2.8 g. of polymer gave 0.2 g. (6.1%) of the 2,4-dinitrophenylhydrazone derivative. The derivative was carefully recrystallized from alcohol and then melted at 160°. Acetaldehyde 2,4-dinitrophenylhydrazone melts at 164.5°4 and a mixture of an authentic specimen with the derivative isolated from the above hydrolysis melted at 162°.

Anal. Calcd. for C₈H₈N₄O₄: C, 42.8; H, 3.57. Found: C, 43.05; H, 3.68.

An authentic specimen of propionaldehyde 2,4-dinitrophenylhydrazone, m. p. 151° (lit. 155°_5}), was mixed with the derivative obtained in the above hydrolysis and the mixture melted at 140-144°.

The alkaline residue remaining in the distilling flask after the steam distillation was filtered to remove aldehyde resin and other insoluble material and analyzed for chloride, sulfite and sulfate. No sulfites were found. Precipitation of the sulfate with barium chloride showed that 3.72-4.22% out of the 16.9% of the sulfur originally present in the polymer had been converted to sulfate. Of the 37.6% of chlorine originally present in the polysulfone, 35.5% was present in this filtrate as chloride ion.

Action of Liquid Ammonia on Vinyl Chloride Polysulfone.—Many experiments were tried adding liquid ammonia to the polymer and vice versa. The liquid ammonia was then allowed to evaporate and the residue treated with water and filtered. Extensive analyses of the water solution and the insoluble part showed that the chlorine was entirely removed from the polymer as ammonium chloride. Considerable sulfur was removed as ammonium sulfite. The remaining polymeric products were not uniform in character and varied over a considerable range in their sulfur content.

Pyrolysis in Dioxane.—When small quantities of vinyl chloride polysulfone were suspended in dioxane and the mixture heated to boiling under a reflux condenser, gas was evolved. This gas consisted of a mixture of hydrogen chloride and sulfur dioxide. No vinyl chloride could be detected among the volatile products. In fact no organic material except dioxane was carried over through the reflux condenser. Analysis of the residual polymeric materials showed that they varied widely in sulfur content.

Summary

1. Alkaline hydrolysis of vinyl chloride polysulfone produces acetaldehyde which is evidence that the polymeric unit in this material is —CHCl- $CH_2CHClCH_2SO_2$ —.

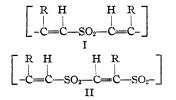
2. The polymer does not give a clean-cut reaction with liquid ammonia and pyrolysis causes loss of both hydrogen chloride and sulfur dioxide. URBANA, ILLINOIS RECEIVED JULY 24, 1939

[CONTRIBUTION FROM THE NOVES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

Acetylene Polysulfones. XI.¹ The Compound $C_{10}H_{16}SO_2$ from 1-Pentynepolysulfone and Some Experiments on Other Acetylenepolysulfones

By C. S. MARVEL AND W. W. WILLIAMS

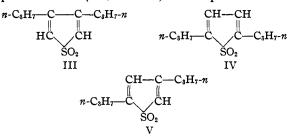
When acetylenes of the type $RC \equiv CH$ combine with sulfur dioxide, the polysulfone formed has one remaining double union for each acetylene unit.² The arrangement of these units in the polymer may be either that shown in formula I or



that in formula II or the polymer may consist of a random mixture of these units. The present work was undertaken in order to add to our knowledge concerning these compounds.

It was found² that heating a solution of 1-pentynepolysulfone $(C_6H_9SO_2)_n$ gave a crystalline solid of the composition $C_{10}H_{16}SO_2$ which tenta-(1) For the tenth communication on polysulfones, see TBIS

JOURNAL, **81**, 2709 (1939). (2) Ryden and Marvel, *ibid.*, **58**, 2047 (1986). tively was considered to be a di-*n*-propylthiophene sulfone (III, IV or V). This product must



be formed by the loss of sulfur dioxide from two units of polymer and hence knowledge of its structure would make it possible to assign a definite formula for the polymer.

A more detailed study of the pyrolysis of 1pentynepolysulfone in dioxane has been made. The reaction proceeds to some equilibrium stage. Isolation of the unchanged polymer and repetition of the pyrolysis in fresh dioxane gives more of the decomposition product. By using this stepwise

⁽⁴⁾ Strain. THIS JOURNAL, 57, 758 (1935).

