tenth grams of magnesium in 25 cc. of ether in a three-necked flask equipped with a mercury-sealed stirrer, a reflux condenser, and a dropping funnel, was converted into phenylmagnesium bromide by 7.3 g. of bromobenzene dissolved in 25 cc. of ether. Two grams of VI dissolved in 40 cc. of dry, thiophene-free benzene, was added dropwise to the Grignard reagent. The water was drained from the reflux condenser, and the reaction mixture was heated for six hours. Stirring was maintained constantly. The ether was removed from the reaction mixture in this way. Stirring was discontinued, and the reaction mixture was refluxed for fourteen hours and decomposed by pouring into a beaker of ice containing a little sulfuric acid. A small precipitate of the imine hydrobromide formed and was collected on a filter. The benzene layer was separated from the water layer, and the aqueous layer was extracted with ether. The combined ether–benzene solution was dried quickly over calcium chloride, and the solvents were removed by distillation. The residue crystallized on cooling, more of the imine hydrobromide being obtained. This was crystallized from benzene. Crystallization was also carried out by dissolving it in a minimum amount of methyl alcohol and adding several volumes of ether. The latter method produced colorless needles: yield 1.3 g.; m. p. 110–130°, with decomposition.

Anal. Calcd. for $C_{20}H_{24}ONBr$: C, 64.18; H, 6.42; N, 3.74. Found: C, 64.18; H, 6.68; N, 3.98.

Methyl bromide was shown to be evolved by melting a sample and passing the evolved gas into quinoline. Methylquinolinium bromide was obtained and identified by a mixed melting point determination.

The aqueous solution was allowed to stand in an open beaker; as evaporation proceeded an oil formed. This was taken up in ether; the ether solution was shaken with a solution of cupric acetate and became deep green in color. Evaporation of the ether solution left a dark green copper derivative. This was dissolved in ether and decomposed by shaking with hydrochloric acid. The ether solution was dried over calcium chloride and evaporated. The remaining oil gave a strong enol test but did not crystallize. The oil was again converted into the copper derivative, and the derivative was recrystallized by dissolving it in hot benzene, adding ligroin and cooling. The composition was that calculated for the copper derivative of VIII.

Anal. Calcd. for $(C_{19}H_{19}O_2)_2Cu$: C, 73.34; H, 6.16; Cu, 10.2. Found: C, 73.41; H, 6.58; Cu, 10.1.

The copper was determined by weighing the copper oxide remaining after the combustion determination. In another experiment, 3 g. of the hydrobromide was obtained from 3 g. of nitrile (VI).

The product obtained from melting the hydrobromide, which is probably the imine, could not be induced to crystallize. However, hydrolysis of this substance with alcoholic hydrochloric acid converted it into an oil (VIII) which formed a copper derivative and gave a strong ferric chloride test.

The imine hydrobromide was likewise converted, by boiling with alcoholic hydrochloric acid, into an oil (VIII) which gave a ferric chloride test and formed a copper derivative.

Summary

The isomeric β-methoxy-β-mesitylacrylonitriles (I) react with phenylmagnesium bromide to give the corresponding imino hydrobromide (II) and its hydrolysis product, the keto ether (III), as well as the diketone (IV) and its imino derivative (V). The three last-named products have been synthesized by other methods.

Similar results were obtained with α-methyl-β-methoxy-β-mesitylacrylonitrile (VI) and phenylmagnesium bromide.

URBANA, ILLINOIS RECEIVED MARCH 17, 1938

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

The Reaction between Sulfur Dioxide and Olefins. VII.[1] Copolymers from Mixtures of Olefins, Acetylenes, and Olefin Derivatives with Sulfur Dioxide

BY C. S. MARVEL, S. JACK DAVIS AND F. J. GLAVIS

Many copolymers of mixed vinyl derivatives have been described in the literature. The physical and chemical properties of these copolymers are sometimes quite different from those which might be expected from an examination of the polymers made from the individual vinyl derivatives. It has therefore seemed desirable to investigate some of the copolymers from mixtures of olefins or olefinic derivatives and sulfur dioxide in order to learn more about this unusual polymerization reaction.

