

mp 120–121°. The spectral properties and dipole moment of 7.13 D support the chloronium ylide structure for **13**; also, **13** rearranges to imidazole **12** on warming in a solvent.

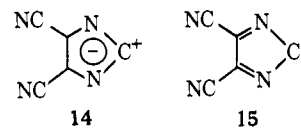
Bromobenzene also gives three products; the bromonium ylide **13** (X = Br, mp 143–144°) appears more stable to rearrangement since essentially no imidazole **12** (X = Br) is formed under minimum reaction conditions for nitrogen elimination. The thermally stable iodonium ylide, **13** (X = I, mp 221–222°), is the primary product from reaction of **3** with iodobenzene. Although no fluoronium ylide could be detected in the products from **3** decomposition in fluorobenzene, imidazole **12** (X = F, mp 93–94°) was formed in 23% yield, perhaps from **13** (X = F) or by attack on fluorine with concerted rearrangement. Imidazole **11** (X = F) was formed in 50% yield and was shown by ¹⁹F nmr to be a mixture of ortho, para, and meta isomers in the ratio 58:8:34.

Although stable iodonium ylides have been prepared from diazo ketones and aryl iodides or active methylene compounds and iodosobenzene,⁴ no stable chloronium or bromonium ylides have been reported.⁵ Preliminary examination of our halonium ylides indicates that they react similarly to the known iodonium ylides.

Aliphatic halides react with **3** to give only 1-alkyl-2-halo-4,5-dicyanoimidazoles, with no attack on carbon-hydrogen bonds. For example, 1,2-dichloroethane gives 1-(2-chloroethyl)-2-chloro-4,5-dicyanoimidazole, (10, mp 90–90.5°), in 81% yield. Benzotrifluoride gives the imidazole **7**, mp 44–44.5°, corresponding to carbon-fluoride insertion, as well as 2-(*m*-(trifluoromethyl)phenyl)-4,5-dicyanoimidazole (**8**). The meta orientation is expected from attack by an electrophilic species⁶ rather than a radical type intermediate.⁷ Contrary to expectations, boiling ethanol reduces **3** to give 4,5-dicyanoimidazole⁸ and acetaldehyde but no 2-ethoxy-4,5-dicyanoimidazole. Since this reaction appears to proceed at a faster rate than the other pyrolysis reactions, we believe that **3** is itself abstracting a hydride ion from ethanol or is first adding ethanol.

The electron-rich olefin *cis*-1,2-dimethoxyethylene reacts with **3** at room temperature forming a single product, mp 157–157.5°, believed to be **4**. Butadiene also adds to **3** without elimination of nitrogen. The nmr spectrum of the product (CD₃SOCD₃), δ 7.2 (m, 1), 6.2 (m, 2), 4.5 (m, 2), indicates structure **5** rather than an open-chain azo compound.

In thermal reactions of **3**, nitrogen loss and C–C (or C–X) bond formation could be concerted. However, we prefer the interpretation that nitrogen is lost first to form an intermediate that is a resonance hybrid best represented by the zwitterion structure **14**, in which the negative charge is delocalized as an aromatic 6π electron imidazole anion and further by the two cyano groups, while the carbonium ion is localized as a highly



reactive center for electrophilic attack. The insertion into aliphatic C–H bonds suggests considerable contribution from the carbene canonical form **15**.

The extensive chemistry of this unusual diazo reagent and the character of the intermediate formed by nitrogen loss are currently under investigation.

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A Mild Procedure for the Conversion of Epoxides to Allylic Alcohols. The First Organoselenium Reagent

Sir:

We recently reported^{1,2} several new thermal rearrangements of allylic organoselenium compounds and noted that they proceeded considerably faster than the related sulfur cases. In keeping with this trend, we found that alkyl phenyl selenoxides bearing a β-hydrogen undergo syn elimination to form olefins under much milder conditions than the corresponding sulfonoxides.^{3,4} All of the selenoxides we have investigated eliminate readily at room temperature. Herein is described a new procedure for the conversion of epoxides to allylic alcohols, based on this facile elimination. This is the first of several synthetic applications we have discovered for this gentle olefin-forming process.