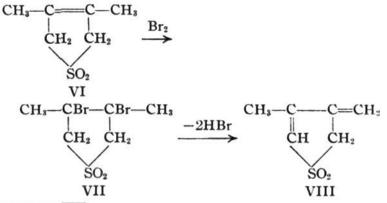
⁽⁵⁾ Allen, ibid., 52, 2955 (1930).

procedure it has been possible to increase the yield of the crystalline sulfone to 22% on the basis of the polysulfone which is used up in the process. It has not been possible to obtain other crystalline products from 1-pentynepolysulfone. Neither has it been possible to pyrolyze other acetylenepolysulfones to give a product similar to the $C_{10}H_{16}SO_2$ compound.

Evidence that this crystalline degradation product has an α,β -unsaturated sulfone linkage has been obtained by a study of its addition reactions. Sodiomalonic ester adds readily to give a product of the expected composition.³ Reduction of the cyclic sulfone with zinc and acetic acid yields a dihydro compound. This reaction must proceed by a 1,4-addition of hydrogen with a resulting shift of the double union to the 3,4-position in the ring (III, IV or V) as otherwise this reduction would be expected to give a tetrahydro compound.

Catalytic reduction of the cyclic sulfone using hydrogen at three atmospheres and a platinum oxide-platinum black catalyst⁴ gave another dihydro compound. The catalyst was poisoned rather quickly during this reaction. Since this dihydro compound is isomeric with the one formed by a 1,4-addition of hydrogen, it must be the 1,2addition product. However, if it is the result of 1,2-addition of hydrogen to one of the structures III, IV or V, the resulting molecule would still be an α,β -unsaturated compound and would be expected to reduce with zinc and acetic acid. This could not be accomplished.

One or the other of these reduction products may be derived from a rearranged form of the cyclic sulfone. Backer and Strating⁵ have shown that the cyclic sulfone (VIII) obtained by the addition of sulfur dioxide to 2,3-dimethylbutadiene



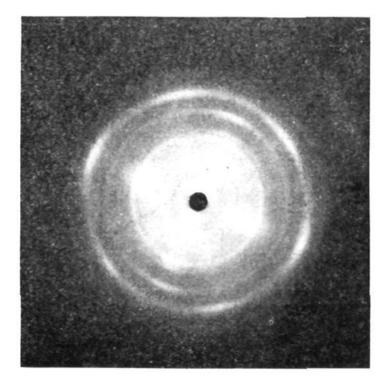
⁽³⁾ Kohler and Potter, THIS JOURNAL, **57**, 1316 (1935), have shown this reaction is characteristic of α,β -unsaturated sulfones. (4) Adams, Vorhees and Shriner, "Org. Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1932, p. 452.

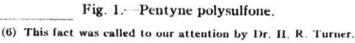
followed by bromination and removal of two molecules of hydrogen bromide has only one double bond in the ring.

The sulfone (III, IV or V) obtained by the pyrolysis of 1-pentynepolysulfone might have a similar structure but the fact that Backer and Strating's compound (VIII) adds bromine, whereas our compound does not, seems to cast doubt on this possibility.

The polysulfones derived from acetylenes have an α,β -unsaturated sulfone linkage⁶ (I or II) and therefore would be expected to show the characteristics of simpler molecules containing this system.³ Attempts to add sodiomalonic ester, the Grignard reagent and hydrogen from zinc and acetic acid all resulted in degradation of the polymers without the formation of products which could be characterized.

X-Ray diffraction patterns of the polysulfones from 1-pentyne, 1-hexyne, 1-heptyne, 1-nonyne and 1-pentadecyne have been furnished us by Dr. S. T. Gross. Fibered samples obtained by extruding the hot sample through a conical orifice were used. The patterns were prepared at 5 cm. using radiation from a copper target Phillips metallix diffraction X-ray tube. A nickel filter furnishing approximately monochromatic K-radiation was used. An analysis of the patterns will be reported later by Dr. Gross. It is of interest to note that the patterns are much better defined than any which have been obtained with olefin polysulfones. It is possible that the many asymmet-





⁽⁵⁾ Backer and Strating, Rec. trav. chim., 53, 525 (1934); 54, 170 (1935).

