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Telomerization Studies with Allyl Ethene Sulfonate and Allyl Allyl Sulfonate*

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SUMMARY

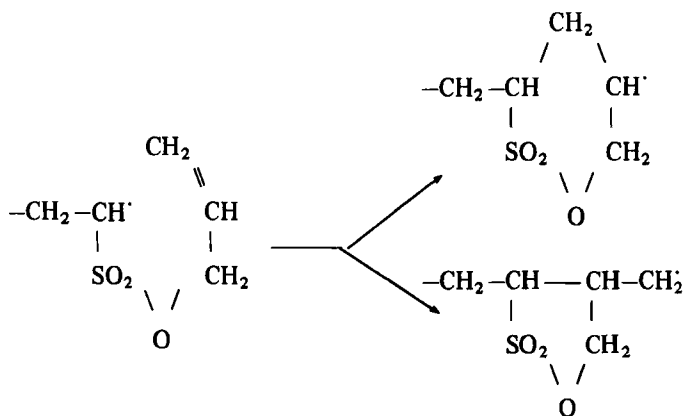
Telomerization of allyl ethene sulfonate (AES) in the presence of butyl mercaptan yielded a mixture of two products: the first was a five-membered ring sultone containing a sulfide group and the second a five-membered ring sulfonium salt formed by reaction of the sultone of the first product with its own sulfide function. If cyclotelomerizations and cyclopolymerizations give the same ring structures, these results indicate that the cyclic units in poly-AES are five-membered rings. Telomerization of allyl allyl sulfonate (AAS) in the presence of butyl mercaptan yielded a mixture of two products formed by addition of butyl mercaptan to one of the two allyl functions. Telomerization of AAS in bromotrichloromethane yielded a small amount of 1,5-hexachloro-3-bromopentane formed via fission of an oxygen-carbon bond, and a rearranged adduct. The rearrangement of the allyl group to a propenyl group in the case of AAS was not observed when allyl ethane sulfonate or propyl allyl sulfonate were telomerized under the same conditions. Therefore a mechanism is proposed in which the rearrangement of the allyl double bond in AAS is due to the presence of a second double bond in the same molecule. This observation also indicates that poly-AAS might have a more complicated structure than expected from a simple cyclopolymerization mechanism.

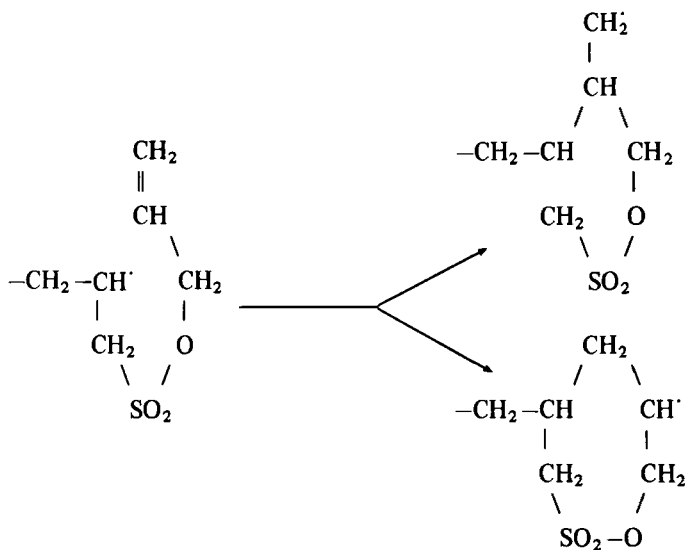
*Presented at the 5th IUPAC Microsymposium on Cyclopolymers and Cyclopolymerization, Prague, Czechoslovakia, September, 1969.

INTRODUCTION

In previous papers we reported that allyl ethene sulfonate (AES) (I) and allyl allyl sulfonate (AAS) (II) are polymerized under the influence of azoisobutyronitrile (AIBN) to linear polymers containing cyclic structures formed by alternating inter- and intramolecular propagation steps [1-3]. In those papers it was proposed that the cyclic structures in both poly-AES and poly-AAS were six-membered rings. However, it is obvious that the rings in poly-AES could also be five-membered and those in poly-AAS seven-membered.

