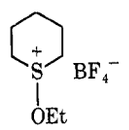
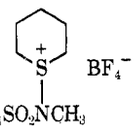
sulfur dioxide (which is acidic) readily reduced sulfoxides to sulfides.[12] Compared to the free sulfoxide, the protonated sulfoxide has a more electrophilic sulfur and a better leaving group on sulfur ($^-OH$ *vs.* $O^{2-}$). Similar advantages should also be available in O-alkylated sulfoxides. It was found that alkoxysulfonium salts were rapidly and quantitatively reduced to sulfides by saturated aqueous solutions of either sodium hydrogen sulfite or sodium sulfite. The reactions of alkoxysulfonium salts are much faster than the direct reductions of sulfoxides by hydrogen sulfite; *e.g.*, the reduction of **1** is complete



**1**



**2**

in a few minutes at room temperature, whereas reduction of thiane 1-oxide is only 27% complete after 135 min. Other leaving groups on sulfur also facilitate the reaction. The aminosulfonium salt **2**[13] was quickly and cleanly converted to thiane by sulfite solutions.

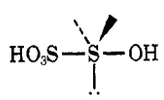
The relative rates of reduction of a series of sulfoxides under standardized conditions were examined in a semiquantitative fashion; partial data which reflect the trends found are summarized in Table I. These

TABLE I
REDUCTION BY SATURATED AQUEOUS SODIUM HYDROGEN SULFITE

| Sulfoxide | % Reduction after 60 min |
|---|---|
| Diethyl sulfoxide | 45 |
| Isopropyl methyl sulfoxide | 8 |
| Thietane 1-oxide | 18 |
| Thiolane 1-oxide | 100[a] |
| Thiane 1-oxide | 16 |
| Thiepane 1-oxide | 52 |

[a] Reduction complete at 10 min.

data appear to indicate that the reduction proceeds *via* a pathway involving substitution at the sulfoxide sulfur, which occurs in, or prior to, the rate-determining step. Branching at the carbon $\alpha$ to the sulfoxide has a retarding effect on the reaction. In the cyclic sulfoxides, the rate reaches a maximum in the case of the five-membered ring. In reactions which involve rehybridization from $sp^3$ to $sp^2$ of a carbon reaction center, five-membered rings react faster than four- or six-membered ones, and branching is known to retard rates.[14] Whether **3** represents a transition state



**3**

or an energetically contiguous intermediate, the response to substitution pattern and ring size should follow along the same general trends as observed for SN2 reactions at carbon. It appears to be typical of the thiolane ring system to display increased reactivity. In the case of thermally induced pyramidal inversion of cyclic sulfonium salts, the five-membered rings were found to invert slightly faster than a six-membered one.[15] In the hydrogen chloride catalyzed stereomutation of sulfoxides, the thiolane 1-oxides react some 300 times faster than thiane 1-oxides.[15] In periodate oxidations of sulfides to sulfoxides, thiolane reacts faster than either thietane or thiane.[16]

For preparative purposes, especially when stereoselectivity is not a consideration, the bisulfite reductions are conveniently run on a steam bath. A cosolvent such as dioxane or methanol may be added in the case of poorly soluble sulfoxides.

(12) Sulfurdioxide in ethanol or chloroform failed to reduce sulfoxides.
(13) For method of preparation see C. R. Johnson, J. J. Rigau, M. Haake, D. McCants, Jr., J. E. Keiser, and A. Gertsema, *Tetrahedron Lett.*, 3719 (1968).
(14) E. L. Eliel, "Stereochemistry of Carbon Compounds," McGraw-Hill, New York, N. Y., 1962, p 268.

### Experimental Section

**Reduction of *n*-Butyl Sulfoxide.**—*n*-Butyl sulfoxide (4 g) was added to a solution of 16 g of sodium hydrogen sulfite in 40 ml of water. The mixture was heated on a steam bath with stirring for 40 hr. The mixture was cooled and extracted several times with chloroform. Vpc analysis showed the extract to contain no sulfoxide. Distillation provided 2.5 g (70 %) of pure *n*-butyl sulfide.