Treatment of mixtures of olefins with sulfur dioxide in the presence of suitable peroxide catalysts gave polymeric products. These products had approximately the composition which would be expected for copolymers if the olefins had combined in the ratio in which they were introduced into the reaction mixtures. When an equimolecular mixture of olefins was used the product was shown definitely to be a copolymer of the type

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[1] For the sixth communication in this series see THIS JOURNAL, 59, 1014 (1937).

olefin(1)-SO_2-olefin(2)-SO_2-. When the olefins were not used in equimolecular proportions the products obtained had solubilities and melting points which indicated that they were truly copolymers and not mixtures of a copolymer and a simple polymer. However, this second possibility has not been rigorously excluded.

Four series of copolymers were made from sulfur dioxide and the following mixtures of olefins and olefinic derivatives: methylpropene and cyclohexene; methyl 10-hendecenoate and 1-pentene; 10-hendecenoic acid and 1-pentene; and hendec-10-en-1-ol and 1-pentene. Another combination less extensively studied was phenylacetylene and 1-pentene.

The copolymers obtained from mixtures of cyclohexene and methylpropene are of especial interest since it has been reported[2] that methylpropene inhibits the photochemical and catalyzed reactions between sulfur dioxide and other olefins. Methylpropenepolysulfone is insoluble in all common solvents and melts at 340°.[3] Cyclohexenepolysulfone is soluble in chloroform and benzene and melts at about 200°.[4] A product made from a mixture containing one equivalent of cyclohexene to eighteen equivalents of methylpropene was insoluble in common solvents but it melted at about 250°. When the ratio of these olefins was made two to one the polymer obtained melted at about 205–210° and was soluble in chloroform. With the olefin ratio two to three the resulting polymer melted at about 200° and was soluble in chloroform. None of the copolymers was soluble in benzene as is pure cyclohexenepolysulfone.

Another interesting case of the change in the physical properties of the copolymers with change in composition was found in the series prepared from a mixture of methyl 10-hendecenoate, 1-pentene and sulfur dioxide. Methyl 10-hendecenoate polysulfone was a sticky, glassy, semi-solid which became fluid at 95–115° and was soluble in hot methyl alcohol.[1] 1-Pentenepolysulfone melted at 150–160°[3] and was soluble in acetone but insoluble in alcohol. The copolymer prepared from a mixture of one equivalent of methyl 10-hendecenoate and five equivalents of 1-pentene was a solid soluble in acetone, insoluble in hot alcohol but melting almost as low (100–115°) as the temperature at which the polysulfone of methyl 10-hendecenoate became fluid. The effectiveness of small amounts of this ester in producing low melting copolymers was further evidenced by the polysulfone obtained from a mixture containing only one equivalent of the ester to one hundred equivalents of 1-pentene, which still melted slightly lower (135–150°) than did 1-pentenepolysulfone. In all of the copolymers studied the solubilities were more nearly those of the polysulfone from the major constituent, whereas the melting points were often markedly affected by small amounts of one constituent.

Attempts to determine the way the individual fragments were joined in the copolymers from cyclohexene and methylpropene were not successful. Cyclohexenepolysulfone was degraded by the action of liquid ammonia to give a product which analysis and molecular weight showed to be made up of three cyclohexene and two sulfur dioxide units. No identifiable products were obtained from the action of liquid ammonia on methylpropenepolysulfone. When the copolymers from cyclohexene and methylpropene were treated with alkali, only the individual olefins could be identified among the cleavage products.

