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

Polysulfones from Acetylenes and Sulfur Dioxide[1]

BY L. L. RYDEN AND C. S. MARVEL

In an earlier communication,[1] we have shown that one acetylene, 1-heptyne, combines with sulfur dioxide in a one-to-one ratio to yield a polymeric product. This reaction has now been studied with a wide variety of substituted acetylenes and it appears to be a general reaction for monosubstituted acetylenic hydrocarbons.

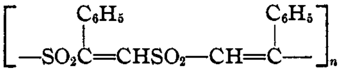
The monoalkylacetylenes, RC≡CH, in which R is a normal alkyl group containing one to five carbon atoms, have been found to combine readily with sulfur dioxide in the presence of alcohol and paraldehyde which contains peroxides. Phenylacetylene also combines readily with sulfur dioxide under the same conditions used for alkylacetylenes. Disubstituted acetylenes apparently do not enter into the reaction as shown by failure to obtain sulfur dioxide addition products from 2-butyne, 2-hexyne and methylphenylacetylene. Ethyl acetylenedicarboxylate also failed to react with sulfur dioxide. Further experiments on monosubstituted acetylenes will have to be made before the exact limits of the reaction can be set forth.

The products of the addition of sulfur dioxide to monosubstituted acetylenes are presumably polysulfones. They still contain one double bond for each hydrocarbon residue in the polymer, since oxidation gives the acid which would be expected from this structure. That the addition of sulfur

$$(\underset{|}{\mathrm{RC}}{=}\mathrm{CH{-}SO_2{-}})_n \xrightarrow{\text{Oxid.}} \mathrm{RCOOH}$$

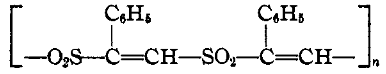
dioxide is to the acetylene and not to an allene which might result from a rearrangement of the acetylene is established by the above observation. Moreover, phenylacetylene, which could not rearrange to an allene, adds sulfur dioxide, and allene itself fails to combine with this reagent.

The polymers are readily hydrolyzed with 10% aqueous sodium hydroxide, but all of the products of this hydrolysis are not known. The phenylacetylenepolysulfone was most extensively investigated, since it was thought that the presence of the phenyl group would give products which were more readily identifiable. The products which have been isolated are benzylmethylsulfone (8%), acetophenone (trace), benzoic acid (20%) and sodium sulfite (50%). The remainder of the sulfur was present in the tarry organic products which are produced in the hydrolysis. The fact that almost exactly half of the sulfur is isolated as sulfur dioxide and half as organic sulfur compounds indicates that there is possibly the same type of alternation in the manner of combination of phenylacetylene and sulfur dioxide to give a polymer of structure I as was previously demonstrated in the case of propylenepolysulfone.[2] However, this structure does not account for the formation of benzylmethylsulfone on hydrolysis. At least a part of the polymer must have the structure shown in formula II. It seems likely that the acetophenone is produced from one end group of the polymer. Addition of water to stop the polymeric reaction would give at one end of the chain the group $C_6H_5COCH_2SO_2$-, and this would give acetophenone on alkaline hydrolysis.



$$\left[\mathrm{-SO_2}\overset{\mathrm{C_6H_5}}{\overset{|}{\mathrm{C}}}\mathrm{{=}CHSO_2{-}CH{=}}\overset{\mathrm{C_6H_5}}{\overset{|}{\mathrm{C}}}\mathrm{-}\right]_n$$

I



$$\left[\mathrm{-O_2S-}\overset{\mathrm{C_6H_5}}{\overset{|}{\mathrm{C}}}\mathrm{{=}CH{-}SO_2{-}}\overset{\mathrm{C_6H_5}}{\overset{|}{\mathrm{C}}}\mathrm{{=}CH-}\right]_n$$

II

Hydrolysis of 1-pentynepolysulfone gave a trace of methyl *n*-propyl ketone which also probably came from the end group of the molecule. About 40–50% of the sulfur was removed as sulfur dioxide. No other products of hydrolysis have been identified. An attempt was made to reduce 1-pentynepolysulfone with hydrogen over a platinum catalyst to see whether the reduction product could be shown to be identical with 1-pentenepolysulfone. No reduction occurred at room temperature in dioxane. The polymer lost sulfur dioxide when heated. Almost exactly half of the sulfur was eliminated as sulfur dioxide at the boiling point of dioxane. The only product besides sulfur dioxide which could be isolated after decomposition with heat was a crystalline material which analysis and molecular weight showed to be $C_{10}H_{16}SO_2$. The structure of this compound is yet unknown.