Infrared spectroscopy, which has been used successfully in other cases [4, 5] to determine the ring size in cyclopolymers, could not be used here because five- and six-membered ring sulfones do not show characteristic differences in their IR spectra. In order to determine the most probable ring size of the cyclic units in poly-AES and poly-AAS, telomerizations of AES and AAS in the presence of different chain transfer reagents were investigated. Other cyclic telomerizations have been reported recently by Aso and co-workers [6, 7], by Cadogan and co-workers [8], and by Julia and Maumy [9].





RESULTS AND DISCUSSION

Telomerization of AES

When a mixture of equimolar amounts of AES and butyl mercaptan was treated with AIBN in benzene at 60°C , two reaction products were formed. The first, a liquid with a bp of $150^{\circ}/0.01$ mm, was obtained in 49% yield. By means of mass spectroscopy its molecular weight was found to be 238, which corresponds to the sum of the molecular weights of butyl mercaptan and AES.

Figure 1 shows its IR spectrum and Fig. 2 its NMR spectrum. From these spectra it can be deduced that the substance still contains a sulfonic ester group (strong absorption at 1165 and 1350 cm^{-1}) and that it does not contain double bonds (no absorption at 1650 cm^{-1} in the IR spectrum and no peaks at δ 5-6 in the NMR spectrum). In the NMR spectrum the doublet at δ 1.42, integrating for 3 hydrogens, indicates the presence of a methyl group placed on a carbon atom carrying one hydrogen.

These observations are in agreement with a five-membered ring sulfone (III) which is formed by the mechanism shown.

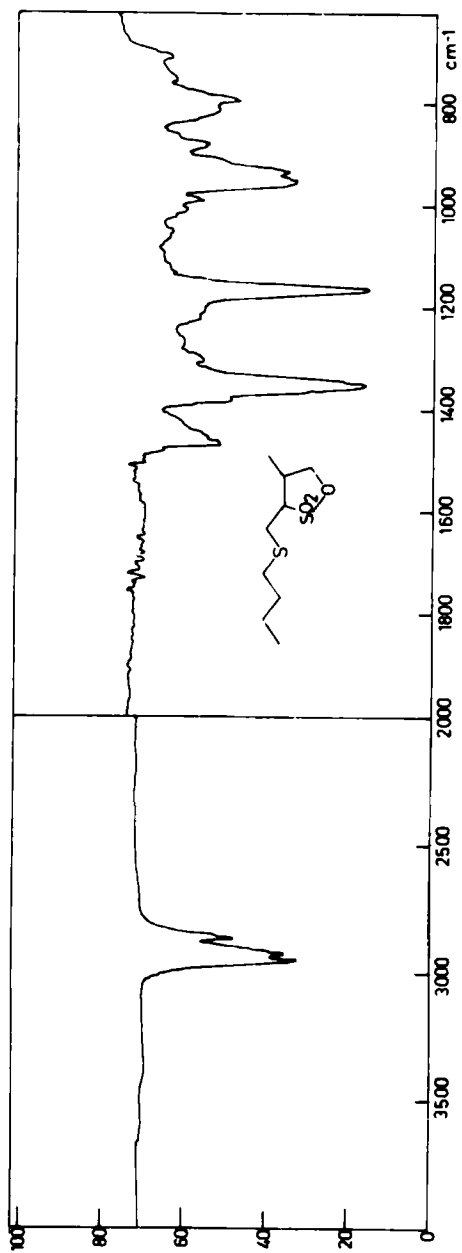


Fig. 1. Infrared spectrum of Compound III.

