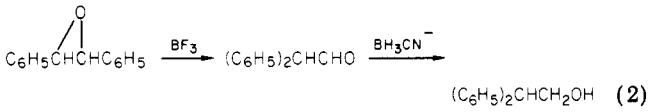
Table I. Reductions of Epoxides with Cyanoborohydride–Boron Trifluoride Etherate

| entry | epoxide | T, °C (time, h) | product(s) (rel ratio)[a] | | % yield[b] |
|---|---|---|---|---|---|
| 1 | cyclohexene | 5 (0.75) | cyclohexanol | | 63, 96[c] |
| 2 | cyclooctene | 5 (4) | cyclooctanol | | 60 |
| 3 | cyclododecene | 66 (22) | cyclododecanol | | 94 |
| 4 | cyclooctadiene (monoepoxide) | 25 (20) | cyclooctan-2-en-1-ol (89) | cyclooctan-3-en-1-ol (11) | 79 |
| 5 | 1-methylcyclohexene | 25 (6) | 2-methylcyclohexanol, cis (97),[d] trans (trace) | 1-methylcyclohexanol (3) | 87 |
| 6 | styrene | 5 (4) | 2-phenylethanol (97) | 1-phenylethanol (3) | 79 |
| 7 | β-methylstyrene | 25 (4) | 2-phenyl-1-propanol (99) | 2-phenyl-2-propanol (1) | 94 |
| 8 | 1-dodecene | 66 (4) | 1-dodecanol (89) | 2-dodecanol (11) | 83 |
| 9 | 2-methylundecene | 66 (2) | 2-methyl-1-undecanol (95) | 2-methyl-2-undecanol (5) | 73 |
| 10 | *trans*-stilbene | 66 (4) | 1,2-diphenylethanol (12) | 2,2-diphenylethanol (88) | 80 |

[a] Ratios of products determined by GC. [b] Yields represent isolated, distilled products unless otherwise indicated. [c] GC yield, corrected for detector response. [d] Analyzed as the acetates.

rangement to diphenylacetaldehyde prior to reduction[7] (eq 2). In addition, the reduction of styrene oxide with



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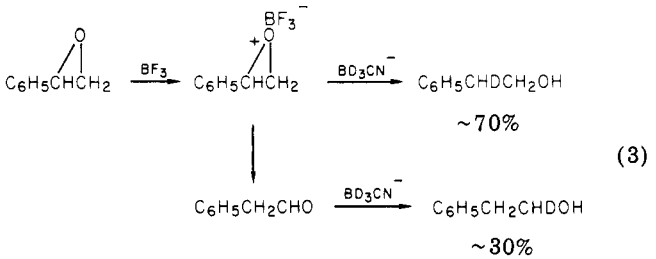


(3)

$NaBD_3CN$ afforded 2-phenylethanol-*d* with approximately 30% of the deuterium located at the 1-carbon, indicating partial rearrangement prior to reduction (eq 3). Note that such rearrangement and subsequent reduction results in production of the same product (2-phenylethanol) in the absence of the deuterium tag. Norbornene epoxide gave a complex mixture of products, some of which contained fluorine. In no other cases was evidence of rearrangement observed.

In conclusion, $BH_3CN^-$–$BF_3OEt_2$ provides an effective combination for the regio- and stereoselective cleavage of most epoxides to the less substituted alcohols resulting from anti ring opening. Further, the inertness of $BH_3CN^-$ toward several other functional groups in acidic media (ester, acid, amide, cyano, nitro)[4,8] recommends the reagent system when chemoselectivity is important.

## Experimental Section

**General Methods.** The epoxides used were either commercially available or prepared from the corresponding alkene and *m*-chloroperbenzoic acid in $CHCl_3$.[9] GC analyses were performed on either a Hewlett-Packard Model 5750 or a Varian Model 3700 equipped with a Columbia Scientific Industries Model CSI 38 digital integrator, and product identification was accomplished by comparison with authentic samples.