Pyrolysis in boiling dioxane removed approxi-

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[1] This is the fourth communication on polysulfones. For the third, see THIS JOURNAL, 57, 2311 (1935).

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

mately half of the sulfur from 1-heptynepolysulfone as sulfur dioxide. Phenylacetylenepolysulfone was insoluble in dioxane, but heating the polymer alone at 140° for the forty-five minutes liberated 62–73% of the sulfur as sulfur dioxide. No definite products could be isolated from the organic residue. When 1-pentynepolysulfone was heated to 200° until frothing ceased, only 50% of the sulfur was removed as sulfur dioxide. The evidence is as yet too meager to ascribe definite formulas to these acetylene–sulfur dioxide polymers but there is apparently considerable difference between the alkyl substituted and aryl substituted products.

No satisfactory molecular weight determinations have been made on any of the acetylene derivatives.

Experimental Part

Preparation of Polysulfones from Acetylenes.—Ten cubic centimeters each of liquid sulfur dioxide and the substituted acetylene were placed in a pressure bottle, and 5 cc. of ethyl alcohol was added. The bottles were sealed and allowed to stand overnight, then cooled and opened to permit the addition of 1 to 5 cc. of paraldehyde which contained peroxides. The amount of paraldehyde to be added varied roughly with various samples. Fresh paraldehyde was inert, but older samples which had been exposed to the air were very effective catalysts for the addition reaction. The flasks were sealed and allowed to come to room temperature. The contents of the flask were usually solid at this time. With 1-pentyne and 1-hexyne, the reaction was distinctly exothermic.

The reaction mixtures were poured into water and the products collected on a filter. The excess of sulfur dioxide and paraldehyde was removed by triturating with alcohol and ether several times. The polymer from 1-pentyne was further purified by dissolving in dioxane and reprecipitating by the addition of water. The products from 1-hexyne and 1-heptyne were purified similarly with acetone as the solvent.

The polysulfones from methyl-, ethyl- and propylacetylene were white, powdery, amorphous substances. The butyl- and amyl-acetylene derivatives were more flaky and were not easily ground to powder.

The products which have been prepared are listed in Table I.

Under the same experimental conditions which gave addition products when the monosubstituted acetylenes were used, no polysulfones could be obtained from dimethylacetylene, 2-hexyne, methylphenylacetylene, diethyl acetylenedicarboxylate or allene and sulfur dioxide. Acetylene itself was not investigated.

The polysulfones derived from methyl-, ethyl- and phenyl-acetylene were insoluble in water, alcohol, ether, acetone, carbon tetrachloride, chloroform, benzene and cold concentrated sulfuric acid. The polysulfones from *n*-propyl-, *n*-butyl- and *n*-amyl-acetylene were soluble in dioxane and could be precipitated from this solvent by the addition of water. Acetone could be substituted for dioxane when *n*-butyl- and *n*-amylacetylenes were used.

TABLE I

POLYSULFONES FROM MONOSUBSTITUTED ACETYLENES

RC≡CH R=	Yield, %	Temp. of decomp.[a] °C.	Empirical formula	S analyses, % Calcd.	Found	
Methyl	40	250–260	$C_3H_4SO_2$	30.8	29.4[b]	
Ethyl	30	210–215	$C_4H_6SO_2$	27.0	26.4	26.3
n-Propyl	60	203–208	$C_5H_8SO_2$	24.2	23.8	23.6
n-Butyl	90	195–205	$C_6H_{10}SO_2$	21.9	21.5	21.3
n-Amyl	75	164–170	[c]	..	..	..
Phenyl	50	250–275	$C_8H_6SO_2$	19.3	18.5	18.7

[a] These decomposition temperatures were determined by heating a sample in a capillary melting point tube in an oil-bath which was heated rapidly. The temperature of decomposition varies widely, depending on the rate of heating. [b] Calcd.: C, 34.6; H, 3.85. Found: C, 34.52, 34.23; H, 3.95, 3.94. [c] Analysis reported previously; see ref. 1.