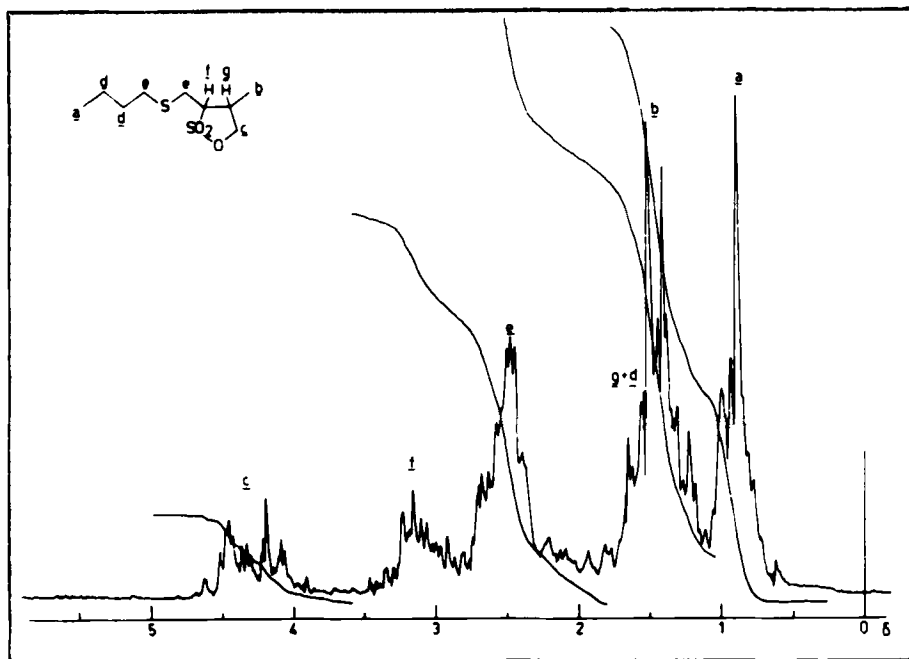
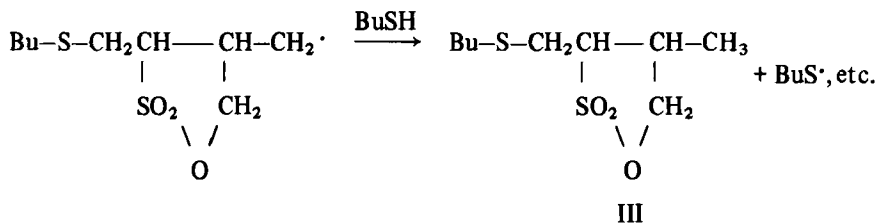
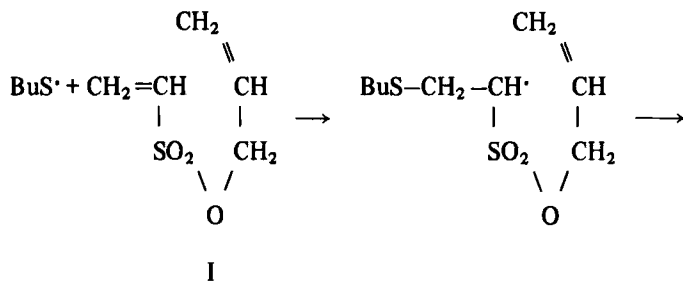
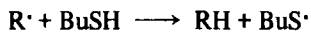


Fig. 2. NMR spectrum of Compound III.

