Reaction of (I) with Benzoyl Chloride. A sample of 5.3 g carefully dried and ground copper acetylenide (I) was stirred at 60°C in an argon stream with 5.2 g Et_3N and 3.8 g benzoyl chloride in 40 ml dry benzene. After 2 h, 10 ml pyridine was added and the mixture was heated for an additional 5 h at 78°C. Then, the mixture was filtered, washed with dilute hydrochloric acid obtained by mixing one part conc. HCl with five parts water, and dried over $MgSO_4$. After removal of the solvent, the residue was recrystallized from methanol and subjected to chromatography on a column packed with alumina (grade II activity). The column was eluted with chloroform to yield: (II) as light brown crystals, mp 86-87°C, which are readily soluble in chloroform but less readily in ethanol and hexane. Found: C 68.43; H 4.41; N 4.54%. $C_{16}H_{11}NO_4$. Calculated: C 68.33; H 3.94; N 4.97%. PMR spectrum (δ, ppm): 7.50-7.15 m (Ph), 6.61 d (CHCO), 5.82 d (OCH), $^3J = 3.5$ Hz.

Ester (III), mp 141-142°C. Found: C 62.66; H 4.09; N 6.38%. $C_{13}H_9NO_4$. Calculated: C 62.34; H 3.92; N 6.06%.

Product (IV), mp 138-139°C as a white powder soluble in chloroform: Found: C 61.11; H 4.25; N 7.58%. $C_{18}H_{12}N_2O_6$. Calculated: C 61.36; H 3.73; N 7.96%. PMR spectrum (δ, ppm): 6.92 m ($C_6H_4NO_2$), 4.76 s (CH_2O).

The yields of (II), (III), and (IV) were 52%, 20%, and 28%, respectively.

CONCLUSIONS

The reaction of copper p-nitrophenoxypropynylide with benzoyl chloride proceeds with the formation of 1-p-nitrophenoxy-3-benzoylpropadiene, p-nitrophenyl benzoate, and 1,6-bis(p-nitrophenoxy)-2,4-hexadiyne. p-Nitrophenyl benzoate may be obtained as a result of the thermal fragmentation of 1-p-nitro-3-benzoylpropadiene.

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REDUCTION OF SEVERAL THIOLENE 1,1-DIOXIDES BY LITHIUM IN LIQUID AMMONIA

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In the present communication, the reduction of three simple thiolene 1,1-dioxides is examined in order to elucidate the basic features of this reaction.

The treatment of butadiene derivative (I) with ~5 equiv. lithium in NH_3 at −65°C leads to a high yield of a mixture of sulfinates (II) characterized as benzylsulfones (III). The PMR spectra of (III) consists of a double set of $\underline{CH_3}CH$ and $\underline{CH_2}CH$ doublets in ~1:4 ratio, of which the stronger, relatively downfield signals at δ 1.68 and 3.57 ppm were assigned to the Z isomer of (III). This isomer was separated as a pure compound by fractional crystallization of the mixture of E and Z isomers (see Scheme 1).

In contrast to (I), the unsymmetrical isoprene (IV) and piperylene derivatives (V) may undergo reductive cleavage, in the general case, at two different C—S bonds. However, the reduction of these compounds proceeds regioselectively with cleavage only of the C^5—S bond and formation of sulfinates (VI). This conclusion was drawn from a gas chromatographic and PMR spectral comparison of the products of the retro desulfonylation [1] of the corresponding salts (VI) of allylsulfinic acids (VII).

As a result of this reaction, (IV) yields olefin (IX) in a mixture with its regioisomer (VIII), which is apparently formed due to the reductive cleavage of the C—S bond in the cor-

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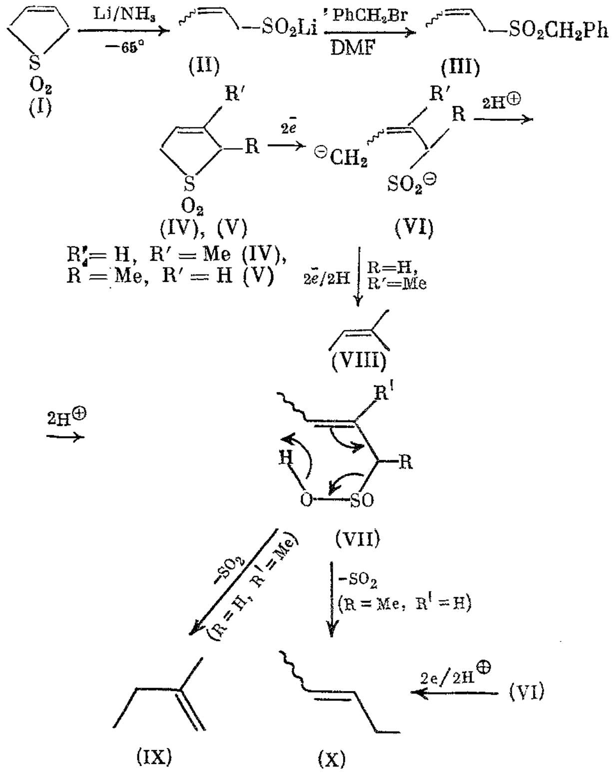
responding precursor (VI). Analogously, (V) yields a mixture of E and Z amylenes (X). The formation of (X) may be attributed to desulfonylation of the corresponding allylsulfinic acids (VII) and partially to hydrogenolysis of the corresponding sulfinates (VI).

