fractioned rubber (17.40 to 17.65) prepared in this Laboratory.

These results indicate quite clearly that a single diffusion of rubber into ether is insufficient completely to separate sol from gel rubber. They also show that while there is no absolute criterion by which the fractional precipitation method may be judged, it is decidedly more efficient than the ether diffusion method.

Summary

Sol rubber prepared by a single diffusion in ether can be separated into two components by fractional precipitation, whereas sol rubber prepared by a single fractional precipitation completely diffuses in ether, thus indicating the superiority of the fractional precipitation method as a means of preparing sol rubber.

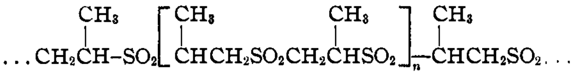
COLUMBUS, OHIO RECEIVED FEBRUARY 23, 1937

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

The Reaction between Sulfur Dioxide and Olefins. V.[1] The Structure of the Polysulfones from Olefins of the Type $RCH{=}CH_2$

BY F. J. GLAVIS, L. L. RYDEN AND C. S. MARVEL

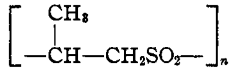
It has been demonstrated[2] that propylene and sulfur dioxide combine to form a polysulfone (I)



$$\ldots CH_2\overset{CH_3}{\overset{|}{C}}H\text{-}SO_2\left[\overset{CH_3}{\overset{|}{C}}HCH_2SO_2CH_2\overset{CH_3}{\overset{|}{C}}HSO_2\right]_n\overset{CH_3}{\overset{|}{C}}HCH_2SO_2\ldots$$

I

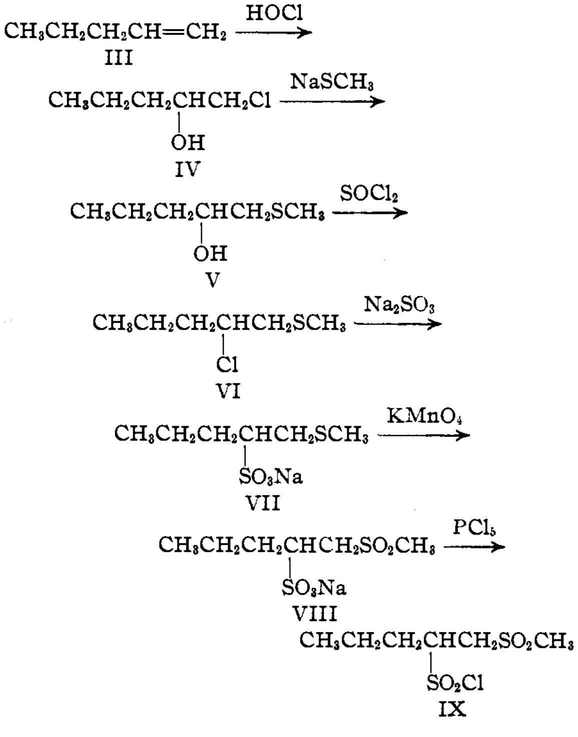
in which the propylene units are oriented so that like parts of the hydrocarbon residues are linked through the sulfone groups. The hydrolysis of the polysulfone with alkali gave products which could not be reconciled with the structure II,



$$\left[-\overset{CH_3}{\overset{|}{C}}H-CH_2SO_2-\right]_n \quad \text{II}$$

which had previously been assigned to the addition product.[3] The experiments described in this communication were undertaken to determine whether the polysulfones from other olefins of the type $RCH{=}CH_2$ would be structurally comparable to propylenepolysulfone (I), or would have a simple symmetrical unit similar to that indicated in formula II.

