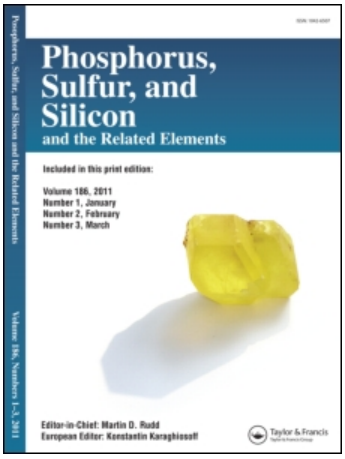

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MICROWAVE-CATALYZED REACTION OF NORBORNANE OXIDE WITH (CHLOROMETHYL) METHYL SULFIDE

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Microwave-catalyzed reaction of (chloromethyl) methyl sulfide with exo-norbornane oxide furnishes fourteen compounds. The probable mechanism of their formation and their mass spectral characterization are presented in this communication.

Keywords: Epoxide ring cleavage; free radical reactions; microwave catalysis

Oxiranes comprise an extremely versatile group of intermediates and as such have attracted considerable attention.[1] Because of their ready availability and exceptional reactivity, epoxides have found varied applications in synthetic organic chemistry. The oxirane ring can be opened under almost all conditions: electrophilic, nucleophilic, neutral, gas-phase, thermal, and free radical conditions (Figure 1a).[1a] The structures of the free radical species generated from the oxiranes and thiiranes have been discussed (Figure 1b).[2] An excellent review on the preparation and synthetic applications of the oxiranes has appeared.[1f] Recently, we investigated the free radical cleavage of styrene oxide with trifluoromethylthiocopper and dimethyl hydrogenphosphonate and reported the formation of products arising from the C—C and C—O bond fission.[3–6] However, their reaction with phosphorus compounds has found only a limited application, including their routine use in the Michaelis-Becker reaction.[7,8] Tri-coordinated pentavalent phosphorus compounds or in situ generated intermediates are known to react with oxiranes as well.[7,8]

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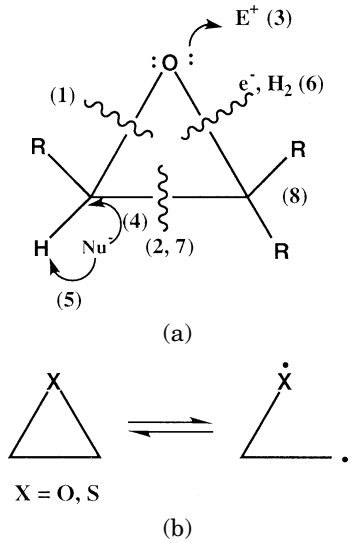

FIGURE 1 (a) Types of oxirane cleavages and reactions: (1, 2) Homolytic cleavages (free radical, photolytic, thermal), (3) Electrophilic attack on the ring oxygen, (4) Nucleophilic attack on the ring carbon, (5) Nucleophilic attack on the ring hydrogen, (6) Reactions with electrons and surface reactions, (7) Cycloadditions, and (8) Reactions of the substituent. (b) Structure of oxirane and thiirane and their diradical equivalents.

The in situ generated electrical energy from microwaves has been used to thermally catalyze chemical reactions. This type of energy transfer depends on the nature and properties of the reacting molecules.[9] Since the advent of commercial microwave cookers, the microwave thermal process is finding increasing and interesting applications in synthetic organic chemistry.[10] The popularity of the microwave-induced chemistry appears to rest primarily on its dramatic reduction of the reaction time and the possibility of carrying out reactions in solid phase.[11] Also, the use of the microwave technique results in a significant reduction of the hazardous laboratory waste.