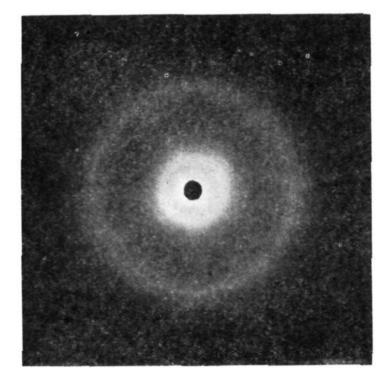


Fig. 2.—Hexyne polysulfone.

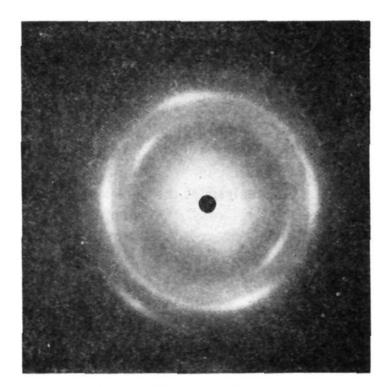


Fig. 3.—Heptyne polysulfone.

ric centers in the latter are responsible for their less sharp patterns.

Attempts to prepare a polysulfone from acetylene itself proved futile.

Experimental

Heat Degradation of 1-Pentynepolysulfone.—In general the polymer was decomposed by boiling its dioxane solution as previously described.² The yields have been improved and the details of a typical experiment follow.

A solution of 10 g. of 1-pentynepolysulfone in 500 cc. of dioxane was heated under reflux condenser for about fifty hours. The evolution of sulfur dioxide had nearly stopped at this time. The dioxane was removed by boiling under reduced pressure and ether was added to the brownish residue. The ether solution was filtered and the residue

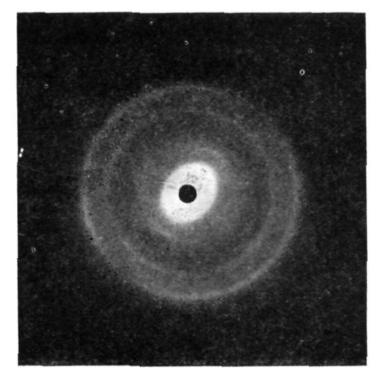


Fig. 4.-Nonyne polysulfone.

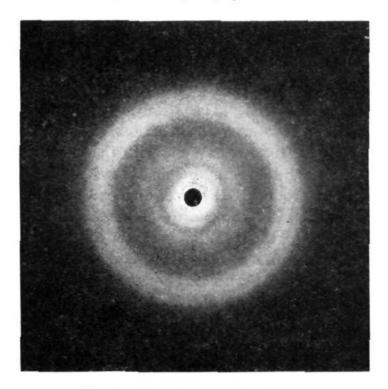


Fig. 5.-Pentadecyne polysulfone.

again extracted with ether. The ether extracts were combined, washed with 5% sodium hydroxide solution and then with water. The alkaline extract turned orange-red during the extraction. The ether layer was dried over anhydrous sodium sulfate, filtered and most of the ether removed by distillation on a steam cone. The last of the ether was removed in a desiccator under reduced pressure. The brownish residue containing some crystals was allowed to stand for about a day in the refrigerator to permit as much crystallization as would occur. This residue, which resembled apple butter, was spread on a clay plate and allowed to stand about a day. The residual material was scraped off and crystallized from dilute alcohol. Norite was used to remove the color. The material thus obtained amounted to 0.3 to 0.4 g. (3.5-5.3%) of product melting at 88°.

In one run 10 g. of polysulfone in 400 cc. of purified

dioxane was heated under a reflux condenser in a current of nitrogen for about one hundred twenty-five hours. The evolved sulfur dioxide was led into standard alkali and titration showed that 8.5% of the total sulfur dioxide in the polymer came off in this time. Evaporation of the dioxane and extraction of the residue with ether left 6.6 g. of polymer which sulfur analysis showed to be essentially unchanged. The yield of crystalline monosulfone in this run was 0.3 g. (3.48% on total polymer or 11.5% on polymer destroyed).

In another set of experiments 30-g. samples of the polymer in 500 cc. of dioxane were heated for about twentyfour hours, then the unchanged polymer was isolated, put in fresh dioxane and heated again for twenty-four hours. This was repeated until practically no unchanged polymer was left. Only one such experiment is recorded for illustration.