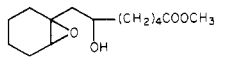
**Reduction of Epoxides. General Procedure.** The general reaction procedure was straightforward. A solution of the epoxide (10 mmol), $NaBH_3CN$ (14–30 mmol), and a small quantity of bromocresol green indicator in 40 mL of dry THF was stirred, while $BF_3OEt_2$ in a few milliliters of THF was added dropwise until a color change to yellow was noted and stirring was continued at the temperatures in Table I for the durations listed. For some examples, additional $BF_3OEt_2$ was required periodically to maintain the acidity. Upon completion the reactions were diluted with brine and exhaustedly extracted with ether. After the solution was dried ($Na_2SO_4$), solvent was removed on a rotary evaporator and the residue distilled on a Kugelrohr apparatus and analyzed by GC.

**Acknowledgment.** We thank the Petroleum Research Foundation, administered by the American Chemical Society, and the National Science Foundation for support of this work.

**Registry No.** Cyclohexene epoxide, 286-20-4; cyclooctene epoxide, 286-62-4; cyclododecene epoxide, 286-99-7; cyclooctadiene epoxide, 637-90-1; 1-methylcyclohexene epoxide, 1713-33-3; styrene epoxide, 96-09-3; 3-methylstyrene epoxide, 4436-22-0; 1-dodecene epoxide, 2855-19-8; 2-methylundecene epoxide, 54125-40-5; *trans*-stilbene epoxide, 1439-07-2; sodium cyanoborohydride, 25895-60-7; boron trifluoride etherate, 109-63-7.

(7) (a) House, H. O.; Reif, D. J. "Organic Syntheses", Collect. Vol. 4; Wiley: New York, 1963; p 375. Collins, D. J. *J. Chem. Soc.* **1959**, 3919. (b) Reduction of *trans*-stilbene oxide with $R_3SiH/BF_3$ also proceeds via initial rearrangement to 1,1-diphenylethanal; Fry, J. F.; Marz, T. J. *Tetrahedron Lett.* **1979**, 849.

(8) The method has been successfully utilized to convert epoxide i to ii (70% + 30% of the tertiary alcohol; 80% yield); G. C. de Magalhaes (University of Brasilia), personal communication. In this case the amount of attack at the less substituted site is perhaps augmented by hydride deliverance at this position by cyanoborohydride complexed to the secondary alcohol.



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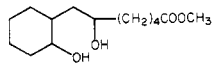

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(9) Fieser, L.; Fieser, M. "Reagents for Organic Synthesis"; Wiley: New York, 1967; Vol. 1, p 135.

# Organic *N*-Halogeno Compounds. 14.[1] Preparation of *N*-(*N*-Halomethoxycarbonimidoyl)-*S*,*S*-dimethylsulfilimines

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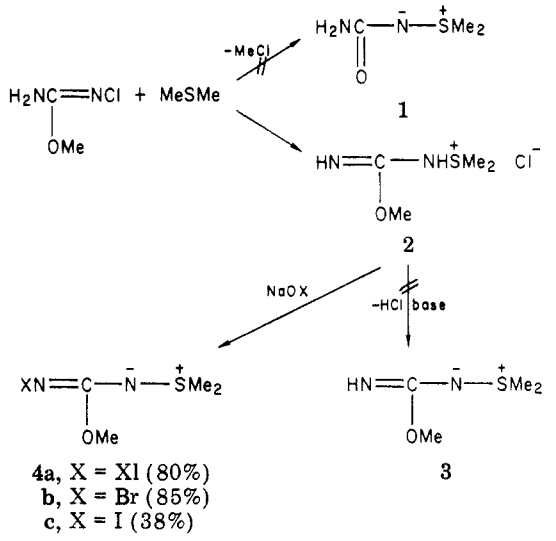
Sulfilimines are unique in reactivity, and many intensive studies on them have been performed.[2] Sulfilimines of

(1) Part 13: T. Fuchigami and T. Nonaka, *Chem. Lett.*, 829 (1979).

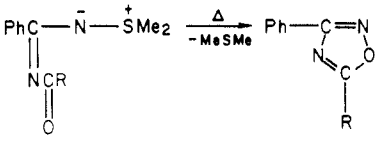
0022-3263/81/1946-5215$01.25/0 

Scheme I

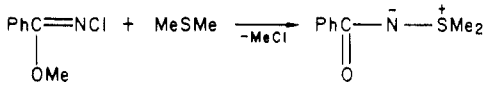


4a, X = Xl (80%)
b, X = Br (85%)
c, X = I (38%)

various types have been synthesized; however, until recently no sulfilimines possessing an additional imino group have been synthesized. In our previous papers,[3,4] we reported the preparation of a new class of sulfilimines stabilized by an imino group from *N*-chlorobenzamidine and dimethyl sulfide, and we found that *N*-acyl derivatives of



the sulfilimine are useful for synthesis of oxadiazoles.[5] About 10 years ago, Papa[6] reported that methyl *N*-chlorobenzimidate reacted with dimethyl sulfide, giving *N*-benzoyl-*S*,*S*-dimethylsulfilimine with liberation of methyl chloride.



