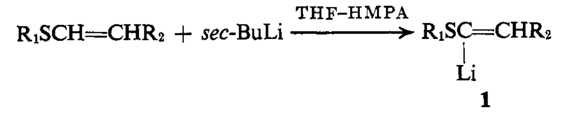

$$R_1SCH{=}CHR_2 + sec\text{-}BuLi \xrightarrow{\text{THF-HMPA}} \underset{\substack{|\\ Li\\ \mathbf{1}}}{R_1SC}{=}CHR_2 \quad (1)$$

at least 6 hr. At −78°, the anion **1** reacts smoothly with halides, aldehydes, and epoxides to provide, after hydrolysis with mercuric ion in aqueous acetonitrile,[1,2] good yields of the corresponding ketones, acyloins, and α,β-unsaturated ketones, respectively, as depicted below (Table I). The procedure is simpler[3] and potentially more versatile than the recently developed ketone syntheses.[4]

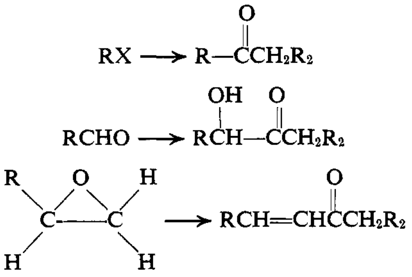

Table I. Reactions of 1-(Alkylthio)vinyllithium with Electrophile

$R_1SCH{=}CHR_2$ R_1	R_2	Electrophile	Product[a]	Yield,[b,c] %
C_2H_5	H	*n*-Octyl bromide	$n\text{-}C_8H_{17}COCH_3$	90
CH_3	$n\text{-}C_8H_{17}$	*n*-Octyl bromide	$n\text{-}C_8H_{17}CO\text{-}n\text{-}C_9H_{19}$	82
CH_3	C_6H_5	*n*-Octyl bromide	$n\text{-}C_8H_{17}COCH_2C_6H_5$	65
C_2H_5	H	1,4-Dibromobutane	$CH_3CO(CH_2)_4COCH_3$	60
C_2H_5	H	1,3-Dibromopropane	3-Methyl-2-cyclohexenone[d]	52
C_2H_5	H	Benzaldehyde	$C_6H_5CHOHCOCH_3$	64
C_2H_5	H	Nonanal	$n\text{-}C_8H_{17}CHOHCOCH_3$	58
CH_3	C_6H_5	Benzaldehyde	$C_6H_5CHOHCOCH_2C_6H_5$	54
CH_3	$n\text{-}C_8H_{17}$	Benzaldehyde	$C_6H_5CHOHCO\text{-}n\text{-}C_9H_{19}$	51
C_2H_5	H	Styrene oxide	$C_6H_5CH{=}CHCOCH_3$	68
CH_3	C_6H_5	Propylene oxide	$CH_3CH{=}CHCOCH_2C_6H_5$	57

[a] All products exhibited spectral and physical properties in accordance with the assigned structures or with reported literature values. [b] Yield of product after isolation by preparative tlc. [c] The yields are not necessarily optimum since each run was performed only once. [d] 2,6-Heptadione could not be obtained after hydrolysis.

Although the potentiality of 1-(alkylthio)vinyllithium as a synthetic equivalent of acyl anion was proposed earlier by Corey,[5] the actual execution utilizing this type of reagent for ketone synthesis has never been developed to a useful level due to the lack of a satisfactory base–solvent system for converting a vinyl sulfide into a reactive anion **1**.[6] In an attempt to find the suitable system, we studied the reaction of ethyl vinyl sulfide with a variety of bases and solvents using octyl bromide as an electrophile (base, solvent, yield of 2-decanone after hydrolysis): *n*-BuLi, THF, 2–3%; *n*-BuLi–TMEDA, THF, 10–20%; *n*-BuLi, THF–HMPA, 68%; *sec*-BuLi, THF, 72%; *sec*-BuLi, THF–HMPA, 90%.