	Heating				
	First	Second	Third	Fourth	Fifth
G. polymer	30	24	18.3	14.0	10.7
Cc. dioxane	500	300	250	200	200
Hours refluxing	24	25	26	25	35
G. polymer lost	6	5.7	4.3	3.3	2.7
G. crystalline C10H16SO2 % yield based on poly-	0.88	0.8	0.71	0.43	0.28
mer used	19.4	18.5	21.8	17.1	13,7

Careful fractional distillation of the dioxane from one of the decomposition experiments showed a low boiling fraction which contained a small amount of 1-pentyne. This was identified as the mercury derivative by means of Johnson and McEwen's reagent.⁷ Known 1-pentyne gave a derivative melting at 117-118°, the alkyne from the pyrolysis gave a derivative melting at 116-119°; the mixture of the two melted at 116-119°.

An acidic substance was always present in the dioxane after the heating period but no definite acidic product could be separated.

Reactions of $C_{10}H_{16}SO_2$.—As noted previously² the sulfone would not add bromine but did decolorize alkaline potassium permanganate solution.

The addition of sodiomalonic ester was accomplished by treating 0.7 g. of ethyl malonate in about 5 cc. of benzene with sodium until the salt was formed. The excess sodium was removed and 60 cc. of benzene added. To the suspension thus obtained was added 0.44 g. of the sulfone. The reaction mixture was heated for three hours on a steambath, cooled, washed with water until the washings were neutral, and the benzene removed. The excess malonic ester was removed by distillation under reduced pressure. When the residue was cooled and dried on a clay plate, 0.56 g. of white crystals remained. Crystallization from alcohol gave a product melting at $104.5-105^\circ$.

Anal. Calcd. for C17H28O6S: S, 8.9. Found: S, 8.6.

Attempts to add a second mole of malonic ester to this product were ineffective and the starting material was recovered.

Reduction with zinc and acetic acid was carried out by dissolving 0.41 g. of the sulfone in 50 cc. of glacial acetic acid and boiling the mixture for seven hours with 10 g. of zinc. The hot mixture was then filtered from undissolved zine, the zinc washed with hot acetic acid, and then the

(7) Johnson and McBwen, THIS JOURNAL, 48, 469 (1926).

combined acetic acid solutions diluted with water. The solution turned cloudy but no crystals separated. The solvent was then removed through a Widmer column and the residue was dissolved in ether. After removal of the ether the residue was finally induced to crystallize from low-boiling petroleum ether. The product thus obtained melted at $49-50^{\circ}$ on a hot-stage microscope. Analysis showed it to be a dihydro derivative of the sulfone.

Anal. Calcd. for $C_{10}H_{18}SO_2$: C, 59.35; H, 8.97. Calcd. for $C_{10}H_{20}SO_2$: C, 58.76; H, 9.87. Found: C, 59.43; H, 9.06.

Catalytic reduction of 2.86 g. of the sulfone in 50 cc. of absolute alcohol with hydrogen in the presence of 0.1 g. of platinum oxide-platinum black⁴ in a low pressure reduction apparatus⁸ for twenty hours gave a solution with a faint odor of hydrogen sulfide. The platinum catalyst was removed by filtration. The solution was cooled in a dry ice-acetone bath and the solid collected in a filter. The solid thus obtained was twice recrystallized from ether by cooling the solution in a dry ice-acetone bath. This product melted at 56.5-57° on a hot-stage microscope.

Anal. Calcd. for $C_{10}H_{18}SO_2$: C, 59.35; H, 8.97. Found: C, 59.55, 59.43; H, 8.88, 8.90.

A mixture of this compound with the dihydro derivative which melted at $49-50^{\circ}$ melted below 44° . This dihydro compound could not be further reduced with zinc and acetic acid.

Attempts to Add Reagents to the Acetylene Polysulfones.—When 5 g. of 1-pentynepolysulfone in 225 cc. of glacial acetic acid was boiled under a reflux condenser with 15 g. of powdered zinc for thirteen hours, some hydrogen sulfide was liberated. After isolating the polymer it was found to have the melting point (200–208°) characteristic of the original 1-pentynepolysulfone.² Attempts to reduce 1-nonynepolysulfone with zinc and acetic acid were also unsuccessful. Similarly attempts to reduce dioxane solutions of 1-nonynepolysulfone, propynepolysulfone and 1-pentynepolysulfone with hydrogen in the presence of platinum oxide–platinum black^{4,8} were unsuccessful.