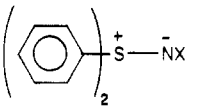
In view of the above facts, we have investigated the possible formation of sulfilimines **1** and **3** from *N*-chloro-*O*-methylisourea and dimethyl sulfide (Scheme I).

*N*-Chloro-*O*-methylisourea reacted readily with dimethyl sulfide in anhydrous acetonitrile to form [(methoxycarbonimidoyl)amino]dimethylsulfonium chloride (**2**) in 80% yield. In this reaction, no evolution of methyl chloride was observed, which was quite different from the reaction of *N*-chlorobenzimidate with dimethyl sulfide. We tried to prepare *N*-(methoxycarbonimidoyl)-*S*,*S*-dimethylsulfilimine (**3**) by treatment of **2** with appropriate bases both in protic and aprotic solvents; however, our attempts to isolate **3** failed because of its instability.

It is well-known that sulfilimines are stabilized by an electron-withdrawing group attached to the ylide nitrogen atom. Attempts were made to prepare *N*-halogeno derivatives **4** instead of **3**. It was found that *N*-chloro- and *N*-bromosulfilimines **4a** and **4b** could be easily prepared in good yields by treatment of **2** with sodium hypochlorite and hypobromite at low temperature. However, the yield of *N*-iodo derivatives **4c** was relatively low.

The structure of **4** was established by elemental analysis and by comparison of IR and NMR spectra of**4** with those of **2**, together with mass spectra. In the IR spectra, the C=N stretching vibration of **2** is at 1640 $cm^{-1}$, while that of **4** is at 1500 $cm^{-1}$. In the NMR spectra, the resonance of the protons of the methyl group adjacent to the positively charged sulfur atom shifts upfield by about 0.25 ppm in going from **2** to **4**. These shifts observed in the IR and NMR spectra are analogous to those in the case of *N*-benzimidoylsulfilimines.[3,4] The reaction seems to be very convenient since **4** can be obtained directly from the sulfonium salt in good yield and adequate purity except for *N*-iodosulfilimine **4c**.

The sulfilimine **4** thus obtained melts at over 100 °C and was found to be relatively stable. Furukawa et al.[7,8] first reported *N*-halosulfilimines such as **5**; however, compounds



of type **4** have not been described. These sulfilimines with reactive functional groups appear to have potentail utility in a variety of organic syntheses.

## Experimental Section

**[(Methoxycarbonimidoyl)amino]dimethylsulfonium Chloride (2).** To a stirred solution of 5.60 g (90 mmol) of dimethyl sulfide in 25 mL of anhydrous acetonitrile was gradually added a solution of 6.52 g (60 mmol) of *N*-chloro-*O*-methylisourea[9] in 10 mL of acetonitrile. The temperature was maintained below 10 °C during the reaction. After about 30 min of continued stirring, active chlorine disappeared, and 8.71 g (80%) of the sulfonium salt **2** precipitated; mp 117–120 °C. This material was purified by recrystallization from methanol–ether: mp 135–136 °C dec; IR (KBr) 3250, 3100 (NH), 1640 $cm^{-1}$ (C=N); 60-MHz $^1H$ NMR ($Me_2SO$-$d_6$) $\delta$ 2.97 (s, 6 H, MeS), 3.73 (s, 3 H, MeO), 8.42 (s, 2 H, NH); mass spectrum (75 eV), *m/e* 134 ($M^+$ – HCl) and 62 ($Me_2S^+$).

Anal. Calcd for $C_4H_{11}N_2OSCl$: C, 28.15; H, 6.50; N, 16.42. Found: C, 28.14; H, 6.56; N, 16.49.

