

pentane and then from ethyl acetate; m. p. 204–208°; yield, 700 mg.

Anal. Calcd. for $\text{C}_{24}\text{H}_{40}\text{O}_4$: C, 73.4; H, 10.3. Found: C, 73.4; H, 10.4.

This compound was saturated as evidenced by the facts that it did not take up bromine and was recovered unchanged upon attempted hydrogenation with Adams catalyst in acetic acid.

neo-Lithobilianic Acid.—To a solution of 500 mg. of 11,12-dihydroxycholanic acid in 25 cc. of acetic acid was added a solution of 500 mg. of chromic anhydride in 15 cc. of 65% acetic acid. This mixture was allowed to stand at room temperature for one hour. The excess chromic anhydride was destroyed by adding zinc dust. The mixture was filtered and the filtrate was evaporated *in vacuo*. The residue was taken up in ether, washed with water, dried and the solvent was removed. The residue was crystallized from ether; m. p. 257–259°.

Anal. Calcd. for $\text{C}_{24}\text{H}_{38}\text{O}_6$: C, 68.2; H, 9.1. Found: C, 68.4; H, 9.1.

In a similar manner 11-hydroxy-12-ketocholanic acid was oxidized to give a 25% yield of *neo-lithobilianic acid*; m. p. and mixed m. p. with the above acid, 257°.

Anal. Calcd. for $\text{C}_{24}\text{H}_{38}\text{O}_6$: C, 68.2; H, 9.1. Found: C, 68.4; H, 9.2.

3(α),11,12-Trihydroxycholanic Acid.—A mixture of 2.5 g. of 3(α),11,12-dihydroxy-12-ketocholanic acid, 10 cc. of 85% hydrazine hydrate and a solution of 3.5 g. of sodium in 70 cc. of absolute ethanol was heated in a sealed tube for eight hours at 200°. The reaction mixture was worked up as described for 11,12-dihydroxycholanic acid. The product was crystallized from ether-pentane; m. p. 136° (bubbles); wt., 686 mg. It was also crystallized from ethyl acetate. This compound did not react with bromine and was recovered unchanged upon attempted catalytic reduction.

Anal. Calcd. for $\text{C}_{24}\text{H}_{40}\text{O}_5$: C, 70.5; H, 9.9. Found: C, 70.3; H, 9.8.

Oxidation of 3(α),11,12-Trihydroxycholanic Acid.—To a solution of 0.4 g. of 3(α),11,12-trihydroxycholanic acid in 40 cc. of acetic acid was added a solution of 0.4 g. of

chromic anhydride in 15 cc. of 65% acetic acid. This was allowed to stand at room temperature for one hour. Water was added to the mixture, and the precipitated solid was extracted with ether. The ether layer was washed with water and evaporated. A Clemmensen reduction was run on the residue by refluxing it with 50 cc. of ethanol, 10 g. of amalgamated zinc and adding 60 cc. of concentrated hydrochloric acid over a period of four hours. The zinc was filtered, and water was added to the filtrate. The product was extracted with ether and the ether layer was washed with water and evaporated. The residue was hydrolyzed with alcoholic potassium hydroxide. The free acid was crystallized from ether-pentane; m. p. and mixed m. p. with the *neo-lithobilianic acid* previously prepared, 256–259°.

Anal. Calcd. for $\text{C}_{24}\text{H}_{38}\text{O}_6$: C, 68.2; H, 9.1. Found: C, 68.0; H, 9.0.

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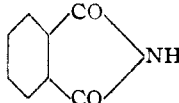
Non-peroxide Catalysts for the Reaction between Sulfur Dioxide and Olefins¹

BY C. S. MARVEL, L. F. AUDRIETH AND W. H. SHARKEY

A tertiary amine oxide, R_3NO , may be considered as a nitrogen analog of a peroxide and this has led us to try representatives of this group of compounds as catalysts for the addition of sulfur dioxide to an olefin or an acetylene to produce polymeric sulfones.

Trimethylamine oxide and dimethylaniline oxide proved to be catalysts for the reaction with such representative compounds as 1-pentene, 1-hexene, 1-heptene, 2-butene and 1-pentyne. The

(1) This is the thirteenth communication on the reaction between sulfur dioxide and olefins. For the twelfth see *THIS JOURNAL*, **61**, 2714 (1939).