The product (I) of the action of liquid ammonia on cyclohexenepolysulfone is of interest since it is not the simple cyclic disulfone (II) containing two units of olefin and two of sulfur dioxide which would be expected from the reaction if it proceeded in the manner noted in all other cases which have been studied previously.[5] When this product (I) of the liquid ammonia breakdown of cyclohexenepolysulfone was recrystallized from glacial acetic acid it was converted into the expected cyclic disulfone (II). When an attempt was made to synthesize this cyclic disulfone by the method which had been used successfully in earlier work for related compounds,[5] the product of the action of sulfur chloride and sodium sulfide on cyclohexene did not prove to be the expected 1,4-dithiane. Analysis showed that it contained three cyclohexene units and two sulfur atoms (IV). Oxidation converted this product into the same compound which had been obtained by the action of liquid ammonia on cyclohexenepolysulfone. We believe these reactions may be formulated as follows.

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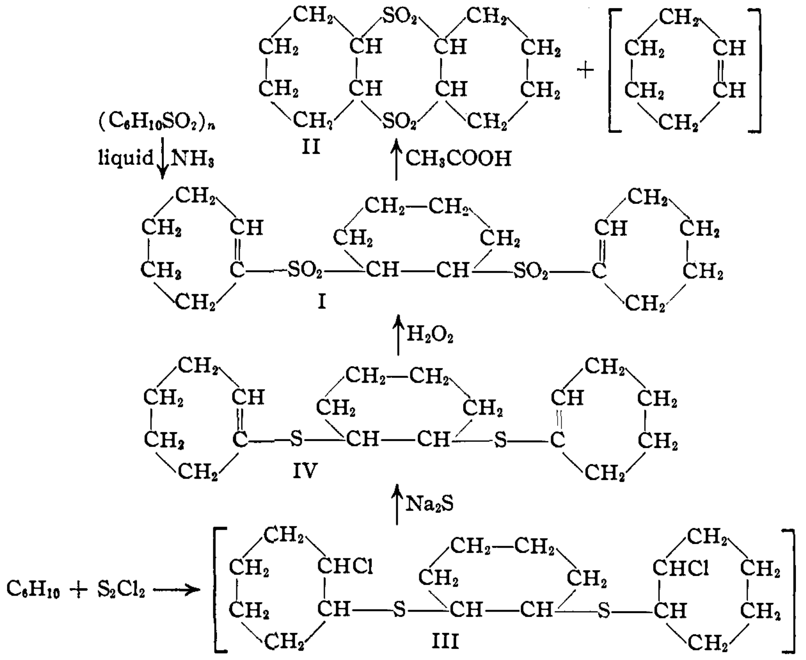
[2] Fitch, U. S. Patent 2,045,592 (1932); Snow and Frey, *Ind. Eng. Chem.*, **30**, 176 (1938).

[3] Ryden and Marvel [This Journal, **58**, 2311 (1936)] give the decomposition point of this polymer as about 300°.

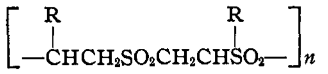
[4] Frederick, Cogan and Marvel, *ibid.*, **56**, 1815 (1934).

[5] Glavis, Ryden and Marvel, *ibid.*, **59**, 707 (1937).



No attempt was made to isolate the first product of the action of sulfur chloride on cyclohexene and it may be that the compound shown in formula III was not an intermediate step. The cyclohexene which must have been formed when the linear disulfone (I) was converted into the simple cyclic disulfone (II) has not been isolated. It seems probable that it was converted to cyclohexyl acetate by the excess acetic acid.

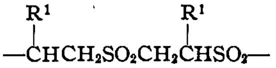
It was possible to show definitely the manner in which 1-pentene, 10-hendecenoic acid and sulfur dioxide combine to give a copolymer. Previous work[5,6] has shown that olefins of the type $RCH{=}CH_2$ always combine with sulfur dioxide to give a polymer of the "head to head, tail to tail" type (V).



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

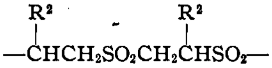
V

If an equimolecular mixture of two olefins $R^1CH{=}CH_2$ and $R^2CH{=}CH_2$ combined with sulfur dioxide in the same manner, it would be expected that three units (VI, VII and VIII) would be found in the final polymer in the ratio of 25, 25 and 50%, respectively.



