

Institute that heating the sulfur precipitate in an autoclave is not attended with losses and that it is thereby converted into a readily soluble form.

The exchange experiments were carried out in sealed U-tubes one leg of each containing a solution of about 3 mg. of radiosulfur in 300 mg. of c. p. carbon disulfide. The filled tubes were heated in a thermostat at 100° for forty-two to sixty-eight hours, and after the heating period about one-half of the carbon disulfide was caused to distil into the empty leg of the tube by cooling it with liquid air. The contents of the two legs were subjected to a Carius combustion, and the resulting sulfuric acid was then converted into dry lithium sulfate. Thin layers of the lithium sulfate, all of equal area, about 20 sq. cm., were prepared on metal plates for the measurement of the activity. Lithium rather than the more easily prepared barium sulfate was used in the radioactivity measurements because the barium absorbs the weak (107 Kev. maximum) beta radiation³ of sulfur more extensively than does lithium. The thickness of the mounted lithium sulfate samples was >0.015 g./sq. cm. and was such that the beta particles from the bottom of a sample could not penetrate to the top and from there reach the electroscop chamber. This arrangement greatly simplifies the quantitative treatment of the results.

In our current experiments with radiosulfur it has been found possible to make the mounted samples of elementary sulfur by reducing barium sulfate to the sulfide with hydrogen at about 900°. Barium sulfide is then treated in the manner described above for the recovery of the sulfur. The reduction procedure was suggested to us by Professor J. E. Bell of this Institute, and the technique for its use was developed by Mr. J. B. Hatcher. Complete reduction of barium sulfate is not attained if the salt melts.

The activity of the lithium sulfate samples was measured with a lead shielded quartz fiber Lauritsen electroscop. A thin aluminum foil, 0.15 mg./sq. cm., served as the window on the ionization chamber. The background was about 0.001 div./min. and varied no more than 30% in a two-week period. By taking background readings immediately before and after readings with the samples, the activities of the latter were determined to ± 0.0002 div./sec. The results, corrected for background, are shown in Table I. The same range of the electroscop scale was used throughout in determining the effect due to the background and to the samples, and therefore no correction for linearity of scale was required.

TABLE I

RADIOACTIVITY OF DISTILLATES AND RESIDUES FROM HEATED SOLUTIONS OF RADIOSULFUR IN CARBON DISULFIDE

Expt.	Activity in div./sec.	Time soln. heated at 100°, hours
1 Distillate	0.000014	42
Residue	.0095	
2 Distillate	— .00017	48
Residue	.0028	
3 Distillate	.00009	68
Residue	.0102	

(3) W. F. Libby and D. D. Lee, *Phys. Rev.*, **55**, 245 (1939).

It is evident from the results that there is practically no interchange between sulfur and carbon disulfide even at 100°. The extent of any interchange must be less than 2%, that is, it must be less than the experimental error of the activity measurements. It is also clear that carbon disulfide may be used as a solvent for radiosulfur without fear of loss by interchange.

GATES AND CRELLIN LABORATORIES OF CHEMISTRY
CALIFORNIA INSTITUTE OF TECHNOLOGY
PASADENA, CALIFORNIA, AND
RADIATION LABORATORY
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA

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Note on the Formation of bis-(β -Diethylaminoethyl) Sulfide

BY ELTON S. COOK AND CORNELIUS W. KREKE

In an attempt to prepare β -diethylaminoethyl mercaptan from 1-bromo-2-diethylaminoethane hydrobromide and sodium hydrosulfide in the presence of sodium ethylate, Lischer and Jordan¹ obtained β, β' -diethylaminodiethyl disulfide. We have tried to prepare the mercaptan using sodium sulfide and hydrogen sulfide by a method based on that employed by Bennett² for the preparation of monothioethylene glycol. We did not obtain the desired mercaptan but isolated *bis*-(β -diethylaminoethyl) sulfide.

Experimental Part

1-Bromo-2-diethylaminoethane hydrobromide was prepared by heating redistilled β -diethylaminoethyl alcohol and 66% hydrobromic acid at 135° according to the method of Meyer and Hopff.³ We found that 40% hydrobromic acid could not be used satisfactorily. The presence of a trace of free bromine greatly facilitated the reaction.

bis-(β -Diethylaminoethyl) Sulfide Dihydrochloride.—One hundred and fifty grams of sodium sulfide ($\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$) was heated to 130° for fifteen minutes and saturated with hydrogen sulfide. The solution was cooled to 60–65°, the passage of hydrogen sulfide being continued during the cooling. Then 10.2 g. of 1-bromo-2-diethylaminoethane hydrobromide was added slowly with stirring and the mixture was kept at 55° for fifteen minutes. The mixture was cooled and extracted immediately three times with 100-cc. portions of ether. The ether solution was dried over anhydrous sodium sulfate, the ether removed, and the dried oily residue was taken up in absolute ether. Dry hydrogen chloride was passed in and the dihydrochloride precipitated readily. It was crystallized from absolute alcohol by the addition of absolute ether:

(1) C. F. Lischer and C. N. Jordan, *THIS JOURNAL*, **59**, 1623 (1937).

