positions of the sulfonate and hydroxyl units along the chain will determine whether or not cyclization will occur. Probably the residual vinyl alcohol units represent isolated hydroxyl groups.

Summary

1. Polyvinyl sulfonates have been treated with primary and secondary amines to yield polymers composed of N-substituted vinylamine units and cyclic ether units. Unreacted vinyl alcohol and vinyl sulfonate units may be present.

2. Evidence has been presented which substantiates the structures proposed for the polymers.

3. The aminated polymers prepared from alkyl primary or secondary amines are insoluble in water but soluble in dilute acid. Those prepared from primary or secondary amines containing aryl groups are insoluble in water and in dilute acid.

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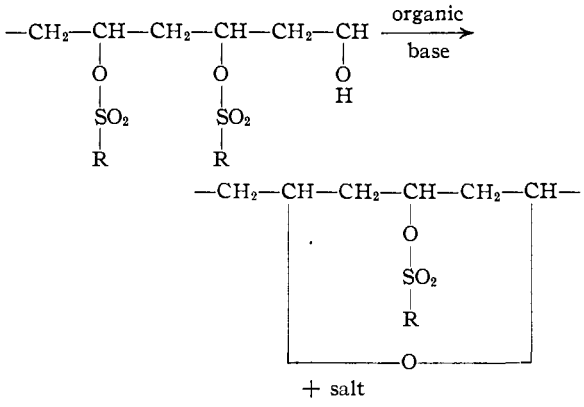
Preparation and Reactions of Sulfonic Esters. IV. Preparation of Cyclic Ethers[1]

BY D. D. REYNOLDS AND W. O. KENYON

Introduction

In a previous publication[2] polymers have been described for which a structure containing cyclic ether units was postulated. The cyclic ether is believed to be of the tetrahydropyran type. Evidence was reported which substantiated the structures assigned. Such ether structures were formed by an intramolecular reaction involving the hydroxyl group of a vinyl alcohol unit and the alkylsulfonyl or arylsulfonyl radical of a suitably situated vinyl sulfonate unit, as illustrated in the equation



In order to elucidate the reactions leading to such compounds, a study was made of the preparation of non-polymeric cyclic ethers of the tetrahydropyran and tetrahydrofuran types. During its course a method for the preparation of cyclic ethers was developed which involves the reaction of a glycol with one mole of a sulfonyl chloride in the presence of a suitable tertiary amine. The products obtained are listed in Table I.

(1) Presented before the Division of Organic Chemistry of the American Chemical Society, Atlantic City, N. J. meeting, September, 1949.

(2) D. D. Reynolds and W. O. Kenyon, THIS JOURNAL, **72**, 1587 (1950).

Experimental

Materials. 2,6-Heptanediol was prepared by the method of Perkins[3] from heptane-2-ol-6-one but using hydrogen and Raney nickel at 50 to 80° and 3500 p. s. i. instead of sodium amalgam in alcohol as the reductant.

1,5-Pentanediol was purchased from E. I. du Pont de Nemours and Co., Inc.

2,5-Hexanediol and **2,4-pentanediol** were prepared by the reduction of the corresponding ketones with hydrogen over Raney nickel at 100° and 4000 p. s. i.

1,4-Butanediol was prepared by the reduction of butynediol by hydrogen over Raney nickel at 3000 p. s. i. at 50 to 100°.

1,3-Propanediol was Eastman Kodak Co. white label grade.

Sulfonyl chlorides were Eastman white label grade.

Anhydrous pyridine and **anhydrous 2,6-lutidine** were obtained by distillation of Eastman white label grade products over calcium hydride.

I. Procedure.—One mole of a glycol was refluxed with four moles of a tertiary amine while one mole of an alkyl- or arylsulfonyl chloride was added dropwise. The cyclic ether which formed was separated, and purified by distillation.

The sulfur oxide–tertiary amine complex formed when methanesulfonyl chloride is used can be removed from the cyclic ether by washing with water.

II. Preparation of Monobenzenesulfonate of 1,5-Pentanediol.—Two liters of anhydrous ether, 600 g. of 1,5-pentanediol and 500 cc. of anhydrous pyridine were stirred in a 5-liter, 3-necked flask equipped with a thermometer and a dropping funnel. The temperature was maintained at 5°, and 300 g. of benzenesulfonyl chloride was added dropwise over a three-hour period. Stirring was continued for an hour. The product was washed three times with water, once with dilute hydrochloric acid, and twice more with water. The ether layer was dried over calcium chloride, then over magnesium sulfate, and the ether was removed *in vacuo*, yield 300 g. of viscous product.

