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

The Reaction between Sulfur Dioxide and Olefins and Acetylenes. VI.[1] Ascaridole as a Catalyst for the Reaction

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Previous work[2] has demonstrated that oxygen and various peroxides are catalysts for the addition reaction between sulfur dioxide and olefins and acetylenes. In this communication, we report experiments which prove that ascaridole, a naturally occurring terpene peroxide, is a very effective catalyst for the above reaction with olefins of the type $RCH{=}CH_2$, and for certain monosubstituted acetylenes.

The most striking illustration of the effectiveness of ascaridole is furnished in the case of the reactions between sulfur dioxide and olefin derivatives containing carboxyl, cyano, carbethoxy and phenolic groups. Previously[3] it was shown that these types of olefin derivatives did not combine with sulfur dioxide when paraldehyde, which contained peroxides, was used as a catalyst. However, with ascaridole as a catalyst, polysulfones have now been obtained from undecylenic acid, allylacetic acid, allyl cyanide, methyl undecylenate and *o*-allylphenol in good yields. In the case of simple olefins, ascaridole is very effective when the double bond is in the terminal position as in 1-pentene, but does not seem to be superior to other peroxides when the double bond is buried in the molecule, as in 2-pentene and cyclohexene. The polysulfones obtained when ascaridole is used as a catalyst are the same as those obtained with other peroxides.

No catalyst has yet been found which will promote a reaction between a tri- or tetra-substituted olefin and sulfur dioxide. Conjugation of the double bond with a carbonyl group also seems to block the addition reaction, as no polysulfones have yet been prepared from ethyl crotonate, crotonaldehyde, methyl acrylate or acrolein and sulfur dioxide.

Ascaridole seems to be superior to any other catalyst which has been found for promoting the addition of sulfur dioxide to acetylenes. In this series, paraldehyde which contains peroxides catalyzes the same reactions, but to a somewhat less degree. Either catalyst will promote the reaction between sulfur dioxide and acetylenes of the type $RCH_2C{\equiv}CH$, even when R is a normal alkyl group of twelve carbon atoms. Phenylacetylene also adds sulfur dioxide in the presence of either of these catalysts. However, no satisfactory yields of addition products have been obtained from acetylenes of the type $RC{\equiv}CR$ or $R_2CHC{\equiv}CH$ with either of these catalysts.

The synthesis of 1-pentadecyne is reported in the experimental part of this communication.

Experimental

Preparation of the Polymers.—To a mixture of equal volumes of the liquid olefin, olefin derivative or acetylene and liquid sulfur dioxide, were added a little alcohol (to prevent darkening) and some ascaridole. The reaction mixture was placed in a pressure bottle, sealed and allowed to stand at room temperature. Typical experiments with individual compounds are described in Table I. In general, the compounds were isolated as described in previous papers from this Laboratory.

Using the same general experimental conditions described above, it has not yet been possible to obtain polysulfones from oleyl alcohol, allyl bromide, crotonaldehyde, acrolein, methyl vinyl ketone, methyl acrylate, ethyl crotonate, dimethylacetylene, *t*-butylacetylene or cyclohexylacetylene.

Purification and Properties of New Polysulfones.—*o*-Allylanisole polysulfone is soluble in dioxane, and was purified by dissolving it in this solvent and reprecipitating with water. The compound melted to a clear, glassy substance, and did not decompose below 200°.

o-Allylphenol polysulfone is soluble in acetone, ether, ethyl acetate, ethyl alcohol and 0.1 *N* sodium hydroxide solution. It could be reprecipitated from the alkaline solution by addition of acid.

p-Bromoallylbenzene polysulfone is insoluble in all common organic solvents. It was purified by washing with alcohol and ether.

Allylacetic acid polysulfone separated as a white, rubbery polymer in the reaction flask. It was purified by removing some impurities by steam distillation and then dissolving in dioxane and precipitating it by adding water. This polymer is soluble in ethyl alcohol. It can be dissolved in alkali and reprecipitated.

Allyl cyanide polysulfone separated in the reaction flask as a white, insoluble powder. It was purified by washing with alcohol and ether. It was insoluble in all of the common organic solvents which were tried.

Undecylenic acid polysulfone is slightly soluble in alcohol and insoluble in most other common organic solvents.

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(1) For the fifth communication on this subject, see Glavis, Ryden and Marvel, THIS JOURNAL, **59**, 707 (1937).

(2) (a) Seyer and King, *ibid.*, **55**, 3140 (1933); (b) Frederick, Cogan and Marvel, *ibid.*, **56**, 1815 (1934); (c) Staudinger and Ritzenthaler, *Ber.*, **68B**, 455 (1935); (d) Ryden and Marvel, THIS JOURNAL, **58**, 2047 (1936); (e) Fitch, U. S. Patent 2,045,592 (1936).

(3) Ryden and Marvel, THIS JOURNAL, **57**, 2311 (1935).

