TABLE I

VALUES OF E_χ/E_t IN TERMS OF THE FRACTIONAL ABSORBING SPACE (χ) AND THE TRUE OPTICAL DENSITY ($\log_{10}(I_0/I)_\nu$

For the significance of the italicized figures see text.

χ	E_χ/E_t															
0.05	0.220	*0.110*	*0.075*	*0.055*	*0.045*	*0.040*	*0.035*	*0.030*	*0.025*	*0.020*	*0.020*	*0.020*	*0.020*	*0.015*	*0.015*	*0.010*
.10	.430	.230	*.160*	*.115*	*.090*	*.075*	*.060*	*.055*	*.050*	*.045*	*.040*	*.035*	*.030*	*.030*	*.030*	*.025*
.20	.645	.430	.315	*.240*	*.190*	*.160*	*.135*	*.120*	*.105*	*.095*	*.085*	*.080*	*.075*	*.070*	*.065*	*.050*
.30	.760	.585	.450	.365	*.305*	*.255*	*.220*	*.195*	*.170*	*.155*	*.140*	*.130*	*.125*	*.110*	*.105*	*.075*
.40	.850	.690	.580	.485	.415	.355	.310	*.275*	*.245*	*.220*	*.205*	*.185*	*.185*	*.160*	*.145*	*.110*
.50	.885	.780	.680	.590	.520	.460	.410	.365	.325	*.295*	*.270*	*.250*	*.240*	*.215*	*.200*	*.150*
.60	.920	.845	.770	.690	.625	.565	.510	.460	.425	.395	.355	.325	.305	*.285*	*.265*	*.200*
.70	.960	.900	.840	.775	.720	.670	.620	.570	.525	.495	.455	.420	.390	.365	.340	.255
.80	.975	.935	.900	.860	.820	.775	.735	.695	.650	.605	.575	.535	.510	.475	.445	.345
.90	.985	.970	.955	.935	.910	.890	.860	.830	.800	.775	.750	.705	.675	.645	.610	.485
.95	.995	.990	.980	.960	.950	.940	.925	.910	.895	.870	.855	.825	.810	.775	.745	.635
.99	1.000	1.000	.995	.990	.990	.990	.990	.985	.975	.975	.970	.960	.960	.945	.935	.860
$\log_{10}(I_0/I)_\nu$	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0	1.1	1.2	1.3	1.4	1.5	2.0

flat when the term $\chi e^{-\epsilon_t cl/\chi}$ is negligible in comparison with $(1 - \chi)$ in equation (4). The figures in Table I are italicized where the ϵ_t dependent term is less than 1% of $(1 - \chi)$; and under these conditions the absorption curve will be flat and no absorption bands detectable.

A non-uniform concentration is more likely to occur in mulls or other powder preparations than in films deposited from solution or by pressure, but in such films there may be significant differences in sample thickness at different positions in the radiation beam. For these conditions, where l is variable but c is constant, an equation identical in form with (4) may be derived, and the effects on the intensity of absorption will be comparable with those discussed above.

Significance in Ultraviolet Spectrophotometry.—The spectrophotometry of solid samples in the ultraviolet has received less attention than in the infrared, both on account of the larger selection of suitable solvents, and because of the greater magnitude of the scattering errors. However, in the application of microspectrophotometry to the study of biological cell structure[9] an inhomogeneous distribution of the absorbing material in the field of the microscope is likely to be encountered. Under these circumstances, this effect would lead to low values for the concentrations of the ultraviolet absorbing cell constituents if such concentrations are evaluated in terms of molecular extinction coefficients based on measurements made in homogeneous solution.

Concluding Remarks.—Under most experimental conditions, the difficulties of correcting adequately for the loss of light by scattering offer the most serious deterrent to the evaluation of absolute absorption intensities in non-isotropic systems, but even if adequate corrections for scattering losses could be made (as for example by the use of mulling agents of the correct refractive index) caution must still be exercised in the application to such systems of the radiation absorption laws established for true solutions. Since the effect of freely transmitting spaces in the sample varies rapidly with the (true) optical density, both the shapes and *relative* intensities of absorption bands will also be modified and this can be of significance in qualitative as well as in quantitative spectrophotometric analysis.

To simplify the mathematical treatment in the above discussion a sharp distinction has been drawn between the absorbing and the freely transmitting regions of the sample preparation, but the same conditions must exist in principle wherever a concentration gradient is present.

(9) See Discussions of the Faraday Society, No. 9, Aberdeen University Press, Aberdeen, Scotland, 1950.

Acknowledgment.—Helpful discussions of this problem with Dr. H. G. Bernstein, Dr. C. Sandorfy and Dr. T. Y. Wu of the National Research Council of Canada are gratefully acknowledged.