***trans*-2-Methylthiolane 1-Oxide.**—Mixtures[10] enriched in the trans sulfoxide were treated briefly (10 to 20 min) with aqueous sodium hydrogen sulfite at room temperature. The reactions were followed by vpc analysis. The 2-methylthiolane was extracted with pentane. Pure *trans*-2-methylthiolane 1-oxide was obtained by extraction with chloroform.

Reaction of *trans*-2-methylthiolane 1-oxide with trimethyloxonium fluoroborate in methylene chloride gave *trans*-2-methyl-1-methoxythioniacyclopentane fluoroborate, mp 82–83°.

*Anal.* Calcd for $C_6H_{13}BF_4OS$: C, 32.75; H, 5.95. Found: C, 33.01; H, 6.24.

***cis*-2-Methylthiolane 1-Oxide.**—Hydrolysis of the above salt with aqueous sodium hydroxide gave pure cis sulfoxide, which was converted to *cis*-2-methyl-1-methoxythioiacyclopentane fluoroborate, mp 53–54°.

*Anal.* Calcd for $C_6H_{13}BF_4OS$: C, 32.25; H, 5.95. Found: C, 32.63; H, 5.96.

Basic hydrolysis of this salt gave 100% of the trans sulfoxide.

**1-Ethoxythioniacyclohexane fluoroborate (2)** was prepared by reaction of thiane 1-oxide with triethyloxonium fluoroborate in methylene chloride. The very hygroscopic salt had mp 35–37°.

*Anal.* Calcd for $C_7H_{15}BF_4OS$: C, 35.92; H, 6.46. Found: C, 36.20; H, 6.59.

**Registry No.**—**2**, 33143-36-1; sodium hydrogen sulfite, 7631-90-5; *n*-butyl sulfoxide, 2168-93-6; *trans*-2-methylthiolane 1-oxide, 25859-45-4; *trans*-2-methyl-1-methoxythioniacyclopentane fluoroborate, 33213-38-6; *cis*-2-methylthiolane 1-oxide, 25859-44-3; *cis*-2-methyl-1-methoxythioniacyclopentane fluoroborate, 33143-40-7.

(15) A. Garbesi, N. Corsi, and A. Fava, *Helv. Chim. Acta*, 1499 (1970).
(16) C. R. Johnson and P. E. Rogers, unpublished results.

## Cyclization of Dimethyl-1,6-octadienes

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*Received August 9, 1971*

In this paper, we describe the cyclization of 5,7-dimethyl-1,6-octadiene (**1**) and 3,7-dimethyl-1,6-octa-

diene (2) with formic acid in the presence of $BF_3$ etherate or a strong mineral acid as a catalyst.

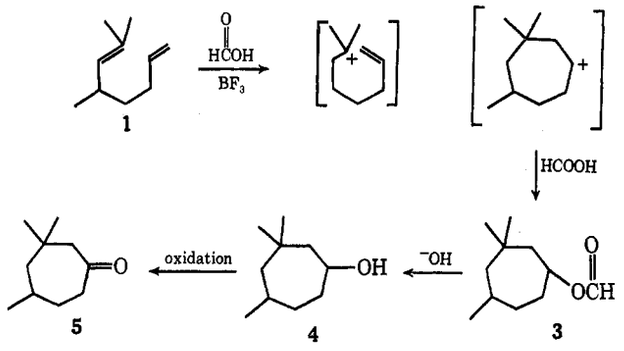
Diene **1**, when treated with excess of formic acid in the presence of a catalytic amount of $BF_3$ or mineral acid at 50° for 6 hr gave a mixture of 3,3,5-trimethylcycloheptanyl formates **3a,b** in about 50% conversion (two peaks by glc[1] analysis). The formates **3a,b** were hydrolyzed with aqueous methanolic sodium hydroxide to yield a mixture of alcohols **4a,b** (two peaks by glc[1]) which were oxidized with chromic acid at 30° to give 3,3,5-trimethylcycloheptanone (**5**) (single peak by glc[1]). The semicarbazone of **5** gave mp 196–198° (lit.[2] 196–197°).