III. Treatment of Monobenzenesulfonate of 1,5-Pentanediol with 2,6-Lutidine.—One hundred and fifty grams of the product prepared in Experiment II was mixed with 300 g. of 2,6-lutidine and fractionally distilled. After removal of a small amount of residual ether, 32.4 g. of tetrahydropyran fraction, b. p. 70 to 90°, was collected. Redistillation of this fraction yielded 21 g. of pure tetrahydropyran. The residue which remained from the first distillation after removal of the tetrahydropyran separated at room temperature into two layers of approxi-

(3) W. H. Perkin, *J. Chem. Soc.*, **105**, 1360 (1914).

TABLE I

PRODUCTS OBTAINED BY REACTING GLYCOLS WITH SULFONYL CHLORIDES IN THE PRESENCE OF TERTIARY AMINES

No.	Glycol	Tertiary amine	Sulfonyl chloride	Product	Yield, %	B. p., °C.
1	1,4-Butanediol	Pyridine	$C_6H_5SO_2Cl$	Tetrahydrofuran	34.7	65–66
2	1,4-Butanediol	2,6-Lutidine	$C_6H_5SO_2Cl$	Tetrahydrofuran	58.3	65–66
3	2,5-Hexanediol	Pyridine	$C_6H_5SO_2Cl$	α,α'-Dimethyltetrahydrofuran	86.0	92–94
4	2,5-Hexanediol	Pyridine	$C_7H_7SO_2Cl$	α,α'-Dimethyltetrahydrofuran	82.5	92–93
5	2,5-Hexanediol	2,6-Lutidine	CH_3SO_2Cl	α,α'-Dimethyltetrahydrofuran	64.0	92–94
6	1,5-Pentanediol	Pyridine	$C_6H_5SO_2Cl$	Tetrahydropyran	5.8	87.5–88.5
7	1,5-Pentanediol	β-Picoline	$C_6H_5SO_2Cl$	Tetrahydropyran	3.5	87.5–88.5
8	1,5-Pentanediol	γ-Picoline	$C_6H_5SO_2Cl$	Tetrahydropyran	3.5	87.5–88.5
9	1,5-Pentanediol	α-Picoline	$C_6H_5SO_2Cl$	Tetrahydropyran	11.6	87.5–88.5
10	1,5-Pentanediol	2,4-Lutidine	$C_6H_5SO_2Cl$	Tetrahydropyran	40.7	87.5–88.5
11	1,5-Pentanediol	2,6-Lutidine	$C_6H_5SO_2Cl$	Tetrahydropyran	50.0	87.5–88.5
12	1,5-Pentanediol	2,6-Lutidine + pyridine	$C_6H_5S_2OCl$	Tetrahydropyran	5	87–89
13	1,5-Pentanediol	2,6-Lutidine + pyridine·HCl	$C_6H_5SO_2Cl$	Tetrahydropyran	50.0	87.5–88.5
14	2,6-Heptanediol	Pyridine	$C_6H_5SO_2Cl$	α,α'-Dimethyltetrahydropyran	26.2	115–116
15	Trimethylene	Pyridine or 2,6-lutidine	$C_6H_5SO_2Cl$	Allyl chloride	50.0	45
16	2,4-Pentanediol	Pyridine	$C_6H_5SO_2Cl$	1,3-Pentadiene	6.9	39–41

mately equal volume. The separated lower layer solidified to a crystalline mass. It was decolorized and crystallized from ethanol and then recrystallized from alcohol–ether. *Anal.* Calcd. for $C_{13}H_{15}SO_3N$: N, 5.3; S, 11.3. Found: N, 5.28; S, 12.0. This 2,6-lutidine salt of benzenesulfonic acid results from the cyclization reaction. A mixed melting point with a known sample showed no lowering.

IV. Treatment of Monobenzenesulfonate of 1,5-Pentanediol with Pyridine.—One hundred and fifty grams of the monobenzenesulfonate was mixed with 300 cc. of pyridine and distilled as previously described. Distillation yielded 10 cc. of ether, and a second fraction, b. p. 35 to 100°, principally 90 to 100°. The latter gave only a trace of tetrahydropyran when refractionated. The cooled residue in the distillation flask was a viscous sirup. Pyridine was removed by vacuum distillation. The residue crystallized when cooled. It was decolorized and recrystallized from ethanol, yielding a white product. Analyses indicated a quaternary pyridinium derivative of the monobenzenesulfonate of 1,5-pentanediol. *Anal.* Calcd. for $C_{16}H_{21}SO_4N$: C, 59.4; H, 6.5; N, 4.3; S, 9.9. Found: C, 60.0; H, 6.4; N, 4.2; S, 10.0. This quaternary salt was very hygroscopic.