All of these new polysulfones were sensitive to alkalies. The products did not dissolve in cold, aqueous, 10% sodium hydroxide, but on warming the mixture the sulfones dissolved and were hydrolyzed rapidly.

Oxidation of the Polysulfones from Acetylenes.—Five grams of 1-pentynepolysulfone was boiled for fifteen minutes with a solution of 24 g. of potassium permanganate in 500 cc. of water. The hydrated manganese dioxide was removed by filtration, and the solution was acidified with phosphoric acid. The distillate was distinctly acid. The Duclaux constants[3] for the volatile acid were 17.7, 16.0 and 14.1, whereas the values reported for *n*-butyric acid are 17.9, 15.9 and 14.6. To confirm the identification of the volatile acid the sodium salt was prepared and converted to the *p*-bromophenacyl derivative, which melted at 63°. A mixture of this product with an authentic specimen of the *p*-bromophenacyl ester of *n*-butyric acid melted at 63°.[4]

Similarly, 2 g. of 1-butynepolysulfone was oxidized with 12 g. of potassium permanganate. The product of this reaction was identified as propionic acid by the Duclaux constants, and preparation of the *p*-bromophenacyl ester which melted at 62°. There was no depression in the melting point when this ester was mixed with an authentic sample of the *p*-bromophenacyl ester of propionic acid.

When 1 g. of phenylacetylenepolysulfone was boiled with 1 g. of potassium permanganate in 20 cc. of water in a like manner, benzoic acid was obtained, m. p. 121.5°.

Hydrolysis of the Polysulfones.—Two grams of phenylacetylenepolysulfone was added to a solution of 2 g. of sodium hydroxide in 75 cc. of water, and the mixture was distilled. A very small amount of oily material came over with the water. The distillates from several such runs were combined, extracted with ether and the extract was concentrated and treated with 2,4-dinitrophenylhydrazine. The 2,4-dinitrophenylhydrazone, after crys-

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(3) Duclaux, *Ann. chim. phys.*, [5] **2**, 289 (1874); Upson, Plum and Shott, THIS JOURNAL, **39**, 731 (1917); Lamb, *ibid.*, **39**, 746 (1917).

(4) Judefind and Reid, *ibid.*, **42**, 1043 (1920).

tallization from alcohol, melted at 238°, and showed no depression of melting point when mixed with an authentic specimen of the 2,4-dinitrophenylhydrazone of acetophenone.[5]

In another experiment, 4 g. of phenylacetylenepolysulfone was hydrolyzed by boiling with 60 cc. of 3% sodium hydroxide solution for thirty minutes. The volatile material was distilled with steam and the alkaline residue was extracted with ether. From this extract a solid was obtained. After recrystallization from benzene it melted at 124°, and showed no depression of melting point when mixed with an authentic specimen of benzylmethylsulfone (m. p. 124.5°).[6]

Anal. Calcd. for $C_8H_{10}SO_2$: C, 56.47; H, 5.88. Found: C, 56.38; H, 5.75.

The yield of benzylmethylsulfone was 0.28 g. (8%).

In another similar alkaline hydrolysis 2 g. of phenylacetylenepolysulfone was refluxed two hours with 50 cc. of 10% sodium hydroxide. The hydrolysate was extracted with ether to remove neutral compounds. Hydrogen peroxide was added to oxidize the sulfite, the solution was acidified with hydrochloric acid and the benzoic acid was extracted with ether. The ether was evaporated and the benzoic acid was extracted from the tarry residue with hot water and determined by titrating with 0.1 *N* sodium hydroxide. Twenty-five cubic centimers of base was used. This is equivalent to 2.5 millimoles (0.305 g.), or, roughly, 20% of the theoretical amount of benzoic acid.

The amount of sulfite which had been produced in the hydrolysis was determined by oxidation with hydrogen peroxide and precipitation as the sulfate. The barium sulfate weighed 1.253 g. (5.37 millimoles). This accounts for 45% of the sulfur in the polymer.

In another experiment, analyses were run on the dried residue (after extraction with ether). This showed that 25% of the sulfur was removed by extraction with ether. An aliquot part of the dried residue was extracted with alcohol. This process removed 25% of the total sulfur, leaving a residue containing 50% of the total sulfur as sodium sulfite.