(2) G. M. Bennett, *J. Chem. Soc.*, **119**, 418 (1921).

(3) K. H. Meyer and H. Hopff, *Ber.*, **54B**, 2274 (1921).

yield, 2.12 g. (36%) of white crystalline powder, m. p. 245.5–247.5° (corr.).⁴ With Grote's reagent⁵ a faint orange color developed only after addition of potassium cyanide, as is characteristic of monosulfides.

Anal. Calcd. for $C_{12}H_{20}Cl_2N_2S$: S, 10.53; Cl, 23.23. Found: S, 10.24; Cl, 23.31, 23.35.

bis-(β -Diethylaminoethyl) sulfide dihydrobromide was prepared similarly to the dihydrochloride as a white crystalline powder, m. p. 237.3–237.8° (corr.).

Anal. Calcd. for $C_{12}H_{20}Br_2N_2S$: Br, 40.56. Found: Br, 41.06.

(4) W. E. Lawson and E. E. Reid, *THIS JOURNAL*, **47**, 2821 (1925), give 247° (corr.) as the melting point of the compound prepared from β, β' -dichlorodiethyl sulfide and diethylamine.

(5) I. W. Grote, *J. Biol. Chem.*, **93**, 25 (1931).

RESEARCH LABORATORIES
INSTITUTUM DIVI THOMAE
CINCINNATI, OHIO

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Relations between Rotatory Power and Structure in the Sugar Group. XXXIV. The Possibility of Different Conformations of the Pyranoid Ring¹

BY C. S. HUDSON

In a preceding article by Eugene Pacsu² he suggests that the exceptional character of the rotations of the α - and β -forms of substances having the pyranoid ring structure in the mannose series may be due to a difference in the conformation of the atoms forming the ring. I thank Dr. Pacsu, with whom I have conferred often during the progress of his research, for this opportunity to publish concurrently the reasons which have led me to take the same viewpoint on this question.

In 1930³ I expressed the view that the exceptional character of these rotations indicated that the substances had different ring structures, and I assumed that the α -forms were of the furanoid and the β -forms of the pyranoid type. The experiments of Haworth and Hirst⁴ and their collaborators, designed to test this view, yielded results which showed that it is not tenable and that the substances in question possess only the pyranoid ring. From then on I have searched for an explanation of these unusual rotations that would be compatible with a pyranoid ring structure. The discovery⁵ of a crystalline molecular compound of the α - and β -forms of methyl xyloside suggested the possibility that some of the

(1) Publication authorized by the Surgeon General, U. S. Public Health Service. No. XXXIII was published in *THIS JOURNAL*, **61**, 1658 (1939).

(2) Pacsu, *THIS JOURNAL*, **61**, 2669 (1939).

(3) Hudson, *ibid.*, **52**, 1680 (1930).

(4) Haworth and Hirst, *J. Chem. Soc.*, 2615 (1930), *et seq.*

(5) Hockett and Hudson, *THIS JOURNAL*, **53**, 4454 (1931).

supposedly pure substances of the mannose series might be compounds of this nature, an hypothesis which easily could account for the exceptional rotations. Many efforts by various ways to separate α -methyl mannopyranoside into components and similar experiments on its tetraacetate and on the tetraacetate of β -methyl mannopyranoside, led to negative results; the hypothesis of the compound nature of any of these substances thus became very improbable but nevertheless the failures did not eliminate it as a possibility. Positive proof that they are true chemical individuals, not molecular compounds, was obtained in the course of experiments⁶ on the oxidation of methyl glycosides by periodic acid; their exceptional rotations, as compared with those of their glucose analogs, are not attributable either to ring-size or to any lack of chemical individuality. As was pointed out some years ago,⁷ there are several differences of rotation in the mannose pyranoid series that conform closely with analogous differences in the glucose series, provided one compares substances of α -classification only, or of β -classification only. Pacsu now finds similar relationships in the fructose and sorbose pyranoid series. It would seem therefore that the agreement of rotational differences within the α - or the β -series, when coupled with the known disagreement across an α - β pair, probably indicates differences in pyranoid ring conformation.

(6) Jackson and Hudson, *ibid.*, **61**, 959 (1939).

(7) Hudson, *ibid.*, **43**, 1424 (1926).

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The Preparation of Seleno Ortho- and Meta-Cresols

BY DUNCAN G. FOSTER

In preparing a series of compounds for the measurement of vapor-phase absorption spectra it developed that the two compounds seleno *o*- and *m*-cresol, $CH_3C_6H_4SeH$, had never been described in the literature. The writer has prepared them by the standard method of treating the tolyl Grignard reagents with elementary selenium,¹ operating in a current of hydrogen. When hydrogen was not used no selenocresols were obtained, but only high-boiling selenides, which perhaps explains why they are not reported.

(1) Taboury, *Ann. chim. phys.*, **15**, 5 (1908).