POLYSULFONES FROM VARIOUS CATALYSTS					
Unsatd. compound	Amount, cc.	Catalyst to be tested	Amount in grams	Time, hr.	Yield of polysulfone, g.
1-Pentene	5	NH ₂ OH·HCl	0.5	12	1.13
1-Pentene	5	(CH ₃) ₃ NO	.5	12	4.5
1-Pentene	5		.5	12	3.5
1-Pentene	5	(CH ₃) ₃ NO	.2	18	3.09
1-Pentene	5	(CH ₃) ₃ NO	.2		
		HCl	2 cc., sp. gr. 1.19	18	5.17
1-Pentene	5	C ₆ H ₅ (CH ₃) ₂ NO	5 cc., soln. in concd. HCl	12	1.0
1-Hexene	5	(CH ₃) ₃ NO	0.2	12	6.15
		HCl	2 cc. dil.		
1-Heptene	5	(CH ₃) ₃ NO	0.2	12	5.04
		HCl	2 cc., sp. gr. 1.19		
1-Pentyne	10	(CH ₃) ₃ NO	0.5	18	13.38
2-Butene	10	(CH ₃) ₃ NO	.5	18	16.00
2-Pentene	10	(CH ₃) ₃ NO	.5	18	2.69
1-Heptene	5	(CH ₃) ₄ NCl	.2	16	5.38
1-Pentene	5	(CH ₃) ₄ NCl	.2	12	3.25
1-Pentene	5	(C ₂ H ₅) ₄ NBr	.2	60	4.42
1-Pentene	5	(<i>n</i> -C ₇ H ₁₅)(<i>n</i> -C ₄ H ₉) ₂ NI	.1	60	None
1-Heptene	5	(<i>n</i> -C ₇ H ₁₅)(<i>n</i> -C ₄ H ₉) ₂ NI	.1	16	None

addition of halogen acid² to give the salt of the amine oxide increased the catalytic activity to a marked extent. Even hydroxylamine hydrochloride proved to have some activity as a catalyst for the reaction. More surprising was the fact that both tetramethylammonium chloride and tetraethylammonium bromide were catalysts for the reaction. Their activity, however, was not great. Tests with some quaternary ammonium iodides showed these were not catalysts for the addition reaction. Phthalimide also showed some catalytic activity.

Experimental

Trimethylamine oxide and dimethylaniline oxide were made by the method described by Hickinbottom.³

The polymerization reactions were carried out in pressure bottles. The unsaturated compounds and sulfur dioxide with a little ethyl alcohol were placed in the bottle with the substance to be tested as a catalyst. The sealed reaction mixture was allowed to stand for the specified time, then opened, the excess sulfur dioxide allowed to evaporate and the product isolated by the usual procedure. The results are summarized in the following table.

Trimethylamine oxide did not catalyze the addition of sulfur dioxide to vinyl chloride. Hydrazine, phenylhydrazine, cupferron, phenylglyoxal oxime, azoxybenzene, nitrobenzene, semicarbazide hydrochloride, dimethyl

formamide, and hydrazocarbamide showed no catalytic activity at ordinary temperatures.

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Association Effects in the Raman Spectra of Solutions of Thiophenol in Donor Solvents

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While the O-H stretching vibration gives strong absorption in the infrared and is quite suitable for use in the study of hydrogen bonding, the O-H frequencies in Raman spectra produce broad bands, so diffuse that in a great number of cases they are not even observed. On the other hand, the Raman spectra of mercaptans show a strong S-H line at 2570 cm.⁻¹ which is in a region not occupied by other fundamentals. For this reason it was hoped that a hydrogen bond study could be made of solutions of thiophenol such as Gordy and Stanford¹ had done in the infrared. Consequently, Raman spectra were obtained for pure thiophenol and for its solutions in benzene, dioxane, diisopropyl ether, pyridine, dibenzylamine and diisobutyl ketone. All compounds used were of good quality and were distilled before mixing. The apparatus and experimental technique used in obtaining the spectra are discussed

(2) Kharasch and Sternfeld [THIS JOURNAL, **62**, 2559 (1940)] have shown that the addition of hydrochloric acid increases the activity of the peroxide, ascaridole, as a catalyst for polysulfone formation.

(3) Hickinbottom, "Reactions of Organic Compounds," Longmans, Green and Company, New York, N. Y., 1938, p. 277.

(1) Gordy and Stanford, THIS JOURNAL, **62**, 497 (1940).