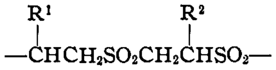
$$-\overset{R^1}{\overset{|}{C}}HCH_2SO_2CH_2\overset{R^1}{\overset{|}{C}}HSO_2-$$

VI



$$-\overset{R^2}{\overset{|}{C}}HCH_2SO_2CH_2\overset{R^2}{\overset{|}{C}}HSO_2-$$

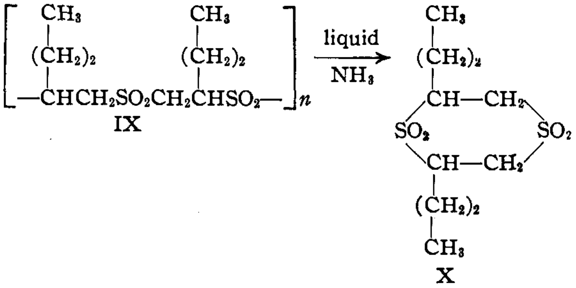
VII

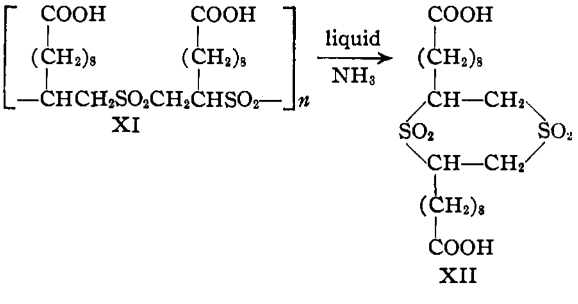


$$-\overset{R^1}{\overset{|}{C}}HCH_2SO_2CH_2\overset{R^2}{\overset{|}{C}}HSO_2-$$

VIII

It was possible to test this assumption with the copolymer prepared from sulfur dioxide and equimolecular portions of 1-pentene and 10-hendecenoic acid since this polymer was converted readily to a cyclic disulfone on treatment with liquid ammonia. Previously[5] it has been found that liquid ammonia converts 1-pentenepolysulfone (IX) to a cyclic disulfone (X) which is alkali insoluble. It has now been found that the polysulfone from 10-hendecenoic acid (XI) is broken down in a similar manner to give a simple cyclic disulfone (XII) which is alkali soluble.





When the copolymer prepared from sulfur dioxide and an equimolecular mixture of 1-pentene and 10-hendecenoic acid was treated with liquid ammonia neither of these cyclic disulfones (X, XII) was obtained. The one product which was isolated in better than 75% yields had the composition of the expected cyclic disulfone (XIV) of the general type which would result from a polymer (XIII) in which one molecule of 10-hendecenoic acid and one molecule of 1-pentene are

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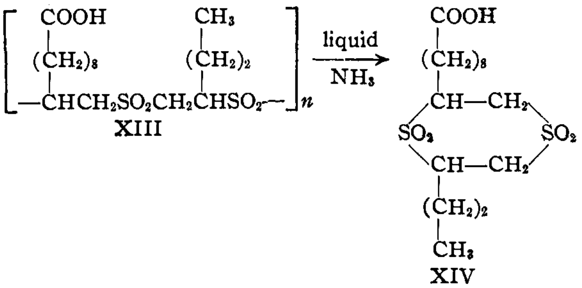
(6) Hunt and Marvel, THIS JOURNAL, 57, 1691 (1935).

joined through their respective terminal CH_2 groups by a sulfone linkage.



XIII

XIV

A copolymer prepared from sulfur dioxide and a mixture containing 5 moles of 1-pentene to 1 mole of 10-hendecenoic acid was treated with liquid ammonia and it was possible to isolate two cyclic disulfones: one alkali insoluble which was identical with the product (X) obtained from pure 1-pentenepolysulfone; the other alkali soluble which was identical with the mixed cyclic disulfone (XIV) obtained from the copolymer containing equimolecular amounts of these two constituents.