Sulfenyl halides have been shown to react with norbornene.[12a] The reaction of norbornene with t-butylhypochlorite, a low-temperature free radical initiator, yields chloronortricyclane and 2-chloro-5-norbornene.[12b] It has been stated that the thiyl radicals add to norbornene via exclusive exo-attack on the double bond.[12c] However, the reaction of exo-norbornane oxide with Li in ethylenediamine gives predominantly exo-norborneol, accompanied by endo-norborneol, nortricyclanol, and 7-hydroxynorbornane.[12d] Samariumthiolate converts epoxides into β-hydroxy sulfides.[13a] Similar results were obtained when

epoxyalkanes were reacted with hydrogen sulfide in the presence of basic catalysts.[13b] But the treatment of α-halothianes with dimethylsulfide yields ω-haloketones and ω-sulfoniumcarbonyl salts.[13c] The above-cited results convincingly suggest that the bicyclo[2.2.1]heptene ring system is highly susceptible to skeletal rearrangements.

In continuation of our interest in the chemistry of the oxirane cleavage reactions[3–6] and with a view to examine whether this reaction can be applied to the decontamination and destruction of mustard, a blister agent, the microwave-catalyzed oxirane ring opening in the presence of (chloromethyl) methyl sulfide has been examined. This communication presents the probable mechanism of the formation of the various compounds formed during the reaction and their gas chromatographic-mass spectral (GC-MS) characterization.

RESULTS AND DISCUSSION

Recently we have shown that the oxirane ring can be cleaved with dimethyl hydrogen phosphonate[4,5] and with trifluoromethylthiocoper.[3,6] It was considered interesting to investigate whether inexpensive oxiranes, such as ethylene oxide, can be used in the decontamination and destruction of mustard, [bis-(2-chloroethyl)sulfide], a known blister agent.[14] This expectation was supported by the fact that the oxiranes react with almost all kinds of reagents.[1] Accordingly, the reaction of exo-norbornane oxide (**1**) with (chloromethyl) methyl sulfide (**2**) was examined and found to furnish 14 compounds (cf. Figure 2). Three compounds, namely bis-(chloromethyl)sulfide (**3**), bis-(methylthio)methane (**4**), and bis-(methylthiomethyl))ether (**5**), are formed from the free radical reaction of (chloromethyl) methyl sulfide (**2**) itself. The probable mechanism of their formation is described in Figure 3. Compound **2** can undergo free radical fission to give chloromethyl and methylthiyl radicals ('a'). It can form chlorine

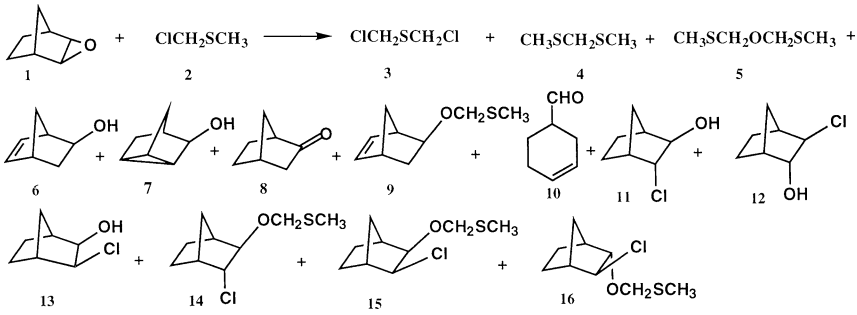

FIGURE 2 Structures of compounds derived from norbornene oxide.

