ture with authentic material); (2) paper chromatography,[1] which showed it to be N-AcGm free of N-AcMm; (3) an X-ray powder diffraction pattern which was identical to that obtained with N-AcGm.

NANA has been obtained by treatment of N-AcGm with oxaloacetate at *p*H 11.0.[4] A solution of N-AcGm (2.5 g. in 10 ml. of water) was therefore adjusted to, and maintained, at *p*H 11.0 at room temperature. Analysis of aliquots (Table I) at 24, 48 and 72 hr. indicated that a substantial amount of N-AcMm was formed during the first day.

TABLE I

ALKALINE EPIMERIZATION[a] OF N-AcGm TO N-AcMm

Compound	Time, hr.	$R_{\text{N-AcGm}}$	N-AcMm formed,[b] %
N-AcGm (*p*H 11.0)	0	1.0	0
	24	1.0, 0.4	19
	48	1.0, 0.4	24
	72	1.0, 0.4	24

[a] Descending chromatography was conducted on borate treated paper with butanol–pyridine–water (6:4:3) for 20 hr. Synthetic N-AcMm exhibits $R_{\text{N-AcGm}}$ 0.4 under these conditions. [b] Estimated enzymatically with NANaldolase and pyruvate.[1] At equilibrium, 10% of the added N-AcMm is converted to NANA, the latter compound determined by the direct Ehrlich reaction. No inhibition of the enzyme was noted with artificial mixtures containing N-AcGm and N-AcMm (5:1).

After 48 hr., 1.95 g. of N-AcGm (m.p. 202–203°) was recovered by fractional crystallization from ethanol. The remaining mixture (0.5 g.) contained about 90% N-AcMm, 10% N-AcGm, and traces of unidentified materials similar to those obtained in the pyridine epimerization. The N-AcMm was identified by: (1) paper chromatography[1]; (2) conversion to the expected quantity of NANA by the addition of pyruvate and NANaldolase; (3) conversion to D-mannosamine, isolated as the crystalline hydrochloride, and identified by ion-exchange chromatography, optical rotation, color reactions and its X-ray powder diffraction pattern. The alkaline epimerization of N-AcGm to N-AcMm may be a suitable method for the preparation of N-AcMm and of D-mannosamine.

The data outlined above indicate that reversible epimerizations of N-AcMm and N-AcGm readily occurs under the conditions which other investigators have used for chemical studies on the structure of NANA. In view of the present findings, and of our previous results,[1] it is concluded that the N-acetylhexosamine moiety of NANA is N-acetyl-D-mannosamine.

[5] Postdoctoral fellow, American Cancer Society.

THE RACKHAM ARTHRITIS RESEARCH UNIT AND
DEPARTMENT OF BIOLOGICAL CHEMISTRY SAUL ROSEMAN
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RECEIVED APRIL 14, 1958

QUANTITATIVE SPECTROMETRY OF AQUEOUS NEPTUNIUM IONS AT ELEVATED TEMPERATURES AND PRESSURES

Sir:

There are reported herein the results of what are believed to be the first quantitative spectral measurements of a liquid phase above its normal boiling point. A solution of neptunyl ion (7.43×10^{-4} *M* $RbNp^{237}O_2(NO_3)_3$ in 0.1 *M* DNO_3–D_2O at 25°)[1] has been examined from 0.6 to 1.3 μ for 45 hours and from 4.5 to 252°. Deuterated solutions were used to decrease both the absorbance and the effect of temperature upon the absorbance of the solvent.[2] The sample was saturated with ozone, then degassed prior to introduction into the pretreated titanium cell assembly. As the temperature was raised Np(VI) was found to be reduced to Np(V) quantitatively and irreversibly.