TABLE I

Unsaturated compound	Used, cc.	SO_2, cc.	Catalyst, cc.		Time of standing, hrs.	Yield of polymers, g.	M. p. of polymers, °C.	Empirical formula	Analysis S, %	
			EtOH	Ascaridole					Calcd.	Found
1-Pentene	5	5	1	0.2	5	4	340	[a]		
2-Pentene	5	5	1	.2	5	0.1	290–300	[a]		
Cyclohexene	5	5	1	.2	5	.2	Above 200	[b]		
Styrene	5	5	1	.2	5	.5	185–190	[c]		
Undecylenyl alcohol	5	5	2	.1	7	7	Above 330	[a]		
o-Allylanisole	5	5	5	.2	8	7	150–160	$C_{10}H_{12}O_3S$	15.1	14.7
o-Allylphenol	5	5	5	.2	4	4	120–160	$C_9H_{10}O_3S$	16.1	15.8
p-Bromoallylbenzene	10	10	2	.2	12	16.5	255	$C_9H_9BrO_2S$	12.2	12.0
Allylacetic acid	5	5	5	.4[d]	4	5	180–230	$C_5H_8O_4S$	19.5	18.8[e]
Allyl cyanide	10	10	2	.2	12	1	222	$C_4H_5NO_2S$	24.45	24.57
Undecylenic acid	5	5	5	.2	1	5.5	255–275	$C_{11}H_{20}O_4S$	12.9	10.2[f]
Methyl undecylenate	5	5	5	.2	10	5		$C_{12}H_{22}O_4S$	12.2	11.81, 11.9[g]
1-Pentyne	10	10	5	.2	10	8	203–208	[h]		
Phenylacetylene	5	5	3	1	1	5	250–275	[h]		
1-Nonyne	6	5	1	0.2	3	2.4	160–169	[a]		
Cyclohexylpropyne	10	10	2	.2	3	15	110–145	$C_9H_{14}O_2S$	17.2	17.5
1-Pentadecyne	5	5	1	.2	5	3.5	120–140	$C_{15}H_{28}O_2S$	11.7	11.5[i]

[a] For the analysis of this compound, see ref. 2d. [b] For the analysis of this compound, see ref. 2b. [c] For the analysis of this compound, see ref. 1. [d] 0.2 cc. of ascaridole was added when the reaction mixture was made up, and after two hours, a second portion of 0.2 cc. was added. [e] Calcd. for $C_5H_8O_4S$: C, 36.6; H, 5.9. Found: C, 37.5, 37.7; H, 4.86, 4.91. [f] Calcd. for $C_{11}H_{20}O_4S$: C, 53.4; H, 8.06. Found: C, 55.4; H, 8.03. [g] This material was prepared and characterized by Mr. S. Jack Davis. Calcd. for $C_{12}H_{22}O_4S$: C, 54.91; H, 8.46. Found: C, 55.48; H, 7.95. [h] For the analysis of this compound, see ref. 3. [i] Calcd. for $C_{15}H_{28}O_2S$: C, 66.0; H, 10.3. Found: C, 64.6; H, 10.1.

It dissolves in 2% sodium hydroxide solution and reprecipitates on acidification. It is a soft, rubbery mass, very difficult to purify, and hence the analyses were somewhat unsatisfactory.

Methyl undecylenate polysulfone is a very soft, glass-like product which is soluble in hot alcohol, but insoluble in the cold. It was purified by dissolving in hot alcohol and allowing to cool. It was finally washed with hot petroleum ether and dried in a vacuum desiccator. The compound is very soluble in acetone and slightly soluble in chloroform, benzene, ether, dioxane, carbon disulfide and carbon tetrachloride. The product gradually becomes sticky as the temperature is raised, and decomposes completely at 230–250°.

1-Pentadecyne polysulfone is a soft, wax-like product soluble in hot acetone and insoluble in the cold.

2-Bromo-1-pentadecene.—A solution of 0.33 mole of lauryl-magnesium bromide in 200 cc. of dry ether was added to 0.3 mole (59 g.) of bromoallyl bromide, and the reaction mixture was worked up as described by Lespieau and Bourguel[4] for the preparation of cyclohexylbromopropene. The yield of product was 22 g., b. p. 145–155° (3–4 mm.); $n^{20}D$ 1.4670; $d^{20}{}_4$, 1.032.

Anal. Calcd. for $C_{15}H_{29}Br$: C, 62.3; H, 10.03. Found: C, 61.3; H, 10.95.

1-Pentadecyne.—Twenty-five grams of 2-bromo-1-pentadecene was added to a solution of 0.3 mole of sodamide in liquid ammonia.[5] The ammonia was allowed to evaporate, and the residue was treated with water, then dilute hydrochloric acid. The acetylene was taken up in ether and distilled. The yield was 2 cc. of material boiling at 112–113° (5 mm.); $n^{20}D$ 1.4410; $d^{20}{}_4$, 0.8261.

The mercury derivative, prepared by the procedure of Johnson and McEwen,[6] melted at 93°.

Anal. Calcd. for $C_{30}H_{56}Hg$: Hg, 32.6. Found: Hg, 32.1.

Summary

Ascaridole has been shown to be an active catalyst for reaction between sulfur dioxide and olefins of the type $RCH{=}CH_2$, and sulfur dioxide and acetylenes of the type $RC{\equiv}CH$.

o-Allylanisole, *o*-allylphenol, *p*-bromoallylbenzene, allylacetic acid, allyl cyanide, undecylenic acid, methyl undecylenate and 1-pentadecyne, when treated with sulfur dioxide in the presence of ascaridole, give good yields of polysulfones.

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[4] Lespieau and Bourguel, "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, 1932, p. 180.

[5] Vaughn, Vogt and Nieuwland, THIS JOURNAL, **56**, 2120 (1934).

[6] Johnson and McEwen, *ibid.*, **48**, 469 (1926).