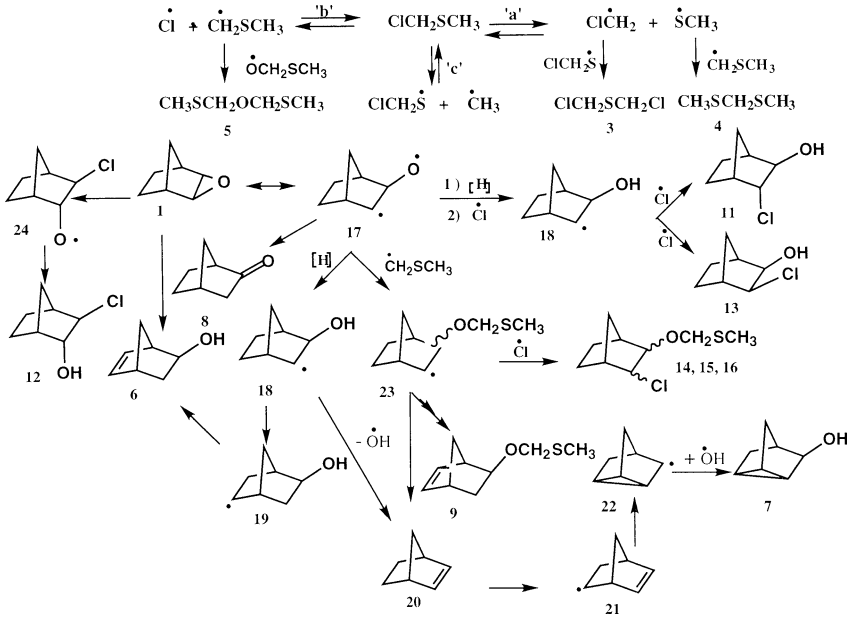

FIGURE 3 Probable mechanism of formation of compounds from norbornene oxide.

and (methylthio)methyl radicals ('b'). It can also undergo cleavage to give (chloromethylthio) and methyl radicals ('c'). The joining of the (chloromethylthiyl) radical with (chloromethyl) radical thus formed leads to bis-(chloromethyl)sulfide (**3**). While bis-(methylthio)methane (**4**) arises from the coupling of the methylthio and (methylthiomethyl) radicals, bis-(methylthiomethyl) ether (**5**) originates from the reaction of (methylthiomethyl) and [(methylthio)methoxy] radicals, the latter arising from (methylthiomethoxy)norbornyl radical (**23**), which itself is generated from the reaction of **17** with methylthiomethyl radical (cf. Figure 3). The diradical structures similar to **17** have been proposed previously.[2] There is nothing strange about the presence of compounds **6**, **7**, **8**, and **10** in the reaction product formed from the substrate. They are artifacts formed either during the course of the reaction or generated during the chromatographic analysis.[15]

Figure 3 attempts to rationalize the formation of nortricyclanol (**7**) via intermediates **18**, **20**, **21**, and **22**. It has been suggested that intermediates **21** and **22** represent equivalent structures.[16] The passage from norbornene (**20**) to dehydronorbornyl radical (**21**) to nortricyclyl radical (**22**) has been previously suggested by J. D. Roberts and coworkers.[16a] In fact, **20** has been transformed into **7** by H. C. Brown and coworkers.[12d]

Compound **9** is formed via intermediates **17** and **23** through a sequence of reactions. It now remains to explain the presence of two sets of isomers, each set containing three isomers. The first set is composed of three chloronorborneols; **11**, **12**, and **13**. Their genesis is described in Figures 3 and 4. If the attack on the substrate by the chlorine radical occurs from the top, then that would result in intermediate **24**, which then goes on to abstract hydrogen to form **12**. The formation of its isomer, namely **11**, can be explained either by invoking the diradical structure of the epoxide, namely **17**, or by assuming the attack to occur from below to form intermediate**25**, which furnishes **11** after the abstraction of hydrogen (Figure 4). However, the intermediate **26** yields **13** after the abstraction of hydrogen. On the other hand, the origin of the second set of three isomers, namely **14**, **15**, and **16**, can be ascribed to the reaction of the intermediates **24**, **25**, and **26** with the methylthiomethyl (CH_3SCH_2) radical, the formation of which is explained in Figure 3.

