnikov product, *n*-hexyl *t*-butyl ether. Similar results were observed with mercuric trifluoroacetate.

In conclusion, the present developments make available a new, highly convenient synthetic route for the conversion of olefins into the Markovnikov ethers. Even more exciting is the promise that solvomercuration–demercuration can be developed into a highly versatile, general approach for additions to the double bond in the Markovnikov direction without isomerizations or rearrangements. We are actively exploring this possibility.

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(4) E. J. Smutny and A. Bondi, *J. Phys. Chem.*, **65**, 546 (1961).

(5) It is perfectly satisfactory for use in subsequent preparations without further treatment.

(6) D. A. Shearer and G. F. Wright, *Can. J. Chem.*, **33**, 1002 (1955), report mp 165–167°.

(7) This high solubility in inert solvents promises to make this salt highly useful for extending the scope of the solvomercuration–demercuration reaction.

(8) E. Tobler and D. J. Foster, *Helv. Chim. Acta*, **48**, 366 (1965).

(9) Postdoctorate research associate on a program supported by Esso Research and Engineering Co.

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The Solvomercuration–Demercuration of Representative Olefins in the Presence of Acetonitrile. A Convenient Procedure for the Synthesis of Amines

Sir:

The solvomercuration–demercuration of representative olefins in the presence of water provides a convenient procedure for the Markovnikov hydration of the carbon–carbon double bond.[1] Similarly, the solvomercuration–demercuration of olefins in the presence of alcohols provides a highly convenient route

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(1) H. C. Brown and P. J. Geoghegan, Jr., *J. Amer. Chem. Soc.*, **89**, 1522 (1967).