Diene **2** when treated with formic acid in the presence of a catalytic amount of $BF_3$ etherate at 50–60° for 4 hr, gave in 45% conversion a mixture of formates **6** and **7** which appeared as a single major peak on glc.[1] Hydrolysis of the mixture with 25% methanolic sodium hydroxide gave the corresponding alcohols **8** and **9**, which were shown to be in 4:1 ratio respectively by glc (10% Apeizon column, 20 ft × 1/4 in.).

The mixture of alcohols **8** and **9** was oxidized with chromic acid at 30° to give the corresponding ketones **10** and **11**, which were separated by preparative glc (10% Apeizon column). The structure of the major component, 3,3-dimethylcyclohexyl methyl ketone (**10**) was supported by the spectral data (see Experimental Section). The nmr spectrum of **11** was superimposable with that of tetrahydroeucarvone[3] prepared by the hydrogenation of eucarvone. The DNP derivative had mp 135–137° (lit.[4] 137–138°).

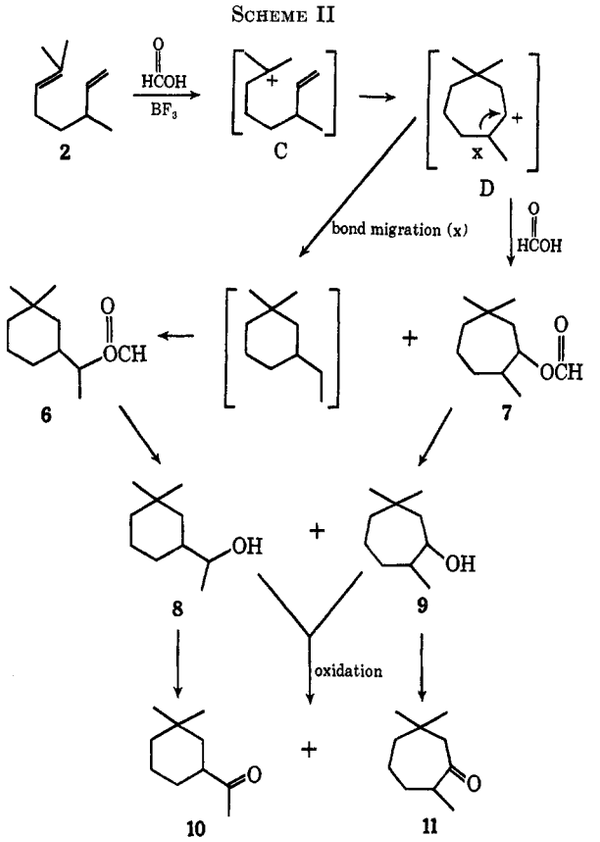
**Mechanism.**—The products obtained in treating 5,7-dimethyl-1,6-octadiene (**1**) and 3,7-dimethyl-1,6-octadiene (**2**) with formic acid and $BF_3$ etherate could be accounted for by the mechanism shown in Schemes I and II, respectively.

SCHEME I




In connection with this work, it was of interest to see if the solvolysis of tetrahydroeucarvanyl tosylate **12** would yield the rearranged product **6**. Tetrahydroeucarvanol, which was obtained by the reduction of tetrahydroeucarvone with lithium aluminum hydride, on treatment with *p*-toluenesulfonyl chloride and pyridine gave the corresponding tosylate **12**, which when treated with sodium formate and formic acid under nitrogen atmosphere at 75° for 6 hr gave a mixture of formates along with a mixture of olefins. The formates were hydrolyzed with methanolic sodium hydroxide and then oxidized with chromic acid to give a mixture of ketones which were separated by preparative vpc and were identified as **10** and **11**.