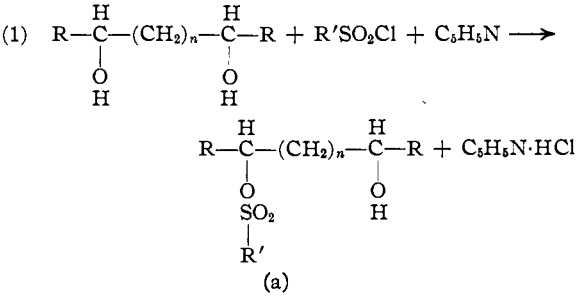
V. Attempt to Prepare Trimethylene Oxide.—Trimethylene glycol (76 g.) dissolved in 300 g. of anhydrous pyridine was refluxed and benzenesulfonyl chloride (176 g.) was added over a one and one-half-hour period. Upon distillation, a low-boiling fraction was collected which, when redistilled, yielded 39 g. of allyl chloride, b. p. 45 to 46°. No trimethylene oxide was isolated. An experiment with 2,6-lutidine instead of pyridine gave allyl chloride but no trimethylene oxide.

VI. Attempt to Prepare α,α'-Dimethyltrimethylene Oxide.—2,4-Pentanediol (104 g.) and 300 g. of anhydrous pyridine were refluxed and 176 g. of benzenesulfonyl chloride was added during one and one-half hours. Upon distillation, the temperature rose immediately to the boiling point of pyridine, and 165 g. of pyridine was collected. The temperature of the reaction mixture then rose to 195° and the distillation temperature fell to 44°. This low-boiling fraction was collected and redistilled, yielding 4.7 g., b. p. 39 to 41°. Carbon and hydrogen analyses indicated 1,3-pentadiene.

Discussion

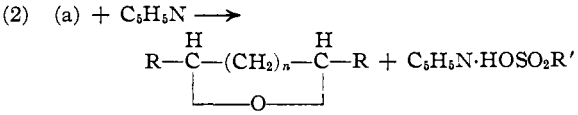
When a monohydric alcohol reacts with a sulfonyl chloride in the presence of a tertiary amine, the initial reaction is usually the formation of a sulfonic ester. If reaction conditions are not controlled, the following side reactions[4] may occur to an extent sufficient to reduce the yield of sulfonic ester: quaternization of the ester by the tertiary amine; replacement of sulfonoxy group by halogen from the amine hydrohalide to form an organic halide; or splitting of the initially-formed ester into an unsaturate and sulfonic acid. These three side reactions are usually controlled by preparing the sulfonic ester at temperatures below 10°. Even lower temperatures are required for the preparation of benzyl, ethyl and 2,4-dinitrophenyl-*p*-toluenesulfonates.[4]

The preparations of cyclic ethers described in this paper were carried out at reflux temperatures. The initial esterification (1)

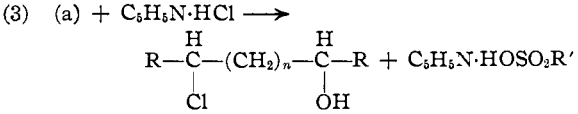


(a)

where R = H or CH_3, and R′ = CH_3, C_6H_5 and $CH_3C_6H_4$, may be followed by the desired cyclization reaction (2)

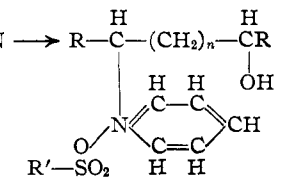


or by undesired side reactions (3), (4) and (5).



(4) R. S. Tipson, *J. Org. Chem.*, **9**, 235 (1944).

(4) (a) + C_5H_5N ⟶
unsaturated alcohol + $C_5H_5N \cdot HOSO_2R'$

(5) (a) + C_5H_5N ⟶ 

For simplicity in these examples, pyridine was employed as the tertiary, cyclic base. Other bases such as picolines, lutidines or quinolines could be similarly used.

The yield of cyclic ether obtained (Reaction 2) will depend upon the relative rates of Reactions 2, 3, 4 and 5. These rates will be determined by the nature of the sulfonoxyl group, *i. e.*, whether it is primary or secondary (R = H or CH_3), by the nature of the organic base, by the particular sulfonic acid ester used, *i. e.*, R′ = CH_3^-, $C_6H_5^-$ or $CH_3C_6H_4^-$ and by the size of the cyclic ether ring to be formed, *i. e.*, n = 1, 2 or 3.