The sharp, strong 0.98 μ absorption band of Np(V) is slightly asymmetric, the integrated absorbance of the long wave length side being 1–2% greater than the short wave length side, both at 25 and 251°. The position of the maximum shifts, at a decreasing rate, from 9797 Å. at 25° to 9741 Å. at 251°. The half intensity band width shows a striking behavior with increasing temperature, first decreasing (12%) from 60 cm.$^{-1}$ at 25° to a minimum of 53 cm.$^{-1}$ at about 175°, then slowly increasing to 57 cm.$^{-1}$ at 251°. The product of the absorbance at the band maximum and the half intensity band width, normalized for solvent background and density change, decreases linearly (34%) from 25 to 251°.

From a chemical point of view the above observations suggest an effect of temperature upon the solvation sphere of the NpO_2^+ ion, and a concomitant interaction of the NO_3^- ion present with the NpO_2^+–solvate dipole system.

Several weaker absorption bands belonging to Np(V) and Np(VI) ions have been studied in less detail. The results do indicate clearly, however, a great variability in the effect of temperature upon band profile.

Expansion and refinement of measurements similar to those reported should have manifold implications toward a better understanding of the nature of ions in solution, and forces operative in the liquid state.

The equipment, which has been designed and built at this Laboratory for use with the Cary Model 14 Spectrophotometer, has a working range of 0 to 250° and 0 to 1000 p.s.i. The cell space is 7.62 cm. long × 1.00 cm. diameter, and is fabricated from annealed titanium with colorless synthetic sapphire windows. The entire sample cell and reservoir assembly is suspended in an evacuated chamber, and positioned in a special fused quartz mount. The sample cell at any operating temperature is measured optically against a geometrically similar solvent cell which is thermostated at 25°. Stability and reproducibility of measurements over the design range are comparable to that of operation at room temperature.

A complete discussion of the above results and equipment will be published in articles now in preparation.

I wish to express my appreciation to Dr. R. W.

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[1] The author is indebted to Messrs. P. M. Lantz and G. W. Parker, Chemistry Division, Oak Ridge National Laboratory, for supplying a single crystal of the Np salt, and to Dr. B. M. Benjamin, also of this Laboratory, for the necessary DNO_3 stock solution.

[2] W. C. Waggener, *J. Phys. Chem.*, **62**, 382 (1958); *Anal. Chem.*, in press.

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

CHEMISTRY DIVISION
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W. C. WAGGENER

RECEIVED APRIL 24, 1958

A NEW SYNTHESIS OF SMALL RING CYCLIC SULFIDES

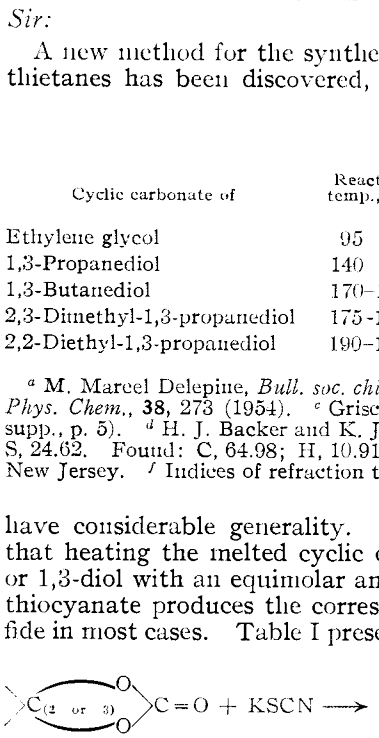
Sir:

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.

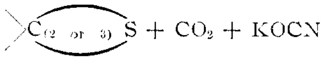
TABLE I

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°.

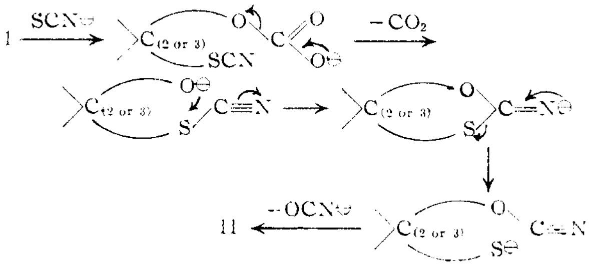


I



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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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,

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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.