

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

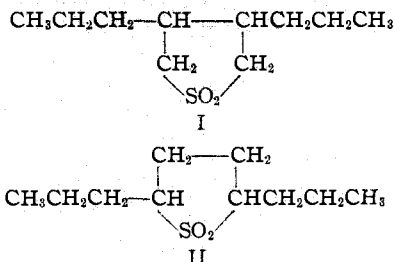
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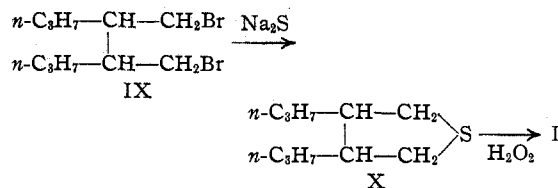
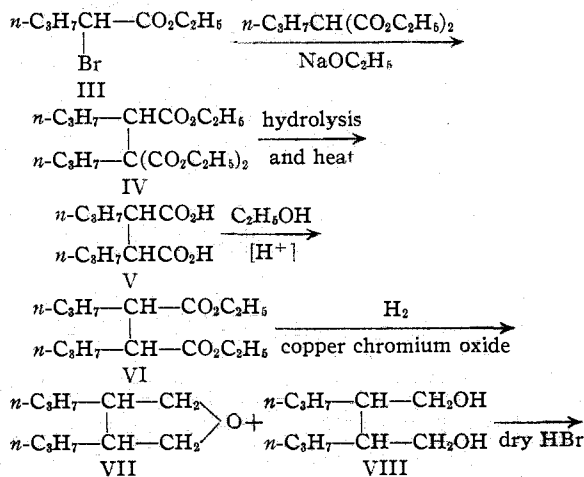
Polysulfones. XII.¹ The Synthesis of 3,4- and 2,5-Di-*n*-propyltetrahydrothiophene-1,1-dioxides

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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).

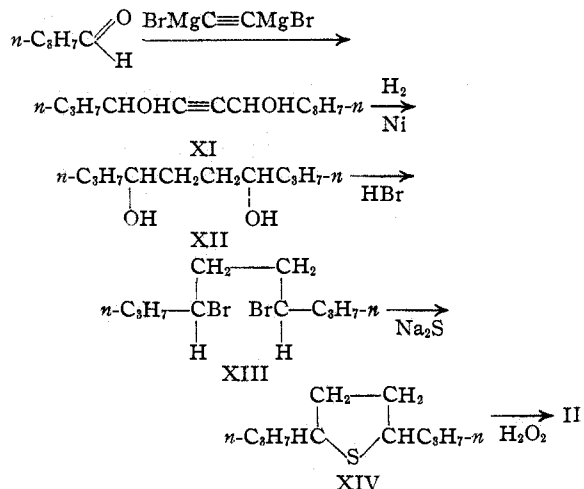


The synthesis of the 3,4-di-*n*-propyl derivative (I) has been accomplished by the following reactions.



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-Di-*n*-propyltetrahydrothiophene-1,1-diox-

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

(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).

ide (II) is a liquid. By use of its refractive index and density it is possible to assign a refractive constant of 8.7 to the sulfone group.

Experimental

4,4,5-Tricarboethoxyoctane (IV).—A regular malonic ester synthesis using 469 g. of ethyl *n*-propylmalonate, 500 cc. of dry xylene, 53.4 g. of sodium and 490 g. of ethyl α -bromovalerate and heating for fifteen hours gave 454.4 g. (59%) of a product boiling at 182–183° (1 mm.); d_{20}^{20} 1.0170; n_D^{20} 1.4393.

Anal. Calcd. for $C_{17}H_{30}O_6$: C, 61.78; H, 9.16. Found: C, 61.91; H, 8.95.

α,α' -Di-*n*-propylsuccinic Acid (V).—A solution of 405 g. of the above ester in 1250 g. of aqueous 40% potassium hydroxide was refluxed overnight. About 300 cc. of water was distilled from the flask and heating was continued for two days, after which time the solution became nearly homogeneous. A few drops of unsaponified material was removed by ether extraction and then the solution was cooled to 0° and hydrochloric acid was added until the solution was distinctly acid to congo paper. When the solution warmed up to room temperature carbon dioxide was evolved rapidly. The organic acid was extracted with ether and the ether evaporated. There remained a nearly quantitative yield of the mixture of diastereoisomers of the desired acid. Recrystallization of a sample from benzene gave the *cis*-form⁵ melting at 115–117°. The *trans*-form never was isolated in an entirely pure form.

Ethyl α,α' -Di-*n*-propylsuccinate (VI).—The mixed isomers of the acid were esterified with ethyl alcohol in the presence of sulfuric acid. The ester was obtained in about 87% yield based on the acid not recovered; b. p. 86–87° (less than 1 mm.); d_{20}^{20} 0.9568; n_D^{20} 1.4302.

Anal. Calcd. for $C_{14}H_{26}O_4$: C, 66.58; H, 10.38. Found: C, 65.53; H, 10.22.