From these experiments it is evident that the copolymerization of equimolecular amounts of 1-pentene and 10-hendecenoic acid with sulfur dioxide does not follow a chance course but must proceed by some directed mechanism which lays down a polymeric molecule of a very definite type (XIII).

Experimental

Preparation of Copolymers from Sulfur Dioxide and Mixtures of Olefins, Acetylenes and Olefinic Derivatives.—All of the copolymers were prepared by placing the reaction mixtures containing 10 cc. of the mixture of olefins, acetylenes or olefinic derivatives, 10 cc. of liquid sulfur dioxide, 0.2 cc. of ascaridole and 2–3 cc. of 95% ethyl alcohol in pressure flasks and allowing them to stand at room temperature for approximately twelve hours. The yields of crude polymers were usually almost quantitative. The copolymers were purified by somewhat different methods depending on the physical properties.

The copolymers from methyl 10-hendecenoate, 1-pentene and sulfur dioxide were extracted repeatedly with hot alcohol and then dried in an Abderhalden dryer.

The copolymers from 10-hendecenoic acid, 1-pentene and sulfur dioxide were insoluble but tended to swell when treated with organic solvents. This was particularly true of those with a high 10-hendecenoic acid content. Washing with cold ether seemed to be the best procedure for purifying these mixtures. The same treatment worked best for the copolymers from hendec-10-en-1-ol, 1-pentene and sulfur dioxide. Some of these polymers were also purified by removing volatile material by steam distillation.

The copolymers from methylpropene, cyclohexene and sulfur dioxide which were soluble in chloroform were dissolved in this solvent and then precipitated with ether. The insoluble polymers were washed successively with chloroform, alcohol and water. It should be mentioned that methylpropene and sulfur dioxide do not give a polysulfone when ascaridole is used as a catalyst but the copolymer with cyclohexene is formed when this catalyst is used.

The copolymers from phenylacetylene, 1-pentene and sulfur dioxide were washed thoroughly with ethyl alcohol and then dried.

The copolymers which have been prepared together with their physical properties and analyses are listed in Table I. In the column headed "S % Calcd." are given the values which would be expected if the compounds combine in exactly the ratio in which they were put into the reaction mixture. It will be noted that not all of these values check and that some are not especially significant, yet these values coupled with the solubility behavior and

TABLE I

PROPERTIES OF COPOLYMERS

Ratio in moles	M. p. of polymer, °C.	Dec. point of polymer, °C.	Solubility of polymer	S, % Calcd.	S, % Found
			Methyl 10-hendecenoate and 1-pentene		
1:700	145–165	...	Sol. in acetone, dioxane,	23.8	22.9
1:100	135–150	...	chloroform and benzene.	23.5	22.9
1:50	125–140	...	Somewhat sol. in glacial	23.4	22.9
1:20	125–135	...	acetic acid and sulfuric	22.8	22.4
1:5	100–115	...	acid. Insol. in carbon tetrachloride, carbon disulfide	20.6	21.6
			Methylpropene and cyclohexene		
18:1	...	250	Insol. chloroform, alcohol, ether	26.3	26.16
1:2	205–210	240	Sol. chloroform. Insol. in	23.2	22.38
3:2	200	240	ether, acetone and petroleum ether	24.5	22.14
			Hendec-10-en-1-ol and 1-pentene		
1:1	90	210–235		17.4	17.3
1:5	115	215–275		20.8	20.7
1:20	150	220–280	Sol. in alcohol and ace-	23.0	23.6
1:50	145	215–280	tone	23.5	23.39
1:100	150	220–280		23.7	23.91
Trace:1	150	220–280		23.87	23.71
			10-Hendecenoic acid and 1-pentene		
1:1	90	230–275		16.75	15.51
1:5	105	190–290	Insol. in all common or-	20.84	20.70
1:20	130	220–290	ganic solvents	22.95	22.86
1:50	140	225–290		23.49	23.31
1:100	140	250–290		23.86	23.45
Trace:1	140	285–305		23.88	23.86
			Phenylacetylene and 1-pentene		
1:1	...	210–215	Sol. dioxane. Slightly sol. in carbon tetrachloride. Insol. benzene, ether, chloroform, acetone, ethyl acetate	21.33	21.77
3:2	...	270–275	Insol. in benzene, ethyl acetate, ether, chloroform, dioxane and acetone	20.5	20.22
1:3	...	210–220	Sol. in chloroform, carbon tetrachloride, dioxane, acetone. Insol. in benzene, ethyl acetate and ether	22.3	22.51