1-Pentenepolysulfone, prepared as described previously,[4] can be hydrolyzed by warming it with 20% sodium hydroxide solution to yield *n*-butyraldehyde and a sodium salt of composition $C_6H_{13}S_2O_4Na$. This salt can be oxidized readily by hydrogen peroxide to give a compound $C_6H_{13}S_2O_5Na$, which, with phosphorus pentachloride, yields a sulfonyl chloride melting at 64–65°. The same sulfonyl chloride (IX) has been synthesized from 1-pentene by the following series of reactions



$$CH_3CH_2CH_2CH{=}CH_2 \xrightarrow{HOCl}$$
III

$$CH_3CH_2CH_2\underset{OH}{\underset{|}{C}}HCH_2Cl \xrightarrow{NaSCH_3}$$
IV

$$CH_3CH_2CH_2\underset{OH}{\underset{|}{C}}HCH_2SCH_3 \xrightarrow{SOCl_2}$$
V

$$CH_3CH_2CH_2\underset{Cl}{\underset{|}{C}}HCH_2SCH_3 \xrightarrow{Na_2SO_3}$$
VI

$$CH_3CH_2CH_2\underset{SO_3Na}{\underset{|}{C}}HCH_2SCH_3 \xrightarrow{KMnO_4}$$
VII

$$CH_3CH_2CH_2\underset{SO_3Na}{\underset{|}{C}}HCH_2SO_2CH_3 \xrightarrow{PCl_5}$$
VIII

$$CH_3CH_2CH_2\underset{SO_2Cl}{\underset{|}{C}}HCH_2SO_2CH_3$$
IX

This synthesis of the sulfonyl chloride (IX) establishes the structure of the sulfonic acid salt $C_6H_{13}S_2O_5Na$ (VIII). Likewise, it shows that the salt $C_6H_{13}S_2O_4Na$ must have the structure shown in formula XII. 1-Pentenepolysulfone must, accordingly, have the structure shown in formula X, and thus be strictly comparable to propylenepolysulfone (I) in the arrangement of the hydrocarbon residues.

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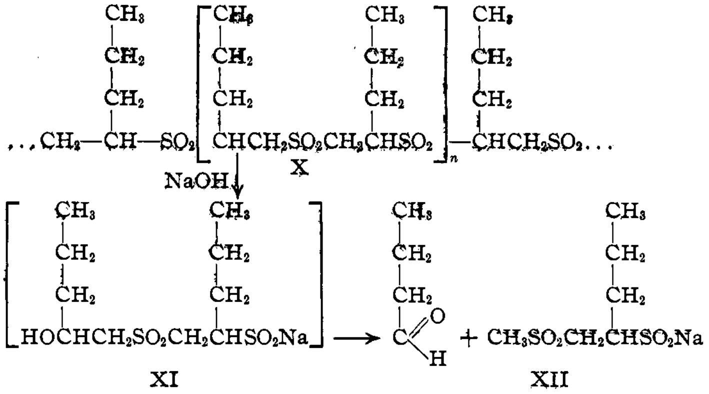
[1] For the fourth paper in this series, see Ryden and Marvel, THIS JOURNAL, **58**, 2047 (1936).

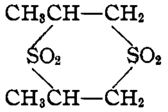
[2] Hunt and Marvel, *ibid.*, **57**, 1691 (1935).

[3] Staudinger and Ritzenthaler, *Ber.*, **68**, 458 (1935).

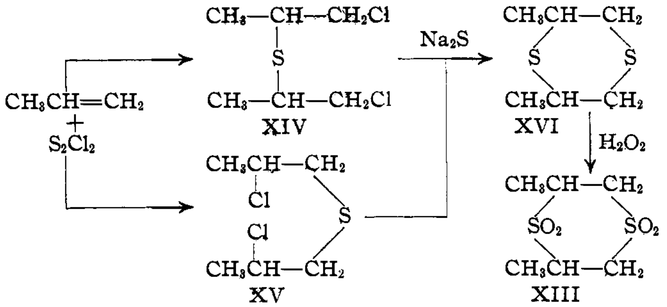
[4] Ryden and Marvel, THIS JOURNAL, **57**, 2311 (1935).