The details of the new ketone synthesis[9] are illustrated by the procedure for the synthesis of 2,7-octadione. To a solution of ethyl vinyl sulfide (0.422 g, 4.80 mmol) in THF–HMPA (9:1, 20 ml) was added *sec*-butyllithium (4.40 mmol in pentane) at −78°, and the solution was held there for 30 min. The resulting orange solution was treated with 1,4-dibromobutane (0.432 g, 2.00 mmol) and the mixture was stirred at −78° for 30 min and 25° for 30 min.[10] Addition of water, extraction with ether, and concentration gave a crude sulfide (0.510 g) which was dissolved in acetonitrile–water (3:1, 20 ml). The solution was treated with mercuric chloride (2.17 g) and the mixture was heated at reflux for 12 hr.[1] Extractive work-up followed by tlc purification (R_f 0.2–0.3, CH_2Cl_2) afforded pure 2,7-octadione as a colorless semisolid (0.170 g, 60%) which was spectroscopically identical with an authentic sample.

We are investigating further extension of this reaction as well as synthetic applications.

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(1) E. J. Corey and J. I. Shulman, *J. Org. Chem.*, **35**, 777 (1970).

(2) In many cases, the alkylated sulfides were isolated and characterized in pure states, but it was found that this delay of the sequence was unnecessary and the crude products were hydrolyzed directly with mercuric chloride to give the desired products efficiently.

(3) Vinyl sulfides are readily available by recently published methods: ref 1; I. Shahak and J. Almog, *Synthesis*, **1**, 170 (1969).

(4) 1,3-Dithiane method: E. J. Corey and D. Seebach, *Angew. Chem., Int. Ed. Engl.*, **4**, 1075, 1077 (1965); dihydro-1,3-oxazine method: A. I. Meyers, E. M. Smith, and A. F. Jurjevich, *J. Amer. Chem. Soc.*, **93**, 2314 (1971); cyanohydrin anion method: G. Stork and L. Maldonado, *ibid.*, **93**, 5286 (1971); epoxysilane method: G. Stork and E. Colvin, *ibid.*, **93**, 2080 (1971); organocopper method: G. H. Posner, C. E. Whitten, and P. E. McFarland, *ibid.*, **94**, 5106 (1972); hydroboration method: H. C. Brown and G. W. Kabalka, *ibid.*, **92**, 714 (1970).

(5) E. J. Corey and D. Seebach, *J. Org. Chem.*, **31**, 4097 (1966).

(6) Indeed, allenic ether, for example, can be readily metalated by sodium amide in liquid ammonia[7] and this is based on the enhanced acidity of sp^2 hydrogen relative to sp^3 hydrogens. It must be borne in mind, however, that to successfully form the anion **1** by metalation, Michael-type addition reaction and some other side reactions[8] must be suppressed.

(7) S. Hoff, L. Brandsma, and J. F. Arens, *Recl. Trav. Chim. Pays-Bas*, **87**, 916, 1179 (1968).

(8) W. E. Parham and R. F. Motter, *J. Amer. Chem. Soc.*, **81**, 2146 (1959); W. E. Parham, M. E. Kalnins, and D. R. Theissen, *J. Org. Chem.*, **27**, 2698 (1962).

(9) The reactivity of this new reagent was found to be very similar to that of 1,3-dithiane anion. Thus, it reacted with alkyl iodides and bromides smoothly at −78°, but proved much less reactive toward chlorides. For example, cyclohexyl chloride was almost inert and the yield of the corresponding ketone was less than 10%.

(10) Most of the color was discharged after 10 min at −78°.