Catalytic Reduction of Ethyl α,α' -Di-*n*-propylsuccinate.

—The ester was reduced by the general method for ester reduction described by Adkins.⁵

A solution of 70.7 g. of ester in 125 cc. of dioxane was refluxed with a few grams of Raney nickel catalyst for two hours to remove catalyst poisons. The nickel catalyst was removed by filtration and 7.1 g. of copper-chromium oxide catalyst was added. The reaction mixture was placed in a steel bomb under a hydrogen pressure of over 4400 lb. per square inch (300 atm.) at a temperature of 260°. The pressure drop noted in about twenty hours indicated the reduction was complete. The catalyst was removed by filtration and the reaction mixture was fractionally distilled through a Widmer column. The first fraction boiling at 55–63° (1–2 mm.) weighed 23.2 g. (54.2%) and was identified as 3,4-di-*n*-propyltetrahydrofuran (VII). Redistillation gave a product, b. p. 40–42° (less than 1 mm.); d_{20}^{20} 0.8683; n_D^{20} 1.4369.

Anal. Calcd. for $C_{10}H_{20}O$: C, 76.84; H, 12.91. Found: C, 76.82; H, 12.92.

After removal of the furan a second fraction boiling at 63–83° (1 mm.) amounting to 26 g. was obtained and a

residue weighing 2 g. remained. Redistillation of the residue gave a liquid boiling at 103° (less than 1 mm.); d_{20}^{20} 0.9378; n_D^{20} 1.4563. Analysis showed this fraction to be the expected 2,3-di-*n*-propyl-1,4-butanediol (VIII).

Anal. Calcd. for $C_{10}H_{22}O_2$: C, 68.89; H, 12.74. Found: C, 68.76; H, 12.71.

1,4-Dibromo-2,3-di-*n*-propylbutane (IX).—No very satisfactory procedure for obtaining the dibromide was worked out in detail. The furan (44.1 g.) and the glycol (6 g.) obtained as above were heated to 125° for about ten hours with dry hydrogen bromide in glacial acetic acid and the samples of impure bromide were obtained. These crude products were mixed and again heated to 125° for fifteen hours with hydrogen bromide in glacial acetic acid but analysis of the best fractions indicated there was incomplete reaction. Finally the crude material from this treatment was heated to 128–154° for about fifty hours with dry hydrogen bromide slowly bubbling through the mixture. This product was washed with sodium carbonate solution, then water and dried. Redistillation gave 34.2 g. of product boiling at 81–94° (about 1 mm.). The best fraction boiling at 94° (about 1 mm.) had the following properties: d_{20}^{20} 1.3834; n_D^{20} 1.4971.

Anal. Calcd. for $C_{10}H_{20}Br_2$: C, 40.00; H, 6.72. Found: C, 40.68; H, 6.88.

3,4-Di-*n*-propyltetrahydrothiophene (X).—In a 200-cc. three-necked flask equipped with a dropping funnel, stirrer, and reflux condenser was placed 125 cc. of an alcoholic solution of sodium sulfide.⁶ The alcohol was heated to boiling and the stirrer started. Then 14.7 g. of 1,4-dibromo-2,3-di-*n*-propylbutane in 15 cc. of absolute alcohol was added from the dropping funnel over a period of one hour. Boiling was continued about ten hours and then the cooled reaction mixture was poured into 265 cc. of 25% sodium chloride solution. The organic sulfide was extracted with petroleum ether (b. p. 35–38°), the extract was dried and then distilled. A second run using 15.5 g. of the bromide and other equivalent reagents was made and mixed with the above. From the two runs 13.4 g. (77.5%) of 3,4-di-*n*-propyltetrahydrothiophene was obtained, b. p. 65–66° (1 mm.); d_{20}^{20} 0.9129; n_D^{20} 1.4830.

Anal. Calcd. for $C_{10}H_{20}S$: C, 69.68; H, 11.70. Found: C, 69.76; H, 11.73.

3,4-Di-*n*-propyltetrahydrothiophene-1,1-dioxide (I).—To a solution of 11.5 g. of the above tetrahydrothiophene derivative in 25 cc. of glacial acetic acid was added cautiously 35 cc. of 100 volume hydrogen peroxide. The heat developed caused the reaction mixture to boil. The mixture was then heated on a steam-bath for about two hours. Cooling the reaction mixture in the icebox caused some crystals to separate. These were collected on a filter, washed with water and dried at 1 mm. pressure. The yield was 8.75 g. The filtrate and washings were extracted several times with ether and the ether extract dried and concentrated. There remained 3.53 g. of oil which was apparently also cyclic sulfone as no odor of the sulfide remained.

The above solid was examined on a hot-stage microscope and found to consist of irregular scales mixed with

(5) Adkins, "Reactions of Hydrogen with Organic Compounds over Copper-Chromium Oxide and Nickel Catalysts," The University of Wisconsin Press, Madison, Wis., 1937.