A further proof that these two polysulfones have similar structural units has been obtained by studying the breakdown of the polymers in liquid ammonia solutions. Propylenepolysulfone dissolves in liquid ammonia, and on evaporation of the solvent and crystallization of the residue from an organic solvent, yields the same cyclic disulfone (XIII) which was previously obtained[2,3] by the

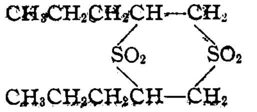

XIII

action of cold alkalies on propylenepolysulfone. This cyclic disulfone (XIII), whose structure was established[2] by alkaline cleavage, has now been synthesized in the following manner

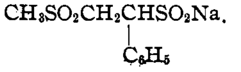


The structure of the intermediate dichlorosulfide is probably that given in formula XV[5] rather than that given in formula XIV, but the same cyclic disulfide (XVI) would be obtained from either.

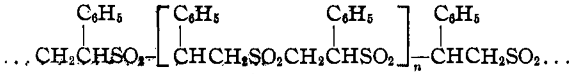
1-Pentenepolysulfone in liquid ammonia is also broken down into a cyclic disulfone (XVII), and the same product was obtained from 1-pentene by the synthesis used above in the case of propylene.


XVII

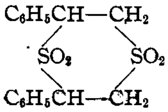
Styrenepolysulfone (XVIII), which has not been described previously, has now been prepared by the general method which has been developed for other polysulfones,[4] and its structure has been established by hydrolysis with alkali to give benzaldehyde and a salt of a sulfone sulfinic acid,


$CH_3SO_2CH_2\underset{C_6H_5}{C}HSO_2Na$.

In liquid ammonia solution, styrenepolysulfone is converted to a cyclic disulfone (XIX), and the


$$\ldots CH_2\overset{C_6H_5}{C}HSO_2-\left[\overset{C_6H_5}{C}HCH_2SO_2CH_2\overset{C_6H_5}{C}HSO_2\right]_n-\overset{C_6H_5}{C}HCH_2SO_2\ldots$$
XVIII

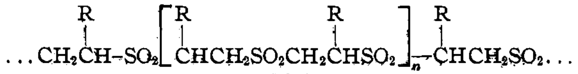
structure of this product was established by its synthesis from styrene by the methods described above for the analogous products from propylene and 1-pentene.


XIX

1-Octenepolysulfone and 1-nonenepolysulfone[4] also undergo rearrangement in liquid ammonia solution to yield dimeric products which are presumably cyclic disulfones of the general structure which has been established in the above cases.

There can no longer be doubt that, in the addition of sulfur dioxide to an olefin of the type RCH=CH$_2$, there is a definite orientation of the hydrocarbon residues, so that like parts are joined through sulfone linkages (XX).

The fact that these olefin–sulfur dioxide addition polymerization reactions so generally yield the "head to head–tail to tail" type of polymer seems to us to make it logical to assume that other addition polymerization reactions may take place in a similar manner, and thus to make it desirable to investigate more carefully the structure of the products of such reactions.


$$\ldots CH_2\overset{R}{C}H-SO_2\left[\overset{R}{C}HCH_2SO_2CH_2\overset{R}{C}HSO_2\right]_n-\overset{R}{C}HCH_2SO_2\ldots$$
XX

Experimental

Styrenepolysulfone.—A mixture of 10 cc. of styrene, 10 cc. of liquid sulfur dioxide, 2 cc. of ethyl alcohol, 2 drops of

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[5] Pope and Smith, *J. Chem. Soc.*, **119**, 396 (1921).

30% hydrogen peroxide and 5 cc. of paraldehyde containing peroxides was placed in a pressure bottle and allowed to stand for twelve to eighteen hours at room temperature. The paraldehyde must be added at the start of the reaction in this preparation as otherwise only polystyrene is formed. The reaction mixture was poured into 100 cc. of ether, and the polymer was collected on a filter. When the reaction mixture was poured into water, it was very difficult to obtain a good product free from water. The yield of polysulfone was 0.5 to 2.5 g. in various experiments. The product darkens on heating and melts, with decomposition, at 185–190°. It is slightly soluble in acetone, but insoluble in most other common organic solvents.

Anal. Calcd. for $(C_8H_8SO_2)_n$: S, 19.05. Found: S, 18.64.