The reaction sequence is exemplified for (*E*)-4-octene oxide (**1**) in Scheme I.

The selenium anion **2** is an excellent nucleophile and easily opens epoxide **1** to the hydroxy selenide **3** (step a).⁵ The hydroxy selenide is not isolated, but is oxidized (step b) by excess hydrogen peroxide to the unstable selenoxide **4**, which decomposes (step c)⁵ to the *E* allylic alcohol **5** in 98% yield.⁶ A striking feature in the decomposition of the β-hydroxy selenoxide **4** is that elimination occurs away from the hydroxyl group. This useful phenomenon appears to be general (Table I), and we never observed more than traces of the possible ketonic products. In the thermal decomposition of several β-hydroxyamine oxides, reported by Cope⁷ and

(1) K. B. Sharpless and R. F. Lauer, *J. Amer. Chem. Soc.*, **94**, 7154 (1972).

(2) K. B. Sharpless and R. F. Lauer, *J. Org. Chem.*, **37**, 3973 (1972).

(3) This work is described elsewhere: K. B. Sharpless, M. W. Young, and R. F. Lauer, submitted for publication.

(4) The unusual thermal lability of selenoxides was also observed recently by Jones and coworkers during their synthesis of a chiral selenoxide: D. Neville Jones, D. Mundy, and R. D. Whitehouse, *Chem. Commun.*, 86 (1970). A similar observation was made during the synthesis of a selenium-containing α-amino acid: R. Walter and J. Roy, *J. Org. Chem.*, **36**, 2561 (1971).

(5) Both step a and step c can be accelerated by refluxing the alcoholic solution (Table I).

(6) In this case and in the other acyclic examples revealed in Table I where disubstituted olefins were formed, the products showed no *ir* band for the *Z* disubstituted olefinic linkage. Thus the *E* isomers are formed with high stereoselectivity. We had previously observed similar stereochemical results with simple alkyl selenoxides.³

(7) A. C. Cope and E. M. Acton, *J. Amer. Chem. Soc.*, **80**, 355 (1958); A. C. Cope, E. Ciganek, and J. Lazar, *ibid.*, **84**, 2591 (1962).

(4) (a) Y. Hayashi, T. Okada, and M. Kawanisi, *Bull. Chem. Soc. Jap.*, **43**, 2506 (1970); (b) F. Karele and O. Neiland, *J. Org. Chem. USSR*, **4**, 1755 (1968).

(5) W. H. Pirkle and G. F. Koser, *J. Amer. Chem. Soc.*, **90**, 3598 (1968), proposed a bromonium ylide intermediate in reaction of 3,5-ditert-butylbenzene 1,4-diazooxide with 2,6-diisopropyl-4-bromophenol.

(6) A. N. Nesmeyanov, L. G. Makarova, and T. P. Tolstoya, *Tetrahedron*, **1**, 145 (1957).

(7) C. S. Rondestvedt, Jr., and H. S. Blanchard, *J. Org. Chem.*, **21**, 229 (1956).

(8) H. Wakamatsu, Y. Yamada, T. Saito, I. Kumashiro, and T. Takenishi, *J. Org. Chem.*, **31**, 2035 (1966).