SCHEME II




### Experimental Section

All the nmr spectra were run on a Varian HA-100 spectrometer. All chemical shifts are reported in parts per million ($\delta$) relative to TMS. The C and H analyses were run by Schwarzkopf Microanalytical Laboratory.

**Cyclization of 5,7-Dimethyl-1,6-octadiene** (**1**).—In a three-necked flask fitted with a condenser, stirrer, thermometer, and dropping funnel 26 g of $BF_3$ etherate was added slowly at room temperature to a mixture of 211 g of formic acid (90%) and 290 g of 5,7-dimethyl-1,6-octadiene. The mixture was stirred for 6 hr at 50–60°. After this period, 150 g of sodium acetate was added and the mixture was stirred for 10 min. After separating the oil layer, the acid layer was diluted with an equal volume of water and extracted with benzene. The combined organic layers were washed once with water and the solvent was removed *in vacuo*. After distilling the hydrocarbons the product was fractionated to give 1749 g (45% conversion) of the pure formates (**3a,b**): bp 80° (5 mm); $n^{20}D$ 1.4490; ir (film) 5.78 and 8.5 $\mu$; nmr 0.92, 1.01 [6 H, 2 singlets, $-C(CH_3)_2$], 0.88 (3 H, doublet, $CHCH_3$), 1.2–2.1 (8 H, multiplet, $CH_2$), 4.81 [1 H, multiplet, HCO(C=O)H], 7.9 [1 H, O(C=O)H].

*Anal.* Calcd for $C_{11}H_{20}O_2$: C, 71.75; H, 10.89. Found: C, 71.55; H, 10.91.

**3,3,5-Trimethylcycloheptanone** (**5**).—To 55.0 g of alcohols (**4a,b**) obtained by hydrolysis of the corresponding formates with methanolic sodium hydroxide was added a solution of 43.2 g of chromic acid, 43.2 g of glacial acetic acid, and 43.2 g of water over a period of 1 hr, maintaining the temperature of 25–30°. The reaction mixture was further stirred at 30° for 3 hr. After

(1) Glc 5% SE-30 column, 20 ft × 1/4 in. at 150°.
(2) G. Buchi and E. M. Burgess, *J. Amer. Chem. Soc.*, **82**, 4333 (1960).
(3) E. J. Corey and H. J. Burke, *ibid.*, **78**, 174 (1956).
(4) J. R. B. Campbell, A. M. Islam, and R. A. Raphael, *J. Chem. Soc.*, 4097 (1956).

this period, 60 ml of water was added and the mixture was steam distilled to give 42.1 g of the crude product, which was fractionated to give 36 g of pure ketone **5** (65% yield), $n^{20}D$ 1.4578, semicarbazone mp 196–198° (lit.[4] 196–197°). The infrared spectrum was superimposable on the spectrum of 3,3,5-trimethylcycloheptanone kindly supplied by Professor Buchi. The mass spectrum showed a parent peak with *m/e* 154, and fragmentation ions with *m/e* 139, 126, 83, 69, 55, 41.

**Cyclization of 3,7-Dimethyl-1,6-octadiene (2).**—In a three-necked flask fitted with stirrer, thermometer, and reflux condenser was added 44 g of $BF_3$ etherate to a stirred mixture of 422 g of 3,7-dimethyl-1,6-octadiene and 307 g of formic acid (90%) over a period of 10 min at room temperature (slightly exothermic). The mixture was then heated to 50–60° and stirred at this temperature for 4 hr. Heating was discontinued and the mixture was stirred for another 30 min. An equal volume of water was added and the oil layer was separated. The water layer was extracted twice with benzene. The combined organic layer was washed neutral with sodium bicarbonate solution, and benzene was removed *in vacuo*. After distilling off hydrocarbons the product was fractionated to give 270 g of the formates **6** and **7** (50% conversion). The mixture of formates (**6**, **7**) showed a single peak by glc analysis (20 ft ×, 1/4 in., SE-30, 5%, packed column). The infrared spectrum (film) showed absorption bands at 5.78 and 8.5 μ. The mass spectrum exhibited a peak at *m/e* 138 (M − 46).