1-Octenepolysulfone.—A mixture of 10 cc. of 1-octene, 10 cc. of liquid sulfur dioxide, 2 cc. of ethyl alcohol, 2 cc. of 3% hydrogen peroxide and 5 cc. of "old" paraldehyde was allowed to stand as described above. The product was precipitated by pouring the reaction mixture into water. The yield was 2 to 4 g. in various runs. This product is first rather pliable, but eventually sets to a very hard product. It is soluble in acetone, but not in other common organic solvents. It becomes opaque at 100°, and melts, with decomposition, at 175–200°.

Anal. Calcd. for $(C_8H_{16}SO_2)_n$: S, 18.18. Found: S, 17.82.

Alkaline Hydrolysis of 1-Pentenepolysulfone.—A suspension of 2 g. of 1-pentenepolysulfone in 10 cc. of 20% sodium hydroxide was heated to boiling, and a current of steam was passed through the mixture. The distillate was condensed and collected in a vessel containing a solution of 1 g. of 2,4-dinitrophenylhydrazine, 75 cc. of alcohol, 10 cc. of concentrated sulfuric acid and water to give a total volume of 250 cc. A precipitate of *n*-butyraldehyde 2,4-dinitrophenylhydrazone came down. The yield was 1.2 g. (85%) of a product melting at 121.5–122°. The literature[6] gives the melting point of *n*-butyraldehyde 2,4-dinitrophenylhydrazone at 122°.

The alkaline residue, after steam distillation had removed all of the butyraldehyde, was evaporated to dryness, and this residue was extracted with hot 95% alcohol. On cooling this solution, a white crystalline salt separated. The yield of salt was about 1 g. (60%). The salt contained one molecule of water of crystallization when dried in a desiccator over phosphorus pentoxide at room temperature, but lost this at 125°. The analyses for carbon, hydrogen and sodium were made on the anhydrous sample.

Anal. Calcd. for $C_6H_{13}S_2O_4Na \cdot H_2O$: H_2O, 7.1. Found: H_2O, 7.0. *Anal.* Calcd. for $C_6H_{13}S_2O_4Na$: C, 30.9; H, 5.5; Na, 9.7. Found: C, 30.4; H, 5.3; Na, 10.1.

Oxidation of the Salt $C_6H_{13}S_2O_4Na$.—To a solution of 10 g. of the above salt in 20 cc. of water was added 30 cc. of 30% hydrogen peroxide solution over a period of about thirty minutes. Considerable heat was liberated during the oxidation. The reaction mixture was allowed to stand for about fifteen minutes, and then evaporated to dryness on a steam-bath. The residue was recrystallized from 200 cc. of hot 95% alcohol. The yield was 7 g. (69%) of a white crystalline salt. The product was dried at 100° at 3 to 4 mm. before analyzing.

Anal. Calcd. for $C_6H_{13}S_2O_5Na$: S, 25.4. Found: S, 25.2.

Preparation of the Sulfonyl Chloride.—The salt obtained in the preceding experiment was recrystallized four times from alcohol and dried. Then 1 g. of this highly purified salt was ground in a mortar with 1 g. of phosphorus pentachloride. One hundred cubic centimeters of ice water was added immediately, and an oily precipitate separated. On stirring the mixture, the oil solidified. The solid was separated and recrystallized from a mixture of petroleum ether and benzene. It melted at 64–65°.

Anal. Calcd. for $C_6H_{13}S_2O_4Cl$: S, 27.12. Found: S, 26.99.

1-Chloro-2-pentanol.—1-Pentene was converted to the chlorohydrin, according to the method which Coleman and Johnstone used for 1-chloro-2-cyclohexanol.[7] From 50 g. of 1-pentene, there was obtained 37 g. (43%) of 1-chloro-2-pentanol, b. p. 68–75° at 30 mm.; d^{20}_{20} 1.037; n^{20}_D 1.4520.

Anal. Calcd. for $C_5H_{11}OCl$: Cl, 26.35. Found: Cl, 26.78.

1-Methylthiol-2-pentanol.—The directions for the preparation of methylthiolethyl alcohol[8] were used for this synthesis. From 35 g. of the above chlorohydrin, there was obtained 18 g. (45%) of a product boiling at 90° under 18 mm.; d^{20}_{20} 0.943; n^{20}_D 1.4792.