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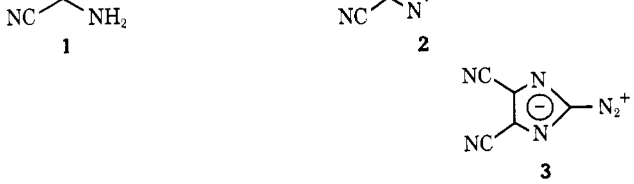
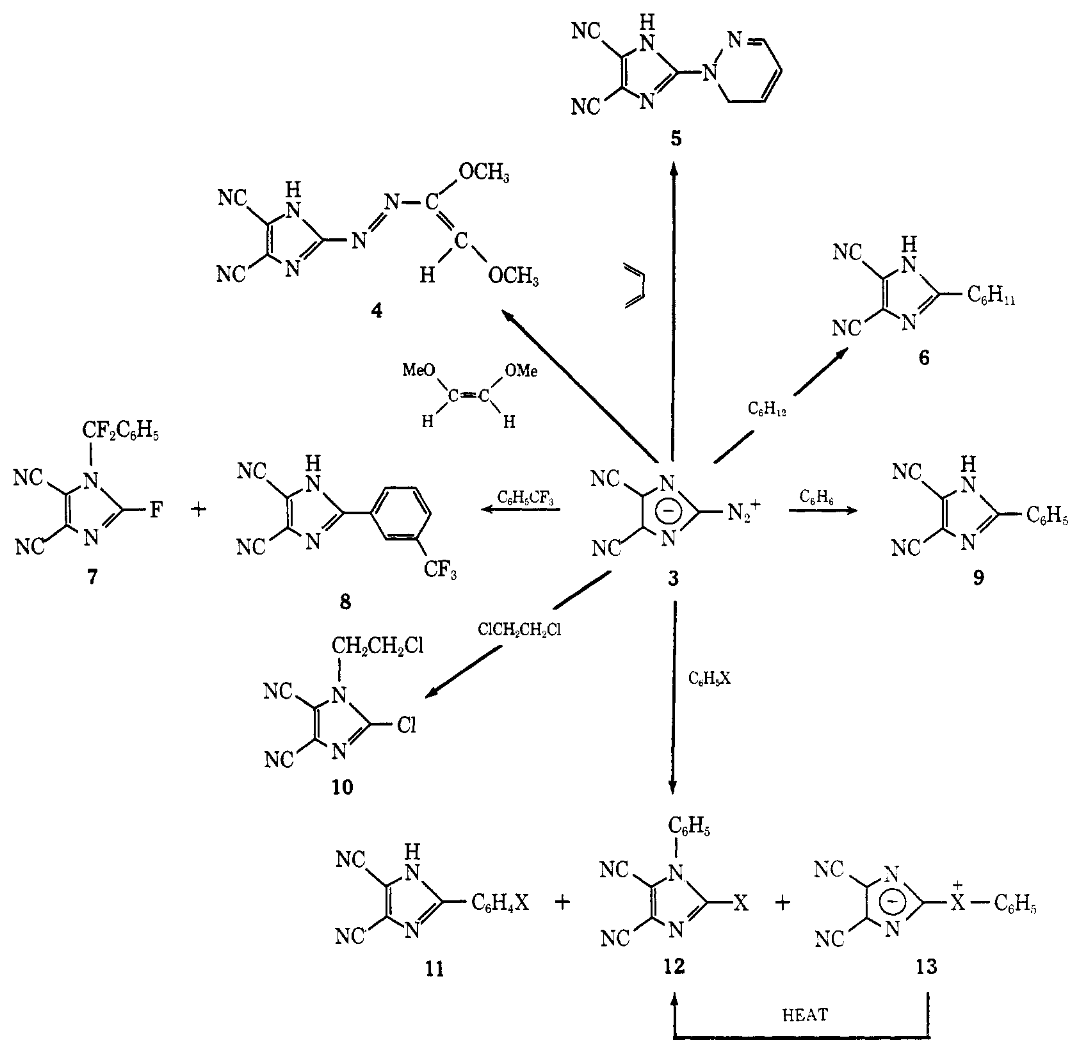
Hydrogen Cyanide Chemistry. V. Diazodicyanoimidazole and Dicyanoimidazole Halonium Ylides

Sir:

We report the synthesis of a new diazo compound, diazodicyanoimidazole (**3**), which eliminates nitrogen at approximately 80° in solution to form a highly reactive intermediate that inserts a 4,5-dicyanoimidazole



Scheme I. Reactions of Diazodicyanoimidazole



moiety into a substrate. This intermediate is unusually electrophilic; it attacks the halogen of aryl halides to form novel halonium ylides as well as products corresponding to 1,2 insertion into C–H and C–X bonds including C–F bonds.

Aminodicyanoimidazole (**2**) is made in 75% yield by condensation of cyanogen chloride with diaminomaleonitrile[1] (**1**) in tetrahydrofuran solution at 0–50°; it is recrystallized from acetonitrile, mp 270° dec.