When compound **1** is treated with pyridinium chloride, it gives 4 chloro-norborneols and nortricyclanol.[17a,17b] When the substrate is reacted with aqueous $HClO_4$, it yields four dihydroxynorbornanes and 7-hydroxy-2-norbornene, while on pyrolysis over neutral alumina at 270°C it furnishes norcamphor (**8**), nortricyclanol (**7**), 3-cyclohexene aldehyde (**10**), nortricyclenone, and three additional compounds.[17c] In the presence of peracids, **1** gives six dihdroxynorbornanes.[17c] In the light of the above discussion, the formation of 14 compounds from **1** on treatment with **2** appears to be reasonable.

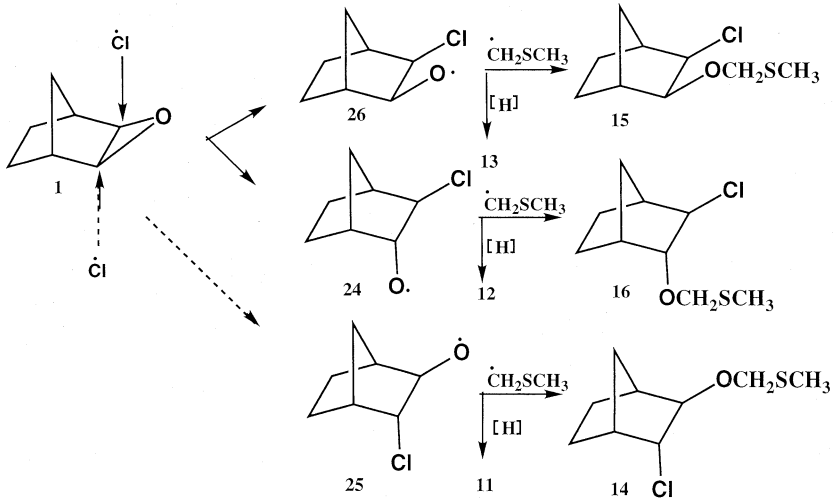

FIGURE 4 Formation of compounds 11 to 13 and 14 to 16.