Anal. Calcd. for $C_6H_{14}SO$: S, 23.88. Found: S, 22.78.

1-Methylthiol-2-chloropentane.—The directions for the preparation of β-chloroethylmethylsulfide[9] were adopted for this synthesis. From 18 g. of the above methylthiol alcohol and 21 g. of thionyl chloride, there was obtained 14 g. (70%) of a product boiling at 84–86° at 20 mm.; d^{20}_{20} 1.0090; n^{20}_D 1.4860.

Anal. Calcd. for $C_6H_{13}SCl$: Cl, 23.26. Found: Cl, 23.48.

Sodium 1-Methylthiol-2-pentanesulfonate.—To a solution of 14 g. of sodium sulfite in 50 cc. of water, 12.5 g. of 1-methylthiol-2-chloropentane was added over a period of about one hour. The mixture was well stirred with a mechanical stirrer, and heating and stirring were maintained for an hour after the addition of the chloro compound. The solution was evaporated over a water-bath, and the residue was recrystallized from 95% alcohol. The yield of salt was about 2 g.

Anal. Calcd. for $C_6H_{13}S_2O_3Na$: S, 10.44. Found: S, 10.68.

1-Methylsulfonepentane-2-sulfonyl Chloride.—To a solution of 3 g. of the above salt in 10 cc. of water was added 1 drop of 10% sodium hydroxide solution, and enough 5% potassium permanganate solution so that the color persisted after the solution was boiled. The excess potassium permanganate was then destroyed with hydrogen peroxide solution, and the reaction mixture was filtered. The filtrate was evaporated to dryness, and the residue was re-

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[6] Brady and Elsmine, *Analyst*, **51**, 77 (1926): Allen, THIS JOURNAL, **52**, 2955 (1930).

[7] Coleman and Johnstone, "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, 1932, p. 151.

[8] Windus and Shildneck, "Organic Syntheses," Vol. XIV, John Wiley and Sons, Inc., New York, 1934, p. 54.

[9] Kirner and Windus, *ibid.*, p. 18.

TABLE I

CYCLIC DISULFONES FROM POLYSULFONES

Polysulfone from	Yield of cyclic disulfone, %	Solvent for crystallization	M. p., °C.	Molecular formula	Analyses, % Calcd. C	H	S	Found C	H	S
Propylene	35	Mixture of dioxane and water	334	[a]						
1-Pentene	40	Alcohol	257	$C_{10}H_{20}S_2O_4$	44.8	7.46	23.8	44.8	7.03	23.5
1-Octene	40	Dioxane and acetic acid	265	$C_{16}H_{32}S_2O_4$	..	..	18.18	..	...	18.02
1-Nonene	14	Alcohol or benzene	260–261	$C_{18}H_{36}S_2O_4$	56.9	9.48	...	57.4	10.02	...
Styrene	25	Alcohol, dioxane and glacial acetic acid	280	$C_{16}H_{16}S_2O_4$	..	..	19.05	..	...	19.35

[a] This product is identical with a product isolated by treatment of propylenepolysulfone with cold sodium hydroxide solution, and reported as melting at 320°.[3]

crystallized from alcohol four times. The yield of recrystallized salt was 1.3 g. (40%). This salt was then converted to the sulfonyl chloride in the manner described for the sulfone–sulfonate salt obtained from the breakdown of 1-pentenepolysulfone.

The sulfonyl chloride from this synthetic salt melted at 64–64.5°, and when a sample of this synthetic product was mixed with the sulfonyl chloride prepared from the breakdown of the polysulfone, the mixture melted at 64–65°.

Alkaline Hydrolysis of Styrenepolysulfone.—A mixture of 10 g. of styrenepolysulfone and 100 cc. of 10% sodium hydroxide solution was distilled with steam. The distillate contained benzaldehyde, which was identified by preparing the 2,4-dinitrophenylhydrazone, which melted at 235°, and showed no depression in melting point when mixed with an authentic specimen of the benzaldehyde derivative.[10] The solution remaining in the distilling flask was filtered and evaporated to dryness. The resulting salt was recrystallized from alcohol. The yield was 4 g. Ten grams of this salt was oxidized by dissolving it in 20 cc. of water and treating with 30 cc. of 30% hydrogen peroxide solution. This reaction mixture was evaporated, and the sulfonic acid salt was recrystallized from alcohol.