breakdown products indicate that copolymers were really produced in all of these cases.

A known mixture of methylpropenepolysulfone and cyclohexenepolysulfone was treated with benzene and the cyclohexenepolysulfone was dissolved leaving behind the methylpropenepolysulfone. A sample of 1 g. of 1-pentenepolysulfone was dissolved in 10 cc. of liquid sulfur dioxide and 10 cc. of 10-hendecenoic acid, 2 cc. of ethyl alcohol and 5 drops of ascaridole were added. After standing for twenty-four hours, the mixed polymers were precipitated by pouring the mixture into water. The excess 10-hendecenoic acid was removed by steam distillation. Treatment of the resulting mixture of polymers with hot ethyl alcohol gave a solution of 10-hendecenoic acid polysulfone and left an insoluble residue of 1-pentenepolysulfone.

Cleavage of Cyclohexene–Methylpropenepolysulfones.—The copolymers from sulfur dioxide and mixtures of cyclohexene and methylpropene were treated with hot sodium hydroxide solution. Both methylpropene and cyclohexene were identified in the decomposition products by means of boiling points and derivatives.

Action of Liquid Ammonia on Cyclohexenepolysulfone.—When cyclohexenepolysulfone was dissolved in liquid ammonia and the reaction mixture allowed to evaporate spontaneously, as was done in other cases[5] where polysulfones were converted to cyclic disulfones by this treatment, no crystalline products were isolated. However, when 15 g. of the cyclohexenepolysulfone was dissolved in liquid ammonia, the solution sealed in a pressure bottle and allowed to stand at about 0° overnight, the polymer was broken down. The pressure bottle was opened, the ammonia allowed to evaporate and the residue was crystallized from 70% alcohol. The yield of product was 3 g., m. p. 145–145.5°. Analysis and molecular weight showed that this product contained three cyclohexene and two sulfur dioxide units.

Anal. Calcd. for $C_{18}H_{28}S_2O_4$: C, 58.06; H, 7.53; S, 17.20; mol. wt., 372. Found: C, 57.49; H, 7.44; S, 18.24; mol. wt. (ebullioscopic in benzene), 358.

Recrystallization of this product from glacial acetic acid converted it into a compound melting at 291° which had the composition of the expected cyclic disulfone.

Anal. Calcd. for $C_{12}H_{20}S_2O_4$: C, 49.32; H, 6.85; S, 21.92; mol. wt., 292. Found: C, 49.18; H, 7.34; S, 22.12; mol. wt. (ebullioscopic in benzene), 291.

This disulfone was also synthesized from cyclohexene by a procedure similar to that described for related products.[5] To 100 g. of sulfur monochloride in a 500-cc. three-necked round-bottomed flask was added slowly and with stirring 125 g. of cyclohexene. The reaction mixture was kept at about 55° during the addition of the olefin and for four hours afterward. A solution of sodium sulfide was prepared from 50.6 g. of sodium in 800 cc. of absolute alcohol by treatment with hydrogen sulfide as described by Bost and Conn.[7] Then the crude reaction mixture from the sulfur chloride cyclohexene reaction was added dropwise to the sodium sulfide solution over a period of two and one-half hours. The temperature of the reaction mixture was maintained at the boiling point of the solvent during this addition and the heating was continued for about twelve hours afterward. The reaction mixture was poured into 1800 cc. of water containing 600 g. of sodium chloride and the organic material was extracted with low boiling petroleum ether. After the solution had been dried over anhydrous sodium sulfate and filtered, the solvent was distilled off and the residue distilled under reduced pressure. The main fraction boiled at 175–180° at 16 mm. and weighed 10 g.; n^{20}D 1.5211; d^{20}_{20} 1.0635. Analysis showed that it was not the expected 1,4-dithiane but contained three cyclohexene units and two sulfur atoms.