TABLE I Compounds Formed from Chlorolemethyl Methyl Sulfide and Epoxy Norbornane

1. Norbornene oxide[a] (**1**, r.t. = 3.38 min, 64.0%); $M^+ = 110$; 95 ($M - CH_3$); 91 (C_7H_7); 82 (C_7H_8); 81 (C_7H_7, 100%); 79 (C_6H_7); 77 (C_6H_5); 67 (C_5H_7); 66 (C_5H_6); 65 (C_5H_5); 54 (C_4H_6); 53 (C_4H_5); and 51 (C_4H_3).
2. **C**hloroemethyl methyl sulfide (**2**, r.t. = 2.04 min, 17.9%); $M^+ = 96$ (100%, ^{37}Cl:98); 81 ($M - CH_3$); 61 ($M - Cl$, 98%); 59 (C_2H_3S); 49 (CH_2Cl); 47 (SCH_3); and 46 (SCH_2).
3. Bis-(Chloromethyl) sulfide (**3**, r.t. = 2. 49 min, 1.3%): $M^+ = 130$ (^{37}Cl peak seen); 115 ($M - CH_3$); 95 ($M - Cl$, 100%); 83 ($CH_3S(H)Cl$); 59 (C_2H_3S); 47 (CH_3S); and 45 (CSH).
4. Bis-(Methylthio)methane (**4**, r.t. = 3. 08 min, 3.3%): $M^+ = 108$ (100%); 93 ($M - CH_3$); 78 (93-CH_3 or CH_2S_2); 61 (CH_3SCH_2); 59 (C_2H_3S); 47 (SCH_3); and 46 (SCH_2).
5. Bis-(Methylthiomethyl) ether (**5**, r.t. = 6. 0 min, 0.6%): $M^+ = 138$ (100%); 91 ($M - SCH_3$); 76 (91-CH_3); 59 (C_2H_3S); and 47 (SCH_3).
6. 5-Norbornene-2-ol[22] (**6**, r.t. = 3. 24 min, 2.1%): $M^+ = 110$; 109 ($M - H$); 95 ($M - CH_3$); 93 ($M - OH$ or C_7H_9); 91 (C_7H_7); 82 ($M - C_2H_4$); 81 ($M - C_2H_5$); 79 (C_6H_7, 100%); 77 (C_6H_5); 67 (C_5H_7); 65 (C_5H_5); 55 (C_4H_7); 53 (C_4H_5); and 51 (C_4H_3).
7. Nortricyclanol[15e,23] (**7**, r.t. = 3. 54 min, 1.9%): $M^+ = 110$; 109 ($M - H$); 95 ($M - CH_3$); 91 (C_7H_7); 81 (C_7H_7); 79 (C_6H_7, 97%); 77 (C_6H_5); 69 (C_5H_9); 67 (C_5H_7); 66 (C_5H_6, 100%); 65 (C_5H_5); 57 (C_4H_9); 55 (C_4H_7); 53 (C_4H_5); and 51 (C_4H_3). (Base peak @ m/e = 79, NIST # 2290).
8. Norbornanone[15a] (**8**, r.t. = 3. 59 min, 3.6%): $M^+ = 110$; 95 ($M - CH_3$); 92 (C_7H_8); 81 (C_7H_7); 79 (C_6H_7); 77 (C_6H_5); 67 (C_5H_7, 97%); 66 (C_5H_6, 100%); 54 (C_4H_6); 53 (C_4H_5); and 51 (C_4H_3). (base peak @ 67 but m/e = 66 (98%)).
9. 2-(Methylthiomethoxy)-5-norbornene (**9**, r.t. = 6. 16 min, 0.6%): $M^+ = 170$; 155 ($M - CH_3$); 140 ($M - OCH_2$); 123 ($M - SCH_3$); 109 ($M - CH_2SCH_3$); 93 (C_7H_9, 100%); 91 (C_7H_7, 99%); 79 (C_6H_7); 77 (C_6H_5); 67 (C_5H_7); 65 (C_5H_5); 61 (CH_2SCH_3); 55 (C_4H_7); and 51 (C_4H_3).
10. 3-Cyclohexene aldehyde[15a] (**10**, r.t. = 6.0 min, 3.4%): $M^+ = 110$; 95 ($M - CH_3$); 92 ($M - H_2O$); 91 (C_7H_7); 81 ($M - CHO$, 100%); 79 (C_6H_7, 98%); 77 (C_6H_5); 57 (C_4H_9); 55 (C_4H_7); and 51 (C_4H_3). (NIST #2305).
11. endo-2-Chloro-exo-3-norbornaneol (**11**, r.t. = 5. 54 min, 0.43%): $M^+ = 146$; 128 ($M - H_2O$); 110 ($M - HCl$); 97 ($M - CH_2Cl$); 93 (C_7H_9); 91 (C_7H_7); 81 (C_6H_9); 79 (C_6H_7); 77 (C_6H_5); 67 (C_5H_7, 100%); 65 (C_5H_5); 57 (C_4H_9); 55 (C_4H_7); and 51 (C_4H_3).
12. exo-3-Chloro-endo-2-norbornaneol (**12**, r.t. = 6. 01 min, 0.3%): $M^+ = 146$; 128 ($M - H_2O$); 110 ($M - HCl$); 97 ($M - CH_2Cl$); 93 (C_7H_9, 98%); 91 (C_7H_7); 81 (C_6H_9); 79 (C_6H_7, 100%); 77 (C_6H_5); 69 (C_5H_9); 67 (C_5H_7); 65 (C_5H_5); 57 (C_4H_9); 55 (C_4H_7); 53 (C_4H_5); and 51 (C_4H_3).
13. exo-2-Chloro-exo-3-norbornaneol (**13**, r.t. = 6.29 min, 0.5%): $M^+ = 146$ (not seen); 128 ($M - H_2O$); 110 ($M - HCl$); 97 ($M - CH_2Cl$); 95 (110-CH_3); 92 (110-H_2O); 91 (C_7H_7); 81 (C_6H_9); 79 (C_6H_7, 100%); 77 (C_6H_5); 67 (C_5H_7); 66 (C_5H_6); 57 (C_4H_9); 55 (C_4H_7); 53 (C_4H_5); and 51 (C_4H_3).
14. endo-2-Chloro-exo-3-(methylthiomethoxy) norbornane (**14**, r.t. = 9.09 min, 0.1%): $M^+ = 206$; 170 ($M - HCl$); 159 ($M - SCH_3$); 142 (170-C_2H_4); 127 (C_7H_8Cl); 110 ($M - Cl$-CH_2SCH_3); 94 (C_7H_{10}); 81 (C_6H_9); 79 (C_6H_7); 77 (C_6H_5); 67 (C_5H_7); 61 (CH_2SCH_3, 100%); and 53 (C_4H_5).
15. exo- 2-Chloro-exo-3-(methylthiomethoxy) norbornane (**15**, r.t. = 9.08 min, 0.1%): $M^+ = 206$; 170 ($M - HCl$); 159 ($M - SCH_3$); 142 (170-C_2H_4); 127 (C_7H_8Cl); 110 ($M - Cl$-CH_2SCH_3); 94 (C_7H_{10}); 81 (C_6H_9); 79 (C_6H_7); 77 (C_6H_5); 67 (C_5H_7); 61 (CH_2SCH_3, 100%); and 53 (C_4H_5).
16. exo-2-Chloro-endo-3-(methylthiomethoxyl) norbornane (**16**, r.t. = 9.26 min, 0.2%): $M^+ = 206$; 170 ($M - HCl$); 159 ($M - SCH_3$); 142 (170-C_2H_4); 129 ($M - OCH_2SCH_3$); 127 (C_7H_8Cl); 110 ($M - Cl$-CH_2SCH_3); 94 (C_7H_{10}); 81 (C_6H_9); 79 (C_6H_7); 77 (C_6H_5); 67 (C_5H_7); 61 (CH_2SCH_3, 100%); and 53 (C_4H_5).