Anal. Calcd. for $C_9H_{11}S_2O_5Na$: S, 22.38. Found: S, 22.51.

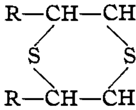
Liquid Ammonia Cleavage of Polysulfones.—Several polysulfones were treated with liquid ammonia to test their solubility. It was observed that those which dissolved were changed by the treatment. The long polymeric molecules were broken up and cyclic disulfones were produced. The experiments were carried out by dissolving about 1 g. of polysulfone in 50–100 cc. of liquid ammonia, and then allowing the solvent to evaporate. The crystalline residue was then recrystallized from an organic solvent. The results are summarized in Table I.

Neither cyclohexenepolysulfone nor isobutylenepolysulfone would dissolve in liquid ammonia, and were recovered unchanged after the treatment. 2-Pentenepolysulfone dissolved slowly in liquid ammonia, and the polymer was destroyed, but no crystalline products could be isolated.

2,6-Disubstituted-1,4-dithians.—Three representatives of this series of compounds were prepared from the olefins by first adding sulfur monochloride according to the procedure of Pope and Smith,[5] and then converting the crude β,β'-dichlorosulfides to the 1,4-dithians by the action of sodium sulfide. In each case, to 72 g. (0.5 mol) of sulfur monochloride was added 1 mol of olefin. After the completion of the addition reaction, the crude mixture was added to a solution of 0.5 mol of sodium sulfide in absolute alcohol, prepared as described by Bost and Conn.[11] The reaction mixture was boiled overnight, and then poured into 2 liters of 25% sodium chloride solution. The dithian derivative was extracted with petroleum ether (b. p. 40–110°), and purified by distillation under reduced pressure. The results of these experiments are given in Table II.

TABLE II

2,6-DISUBSTITUTED-1,4-DITHIANS

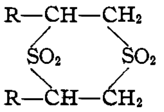


R=	Yield, %	B. p., °C.	Press., mm.	$n^{20}D$	Sp. gr. 20/20	Analyses, % Calcd. S	Found S
CH_3—	14	85– 87	12	1.5420	1.080	43.2	42.5 42.2
n-C_3H_7—	9	145–155	20	1.5255	1.002	31.37	31.5
C_6H_5—	11	190–195	30	1.6060	1.143	23.53	23.15

2,6 - Disubstituted - 1,4 - dithian - 1,4 - bis - (dioxides).—These synthetic cyclic disulfones were obtained by oxidizing about 2 g. of the corresponding 1,4-dithian derivative in 10 cc. of glacial acetic acid with 5 cc. of 30% hydrogen peroxide. The reaction mixture was heated to boiling under a reflux condenser for about fifteen minutes, and diluted with about 50 cc. of water. The precipitate which came down was then recrystallized from dioxane or alcohol. The synthetic product in each case proved to be identical with the product obtained by dissolving the corresponding polysulfone in liquid ammonia. These experiments are recorded in Table III.

TABLE III

COMPARISON OF SYNTHETIC CYCLIC DISULFONES WITH THOSE OBTAINED FROM POLYMERIC SULFONES



R=	Yield from dithian, %	M. p. of synthetic product, °C.	M. p. of product from polymer, °C.	Mixed m. p., °C.
CH_3—	90	332	334	334
n-C_3H_7—	90	254–256	257	257
C_6H_5—	80–85	279	280	279

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(10) Curtius and Dedichen, *J. prakt. Chem.*, **50**, 265 (1894).

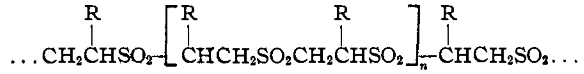
(11) Bost and Conn, "Organic Syntheses," Vol. XV, John Wiley and Sons, Inc., New York, 1935, p. 72.

Summary

1. Those polysulfones prepared from sulfur dioxide and olefins, which dissolve in liquid ammonia, are converted by this treatment into cyclic disulfones.

