

glass for fourteen hours at 135° gave 29% of dicholesteryl ether, with the remainder of the sterol resinified. The ether was obtained in 26% yield and 51% of the cholesterol was recovered when copper chloride was used as a catalyst, and a similar experiment using a small amount of sulfur resulted in an 18% yield of dicholesteryl ether and the recovery of 45% of the starting material.

These experiments indicate that in liquid sulfur dioxide at 100° cholesterol is dehydrated to form dicholesteryl ether. There are no side reactions. It is probably an equilibrium reaction and apparently subject to catalysis. Higher temperatures and longer reaction periods produce cholesterilenes and resinous products, either by a competing reaction¹¹ or by a dismutation of the cholesteryl ether already formed.

(11) For a discussion of the mechanism of dehydration of cholesterol see Bills and McDonald, note 4b; also Kawasaki, note 10.

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Summary

Cholesterol is dehydrated in liquid sulfur dioxide at elevated temperatures with the formation of dicholesteryl ether. The reaction is subject to catalysis.

A good method for the preparation of dicholesteryl ether has been developed.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, PURDUE UNIVERSITY]

The Utilization of Aliphatic Nitro Compounds. VIII. Nitrotriols (Nitroglycerols) Prepared from Simple Aldehydes¹

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In the condensation of nitromethane with formaldehyde to form nitroethanol, a very large excess of nitromethane is required² to prevent the formation of 2-nitro-1,3-propanediol and 2-hydroxymethyl-2-nitro-1,3-propanediol. Higher aldehydes are not so readily condensed with nitromethane. Thus it has not been found possible to prepare nitrotriols by condensing three equivalents of such aldehydes with one of nitromethane; but by first condensing the higher aldehyde with one equivalent of nitromethane followed by treatment with a large excess of formaldehyde, a nitrotriol results.³

The preparation of the nitrotriols is very much the same as that of the nitrodiols.⁴ The reaction is not as sensitive to the alkali concentration, since formaldehyde condenses very readily with nitromethane or with 1-nitro-2-alkanols. The following illustrates the procedure.

2-Hydroxymethyl-2-nitro-1,3-pentenediol.—A mixture of 41 g. of 1-nitro-2-butanol, 25 ml. of 95% ethanol, and 3 g. of potassium carbonate is stirred while 62 g. of 40% formalin is added dropwise. The clear solution after standing for four days at room temperature is neutralized with

4 ml. of concentrated hydrochloric acid, then saturated with sodium chloride and extracted with butanol. Part of the butanol is removed by distillation under diminished pressure and the residue is chilled to bring about crystallization. The crystals are recrystallized from dry butanol. Four nitrotriols, as shown in the table, have been prepared by this procedure.

Nitrotriol, 2-hydroxymethyl-2-nitro-	M. p., °C.	% Nitrogen	
		Calcd.	Found ^a
-1,3-pentenediol	141	7.83	7.51
-1,3-hexanediol	154-6	7.26	6.83
-1,3-nonanediol	145-7	5.97	5.82
-5-methyl-1,3-hexanediol	144-6	6.77	6.64

^a By a modified Kjeldahl method (see Harte, *Ind. Eng. Chem., Anal. Ed.*, 7, 432-3 (1935)).

The nitrotriols are white crystalline substances, very soluble in water, moderately soluble in alcohol, and quite insoluble in ether or in petroleum solvents. Their melting points are somewhat higher than those of the nitrodiols.

Summary

Nitrotriols are prepared by means of an aldol condensation involving two equivalents of formaldehyde with one equivalent of a higher aldehyde and one of nitromethane. The purification of the nitrotriols is much simpler than that of the nitrodiols which are prepared from aldehydes other than formaldehyde.

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(2) Gorski and Makarov, *Ber.*, 67B, 996-1000 (1934); *C. A.* 28, 5039 (1934). The nitroparaffins used in this work were furnished by The Commercial Solvents Corporation.

(3) Charlton and Kenner, *J. Chem. Soc.*, 750 (1932).

(4) Sprang with Degering, *This Journal*, 64, 1735 (1942).