It is conceivable that many of the compounds, may have been formed from the free-radical–catalyzed reactions of norbornene itself (**20**) (Figure 3). Indeed, it has been reported that **20** gives six difluoronorbornanes and three dichloronorbornanes and chloronortricyclane when reacted with XeF_2[18a] and chlorine radicals,[18b] respectively. Although the free radical reactions of **20** generally occur from the nonhindered side of the molecule, products formed from both exo and endo attacks have been identified.[19] It seems that with smaller substituents both cis and trans additions are observed, while with bulky attachments steric factors come into play and favor the attack from the less-hindered exo-face.[19c] These observations have led to the generalization that radical attack on the norbornene system occurs "exclusively from the exo-side but propagating species transfer from the endo as well as from the exo-face."[19b]

Figure 4 endeavors to rationalize the origin of two sets of isomers, each set being composed of three isomers. The formation of the three intermediates, **24**, **25**, and **26**, has already been explained. These three intermediates react with (methylthiomethoxy) radical and furnish the three components in question. The concept of thiyl radicals derived from sulfenyl halides was suggested by N. Kharasch.[20] In view of the known propensity of the bicyclo[2.21]heptenyl system to undergo facile skeletal rearrangements,[21] the free radical addition reactions to the norbornenyl system appear to be nonspecific in that both cis and trans additions appear to be the norm rather than the exception.

The mass spectral breakdown of the norbornyl derivatives has been the subject of detailed investigations.[21] The mass spectrum of nortircyclanol has been described.[15e–f,21b] Table I describes the mass spectral fragmentation of the compounds cited in the narrative. The mass spectral breakdown of bis-(chloromethyl)sulfide (**3**), bis-(methylthio)methane (**4**) and bis-(methylthiomethyl))ether (**5**) is straightforward. The mass spectral fission of endo-2-chloro-exo-3-norborneol (**11**) has been published.[17b]

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