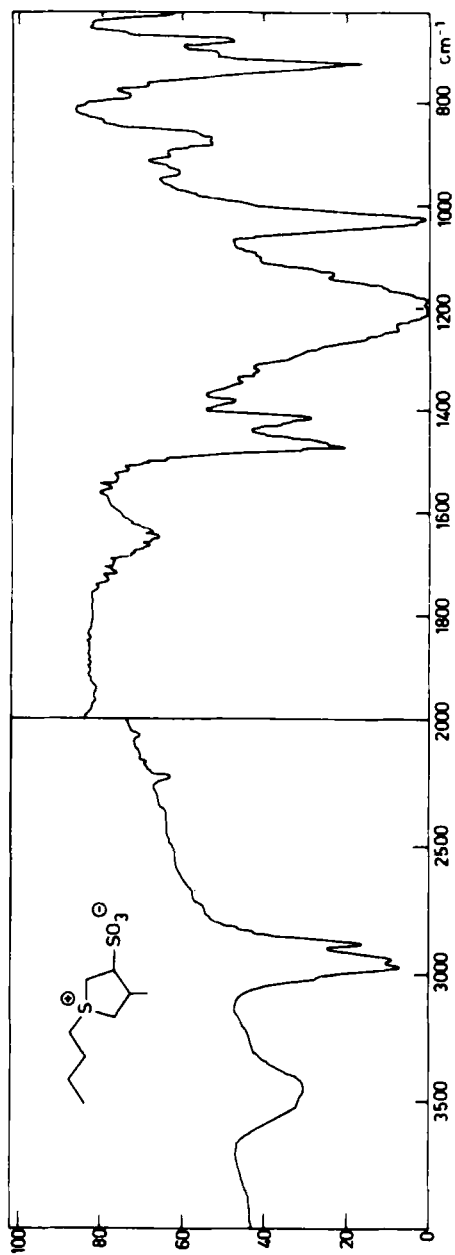


Fig. 3. Infrared spectrum of Compound IV.

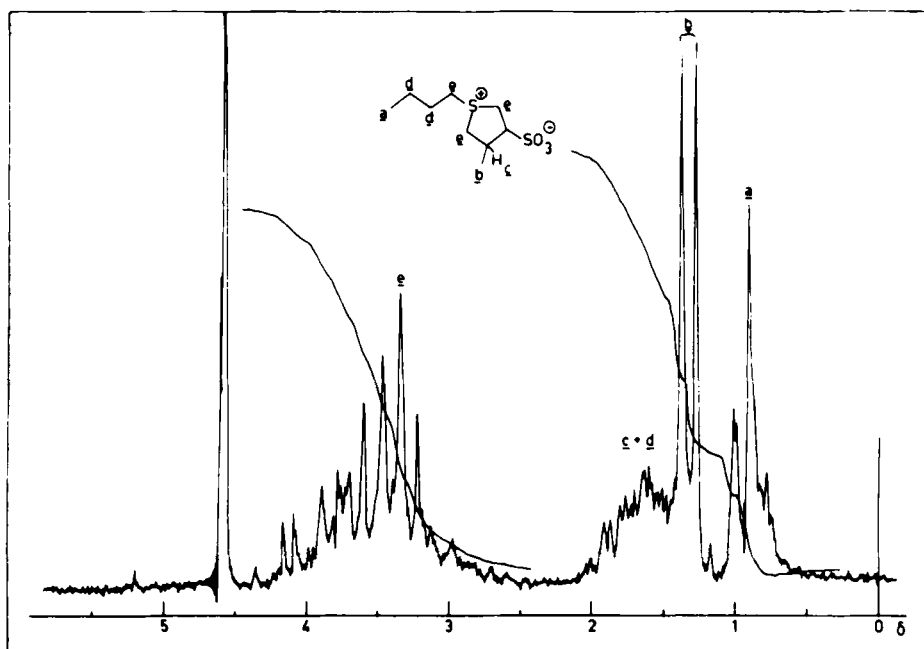
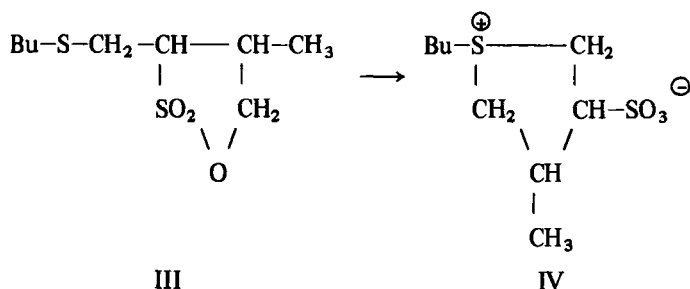


Fig. 4. NMR spectrum of Compound IV.

The second product formed by telomerization of AES with butyl mercaptan was obtained in 28% yield. It is a crystalline substance with mp 238°C, insoluble in common organic solvents, but soluble in water. Mass spectroscopy and elemental analysis showed that this product also was composed of 1 mole of butyl mercaptan and 1 mole of AES. Figure 3 shows its IR spectrum and Fig. 4 its NMR spectrum. The broad peak at 1200 cm⁻¹ in the IR spectrum indicates that instead of a sulfonyl group, the product contains a sulfonic acid salt group. Double bonds are absent and again a doublet at δ 1.34 in the NMR spectrum proves the presence of a methyl group on a carbon atom with 1 hydrogen. These observations are in agreement with a cyclic sulfonium salt in the inner salt form (IV), formed by reaction of the sultone ring of Compound III with its own sulfide function.

