Stoughton of this Laboratory for the help and encouragement he has given this program since its inception.

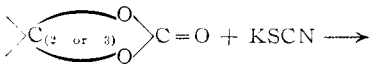
CHEMISTRY DIVISION
OAK RIDGE NATIONAL LABORATORY W. C. WAGGENER
OAK RIDGE, TENNESSEE

RECEIVED APRIL 24, 1958

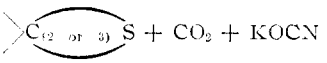
A NEW SYNTHESIS OF SMALL RING CYCLIC SULFIDES

Sir:

A new method for the synthesis of thiiranes and thietanes has been discovered, which promises to have considerable generality. It has been found that heating the melted cyclic carbonate of a 1,2- or 1,3-diol with an equimolar amount of potassium thiocyanate produces the corresponding cyclic sulfide in most cases. Table I presents typical data.

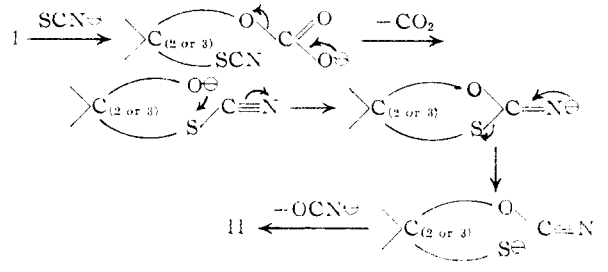


I



II

This method may be compared with the recently reported pyrolysis of 1,3-oxathiolan-2-one over potassium carbonate to yield ethylene sulfide,[1] but the present process is much more convenient because of the easy preparation of the cyclic carbonate from a 1,2- or 1,3-diol and ethylene carbonate or diethyl carbonate.



The pyrolysis is thought to proceed by a mechanism similar to that proposed by van Tamelen for the formation of episulfides from epoxides and thiocyanate ion.[2] Failure to obtain an appreciable amount of cyclic sulfide from the reaction of 4,4,6-trimethyl-1,3-dioxan-2-one with potassium thiocyanate at 185° may be attributed by this mechanism to the α,α,α'-trisubstitution. The chief product in the latter case is 4-methyl-3-penten-2-ol.

Acknowledgment.—We wish to thank the National Science Foundation for a research grant under which this work was carried out and Mr. Donald G. Hummel for supplying us with the cyclic carbonates of 1,3-propanediol, 1,3-butanediol,

TABLE I

Cyclic carbonate of	Reaction temp., °C.	Product	B.p., °C. Obsd.	B.p., °C. Lit.	$n^{20}D$ Obsd.	$n^{20}D$ Lit.	Yield, %
Ethylene glycol	95	Ethylene sulfide	54–54.5	55–56[a]	1.4950	1.49145[a,f]	64.5
1,3-Propanediol	140	Trimethylene sulfide	70–93	95.0[b]	1.4932	1.5102[b]	3.4
1,3-Butanediol	170–180	2-Methylthietane	101–102	105.5–107.5[c]	1.4852	1.4831[c]	15.8
2,3-Dimethyl-1,3-propanediol	175–180	3,3-Dimethylthietane	115–116	120[d]	1.4738[f]	1.4739[d,f]	58.6
2,2-Diethyl-1,3-propanediol	190–195	3,3-Diethylthietane[e]	170.5–173		1.4833		43.8

[a] M. Marcel Delepine, *Bull. soc. chim. France*, 742 (1920). [b] W. E. Haines, R. V. Helm, C. W. Bailey and J. S. Ball, *J. Phys. Chem.*, **38**, 273 (1954). [c] Grischkewitsch-Trochimowski, *J. Russ. Phys.-Chem. Ges.*, **48**, 894 (*Beil.*, XVII–XIX, 1st supp., p. 5). [d] H. J. Backer and K. J. Keuning, *Rec. trav. chim.*, **53**, 810 (1934). [e] Calcd. for $C_7H_{14}S$: C, 64.55; H, 10.83; S, 24.62. Found: C, 64.98; H, 10.91; S, 24.30. Microanalysis by Geller Microanalytical Laboratories, West Englewood, New Jersey. [f] Indices of refraction taken at 18°.

(1) D. D. Reynolds, THIS JOURNAL, **79**, 4951 (1957).

(2) E. E. van Tamelen, *ibid.*, **73**, 3444 (1951).

DEPARTMENT OF CHEMISTRY
KANSAS STATE COLLEGE SCOTT SEARLES, JR.
MANHATTAN, KANSAS EUGENE F. LUTZ

RECEIVED APRIL 25, 1958

HEMOGLOBIN STUDIES. II. A SYNTHETIC MATERIAL WITH HEMOGLOBIN-LIKE PROPERTY[1]

Sir:

It was suggested from the experimental data on hemoglobin and related compounds that the unusual stability of oxyhemoglobin and oxymyoglobin could be due to the low dielectric constant of the immediate surroundings of the bound oxygen molecules.[1] In order to check this hypothesis, a synthetic model material was made by the following procedure.

A solution of the diethyl ester of hemin and an excess of 1-(2-phenylethyl)-imidazole in benzene was reduced by shaking with an aqueous $Na_2S_2O_4$ + KOH solution in a carbon monoxide atmosphere. After centrifugation, the clear, bright-red benzene solution was mixed, in CO-atmosphere, with a 10% solution of polystyrene in benzene, and then dried in a warm stream of CO at 1 atm. pressure. The transparent, solid-like film, which contained the complex molecules of 1-(2-phenylethyl)-imidazolecarbonmonoxyheme diethyl ester imbedded in a matrix of an amorphous mixture of polystyrene and 1-(2-phenylethyl)-imidazole,

(1) Paper I, J. H. Wang, A. Nakahara and E. B. Fleischer, THIS JOURNAL, **80**, 1109 (1958). This work was supported in part first by a grant from Research Corporation, and later by a grant (USPHS-RG-4483) from the Division of Research Grants, Public Health Service.