Anal. Calcd for $C_5H_3N_5$: C, 45.1; H, 2.3; N, 52.6. Found: C, 45.3; H, 2.4 N, 52.6.

Amine **2** is diazotized with sodium nitrite in water–hydrochloric acid. White diazodicyanoimidazole (**3**) precipitates quantitatively. It can be filtered and dried under an air stream or under vacuum. *Dry* **3** *is highly shock sensitive.* To avoid explosions, our preferred procedure is to transfer moist **3** to the reaction vessel and dry it under vacuum. **3** decomposes (explodes) at 150°. For analysis a small sample was recrystallized from CH_3CN. Ir: 4.35, 4.45, 6.95, 7.46, 8.65, 13.57, 15.18 μ; uv: λ_{max} 232 nm (ϵ 9390), 315 (22,300); dipole moment 7.66 D.

Anal. Calcd for C_5N_6: C, 41.7; N, 58.2. Found: C, 41.6; N, 58.2.

When **3** in an organic solvent is heated to approximately 80°, nitrogen is evolved gradually until a stoichiometric amount is liberated in 1–2 hr. For example, when 2.8 g (20 mmol) of **3** in 100 ml of benzene was heated under reflux for 2 hr, 20 mmol of nitrogen was evolved. 2-Phenyl-4,5-dicyanoimidazole (**9**), 3.18 g (85%), crystallized from the solution on cooling and was identical with material prepared by condensation–oxidation of benzaldehyde with **1**.[2] Similarly, 2-cyclohexyl-4,5-dicyanoimidazole (**6**)[3] was obtained in 72% yield by thermolysis of **3** in refluxing cyclohexane (Scheme I).

3 pyrolyzes in halobenzenes to a mixture of products. For example, pyrolysis in chlorobenzene gave 2-(chlorophenyl)-4,5-dicyanoimidazole (**11**, X = Cl, as an isomer mixture) in 50% yield, 1-phenyl-2-chloro-4,5-dicyanoimidazole (**12**, X = Cl) in 21% yield, and chloronium ylide **13** (X = Cl) in 26% yield. Imidazole **11** (X = Cl) was separated by base extraction of the reaction mixture. Imidazole **12** (X = Cl) was separated from **13** (X = Cl) by extraction into hot hexane and was recrystallized from hexane, mp 108–110°. Imidazole **13** was recrystallized from chloroform–petroleum ether,

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[1] R. W. Begland, A. Cairncross, D. S. Donald, D. R. Hartter, W. A. Sheppard, and O. W. Webster, *J. Amer. Chem. Soc.*, **93**, 4953 (1971), and references therein.

[2] L. E. Hinkel, G. O. Richards, and O. Thomas, *J. Chem. Soc.*, 1437 (1937).

[3] The new 2-substituted imidazoles **6**, **8**, and **11** were also prepared by the aldehyde condensation method[2] and compared to products from the thermolysis of **3**. Satisfactory analytical results and spectra (ir, nmr, and uv) were obtained on the imidazoles (mp): **6** (149–150°), **8** (205–206°), **11**, X = *o*-F (246–247°), *m*-F (198–200°), *p*-F (220–221°), *o*-Cl (211–212°), *m*-Cl (227–228.5°), *p*-Cl (300–301°), *o*-Br (182–183°), *m*-Br (212–213°), *p*-Br (226° dec).

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.

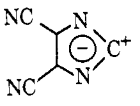
Bromobenzene also gives three products; the bromonium ylide **13** (X = Br, mp 143–144°) appears more stable to rearrangement since essentially no imidazole **12** (X = Br) is formed under minimum reaction conditions for nitrogen elimination. The thermally stable iodonium ylide, **13** (X = I, mp 221–222°), 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 ^{19}F 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 species[6] rather than a radical type intermediate.[7] Contrary to expectations, boiling ethanol reduces **3** to give 4,5-dicyanoimidazole[8] 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 (CD_3SOCD_3), 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 hydrid 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**.



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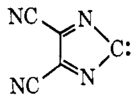

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The extensive chemistry of this unusual diazo reagent and the character of the intermediate formed by nitrogen loss are currently under investigation.

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(4) (a) Y. Hayasi, 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-di-*tert*-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).

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 sulfoxides.[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 Cope[7] and

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(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).