Scheme 1



Thus, the Birch reduction of isoprenic (IV) and piperylenic thiolene dioxides (V) proceeds regioselectively with cleavage of the C^5—S bond.

EXPERIMENTAL

The PMR spectra were taken relative to TMS on a Tesla BS-497 spectrometer at 100 MHz. Gas chromatography was carried out on an LKhM-8M chromatograph using a 50 m × 0.25 mm stainless steel column packed with triethyleneglycol dibutyrate and helium gas carrier at 20°C. Authentic samples of olefins (VIII)-(X) were used.

1-Benzylsulfonyl-2-butenes (III). A sample of 330 mg lithium (47 mg-atom) was added in small portions over 10 min to a suspension of 1.18 g (10 mmoles) (I) [2] in 50 ml ammonia stirred at −65°C until a stable blue color was formed. The excess lithium was decomposed with NH_4Cl and the mixture was evaporated to yield 2.5 g of a mixture of E and Z sulfinates (II) and LiCl. PMR spectrum (CD_3OD, δ, ppm): 1.73 m (3H, CH_3), 2.97 and 3.09 d (J = 7 Hz, 2H, CH_2SO_2), 5.62 m (2H, HC=CH).

A solution of 2.35 g of the mixture of isomers of (II) and 1.7 g $PhCH_2Br$ in 30 ml DMF was maintained for 20 h at 50°C, diluted with water, and extracted with ether. The extract was dried over $MgSO_4$, distilled in vacuum, and the residue (2.8 g) was subjected to chromatography on 70 g silica gel. Elution with 4:1 ether—hexane gave 1.16 g (60%) isomers (III) (Z/E ~ 4:1) as a light yellow oil. PMR spectrum ($CDCl_3$, δ, ppm): 1.59 and 1.68 d (J = 7 Hz, 3H, CH_3), 3.46 and 3.57 d (J = 7 Hz, 2H, CH_2SO_2), 4.13 s (2H, CH_2Ph), 5.46 m (2H, HC=CH), 7.34 s (5H, C_6H_5).

Recrystallization thrice from ether—hexane gave 110 mg of the Z isomer as colorless prisms, mp 55.5-56.5°C. Found: C 63.29; H 6.74; S 15.26%. $C_{11}H_{14}O_2S$. Calculated: C 63.01; H 6.71; S 15.24%.

Olefins (VIII) and (IX) from Thiolene Dioxide (IV). A sample of 280 mg (40 mg-atom) Li was added in small portions over 10 min to a suspension of 1.0 g (7.5 mmoles) (IV) [2] in 50 ml NH_3 stirred at −65°C. The excess lithium was decomposed with NH_4Cl and the ammonia was evaporated. Then, 25 ml 5% H_2SO_4 was added dropwise to the stirred residue at from −5° to 0°C and the mixture was warmed to about 25°C over 30 min and then maintained for an additional 20 min at 40°C with condensation of the gaseous products through a KOH drying tube into a trap at −10°C to give 130 mg (~25%) olefins (VIII) and (IX) in ~2:3 ratio as indicated by gas chromatography and PMR spectroscopy.

Amylenes (X) from Thiolene Dioxide (V). By analogy, 1 g (7.5 mmoles) (V) [2] and 280 mg (40 mg-atom) lithium in 50 ml ammonia upon decomposition of the reduction products by 5% H_2SO_4 gave 100 mg (~20%) olefins (X) with Z/E ratio of ~1:3 as indicated by gas chromatography and PMR spectroscopy.

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CONCLUSIONS

The isoprene and piperylene thiolene dioxide derivatives undergo regioselective oxidative ring cleavage at the C^5—S bond upon reduction using lithium in liquid ammonia.

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MASS SPECTRA OF CYCLIC OXYETHYLENETHIOUREAS

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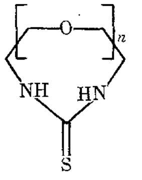
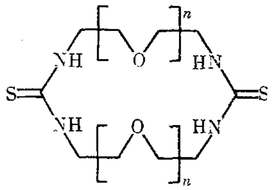
Macrocyclic ethers and their derivatives containing various heteroatoms have attracted the attention in light of their ability to form complexes. Physicochemical methods including mass spectrometry have been widely used to establish the structure of such complexing agents in order to clarify the features of their complexation and selectivity relative to various metal cations [1-4].

In the present work, we studied the electron impact (EI) fragmentation of a series of cyclic oxyethylenethioureas with different numbers of oxyethylene fragments



(I)-(IV)



(V), (VI)

n = 1-4 (I)-(IV), 1 (V), and 2 (VI).

The mass spectra of (I)-(IV) (Table 1) have strong molecular ion peaks (M^+) which are the major peaks in the case of (I)-(III).

Decomposition upon EI is determined by the site of the initial localization of charge, which may be found in these compounds on any of the three heteroatoms present, namely, sulfur, nitrogen and oxygen. Upon charge localization on one of the nitrogen atoms, the cleavage of the adjacent carbon—carbon bond leads to a linear structure of the molecular

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*Deceased.

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