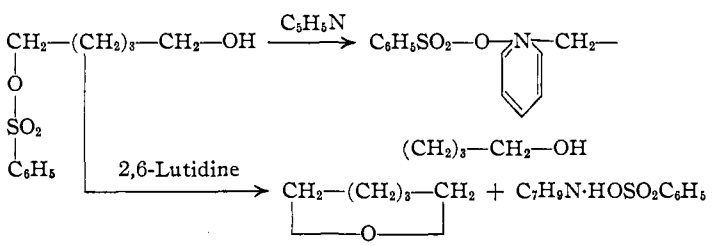
The formation of a five-membered heterocyclic ring of the furan series proceeded readily. 2,5-Hexanediol gave good yields of α,α'-dimethyltetrahydrofuran when reacting in pyridine with methanesulfonyl, benzenesulfonyl or *p*-toluenesulfonyl chloride. The use of 2,4- or 2,6-lutidine instead of pyridine was equally satisfactory. The particular sulfonic acid ester or tertiary cyclic organic base selected appears to be of little significance. The hydroxyl groups in 2,5-hexanediol are secondary, yet 1,4-butanediol, having primary hydroxyl groups, gave a good yield of tetrahydrofuran.

Though the five-membered furan ring formed readily under diverse experimental conditions, the conditions of formation of the six-membered tetrahydropyran ring were more critical.

When 1,5-pentanediol reacted with methanesulfonyl, benzenesulfonyl, or *p*-toluenesulfonyl chloride in pyridine, only a small amount of the tetrahydropyran was obtained. If the pyridine was replaced by β- or γ-picoline, similar results were obtained. α-Picoline gave a somewhat improved yield. The use of 2,4- or 2,6-lutidine as the tertiary amine produced good yields of tetrahydropyran. Specifically, the diol with benzenesulfonyl chloride in pyridine gave a 5.8% yield (Table I, no. 6), while under comparable conditions 2,6-lutidine gave a 50% yield (Table I, no. 11).

This difference is not due to the relative rates of formation of the sulfonic ester (Reaction 1) in the presence of the two amines. A single batch of the monobenzenesulfonate of 1,5-pentanediol (Experiment II) was prepared. One portion reacted with 2,6-lutidine to yield 40% of purified tetrahydropyran (Experiment III), while the other portion, when reacting in pyridine, gave only a trace of tetrahydropyran (Experiment IV). A large quantity of the lutidine salt of benzenesulfonic acid was isolated from Experiment III, while Experiment IV gave a substantial amount of the quaternary pyridinium salt of the monobenzenesulfonate of the diol. An experiment (Table I, no. 12), with equal parts of lutidine and pyridine in the reaction, gave a very low yield of tetrahydropyran.

The preceding experiments indicated that quaternization (Reaction 5) was using up the sulfonic ester and preventing cyclization. Pyridine and the monosubstituted pyridines appeared to favor the side reaction, probably because of their high rate of quaternization. The quaternization rates of the lutidines, especially of the 2,6-isomer, appeared very much less than the rate of the cyclization reaction. These reactions are summarized in the equations

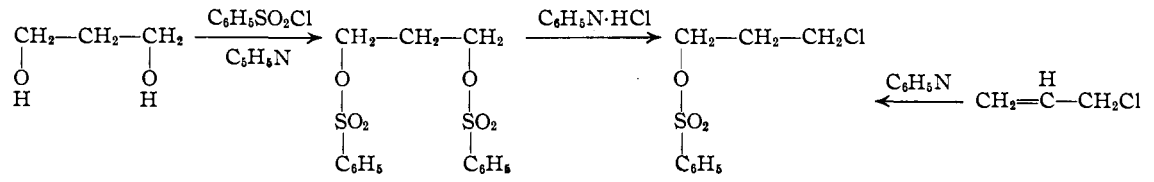


Other experiments not reported here showed that 2,6-lutidine quaternized simple sulfonic esters much more slowly than did pyridine.

To corroborate these results it was necessary to rule out the formation of halides or unsaturates as competing reactions (3 and 4). The reaction of the diol and benzenesulfonyl chloride in 2,6-lutidine containing a large quantity of pyridine hydrochloride (Table I, no. 13) gave the expected 50% yield of tetrahydropyran which is quite comparable to the same reaction without the pyridine salt (Table I, no. 11). Unsaturates were never encountered as by-products of the reactions run with 1,5-pentanediol.