Five grams of 1-pentynepolysulfone was mixed with 100 cc. of 10% sodium hydroxide solution, and the mixture was slowly distilled. The distillate was treated with an alcohol solution of 2,4-dinitrophenylhydrazine and a small amount of the 2,4-dinitrophenylhydrazone of methyl *n*-propyl ketone, m. p. 135–137°, was obtained. This material was mixed with an authentic specimen of the methyl *n*-propyl ketone derivative (m. p. 141°),[5] and the mixture melted at 138–139°. No definite products except sodium sulfite could be identified in the alkaline residue. By making the mixture acid with phosphoric acid, and distilling the sulfur dioxide into standard alkali, it was found that between 40 and 50% of the original sulfur in the 1-pentynepolysulfone was removed as sulfite.

Pyrolysis of the Polysulfones.—A 0.2372-g. sample of 1-pentynepolysulfone was placed in a test-tube fitted with a gas delivery tube dipping into standard alkali. The test-tube was then heated to 200° until frothing in the tube ceased (thirty minutes) and the tube was swept out with air. Titration of the standard alkali showed that 50% of the sulfur of the polymer was liberated as sulfur dioxide. When the polymer was heated at 200° for one hour, 51% of the sulfur dioxide was liberated. When the polymer was heated at 205–215° for one hour, roughly 60% of the sulfur dioxide was eliminated, showing that further decomposition takes place at higher temperatures.

With phenylacetylenepolysulfone, pyrolysis at 140° for forty-five minutes liberated from 62 to 73% of the sulfur dioxide. There seemed to be no really definite stopping place in the decomposition of this derivative.

By dissolving 1-pentynepolysulfone in dioxane and heating the solution to boiling, sulfur dioxide was liberated slowly, and the amount lost approached 50% as a limiting value. 1-Heptynepolysulfone showed a similar behavior. This is shown best by the accompanying curve (Fig. 1).

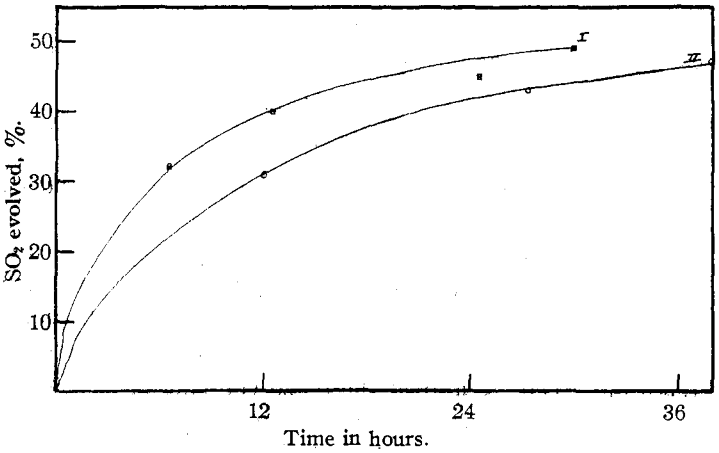

Fig. 1.—I, Pyrolyis of 1-heptynepolysulfone in dioxane; II, pyrolysis of 1-pentynepolysulfone in dioxane.

When 100 g. of 1-pentynepolysulfone was heated in 50 cc. of dioxane until approximately 50% of the sulfur dioxide was evolved and the solution evaporated and poured into ether, a small amount of the original polymer was obtained. In addition, a small amount (0.05 g.) of a crystalline compound, m. p. 88°, was obtained. This product did not add bromine, but did decolorize aqueous potassium permanganate solution.

Anal. Calcd. for $C_{10}H_{16}SO_2$: C, 60.00; H, 8.00; S, 16.00; mol. wt., 200. Found: C, 59.43; H, 7.97; S, 14.73; mol. wt. (Rast), 203.

The structure of this compound has not been determined, but its behavior toward bromine and potassium permanganate solution, together with the analysis and molecular weight, suggest that it may be a dipropylthiophenesulfone.

The polysulfones from 1-heptyne, 1-hexyne and phenylacetylene gave no product of this type.