2. Styrene (phenylethylene) adds sulfur dioxide to give a polysulfone.

3. Evidence is presented to show that polysulfones prepared from olefins of the type $RCH=CH_2$ have the general formula



$$\ldots \mathrm{CH_2\overset{R}{\overset{|}{C}}HSO_2}-\left[\mathrm{\overset{R}{\overset{|}{C}}HCH_2SO_2CH_2\overset{R}{\overset{|}{C}}HSO_2}\right]_n-\mathrm{\overset{R}{\overset{|}{C}}HCH_2SO_2}\ldots$$

in which like parts of the hydrocarbon residues are joined to each other by sulfone linkages.

URBANA, ILLINOIS RECEIVED JANUARY 29, 1937

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY OF PRINCETON UNIVERSITY]

Studies in the Ketone Sugar Series. VI. The Effect of Zinc Chloride on Ketose Acetates

BY FRANCIS B. CRAMER[1] AND EUGENE PACSU

In preparing new sugar derivatives for testing the isorotation rules in the aldose group, Hudson and co-workers have made extensive use of zinc chloride dissolved in acetic anhydride as a reagent in converting the β-acetates into the α-forms. An earlier physico-chemical investigation of the process by Jungius[2] showed that in the case of glucose pentaacetates equilibrium was reached when the proportion was nine moles of the α- to one mole of the β-form. In the case of most aldose acetates the equilibrium contains the two forms in similar proportion. Exceptions are found in the pentaacetates of galactofuranose[3] and galactoseptanose[4] where the equilibrium is in favor of the β-isomers. In 1915, Hudson and Brauns[5] attempted to apply this method to β-pentaacetylfructose. When zinc chloride was added to a solution of this substance in acetic anhydride, only a very small change in rotation was observed whereas a large one was anticipated. Since some coloration occurred, the authors evidently ascribed the change in rotation to slight decomposition and after recovering about one-third of the starting material and conducting confirmatory experiments, concluded that the method was not applicable in the ketose series. It has now been discovered that the small change in rotation observed by Hudson and Brauns was due to the formation of the new isomer described in Part V[6] as the true α-pentaacetylfructopyranose.

The structure of β-pentaacetylfructose is generally accepted as that of a normal acetate possessing a <2, 6> ring. The evidence leading to this conclusion is extensive and will not be reviewed here. To establish the structure of the new fructose acetate as the normal α-pentaacetate, it would be sufficient to show that it differs from the known β-compound only in the configuration of carbon atom 2. If this glycosidic carbon atom were selectively inverted, the β-pentaacetate should result.

When a trace of zinc chloride was added to the acetic anhydride solution of the new fructose acetate, the rotation dropped rapidly, changing sign, and within a few minutes became constant at −107°. From the rotations of α- and β-pentaacetylfructose in acetic anhydride (42.3 and −122°, respectively) it may be calculated that the equilibrium mixture contained 91% of the β-form. When the solution was worked up a large amount of β-pentaacetylfructose was obtained.

Similarly, when pure β-pentaacetylfructose was treated with zinc chloride in acetic anhydride after the manner of Hudson and Brauns,[5] the rotation again became −107°. On carefully working up this mixture, a small amount of the α-compound was isolated in pure form.

This interconversion of the two acetates gives definite proof that the new compound is the true α-pentaacetylfructose <2,6>. Supporting evidence is afforded by the method of preparation, both α- and β-pentaacetates being formed simultaneously by replacing the chlorine atom in β-acetochlorofructose with the acetoxyl radical. In

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[1] This paper is based upon a thesis submitted by Francis B. Cramer to the Faculty of Princeton University in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] Jungius, *Z. physik. Chem.*, **52**, 101 (1905).

[3] Hudson and Johnson, THIS JOURNAL, **37**, 1519 (1915).

[4] Micheel and Suckfüll, *Ann.*, **502**, 85 (1933).

[5] Hudson and Brauns, THIS JOURNAL, **37**, 2736 (1915).

[6] Pacsu and Cramer, *ibid.*, **57**, 1944 (1935).