The carefully dried polysulfones from 1-pentyne, 1hexyne, 1-heptyne, 1-nonyne and phenylacetylene dissolved in an ether solution of ethylmagnesium bromide with the evolution of gas and the formation of amber to red colored solutions. Attempts to follow the gas liberation quantitatively gave unreproducible results. Recovery of the polymers from the solution showed that considerable degradation had taken place in this reaction. No evidence for a simple addition was obtained.

Sodiomalonic ester in dry benzene did not add to 1pentynepolysulfone in the cold and when the mixture was warmed the polymer was degraded.

Attempts to Obtain Acetylene Polysulfone.—Various attempts to bring about the combination of acetylene and sulfur dioxide at atmospheric pressure and under the pressure of a solution of acetylene in acetone and sulfur dioxide were made. Ascaridole was used as a catalyst. Ethyl alcohol was also added to some of the mixtures. In the experiments at atmospheric pressure acetylene was bubbled through the cold reaction mixture. No evidence of polymer formation was ever obtained.

⁽⁸⁾ Adams and Vorhees, ref. 4, p. 53

Summary

1. The pyrolysis of 1-pentynepolysulfone to yield a crystalline sulfone, $C_{10}H_{16}SO_2$, has been studied further and evidence that the new sulfone has a cyclic unsaturated sulfone structure has been described. No similar products have been obtained from other acetylenepolysulfones by pyrolysis.

2. Attempts to add reagents to the α,β -unsaturated sulfone systems present in the acetylene polysulfones resulted in degradation of the polymers.

3. Some X-ray diffraction patterns of typical acetylenic polysulfones have been recorded.

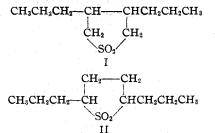
URBANA, ILLINOIS RECEIVED JULY 24, 1939

[CONTRIBUTION FROM THE NOVES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

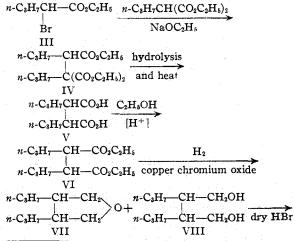
Polysulfones. XII.¹ The Synthesis of 3,4- and 2,5-Di-*n*-propyltetrahydrothiophene-1,1-dioxides

By C. S. MARVEL AND W. W. WILLIAMS

The pyrolysis of 1-pentynepolysulfone in dioxane has yielded a cyclic unsaturated sulfone which is probably a di-*n*-propylthiophene oxide.² The positions of the alkyl groups are uncertain as they may be 3,4, 2,5 or 2,4. In order to have available related compounds of known structure, we have now synthesized the 3,4- and the 2,5-di-*n*-propyltetrahydrothiophene-1,1-dioxides (I and II).



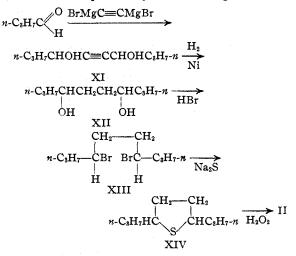
The synthesis of the 3,4-di-*n*-propyl derivative (I) has been accomplished by the following reactions.



⁽¹⁾ For the eleventh communication on polysulfones, see THIS JOURNAL, 61, 2710 (1939).

The di-*n*-propylsuccinic acid has been prepared previously by Bone and Sprankling³ from cyanoacetic ester but the procedure described in the experimental part of this communication worked more smoothly for us.

The synthesis of the 2,5-di-*n*-propyl derivative has been accomplished by the following reactions.



4,7-Decanediol has been prepared previously by Bogert and Slocum⁴ but the details of their process were not available to us at the time the above synthesis was performed.

 $2,5-{\rm Di}\text{-}\textit{n}\text{-}{\rm propyltetrahydrothiophene-1,1-diox-}$

⁽²⁾ Ryden and Marvel, ibid., 58, 2047 (1936); see also ref. 1.

⁽³⁾ Bone and Sprankling, J. Chem. Soc.. 77, 654 (1900).

⁽⁴⁾ Bogert and Slocum. Am. Perfumer, 18, 621 (1924); C. A., 18, 1271 (1924).