Table I^a

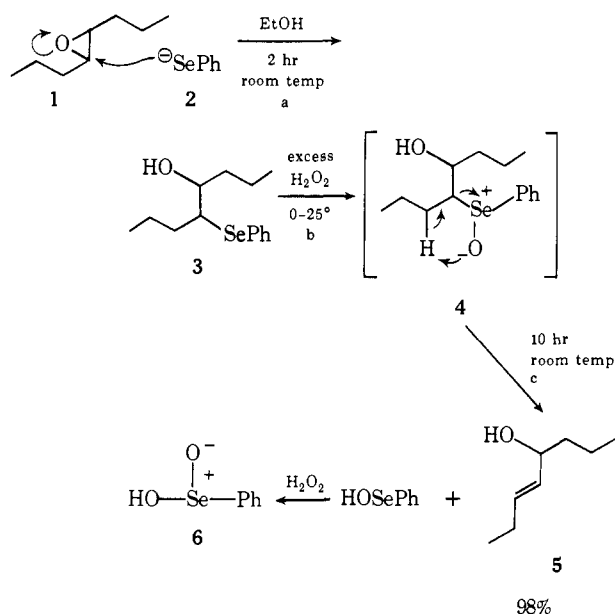
Epoxide ^{b,h}	Product ^b	Yield, ^c %	Solvent ^d	Step a time, hr (temp)	Step c time, hr (temp) ^e
		98	EtOH	2 (room temp)	12 (room temp)
		85	<i>n</i> -BuOH	16 (reflux)	1 (reflux)
		75	<i>n</i> -BuOH	16 (reflux)	4 (room temp)
		(40)	EtOH-THF 1:1	14 (reflux)	2.5 (reflux)
		(51)	EtOH-THF 1:1	8.5 (reflux)	4 (reflux)
8, R =	7, R =	95	EtOH	0.5 (reflux)	12 (room temp)
16, R =	17, R =	(79)	EtOH	2 (reflux)	2 (room temp)
10, R =	9, R =	(50)	EtOH	2 (reflux)	5 (room temp)
		50	EtOH	0.5 (reflux)	0.1 (room temp)

^a The general procedure is described below for the synthesis of allylic alcohol 17. Most of these reactions were carried out on a 8–10 mmol scale, using between 10 and 20 mol equiv of 30% hydrogen peroxide. All steps of the reaction were monitored by tlc. ^b These are all known epoxides except for 16 which was completely characterized, as were all new compounds described in this work. ^c The yields in parentheses are for isolated pure substances, all other yields were determined by glc relative to internal standards. ^d 1-Butanol gave a higher reflux temperature which speeded the opening of more hindered epoxides. ^e In those cases where selenoxide decomposition was speeded by refluxing, heating was begun only after the solutions had ceased bubbling (oxygen evolution). ^f A new steroid, mp 114.5–115.5°, [α]_D²⁵ +24.6° (c 0.22, CHCl₃). ^g Results from a [2,3] sigmatropic rearrangement of the corresponding allylic selenoxide (see ref 1). ^h All new compounds have been adequately characterized by analytical and spectral data.

others,⁸ preference for elimination away from the hydroxyl was also noted but was much less pronounced.

Examination of Table I reveals that this new procedure affords good to excellent yields of allylic alcohols. The crude reaction mixtures are almost free of by-products; so that for most further applications, purification is not necessary.⁹ For example, the crude diol 7 was cyclized following the procedure of Ohloff,¹⁰ to a mixture of cis and trans rose oxides in 78% yield based on the starting epoxy alcohol 8. The natural product, isomyrcenol, (*E*)-2-methyl-6-methylene-3,7-

Scheme I



(8) (a) S. Labadum, P. Potin, F. Winternitz, and R. Wylde, *Bull. Soc. Chim. Fr.*, 111 (1965); (b) P. Potin and R. Wylde, *ibid.*, 4445 (1967); (c) A. M. Mandrou, P. Potin, and R. Wylde-Lachazette, *ibid.*, 1546 (1962).

(9) Contamination by organoselenium compounds, often a severe problem in SeO₂ oxidations, does not occur. At the end of the reaction the selenium is present as phenyl seleninic acid (6) which is extracted by aqueous base. We have found that the aqueous solution of phenyl seleninic acid is readily reduced back to the starting material (diphenyl diselenide) by almost any reducing agent. Thus the only expensive reagent in the entire process is recoverable.

(10) G. Ohloff and B. Lienhard, *Helv. Chim. Acta*, 48, 182 (1965); G. Ohloff, E. Klein, and G. O. Schenck, *Angew. Chem.*, 73, 578 (1961).

octadien-2-ol (9),¹¹ was formed exclusively when the myrcene monoepoxide (10) was subjected to the usual reaction sequence.