***N*-(*N*-Chloromethoxycarbonimidoyl)-*S*,*S*-dimethylsulfilimine (4a).** To a stirred solution of 1.20 g (7 mmol) of **2** in water–dichloromethane (5–30 mL) was gradually added 10 mL (7 mmol) of 0.7 M sodium hypochlorite, the temperature being kept below 5 °C. After about 10 min of stirring, the organic layer was separated, and the aqueous layer was extracted twice with 15-mL portions of dichloromethane. The extracts were dried over sodium sulfate, filtered, and concentrated under reduced pressure to provide 0.94 g (80%) of the *N*-chlorosulfilimine **4a**. Recrystallization from dichloromethane–petroleum ether gave 0.80 g (68%) of **4a** as a white solid: mp 120.0–120.5 °C; IR (KBr) 1500 $cm^{-1}$ (C=N); 60-MHz $^1H$ NMR ($CDCl_3$) $\delta$ 2.70 (s, 6 H, MeS), 3.80 (s, 3 H, MeO); mass spectrum (75 eV), *m/e* (relative intensity) 170 (4, $M^+$ + 2), 168 (11, $M^+$), 62 (100, $Me_2S^+$).

Anal. Calcd for $C_4H_9N_2OSCl$: C, 28.49; H, 5.38; N, 16.16. Found: C, 28.17; H, 5.42; N, 16.46.

***N*-(*N*-Bromomethoxycarbonimidoyl)-*S*,*S*-dimethylsulfilimine (4b).** In a similar manner as described above, **4b** was prepared in 85% yield by the reaction of sodium hypobromite. Recrystallization from dichloromethane–petroleum ether provided **4b** (70%) as a light yellow solid: mp 135.0–135.5 °C dec; IR (KBr) 1500 $cm^{-1}$ (C=N); 60-MHz $^1H$ NMR ($CDCl_3$) $\delta$ 2.73 (s, 6 H, MeS), 3.80 (s, 3 H, MeO); mass spectrum (75 eV), *m/e* (relative intensity)

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(4) T. Fuchigami and K. Odo, *Bull. Chem. Soc. Jpn.*, 50, 1793 (1977).
(5) Gilchrist et al. also reported the formation of heterocyclic compounds by photolysis and thermolysis of *N*-(arylimidoyl)sulfilimines. T. L. Gilchrist, C. J. Moody, and C. W. Rees, *J. Chem. Soc., Perkin Trans. 1*, 1965 (1975).
(6) A. J. Papa, *J. Org. Chem.*, 35, 2837 (1970).
(7) N. Furukawa, T. Yoshimura, and S. Oae, *Tetrahedron Lett.*, 2113 (1973).
(8) T. Yoshimura, N. Furukawa, T. Akasaka, and S. Oae, *Tetrahedron*, 33, 1061 (1977).
(9) J. Goerdeler and F. Bechlars, *Chem. Ber.*, 88, 848 (1955).

214 (17, $M^+ + 2$), 212 (17, $M^+$), 62 (100, $Me_2S^+$).

Anal. Calcd for $C_4H_9N_2OSBr$: C, 22.55; H, 4.26; N, 13.15. Found: C, 22.19; H, 4.21; N, 12.94.

***N*-(*N*-Iodomethoxycarbonimidoyl)-*S*,*S*-dimethylsulfilimine (4c).** *N*-Iodosulfilimine **4c** was obtained only in a low yield (6%) according to the same procedure described above. In methanol as a solvent, **4c** was prepared in 38% yield by the following procedure. To a stirred solution of 0.51 g (3 mmol) of **2** in 5 mL of methanol was gradually added a solution of 0.76 g (3 mmol) of iodine and 0.24 g (6 mmol) of sodium hydroxide in 20 mL of methanol below 5 °C. After being stirred about 20 min, the solution was mixed with water, and the mixture was extracted repeatedly with dichloromethane. After the extracts had been dried and concentrated, the remaining dark brown oily material was solidified with ether, and 0.30 g (38%) of crude **4c** was obtained. Recrystallization twice from dichloromethane–petroleum ether provided 0.15 g (19%) of **4c** as a yellow solid: mp 102.5–103.5 °C dec; IR (KBr) 1500 $cm^{-1}$ (C=N); 60-MHz $^1H$ NMR ($CDCl_3$) $\delta$ 2.77 (s, 6 H, MeS), 3.83 (s, 3 H, MeO); mass spectrum (75 eV), $m/e$ 260 ($M^+$), 62 ($Me_2S^+$).