Anal. Calcd. for $C_{18}H_{28}S_2$: S, 20.79; mol. wt., 308. Found: S, 20.81, 20.88; mol. wt. (ebullioscopic in benzene), 306.5.

Oxidation of this product with hydrogen peroxide as described previously for related compounds[5] gave a sulfone which after crystallization from alcohol melted at 144–144.5° and was identical with the liquid ammonia breakdown product of cyclohexenepolysulfone. This synthetic product on recrystallization from acetic acid also gave the cyclic disulfone melting at 291°.

2,6 - Di - (ω - carboxyoctyl) - 1,4 - dithiane - 1,4 - bis-(dioxide).—Using the general method described previously[5] 10-hendecenoic acid was converted to the dithiane in 1% yield. The physical properties were: b. p. 90–100° at 10–12 mm.; n^{20}D 1.4417; d^{20}_{20} 0.842.

Anal. Calcd. for $C_{22}H_{40}S_2O_4$: S, 14.82. Found: S, 15.15.

Oxidation gave the cyclic disulfone which after crystallization from glacial acetic acid melted at 184–185°.

Anal. Calcd. for $C_{22}H_{40}S_2O_8$: S, 12.9; neut. equiv., 248. Found: S, 12.91; neut. equiv., 243.

This cyclic disulfone was also obtained by the action of liquid ammonia on the polysulfone from 10-hendecenoic acid.

Action of Liquid Ammonia on the Copolymer Prepared from 10-Hendecenoic Acid, 1-Pentene and Sulfur Dioxide.—The copolymer prepared from a mixture of one mole of 10-hendecenoic acid and five moles of 1-pentene on solution in liquid ammonia and subsequent evaporation of the solution gave a considerable amount (80% of the calculated) of alkali insoluble cyclic disulfone which melted at 249–251°. This material was apparently not different from 2,6-di-*n*-propyl-1,4-dithiane-1,4-bis-(dioxide), m. p. 257°, previously obtained from pure 1-pentenepolysulfone.[5] A mixture of the products melted at 250–252°.

There was also formed a small amount (40% of the calculated amount based on the 10-hendecenoic acid used) of alkali soluble cyclic disulfone. This melted at 195° and was shown to be identical with the compound described in the next experiment.

The copolymer prepared from a mixture containing equimolecular quantities of 10-hendecenoic acid and 1-pentene was dissolved in liquid ammonia and then the solution was allowed to evaporate spontaneously. A single alkali soluble product was obtained. The crude yield was above 75%. After two recrystallizations from alcohol the yield was still 63% of a compound, m. p. 198°. This compound was titrated and showed a neutral equiva-

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[7] Bost and Conn, "Organic Syntheses," Volume XV, John Wiley and Sons, Inc., New York, N. Y., 1935, p. 72.

lent of 377 whereas that calculated for a cyclic disulfone having one molecule of 10-hendecenoic acid and one of 1-pentene should have the value 382.

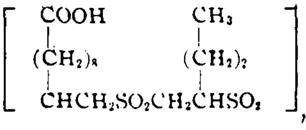
Anal. Calcd. for $C_{16}H_{30}S_2O_6$: S, 16.75. Found: S, 16.97.

No alkali insoluble sulfone was found and no evidence was obtained to indicate that the cyclic disulfone having two units of 10-hendecenoic acid was formed in this reaction.

Summary

1. Mixed olefins and their derivatives or mixtures of an olefin and an acetylene combine with sulfur dioxide to give products which correspond closely in composition to the mixture used and appear to be true copolymers.

