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

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RECEIVED APRIL 24, 1958

A NEW SYNTHESIS OF SMALL RING CYCLIC SULFIDES

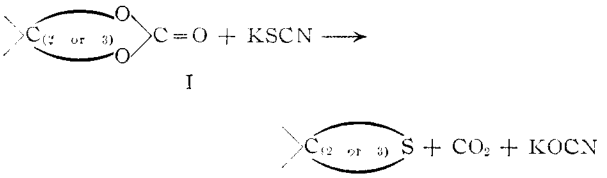
Sir:

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.

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

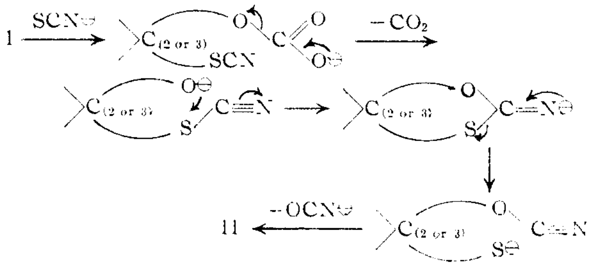
[a] M. Marcel Delepine, *Bull. soc. chim. France*, 742 (1920). [b] W. E. Haines, R. V. Helm, C. W. Bailey and J. S. Ball, *J. Phys. Chem.*, **38**, 273 (1954). [c] Grischkewitsch-Trochimowski, *J. Russ. Phys.-Chem. Ges.*, **48**, 894 (*Beil.*, XVII-XIX, 1st supp., p. 5). [d] H. J. Backer and K. J. Keuning, *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°.



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, 2,2-diethyl-1,3-propanediol and 2-methyl-2,4-pentanediol.

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

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

DEPARTMENT OF CHEMISTRY
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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,

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(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.

showed a carbonmonoxyheme-like absorption spectrum.

After completely removing the bound CO by flushing with nitrogen gas for several hours at room temperature, the film showed a typical hemochromogen spectrum. With polystyrene and 1-(2-phenylethyl)-imidazole mixture of 1:3 weight ratio as the matrix, the absorption maxima are at 5280 and 5560 Å., respectively. When this material was exposed to oxygen or air, it rapidly combined with molecular oxygen to give a product which showed an oxyhemoglobin-type of spectrum with absorption peaks at 5370 and 5630 Å. respectively. The oxygenation is reversible, because the original hemochromogen spectrum can be quantitatively restored by flushing the film with nitrogen or by evacuating at room temperature. The cycle can be carried out repeatedly. For a film with more than 90% of polystyrene, the hemochromogen-like spectrum becomes more diffuse. This film still combines rapidly and reversibly with CO_2 or O_2, and it may also be kept in contact with air-saturated water for days without being oxidized to Fe(III) state.

Although reversible oxygen-addition compounds of Fe(II)-complexes have been reported,[2,3] the present synthetic material appears to be the first successful hemoglobin model which is stable in the presence of water. These results also substantiate our previously suggested picture of the binding sites in hemoglobin and myoglobin.[1]

Besides serving as a protective atmosphere, the function of CO in the preparative procedure for high polystyrene-content films is two-fold: (1) to help each Fe(II) to bind one 1-(2-phenylethyl)-imidazole through the stronger ligand-field of CO[4]; (2) to create a spatial configuration in the matrix near the binding site more favorable to O_2 than to another 1-(2-phenylethyl)-imidazole. This last function of CO is shown by the following observation.

The oxygenation ability of the high polystyrene-content film can be destroyed by heating the film in nitrogen atmosphere. This "denatured" film still readily combines with CO. Its oxygenation ability can be restored by heating in CO-atmosphere, cooling, and subsequently removing the bound CO by prolonged flushing with nitrogen.

A high polystyrene-content film made by the above procedure with free heme to replace the diethyl ester was oxidized immediately to Fe(III)-state on exposure to air. This suggests that, in contrast to the ester, the free hemes are not imbedded in the hydrophobic matrix but are quite exposed.

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[2] K. Kunz and A. J. Kress, *Ber.*, **60**, 367 (1927).

[3] A. H. Corwin and Z. Reyes, THIS JOURNAL, **78**, 2437 (1956).

[4] A. Nakahara, Y. N. Chiu and J. H. Wang, to be published.

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BOOK REVIEWS

The Spectroscopy of Flames. By A. G. GAYDON, D.Sc., F.R.S., Warren Research Fellow of the Royal Society, John Wiley and Sons, Inc., 440 Fourth Avenue, New York 16, N. Y. 1957. ix + 279 pp. 16 × 24.5 cm. Price, $9.00.

This book aims at replacing "Spectroscopy and Combustion Theory" and "Flames, their Structure, Radiation and Temperature" from the same author, but covers slightly different ground. Some regions covered in the other books are not repeated here, but a fuller treatment of more recent work is made.

The last decade has been notable for the development of a number of new experimental techniques for controlling flames and for exciting flame-type spectra in special sources. These techniques include the burners for flat diffusion and flat premixed flames, low-pressure flames, controlled low-temperature flames, flames supported by free atoms, flash photolysis, shock-tube excitation and use of isotope tracer methods. Dr. Gaydon and his colleagues at Imperial College have been associated with the development of many of these techniques and he has included a great deal of invaluable experimental information in the first part of the book.

The subject is presented in such a way that the book may be of service to those engaged in research in the field, but so that it may be read easily by the beginner and the non-specialist. It is with this viewpoint in mind that a chapter is devoted to the theory of spectra and gives a condensate of the most useful results.

Hydrogen and carbon monoxide flames are studied in two separate chapters and a large extension is given to the application of the spectroscopic results to combustion mechanism. A description of the various band systems encountered in organic flames with a discussion of the emitting species, is followed by sections in which the effect of fuel-type, mixture strength and flame conditions are detailed.

A very interesting and fruitful chapter exposes the extensive work done during the past few years about temperature measurements. Electronic, translational, vibrational and rotational temperatures have been determined for a great deal of emitting species in a variety of experimental conditions. All this information is gathered here and criticized very carefully. This work helps elucidate the detailed state of the gases in the reaction zone in order to discriminate the thermal excitation from the chemical excitation. A long discussion includes the author's hypothesis accounting for the chemical reactions involving the different excited free radicals.

The book is mainly concerned with interpretation of the visible and near ultraviolet spectra of flames. The infrared region has been shortly treated although this question had been the subject of a great deal of work. Explosions as well as flames containing nitrogen, halogens and metals are also rapidly reviewed.

Some very useful tables of emission and absorption spectra, molecular constants, and an extensive bibliography are convenient references.

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