DIVISION OF CHEMISTRY
THE NATIONAL RESEARCH COUNCIL OF CANADA
OTTAWA, CANADA

Preparation of Small Quantities of Germanium Tetramethyl

BY J. H. LENGEL AND V. H. DIBELER

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As part of a mass spectrometric study of the Group IV tetramethyl compounds, a satisfactory method was required to prepare small amounts of germanium tetramethyl. Our experience together with that of previous investigators[1,2,3] made it apparent that the Grignard method of preparation was unsuitable for our purposes. Several Grignard preparations made in this laboratory using ethyl ether, *n*-butyl ether, "isoöctane" and tetrahydrofuran as solvents gave only traces. These low yields were principally because of the low boiling point of germanium tetramethyl (approximately 43°) and the difficulty of separation from the ethers.

Dr. Anton B. Burg pointed out to us the suitability of applying vacuum techniques to the reaction between zinc alkyls and germanium tetrachloride, first described by Winkler.[4] Accordingly, two preparations of approximately 10-millimole quantities of germanium tetramethyl were made by using zinc dimethyl and germanium tetrachloride obtained from commercial sources. Mass spectrometric analyses of these compounds showed an estimated total impurity of less than one mole per cent. in each case.

In the first preparation approximately stoichiometric quantities of zinc dimethyl and germanium tetrachloride were distilled *in vacuo* from glass storage ampoules into a

(1) L. M. Dennis and W. I. Patnode, THIS JOURNAL, **52**, 2779 (1930), give references to earlier work.

(2) C. W. Young, J. S. Koehler and D. S. McKinney, *ibid.*, **69**, 1410 (1947).

(3) H. Siebert, *Z. anorg. allgem. Chem.*, **263**, 82 (1950).

(4) C. Winkler, *J. prakt. Chem.*, **144**, (N. F. 36, 204 (1887)).

third ampoule provided with a break-seal and cooled with liquid nitrogen. The ampoule was sealed off, allowed to warm to −78° and then placed in an ice-bath. These precautions were taken to prevent too rapid warming of the mixture. At 0°, a white slush, presumably zinc chloride and germanium tetramethyl, was observed in the ampoule. The ampoule was removed from the ice-bath, attached to a vacuum manifold and opened. A nearly quantitative yield of germanium tetramethyl was evaporated into a receiver cooled with liquid nitrogen. Total non-condensable gases, principally methane, were measured, analyzed with the mass spectrometer, and discarded. A mass spectrometric analysis of the condensable fraction showed only a trace of germanium tetrachloride. The impurities of the combined condensable and non-condensable fractions totaled less than one mole per cent. No zinc compounds volatile at room temperature were observed.

In the second preparation a calculated 100% excess of germanium tetrachloride was used. After sealing off the reaction ampoule, it was immediately removed from the liquid nitrogen and allowed to warm directly to room temperature. Crystals of zinc chloride appeared only after 30 minutes, presumably because of the solubility in the excess germanium tetrachloride. After standing overnight at room temperature the ampoule was attached to the vacuum manifold and was opened. The excess germanium tetrachloride was almost completely removed by a single bulb-to-bulb vacuum distillation through a short column of potassium hydroxide pellets in series with the receiving bulb and attached to the manifold. This proved to be a very convenient way to remove the chloride compounds as the pellets retained sufficient water even under vacuum to hydrolyze the germanium tetrachloride. Mass spectrometric analysis of the product after removal of the chlorides indicated a purity comparable with that of the first preparation.

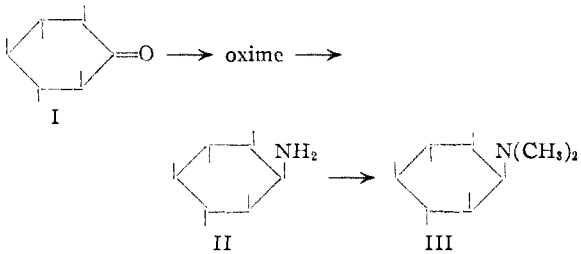
NATIONAL BUREAU OF STANDARDS
WASHINGTON, D. C.

Cyclitol Derivatives. IV. 2-Keto-*myo*-inositol Thiosemicarbazone and 2-Dimethylamino-2-desoxy-*myo*-inositol[1]

BY H. GEORGE LATHAM, JR., EVERETTE L. MAY AND ERICH MOSETTIG

RECEIVED DECEMBER 6, 1951

The first communication[2] of this series included among other N-containing cyclitols, the thiosemicarbazone of D,L-2-keto-*epi*-inositol (*rac*-*epi*-inosose) and an N,N-dimethylinosamine (either D,L-2-dimethylamino-2-desoxy-*epi*-inositol or D,L-4-dimethylamino-4-desoxy-*myo*-inositol) derived from this cyclose. We now wish to report two corresponding isomeric compounds which have been prepared from 2-keto-*myo*-inositol (*scyllo*-inosose) (I).