The best current method for the epoxide-allylic alcohol conversion, discovered by Cope,¹² and thoroughly developed by Crandall¹³ and Rickborn,¹⁴ involves isomerization with strong base. Although often an excellent procedure, the results in Table I reveal several situations where our new, milder method would be preferred. Medium ring epoxides such as 11 give very little allylic alcohol with the base procedure.^{12a,b} Rigid epoxides, similar to α - (12) and β - Δ^2 -cholestene oxides (13) often give mixtures with the base methods,^{14a} whereas we obtained only the allylic alcohols expected from initial (step a) diaxial opening of the epoxides. Terpenoid epoxides, such as 8, 10, and 16, give exclusively the allylic alcohols resulting from attack by base on a methyl proton.^{13b,14a} Finally, the almost neutral selenium procedure should succeed in situations where strong base would not be tolerated.

In a typical procedure, 12.0 g (0.04 mol) of diphenyl diselenide¹⁵ was dissolved in 200 ml of absolute ethanol. Sodium borohydride (3.07 g, 0.081 mol) was added in batches, while stirring mechanically under nitrogen, until the bright yellow solution turned colorless.¹⁶ (*Caution!* reduction of the diselenide is exothermic and vigorous hydrogen evolution occurs.) After addition of the epoxy methyl ether (16) (13.2 g, 0.071 mol) the reaction mixture was refluxed for 2 hr. The solution was cooled and 100 ml of THF added. Then 76 ml (0.83 mol) of 30% hydrogen peroxide was added over a period of 1 hr, while cooling the mixture in an ice bath, such that the temperature did not exceed 20°. After 2 hr the elimination was complete by tlc. The resulting slurry was diluted with water and extracted with ether. The organic phase was washed several times with aqueous sodium carbonate, dried (Na₂SO₄), and con-

centrated to give an orange oil, which upon vacuum distillation (77° (0.3 mm)) gave 10.4 g (79%) of the *E* allylic alcohol (17).

We are finding that organoselenium compounds have great potential as synthetic reagents and will soon report on two other diphenyl diselenide derived reagents.¹⁷ Use of diphenyl diselenide as a stoichiometric reagent should be comparable in expense to the use of triphenylphosphine. However, unlike triphenylphosphine, diphenyl diselenide is easily regenerated from its oxidation products (seleninic acid 6), and this oxidation product, being water soluble, is easily separated from the usual organic products. *Caution!* Selenium compounds are toxic and should be handled accordingly.

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(17) K. B. Sharpless, R. F. Lauer, and A. Y. Teranishi, unpublished results.

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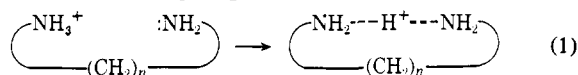
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Quantitative Evaluation of Intramolecular Strong Hydrogen Bonding in the Gas Phase^{1,2}

Sir:

Strong hydrogen bonding and solvation of ions in the gas phase have been the subjects of several recent experimental³ and theoretical investigations.⁴ By studying long range interactions between functional groups in gas-phase basicity studies,^{5,6} we have been able to observe *intramolecular* strong hydrogen bonding and evaluate some of the energetic parameters for formation of such bonds as a function of ring size.

Diaminoalkanes show dramatically higher (by 6–14 kcal/mol) gas-phase basicities (GB's) than primary amines of comparable polarizability (Table I).⁷ This effect must result from intramolecular strong hydrogen bonding between the ammonium ion and the other terminal amino group (eq 1). Allen's *ab initio* calcula-



(1) Presented in part in Abstracts of the 20th Annual Conference on Mass Spectrometry and Allied Topics, Dallas, Texas, June 4–9, 1972.

(2) Supported by NSF Grant No. GP-15628. Acknowledgment is also made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this work.