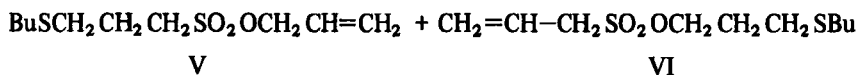
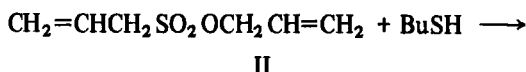


It is known that sultones react with sulfides to form inner sulfonium salts [10]. This mechanism was further confirmed by the fact that sultone (III) could be transformed into the inner sulfonium salt (IV) by boiling in toluene.

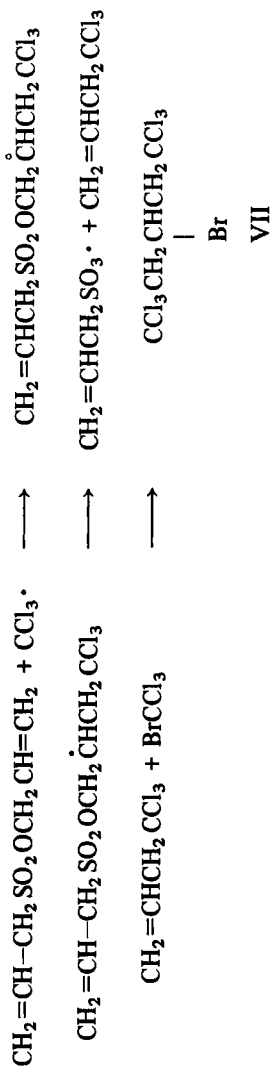
Telomerization of AES in bromotrichloromethane as solvent yielded a small amount (5.2%) of a white crystalline substance, mp 114°C, which contained no double bonds. The NMR spectrum was too complicated to allow a structure determination.

Telomerization of AAS

Telomerization of AAS in the presence of an equimolar amount of butyl mercaptan yielded a mixture of two products which could be separated only by analytical gas chromatography. Mass spectrum and elemental analysis indicated that the substances were adducts of 1 mole of butyl mercaptan to AAS. NMR and IR spectra showed that one allylic double bond was still present. Consequently the structures of the two compounds probably were V and VI.



When AAS was telomerized in bromotrichloromethane with AIBN, two reaction products could be isolated. The first (yield, 7%), a colorless liquid with bp 100°/0.05 mm, had a molecular weight (by mass spectroscopy) of 358 and contained no sulfur. NMR spectrum (Fig. 5) and elemental analysis led to structure VII which could be formed by the



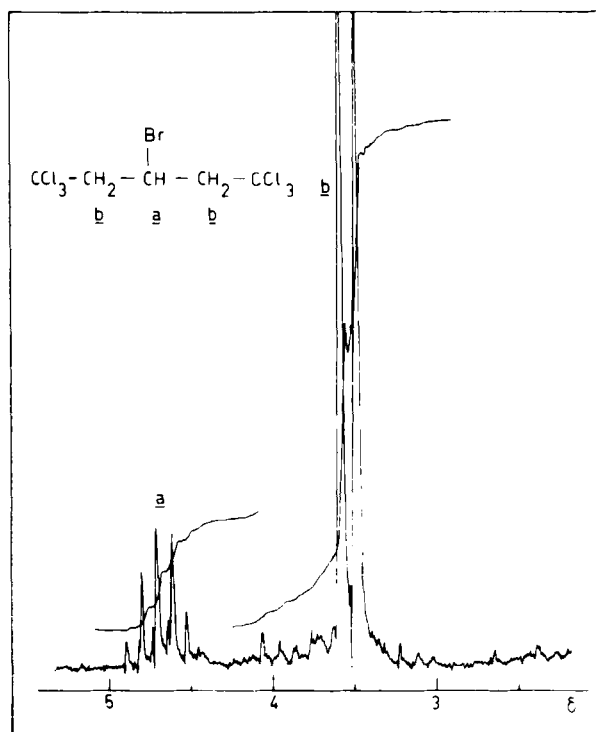
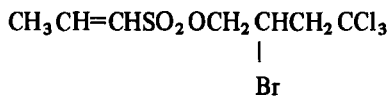


Fig. 5. NMR spectrum of Compound VII.

reaction path shown. The fission of an oxygen-carbon bond in the polymerization of allylic compounds has been observed earlier in the case of allyl acetate [11].