Summary

1. A number of alkylacetylenes and phenylacetylene have been shown to combine with sul-

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(5) Allen, THIS JOURNAL, **52**, 2955 (1930).

(6) Freiman and Sugden, *J. Chem. Soc.*, 263 (1928).

fur dioxide to give polymeric products. No disubstituted acetylene has been found which gives this addition reaction.

2. Some preliminary work on the exact structure of these addition products has been described.

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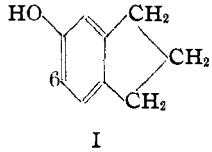
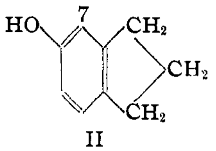
An Investigation of the Mills–Nixon Effect

BY LOUIS F. FIESER AND WARREN C. LOTHROP

In an important and much-discussed[1] paper, Mills and Nixon[2] advanced the hypothesis that hydrindene, or a given substituted hydrindene, is in a condition of less strain when it has the bond structure shown in formula I than when it exists in the alternate Kekulé form (II) in which the carbon atoms common to the two rings are connected by a double bond. As a means of testing the conclusion that I should be the more stable form of 5-hydroxyhydrindene, or the predominant isomer in the tautomeric equilibrium mixture, these investigators studied the diazo coupling of the substance and its behavior on bromination. Since these are reactions characteristic of enolic systems, substitution should occur at the ortho position joined to the hydroxylated carbon atom by a double linkage, that is, position 6 of I and position 7 of II. It was found that, although substitution does not proceed entirely in a single direction, about 90% of the reaction product is the 6-substituted isomer, indicating that I is the more stable form.

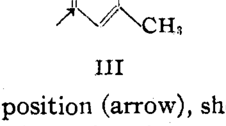


I

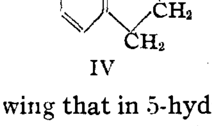


II

The observation loses some of its significance because of the fact, noted by Mills and Nixon, that *as*-*o*-xylenol (II) also is attacked chiefly in the 6-position (arrow), showing that in 5-hydroxyhydrindene the chemical effect of the alicyclic ring may be sufficient, without assistance from a steric factor, to control substitution largely into one of the two available ortho positions. The contrasting behavior of 6-hydroxytetralin (IV), which yields 5-substitution products, afforded the only evidence in the original work of the existence of the Mills–Nixon effect, that is, of a fixation of the bonds in one of the two Kekulé forms as the result of the stereochemical demands of an attached ring. The behavior of IV pointed to the bond structure indicated and, since the 5- and 6-membered rings must be quite similar chemically, the difference was attributed to the different spatial requirements of the two rings. From a theoretical analysis of the configuration of the tetralin molecule, Mills and Nixon concluded, albeit with less conviction than in the other case, that there should be a preference for the Kekulé structure IV.



III



IV

It seemed to us that the preferential formation of one of two possible isomers may be the result of only a moderate preponderance of one tautomeric form, or of even a very slight difference in reactivities, and that the Mills–Nixon effect may be at most a subtle one in comparison to the fixation of bonds resulting from the fusing together of two aromatic nuclei,[3] and we undertook to apply to hydrindene and to tetralin the much more severe test previously employed in investigating naphthalene,[3] anthracene,[4] and phenanthrene.[5] For this purpose phenolic derivatives in which one of the two ortho positions is blocked by an alkyl group were synthesized and tested for their ability to couple with diazotized amines. If the 5-hydroxyhydrindene derivatives V and VI exist in the stable state suggested by Mills and Nixon, coupling at the free ortho position should occur easily in the case of VI, but only following a migration of the double linkages in the case of V.

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(1) Thompson, *Chemistry and Industry*, **52**, 61 (1933); Baker, *J. Chem. Soc.*, 1678, 1684 (1934); 274 (1936); Fries, Walter and Schilling, *Ann.*, **516**, 248 (1935); Hampson and Weissberger, *J. Chem. Soc.*, 393 (1936).

(2) Mills and Nixon, *ibid.*, 2510 (1930).

(3) Fieser and Lothrop, THIS JOURNAL, **57**, 1459 (1935).

(4) Fieser and Lothrop, *ibid.*, **58**, 749 (1936).

(5) Fieser and Young, *ibid.*, **53**, 4120 (1931).