(3) (a) S. K. Searles and P. Kebarle, *J. Phys. Chem.*, **72**, 742 (1968); (b) J. L. Beauchamp, *Annu. Rev. Phys. Chem.*, **22**, 527 (1971); (c) T. H. Morton and J. L. Beauchamp, *J. Amer. Chem. Soc.*, **94**, 3671 (1972).

(4) (a) P. A. Kollman and L. C. Allen, *J. Amer. Chem. Soc.*, **92**, 6101 (1970); (b) W. P. Kraemer and G. H. F. Diercksen, *Chem. Phys. Lett.*, **5**, 463 (1970); (c) N. DePaz, S. Ehrenson, and L. Friedman, *J. Chem. Phys.*, **52**, 3362 (1970).

(5) M. T. Bowers, D. H. Aue, H. M. Webb, and R. T. McIver, *J. Amer. Chem. Soc.*, **93**, 4314 (1971).

(6) D. H. Aue, H. M. Webb, and M. T. Bowers, *J. Amer. Chem. Soc.*, **94**, 4726 (1972).

(7) See ref 6 for an evaluation of polarizability effects on gas-phase basicities.

(11) This terpene was first isolated and characterized by R. M. Silverstein, J. O. Rodin, D. L. Wood, and L. E. Brown, *Tetrahedron*, **22**, 1929 (1966). A recent synthesis gave a mixture of the desired compound and its isomer, 2-methyl-6-methylene-1,7-octadien-3-ol: T. Moore, A. Komatsu, and K. Ueda, U. S. Patent 3,433,839 (1969); *Chem. Abstr.*, **70**, P 114701e (1969).

(12) (a) A. C. Cope, H. H. Lee, and H. E. Petree, *J. Amer. Chem. Soc.*, **80**, 2849 (1958); (b) A. C. Cope, G. A. Berchtold, P. E. Peterson, and S. H. Sharman, *ibid.*, **82**, 6370 (1960); (c) A. C. Cope and J. K. Heeren, *ibid.*, **87**, 3125 (1965); (d) A. C. Cope, M. Brown, and H. H. Lee, *ibid.*, **80**, 2855 (1958).

(13) (a) J. K. Crandall, *J. Org. Chem.*, **29**, 2830 (1964); (b) J. K. Crandall and L. Chang, *ibid.*, **32**, 435, 532 (1967); (c) J. K. Crandall and L. C. Lin, *J. Amer. Chem. Soc.*, **89**, 4526, 4527 (1967).

(14) (a) B. Rickborn and R. P. Thummel, *J. Org. Chem.*, **34**, 3583 (1969); (b) R. P. Thummel and B. Rickborn, *J. Amer. Chem. Soc.*, **92**, 2064 (1970); (c) R. P. Thummel and B. Rickborn, *J. Org. Chem.*, **36**, 1365 (1971); (d) C. L. Kissel and B. Rickborn, *ibid.*, **37**, 2060 (1972).

(15) This odorless, yellow solid was easily prepared on a 2.5 M (based on bromobenzene) scale by a modification of the *Organic Syntheses* procedure for the preparation of selenophenol: D. G. Taster, *Org. Syn.*, **III**, 771 (1955). The above procedure is followed except that the crude ethereal selenophenol solution is not distilled, but rather filtered, then diluted with ~1500 ml of 95% ethanol containing a few pellets of potassium hydroxide. Oxygen or air is bubbled through the stirred solution until the odor of selenophenol disappears (overnight). Filtration affords the yellow diselenide which may be used without further purification. Concentration of the filtrate affords further diselenide; the total yield is ~71%, mp 63°.

(16) B. Sjöberg and S. Herdevall, *Acta Chem. Scand.*, **12**, 1347 (1958). This is a convenient method for reducing diselenides. However, there are a number of less expensive alternatives for reduction to the desired anion 2: see, W. H. H. Günther, *J. Org. Chem.*, **31**, 1202 (1966), and references cited therein. We originally prepared ethanolic solutions of 2 by reaction of selenophenol with NaOEt, but the stench of selenophenol encouraged use of the diselenide route.