Anal. Calcd for $C_4H_9N_2OSI$: C, 18.47; H, 3.49; N, 10.77. Found: C, 18.60; H, 3.43; N, 10.83.

**Registry No. 2**, 79373-16-3; **4a**, 79373-17-4; **4b**, 79373-18-5; **4c**, 79373-19-6; *N*-chloro-*O*-methylisourea, 19224-53-4.

## Tetracyclopentanaphthalene

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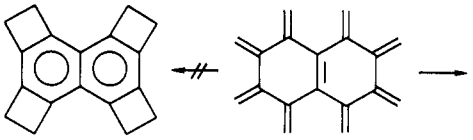
*Received April 3, 1981*

There has been a good deal of recent interest in the preparation and study of cyclobutene-fused aromatic molecules.[1] Hart and co-workers have reported the preparation of compound **3** via a pyrolytic dehydrochlorination which they suggest proceeds through the intermediate naphtharadialene **2**.[2] They find no evidence,



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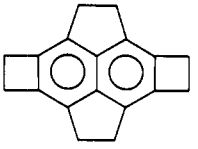

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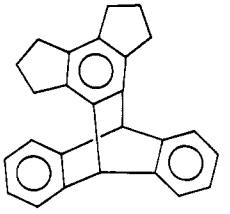
however, for the formation of tetracyclobutanaphthalene **1**. An earlier report on the the synthesis of hexaradialene by a similar route pointed out the absence of any detectable tricyclobutabenzene.[3] We have subsequently demonstrated that this molecule is quite stable when prepared under nonpyrolytic conditions.[4] Thus one might envision that a strategy similar to that used to prepare tricyclobutabenzene might lead to a successful synthesis of tetracyclobutanaphthalene. To test our Diels–Alder approach in the synthesis of a fully annelated naphthalene, we undertook the synthesis of the higher homologue, tetracyclopentanaphthalene (**8**).

The key step in our preparation of this molecule involves the cycloaddition of 3,4:5,6-dicyclopentabenzyne (**5**) to 1,1′-bicyclopentenyl (**6**), (Scheme I). All four of the required cyclopentene rings are preformed in the reacting partners. Considering the relief of strain involved in the cycloaddition and the resonance stabilization gained in the final oxidation step, the energetics of this approach appear quite favorable. A related Diels–Alder reaction has been employed in the preparation of octamethylnaphthalene.[5]

A suitable benzyne precursor appeared to be the amino acid **4** which could be obtained by hydrolysis of the corresponding amino nitrile. This amino nitrile has been reported as the product of a condensation between cyclopentylidenecyclopentanone and malononitrile.[6] The Diels–Alder addition of **5** and **6**, however, proceeded in only 11% yield. To probe the efficiency of the cycloaddition step, we decided to examine the reaction of both the diene and dienophile with partners of established reactivity. The attempted addition of **6** to benzyne was unsuccessful, and none of the expected adduct was obtained. Benzyne **5** was added to anthracene, and the triptycene adduct **9** was obtained in less than 6% yield. It appears that both **5** and **6** are poor partners in [4 + 2] cycloadditions of this type, and the low yield of **7** is understandable.



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The oxidation of **7** to **8** could be effected with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) in benzene. It seemed likely that **8** might form a charge-transfer complex with unreacted DDQ. This complex should be cleaved by treatment with hydrazine, but even on employment of this technique the oxidation yield was only 20%.

Tetracyclopentanaphthalene is a solid which melts with decomposition at 273–274 °C. The ultraviolet spectrum of this compound shows an absorption at 246 nm which is substantially less intense ($\epsilon$ 2240) than the corresponding absorption for compound **3** [240 nm ($\epsilon$ 47 500)] or octamethylnaphthalene [251 nm ($\epsilon$ 50 120)]. The proton NMR spectrum shows two triplets at 3.50 and 2.90 ppm and a quintet at 2.12 ppm. In a study of the NMR spectra of a series of methyl-substituted naphthalenes, it has been established that *peri*-methyl groups (1,8 or 4,5) are significantly deshielded.[7] On this basis we assign the lower field triplet to the $\alpha$-methylene groups. Examination of a model of the molecule indicates that its fairly rigid conformation imposes a serious nonbonded interaction between the methylene groups at peri positions. This

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