I II III

Carter, *et al.*,[3] hydrogenated with Raney nickel both the oxime and the phenylhydrazone of I and obtained a mixture of inosamines. We have hydrogenated I oxime in 50% methanol with platinum oxide and have isolated 2-amino-2-desoxy-*myo*-inositol (inosamine SA) (II).[4]

Methylation of II with formaldehyde and formic acid produced the N,N-dimethyl derivative (III). This tertiary amine, its precursor (II) and the thiosemicarbazone of I have been tested for *in vitro* activity against tuberculosis (Dubos–Davis medium H37Rv).[5] They were not significantly active.

Experimental

Hydrogenation of 2-Keto-*myo*-inositol Oxime.—One gram of the oxime,[6] 0.1 g. of platinum oxide, 10 ml. of water and 10 ml. of methanol absorbed two moles of hydrogen during 10 to 15 hours. Addition of water, warming to solution, filtration and evaporation of the filtrate to one-fourth volume gave 0.5 g. (55%) of 2-amino-2-desoxy-*myo*-inositol (II), m.p. 277–279.5° (cor., evac. tube).

Anal. Calcd. for $C_6H_{13}NO_5$: C, 40.2; H, 7.3. Found: C, 40.7; H, 7.3.

The hydrochloride of II (NIH 3641) melted at 230–233° (Kofler) after undergoing transition at 187–195°, while the N-acetyl derivative melted at 245–248°.[3,4]

2-Dimethylamino-2-desoxy-*myo*-inositol (III) Hydrochloride.—Two grams of II, 2.0 ml. of 37% aqueous formaldehyde and 2.4 ml. of 98% formic acid, heated on the steam-bath for two hours, cooled, treated with a slight excess of concentrated hydrochloric acid and diluted with methanol, then ether, gave 1.7 g. (60%) of the hydrochloride of III. After three recrystallizations from methanol–ether (Norit), it melted at 218–220° (cor.)

Anal. Calcd. for $C_8H_{18}ClNO_5$: C, 39.4; H, 7.4. Found: C, 39.5; H, 7.3.

2-Keto-*myo*-inositol Thiosemicarbazone (NIH 3845).—One gram of I,[6] 0.6 g. of thiosemicarbazide and 15 ml. of water were kept on the steam-bath for 10 minutes and at 5° overnight to give 0.9 g. (70%) of thiosemicarbazone. Recrystallized from water (Norit) it melted at 194.5–196° (cor., dec.).

Anal. Calcd. for $C_7H_{13}N_3O_5S$: C, 33.5; H, 5.2. Found: C, 33.6; H, 5.1.

Acknowledgment.—We are indebted to Dr. Laura C. Stewart of this Institute for the biochemical preparation of 2-keto-*myo*-inositol. Microanalyses are from the Institutes service analytical laboratory under the direction of Dr. William C. Alford.

(1) The nomenclature used is that proposed by H. G. Fletcher, Jr., L. Anderson and H. A. Lardy, *J. Org. Chem.*, **16**, 1238 (1951). Trivial names used previously are also given.

(2) E. L. May and E. Mosettig, *ibid.*, **14**, 1137 (1949).

(3) H. E. Carter, R. K. Clark, B. Lytle and G. E. McCasland, *J. Biol. Chem.*, **175**, 683 (1948).

(4) After our work was completed L. Anderson and H. A. Lardy, THIS JOURNAL, **72**, 3141 (1950), reported the preparation of inosamine SA and assigned to it the structure of II. A recent study by G. E. McCasland, *ibid.*, **73**, 2295 (1951), supports the conclusions of these authors.

(5) Testing was done at the Tuberculosis Research Laboratory, Public Health Service, Cornell University Medical College, New York, N. Y., under the direction of Dr. Bernard D. Davis.

(6) H. E. Carter, C. Belinskey, R. K. Clark, E. H. Flynn, B. Lytle, G. E. McCasland and M. Robbins, *J. Biol. Chem.*, **174**, 415 (1948).

NATIONAL INSTITUTE OF ARTHRITIS AND METABOLIC DISEASES, NATIONAL INSTITUTES OF HEALTH
PUBLIC HEALTH SERVICE
FEDERAL SECURITY AGENCY
BETHESDA 14, MARYLAND

The Reaction of Amines with Nitroguanyl Azide

BY EUGENE LIEBER,[1] CLAUDE C. HERRICK AND EDWARD SHERMAN

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Nitroguanyl azide (I) cyclizes rapidly with a large variety of inorganic and organic bases to form a

(1) U. S. Naval Ordnance Test Station, Inyokern, China Lake, California, to whom all communications concerning this article should be addressed.