2. The copolymer prepared from a mixture of equimolecular quantities of 10-hendecenoic acid and 1-pentene has been shown to have the structure



$$\left[\begin{array}{l}\text{COOH} \qquad\qquad \text{CH}_3 \\ \;| \qquad\qquad\qquad\quad | \\ (\text{CH}_2)_8 \qquad\quad (\text{CH}_2)_2 \\ \;| \qquad\qquad\qquad\quad | \\ \text{CHCH}_2\text{SO}_2\text{CH}_2\text{CHSO}_2\end{array}\right]_n$$

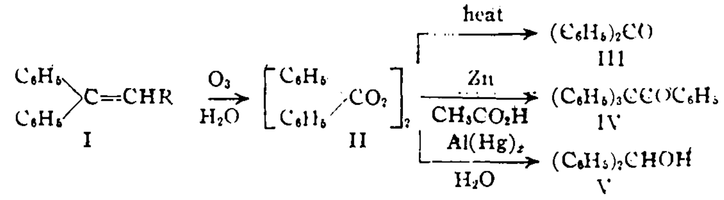
URBANA, ILLINOIS RECEIVED FEBRUARY 14, 1938

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

Diaryl Ketone Peroxides

BY C. S. MARVEL AND VELMA E. NICHOLS

Dimeric and trimeric ketone peroxides from dialkyl and alkyl aryl ketones have been known for some time[1] but the corresponding diaryl ketone peroxides apparently have not been described. While studying the ozonolysis of certain 1,1-diphenyl-1-alkenes (I), we isolated a high-melting neutral compound which proved to be dimeric benzophenone peroxide (II). This communication describes the isolation and the properties of the latter and of several analogous compounds.



It is somewhat surprising that diaryl ketone peroxides have not been noted in earlier ozonolysis reactions since both dialkyl and alkyl aryl ketone peroxides have been prepared by this procedure.[1] After our accidental discovery of benzophenone peroxide, a large number of experiments on the ozonolysis of 1,1-diphenyl-1-propene was carried out. Carbon tetrachloride was used as a solvent for the ozonization. Many changes in experimental conditions of ozonization and of hydrolysis did not greatly affect the yield of benzophenone peroxide, which always amounted to 3–7% of the theoretical.

Benzophenone peroxide was also obtained by the ozonolysis of 1,1-diphenylethene and 1,1-diphenyl-1-butene. It was not obtained by ozonolysis of 1,1-diphenyl-4,4-dimethyl-1,2-pentadiene. Ozonolysis of 1,1-di-*p*-tolylethene, 1,1-di-*m*-tolylethene and 1-phenyl-1-*p*-tolylethene gave the respective ketone peroxides in 3–7% yields. No ketone peroxide was obtained in the ozonolysis of 1,1-dibiphenylethene but some *p*-carboxyphenyl biphenyl ketone was isolated. In all of these ozonolysis experiments small amounts of the acids which might be expected from cleavage of the diaryl ketones were isolated.

All of these diaryl ketone peroxides were quite insoluble in ethanol; were difficultly soluble in ether, acetone, ethyl acetate, and acetic acid; and fairly soluble in hot benzene and carbon tetrachloride. They all melted sharply within the limits of 183 to 225° with some liberation of gas and some evidence of sublimation at the melting point. None exploded at the melting point, although some less pure samples gave off gas at a fairly rapid rate in the melting point tubes.

Benzophenone peroxide when heated for five minutes at its melting point (214–215°) was decomposed completely to give benzophenone (III). It was noted that recrystallization of these peroxides from various solvents always caused con-

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(1) The literature concerning these compounds has been summarized by Rieche: (a) "Alkylperoxyde und Ozonide, Studien uber peroxydischen Sauerstoff," Steinkopff, Dresden. 1931; (b) "Die Bedeutung der organischen Peroxyde für die chemische Wissenschaft und Technik," Ahrens Sammlung, **34**, 1 (1936), Enke, Stuttgart.