The second compound (yield, 39%) was also a colorless liquid with bp $160^{\circ}/0.05$ mm. Its molecular weight (by mass spectroscopy) was 360 and from the NMR spectrum (Fig. 6) it follows that it contains a double bond of the propene type instead of an allylic function. Elemental analysis and spectra are in agreement with Structure VIII.



VIII

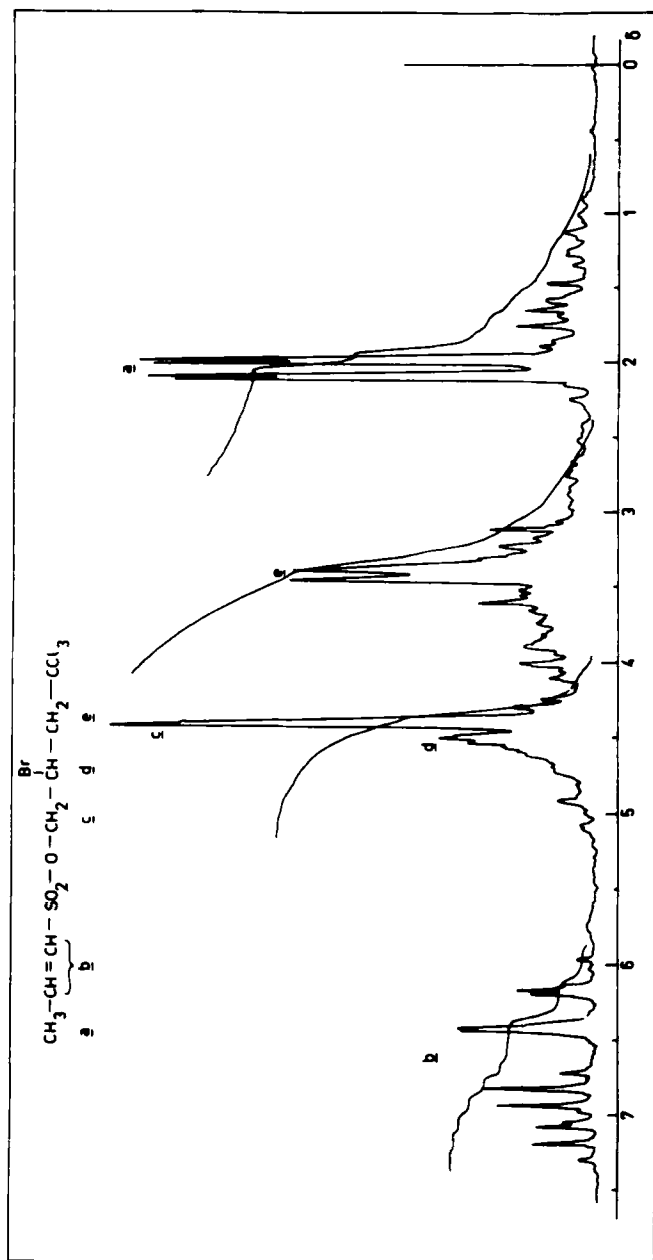


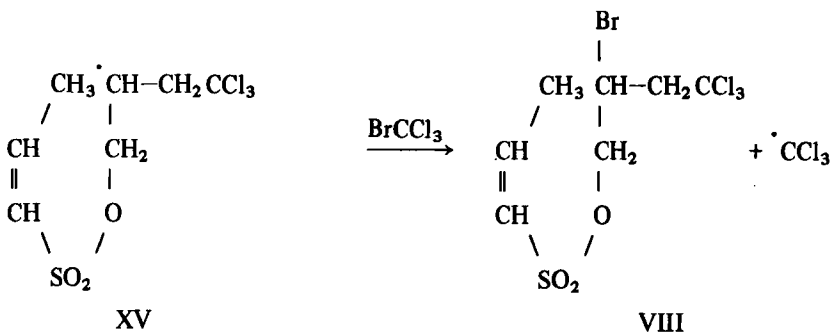
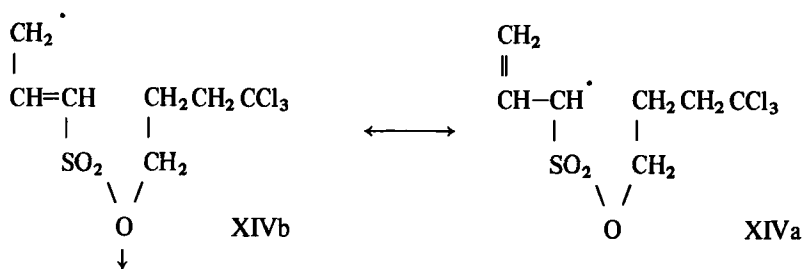
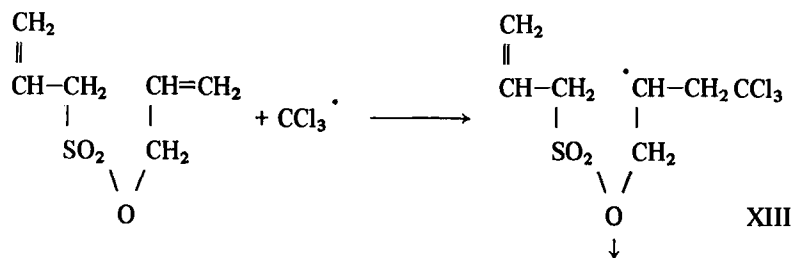
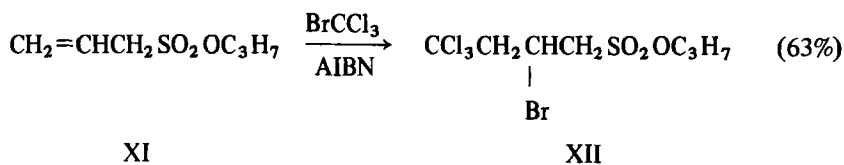
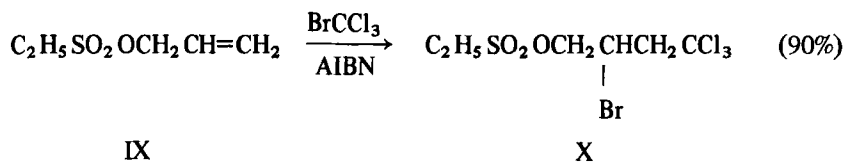
Fig. 6. NMR spectrum of Compound VIII.

The allylic rearrangement in AAS is a very peculiar reaction since it was not found to occur with allyl ethane sulfonate (IX) or with propyl allyl sulfonate (XI) which both gave the expected addition products with bromotrichloromethane. The unique behavior of AAS seems to be due to the fact that in this compound two allylic functions are present in the same molecule. Therefore we suggest a mechanism where a hydrogen atom of an allyl group is transferred to the radical of the same molecule (XIII) with formation of structure XIVa. Another form of the same allyl radical is Structure XIVb. A second hydrogen transfer leads to Structure XV, which reacts with bromotrichloromethane to give VIII.

It was earlier found by several authors that the reactivity of double bonds in monomers capable of undergoing cyclopolymerization is enhanced when compared with monomers in which the same type of double bonds are present alone [1, 2, 12, 13]. This behavior has been attributed to electronic interactions between the two double bonds or between one double bond and a radical [13]. The results of the telomerization of AAS suggest that in telomerizations also, the behavior of a double bond can be influenced by the presence of a second double bond in the same molecule.