(6) Bost and Conn, *Org. Syntheses*, **15**, 72 (1935), John Wiley and Sons, Inc., New York, N. Y., 1935, p. 72.

oily droplets. At 58° it was completely liquid. The solid was purified by dissolving in a little ether and cooling in a dry ice-acetone bath. The glistening white, scale material thus formed melted at 57–59.5° on the hot-stage microscope.

Anal. Calcd. for $C_{10}H_{20}SO_2$: C, 58.77; H, 9.87. Found: C, 58.87; H, 9.80.

5-Decyne-4,7-diol (XI).—To a solution of 1.54 moles of acetylenedimagnesium bromide in ether prepared in the usual manner⁷ was added 216.2 g. of *n*-butyraldehyde over a period of one and one-half hours. The mixture was stirred for nearly a day and then poured onto cracked ice, acidified with hydrochloric acid. The ether layer was worked up in the usual manner and 213 g. (41.8%) of a viscous golden oil of b. p. 113–114° (1 mm.) was obtained; d^{20}_4 , 0.9462; n^{20}_D 1.4678.

Anal. Calcd. for $C_{10}H_{18}O_2$: C, 70.55; H, 10.66. Found: C, 70.58; H, 10.90.

4,7-Decanediol (XII).—The above acetylenic glycol was divided into two parts for reduction with hydrogen over Raney nickel.⁸ In one run 102 g. of glycol, 35 cc. of alcohol and about 5 g. of Raney nickel were placed in the bomb at 25° and 2400 lb. (160 atm.) pressure. The bomb was warmed up to 85° during the reduction. At the end of the reaction the pressure had dropped to 800 lb. (53 atm.). In the other run 111 g. of glycol, 30 cc. of alcohol and about 5 g. of Raney nickel were placed in the bomb at 25° and 4430 lb. (298 atm.) pressure. This run was not heated but the reaction mixture warmed to 75° from the heat of reaction. At the end of the reduction the pressure had dropped to 750 lb. (30 atm.). The two reduction mixtures were united, filtered to remove catalyst and distilled. The portions boiling at 110–112° (1 mm.) solidified in the receiver. The yield was 164 g. (71%). The glycol was recrystallized from petroleum ether (b. p. 65–110°) and then melted at 79–80° on a hot-stage microscope.

Anal. Calcd. for $C_{10}H_{22}O_2$: C, 68.89; H, 12.74. Found: C, 68.94; H, 12.75.

(7) Du Pont, *Ann. chim.*, [8] **30**, 485 (1913); Blomquist and Marvel, *This Journal*, **55**, 1655 (1933).

(8) Covert and Adkins, *Ibid.*, **54**, 4116 (1932).

4,7-Dibromodecane (XIII).—Dry hydrogen bromide was passed through the glycol for four hours at 45–60° and then for eighteen hours at 105–115°. The bromide was then distilled. From 112.6 g. of glycol there was obtained 165 g. (85.3%) of bromide, b. p. 106–109° (1 mm.); d^{20}_4 , 1.3354; n^{20}_D 1.4920.

Anal. Calcd. for $C_{10}H_{20}Br_2$: C, 40.00; H, 6.72; Br, 53.28. Found: C, 40.44; H, 6.77; Br, 52.90.

2,5-Di-*n*-propyltetrahydrothiophene (XIV).—Using the same procedure described for the previous cyclic sulfide, 120 g. of 4,7-dibromodecane gave 52.8 g. (77%) of the desired 2,5-di-*n*-propyltetrahydrothiophene, b. p. 74–75° (1 mm.); d^{20}_4 , 0.8958; n^{20}_D 1.4795.

Anal. Calcd. for $C_{10}H_{20}S$: C, 69.68; H, 11.70. Found: C, 69.61; H, 11.65.

2,5-Di-*n*-propyltetrahydrothiophene-1,1-dioxide (II).—The sulfide was oxidized in the same manner described for its isomer. The yield from 33 g. of sulfide was 38 g. of sulfone, b. p. 123–125° (1 mm.); d^{20}_4 , 1.0408; n^{20}_D 1.4719.

Anal. Calcd. for $C_{10}H_{20}SO_2$: C, 58.77; H, 9.87. Found: C, 58.90; H, 9.95.

Using the Eisenlohr values⁹ 2.42 for each carbon atom and 1.1 for each hydrogen atom the refractive constant for the —SO₂— group in the above sulfone is calculated as 8.7.

Summary

1. 3,4-Di-*n*-propyltetrahydrothiophene-1,1-dioxide and 2,5-di-*n*-propyltetrahydrothiophene-1,1-dioxide have been synthesized and many intermediates in these syntheses have been characterized.

2. Since 2,5-di-*n*-propyltetrahydrothiophene-1,1-dioxide is a liquid it has been possible to calculate a refractive constant of 8.7 for the sulfone group in this compound.

(9) Cohen, "Organic Chemistry," Edward Arnold, London, 1921, Vol. II, pp. 17–40.