*Anal.* Calcd for $C_{11}H_{20}O_2$: C, 71.75; H, 10.89. Found: C, 71.50; H, 11.04.

**Hydrolysis of Formates 6 and 7 to Alcohols 8 and 9.**—The mixture of formates (11.0 g) was refluxed with 25.0 g of sodium hydroxide and 75 ml of 50% aqueous methanol for 2 hr. After recovering methanol, the crude mixture was acidified with 2% acetic acid and extracted with ether. The ether extract was washed once with sodium carbonate solution and once with water and then dried ($MgSO_4$). The solvent was removed *in vacuo* and the residue was distilled to give a mixture of alcohols (**8**, **9**) in 75% yield. Glc analysis indicated two components in an approximate ratio of 4:1. The major peak, isolated by preparative vpc (10% Apeizon, 20 ft × 1/4 in.), was shown to be alcohol **8**: ir (film) hydroxyl band at 2.93 μ; nmr ($CDCl_3$) 0.89, 0.92 [6 H, 2 singlets, $C(CH_3)_2$], 1.08 (3 H, doublet, $CHCH_3$), 1.55 (1 H, broad singlet, for OH), 1.12–1.86 (8 H, multiplet, $-CH_2-$). The mass spectrum showed a parent peak at *m/e* 156.

*Anal.* Calcd for $C_{10}H_{20}O$: C, 76.95; H, 12.81. Found: C, 76.82; H, 12.77.

**Oxidation of Alcohols 8 and 9 to Ketones 10 and 11.**—To 52.0 g of mixture of alcohols (**8**, **9**) was added a solution of 40.0 g of chromic acid, 40.0 g of acetic acid, and 40.0 g of water at 25–30° over a period of 1 hr. The reaction mixture was stirred further for 3 hr at 30°. The mixture was then diluted with 60 ml of water and steam distilled to give 43.0 g of the crude product which was distilled to give a mixture of ketones (**10**, **11**), bp 89° (14 mm). Glc analysis using an Apeizon column (10%) 20 ft × 1/4 in. showed two peaks in a ratio of 4:1, respectively. The infrared spectrum (film) of the major compound, obtained by preparative vpc, exhibited a carbonyl band (5.86 μ); nmr ($CCl_4$) 0.92, 0.95 [6 H, two singlets, $C(CH_3)_2$], 1.12–1.86 (8 H, multiplet, $-CH_2-$), 2.02 [3 H, singlet, $(C{=}O)CH_3$], 2.17–2.55 (1 H, multiplet, $CH(C{=}O)CH_3$]. The mass spectrum showed a peak at *m/e* 154.

*Anal.* Calcd for $C_{10}H_{18}O$: C, 78.00; H, 11.78. Found: C, 77.82; H, 12.01.

The 2,4-dinitrophenylhydrazone had mp 102–103°.

The infrared spectrum (film) of **11**, the minor component isolated by preparative vpc, exhibited a carbonyl band at 5.84 μ. The nmr spectrum ($CDCl_3$) indicated signals at 0.91, 0.96 [6 H, two singlets, $C(CH_3)_2$], 1.02 (3 H, doublet $CHCH_3$), 2.28 (2 H, AB quartet, $J_{AB}$ = 11.5 Hz, =OCHCH), 2.28 (1 H, multiplet, $CHCH_3$), 1.2–1.7 (6 H, multiplet, $-CH_2-$). The 2,4-dinitrophenylhydrazone had mp 136–139° (lit.[3] 137–138°).