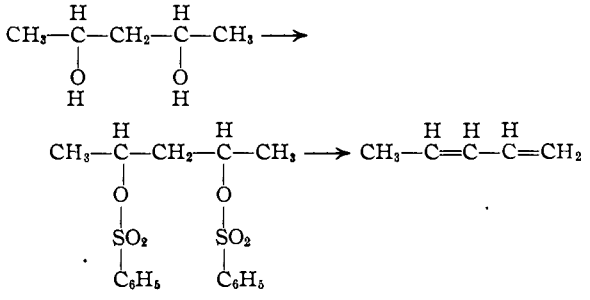
It is well known that sulfonic esters of primary alcohols quaternize much more readily than those of secondary alcohols. The sensitivity of 1,5-pentanediol monobenzenesulfonate to quaternization by pyridine has been indicated, and it was postulated that 2,6-heptanediol monobenzenesulfonate, having secondary alcohol groups, would quaternize less readily with pyridine, and hence would produce α,α'-dimethyltetrahydropyran. This was confirmed by experiment (Table I, no. 14) though the yield was not as great as was expected.

The formation of allyl chloride by the reaction of benzenesulfonyl chloride with trimethylene glycol (Table I, no. 15) illustrates well the reactions competitive with that of cyclization. The rate of formation of the four-membered cyclic oxide was expected to be slow, thus favoring side reactions. Allyl chloride resulted by Reactions 3 and 4, as illustrated by the equation

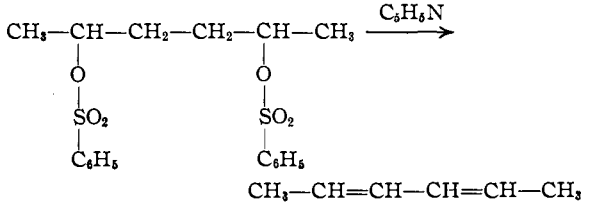


This equation does not necessarily show the sequence of steps in the reaction mechanism. The benzenesulfonyl ester of allyl alcohol may be formed first, and substituted by halogen. Conversely, 3-chloropropanol-1 monobenzenesulfonate may form first. In the experiment (Table I, 15), the 1:1 molar ratio of glycol and benzenesulfonyl chloride needed for cyclization was used instead of the 1:2 ratio needed to form allyl chloride; hence, the halide yield was 50% based on glycol used, or 100% based on the benzenesulfonyl chloride.

The formation of 1,3-pentadiene by the reaction of benzenesulfonyl chloride on 2,4-pentanediol in pyridine can be explained by the steps



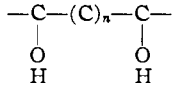
It was shown during this study that the following reaction takes place



which is analogous to the formation of 1,3-pentadiene.

Summary

1. Cyclic ethers may be prepared by refluxing a glycol possessing the nucleus



where n = 2 or 3, with an appropriate tertiary amine and gradual addition of an alkyl- or arylsulfonyl chloride.

2. The following reactions are competitive and the products of the reaction depend upon their relative rates: (1) halogenation, (2) quaternization, (3) dehydrosulfonation to yield an unsaturate, (4) dehydrosulfonation to yield a cyclic ether.

3. The success of the cyclization reaction depends upon the choice of a tertiary amine, which does not quaternize readily with a sulfonic ester. α-Substituted pyridines are very satisfactory. Their tendency to quaternize decreases in the order: α-picoline (2-methylpyridine) > 2,4-lutidine (2,4-dimethylpyridine) > 2,6-lutidine (2,6-dimethylpyridine), the last being the most satisfactory for the cyclization reactions.

4. Rate of quaternization of primary sulfonate groups is greater than the rate of quaternization of secondary sulfonate groups.

5. When n = 2, the rate of cyclization to form a five-membered ring is enough greater than the Reactions 3, 4, and 5 that even pyridine, which quaternizes rapidly, may be used. When n = 2, it makes no difference whether the alcohol group is of primary or secondary type.

6. When n = 3 and the hydroxyl group is primary, the choice of the tertiary amine is of prime importance. If pyridine is used, the rate of quaternization of the intermediate sulfonate is faster than the rate of cyclization and very little cyclic ether is formed. On using a tertiary amine which quaternizes slowly, such as 2,6-lutidine, the rate of quaternization of the intermediate monosulfonate is so slow that the cyclization reaction predominates and good yields of the cyclic ether are obtained.

7. When n = 3 and the hydroxyl group is secondary, the rate of quaternization of the secondary sulfonate group is slow enough that even pyridine may be used.

8. The method described for the preparation of cyclic ethers is of no value when $n < 2$.

9. Pyridine and certain other tertiary amines form relatively stable quaternary salts of the intermediate monoester. These salts may be decomposed at high temperatures to yield a cyclic ether. This method is not satisfactory because of other decomposition reactions at the high temperatures required.

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