CONCLUSIONS

From the telomerization studies of AES with butyl mercaptan it may be concluded that the cyclic units in poly-AES probably are five-membered ring sultones. However, it remains to be proved that cyclotelomerization and cyclopolymerization of nonconjugated dienes always give the same ring size. It would therefore be desirable to study the cyclotelomerization of dienes which have been polymerized to polymers in which the ring size of the cyclic units has been determined by other methods. The telomerization of AAS with butyl mercaptan or with bromotrichloromethane did not give cyclic telomers so that it was not possible to draw conclusions about the ring size of the cyclic units in poly-AAS. The experiments with bromotrichloromethane have demonstrated that telomerization of nonconjugated dienes can give other reaction products than those expected from analogous reactions with analogous monomers containing only one of the double bonds. The rearrangement that occurs in the telomerization of AAS also indicates that poly-AAS might have a more complicated structure than expected from a simple cyclopolymerization mechanism.



EXPERIMENTAL

Synthesis of Monomers

The syntheses of allyl ethene sulfonate (I), allyl allyl sulfonate (II), allyl ethane sulfonate (IX), and propyl allyl sulfonate (X) have been described in previous papers [1-3].

Telomerization of AES (I) with Butyl Mercaptan

A degassed solution of 2.65 g of AES (0.018 mole), 1.62 g of butyl mercaptan (0.018 mole), and 330 mg of AIBN (0.002 mole) was kept at 60°C for 18 hr. A white precipitate of Compound IV was filtered off, washed with benzene, and dried in a vacuum desiccator (1.34 g, 28% mp 238°C after recrystallization in a mixture of water and acetone). The filtrate was concentrated in vacuo and the remaining yellow colored oil distilled in vacuo. 2.32 of Compound III was collected with bp 150°/0.01 mm (49%).

Elemental Analysis. (III): $C_9H_{18}O_3S_2$, MW 238. Calculated: C 45.2; H, 7.52; S, 26.5. Found: C, 47.2; H, 7.35; S, 26.3.

(IV): $C_9H_{18}O_3S_2$, MW 238. Calculated: C, 45.2; H, 7.52; S, 26.5. Found: C, 43.7; H, 7.07; S, 25.2.

Telomerization of AAS (II) with Butyl Mercaptan

A degassed solution of 4.53 g of AAS (0.028 mole), 2.52 g of butyl mercaptan (0.028 mole), and 230 mg of AIBN in 15 ml of benzene was kept at 60° for 16 hr. After evaporation of the solvent, a yellow colored mixture of Compounds V and VI distilled at 160°C/0.01 mm (1.68 g; 24%).

Telomerization of AAS (II) with Bromotrichloromethane

A solution of 3.40 g of AAS (0.021 mole) and 184 mg of AIBN in 40 ml of bromotrichloromethane was kept at 60° for 15 hr. After evaporation of the solvent, the residue was distilled in vacuo. A first fraction (VII) boiled at 100°/0.05 mm (0.5 g, 6.5%), a second fraction (VIII) at 160°/0.05 mm (3.05 g, 39%).

Elemental Analysis. (VIII): $C_7H_{10}BrCl_3O_3S$, MW 360.5. Calculated: C, 23.25; H, 2.82. Found: C, 22.75; H, 2.63.

Telomerization of Allyl Ethane Sulfonate (IX) with Bromotrichloromethane

A solution of 5.70 g of AES and 311 mg of AIBN in 40 ml of bromotrichloromethane was kept at 60° for 15 hr. After evaporation of the solvent, the residue was distilled in vacuo. 11.7 g of Compound X was collected with bp 160°/0.01 mm (89.2%).

Elemental Analysis. (X): C₆H₁₀BrCl₃O₃S, MW 348.5. Calculated: C, 20.7; H, 2.87. Found: C, 21.1; H, 2.84.

Telomerization of Propyl Allyl Sulfonate (XI) with Bromotrichloromethane

A solution of 4.59 g of PAS (0.028 mole) and 230 mg of AIBN in 40 ml of bromotrichloromethane was kept at 60° for 15 hr. After evaporation of the solvent, the residue was distilled in vacuo. 4.8 g of Compound XII was collected with bp 136°/0.01 mm (63.2%).

Elemental Analysis. (XII): C₇H₁₂BrCl₃O₃S, MW 362.5. Calculated: C, 23.2; H, 3.31. Found: C, 23.3; H, 3.15.

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