**Registry No.**—**1**, 33515-77-4; **2**, 33515-78-5; *cis*-**3a**, 33511-45-4; *trans*-**3b**, 33511-46-5; **6**, 25225-08-5; **7**, 33515-80-9; **8**, 25225-09-6; **9**, 33515-82-1; **10**, 25304-14-7; **10** 2,4-DNPH, 25412-05-9; **11**, 4436-59-3.

**Acknowledgment.**—The authors thank Professor G. Stork for helpful discussions with regard to the mechanism of the reaction.

## Preparation of Difluoramino-Substituted Vinyl *N*-Fluorimines[1]

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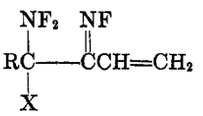
*Received November 5, 1970*

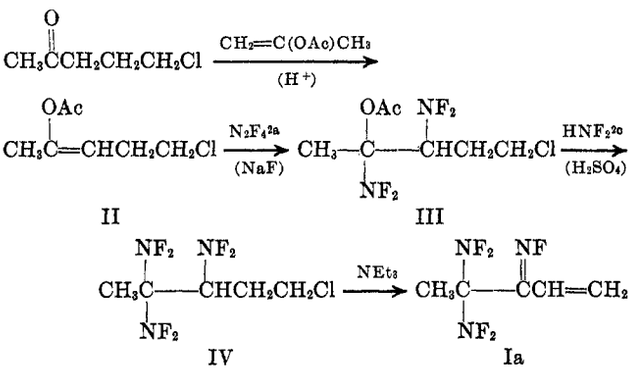
As part of our synthetic studies on poly(difluoramino) compounds,[2] materials polymerizable by way of the vinyl fluorimine function were prepared. The synthesis and characterization of the difluoramino-substituted vinyl fluorimines Ia–e are described here.[3]



Ia, R = $CH_3$; X = $NF_2$
b, R = $CH_3$; X = Cl
c, R = $C_6H_5$; X = $NF_2$
d, R = $C_6H_5$; X = Cl
e, R = $C_6H_5$; X = $-OP(O)(OC_2H_5)_2$

The sequence of reactions by which Ia was prepared from 5-chloro-2-pentanone is shown in Scheme I. The

SCHEME I



2-acetoxy-5-chloro-1-pentene accompanying the mixture of *cis*- and *trans*-2-acetoxy-5-chloro-2-pentene (II) produced in the first step could be converted selectively to 5-chloro-2-pentanone and acetic anhydride with an acid catalyst; distillation then removed these contaminants.

The cis and trans isomers of II were identified by proton nmr on the basis of relative shifts of vinyl and acetoxy methyl protons compared with data from the literature for other enol acetate isomers.[4]

The low yields encountered in the conversion of III to IV are undoubtedly due to fragmentation reactions

(1) This research was supported by the Advanced Research Projects Agency under U. S. Army Missile Command, Redstone Arsenal, Ala., Contract DA-01-021-11909.

(2) (a) R. C. Petry and J. P. Freeman, *J. Org. Chem.*, **32**, 4034 (1967); (b) W. H. Graham and J. P. Freeman, *ibid.*, **34**, 2589 (1969); (c) J. P. Freeman, R. C. Petry, and T. E. Stevens, *J. Amer. Chem. Soc.*, **91**, 4778 (1969); (d) T. E. Stevens, *J. Org. Chem.*, **34**, 2451 (1969).

(3) The polymerization studies are unpublished results of Dr. Mart Baldwin. In summary, these vinyl fluorimines could not be homopolymerized using AIBN initiator but Va, Vb, and Vd copolymerized with methyl methacrylate and with styrene. A 1:5 Ia–MMA comonomer mixture formed a 1:8 copolymer and a 3:1 Vb–styrene comonomer mixture gave a 1:1 copolymer. Vd copolymerized sluggishly with methyl methacrylate.

(4) H. O. House and V. Kramer, *J. Org. Chem.*, **28**, 3362 (1963).