The authors feel that the effect of defects on the measured entropy is also small by several orders of magnitude. The effect of edges and corners depends on the actual structure of the surface. It is simple to consider those systems in which only atomically plane surfaces are present. For the particles that were used in the experiment, assuming an average cube size, it is found that in round numbers there are 8 corner to 600 edge to 15,000 surface ions. The corners, obviously can be neglected. If it is assumed that the effect of the edge is twice that of the surface, then in order to detect the effect of edges with certainty, it would be necessary to make calorimetric measurements by a factor of ten better than now possible. If the surface is heterogeneous, then estimates of the effect of heterogeneity are impossible. However, if the degree of heterogeneity is independent of particle size, then the results which are obtained are valid. For very small particles, such as those which are used as catalysts, there is probably variation in the heterogeneity of the surface. These particles are smaller than those used in these experiments. It appears reasonable that as the particles grow, the distribution of energy over the surface would become independent of size.

In view of the preceding considerations the authors still feel that the ideas presented in the original paper are valid.

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SYNTHESIS AND CONFIGURATION OF DIHYDROSPHINGOSINE[1,2]

Sir:

Dihydrosphingosine is one of the four stereoisomeric forms of 1,3-dihydroxy-2-aminoöctadecane.[3] Recently several papers have appeared describing synthetic methods for obtaining such compounds.[4,5,6,7] However, none of these methods provides evidence as to the stereochemistry of the product and indeed most of them would be presumed to yield a mixture of the two racemic forms.

We have approached the synthesis by a different route. The two racemic α-amino-β-hydroxystearic acids were prepared and characterized as the *threo* and *erythro* isomers by comparison of the properties of a number of derivatives with the corresponding derivatives of threonine (*threo*) and allothreonine (*erythro*). The assignment of configuration was based on the complete agreement in the relative behavior of the C_{18} isomers as compared to the C_4 isomers.[8] Thus the characteristic shifts in infrared spectra from threonine to allothreonine and the relative melting point and solubility behavior of the two isomers and their derivatives are duplicated exactly in the C_{18} series. Furthermore the interconversion and isomerization of the 2-phenyloxazoline derivatives of threonine and allothreonine[9] are given by the C_{18} isomers under identical conditions. These data leave little or no doubt as to the configuration of the two α-amino-β-hydroxystearic acids. This work will be reported in detail shortly.

The methyl esters of the two amino acids were reduced to the corresponding 1,3-dihydroxy-2-aminooctadecanes with lithium aluminum hydride. The N-benzoyl methyl esters under similar conditions yielded the corresponding N-benzyl derivatives, which were readily debenzylated by catalytic reduction. The melting points of these substances are summarized in Table I.

TABLE I

Each of the compounds listed gave C, H, and N analyses agreeing with the theoretical.

	Threo series m.p., °C.	*Erythro* series m.p., °C.
α-Amino-β-hydroxystearic acid	205–206	217–220
N-Benzoyl	92–95	174–176
Methyl ester	77–78	71–73
Methyl ester, N-benzoyl-	86–88	97–99.5
1,3-Dihydroxy-2-aminoöctadecane	99.5–100.5	84–86
N-Benzyl-	55–56	62.5–63.5
Triacetyl-	65–66	90–92
Tribenzoyl-	...	144–45
N-Acetyl-	104.5	120–121

Reduction of the methyl α-amino-β-hydroxystearates over Raney nickel also gave excellent yields of the corresponding bases with no evidence of inversion. These results thus establish with some certainty the configuration of the two DL-1,3-dihydroxy-2-aminoöctadecanes.

Determination of the configuration of the natural compound was made possible by a striking difference in properties of the two racemic bases. The *erythro* base gave readily a tribenzoyl derivative (m.p. 144–145°) in quantitative yield on treatment with benzoyl chloride and pyridine. Under similar conditions natural dihydrosphingosine gives a tribenzoyl derivative melting at 144–145°. In marked contrast to this behavior we have found that the *threo* base gives only a dibenzoyl derivative and have not been able to obtain a tribenzoyl derivative with pyridine and benzoyl chloride under any of a variety of conditions. When a mixture of the *threo* and *erythro* bases was benzoylated only the tribenzoyl derivative of the *erythro* form was obtained. This result affords an explanation for the fact that all of the synthetic 1,3-dihydroxy-2-aminoöctadecane preparations described in the literature gave a tribenzoyl derivative melting at about 146°.

On the basis of these data it is tentatively con-

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[1] This investigation was supported in part by a research grant (RG 2031) from the National Institutes of Health, Public Health Service.

[2] Part of the material in this paper was taken from the thesis submitted to the Graduate College of the University of Illinois by J. Bradley Harrison in partial fulfilment of the requirements for the degree of Doctor of Philosophy in Chemistry.

[3] H. E. Carter, F. J. Glick, W. P. Norris, and G. E. Phillips, *J. Biol. Chem.*, **170**, 285 (1947).

[4] G. I. Gregory and T. Malkin, *J. Chem. Soc.*, 2453 (1951).

[5] N. Fisher, *Chem. and Ind.*, 130 (1952).

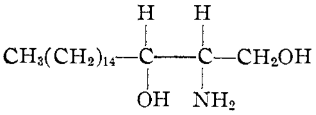
[6] C. A. Grob, E. F. Jenny and H. Utzinger, *Helv. Chim. Acta*, **34**, 2249 (1951).

[7] C. A. Grob and E. F. Jenny, *ibid.*, **35**, 2106 (1952).

[8] J. Bradley Harrison, Ph.D. thesis, University of Illinois, 1952.

[9] D. F. Elliott, *J. Chem. Soc.*, 62 (1950).

cluded that natural dihydrosphingosine has the *erythro* configuration. In conjunction with previous data on the configuration of the amino carbon of dihydrosphingosine[10] it would appear that dihydrosphingosine is *erythro*-D-1,3-dihydroxy-2-aminoöctadecane.



$CH_3(CH_2)_{14}-\underset{OH}{\overset{H}{C}}-\underset{NH_2}{\overset{H}{C}}-CH_2OH$

Recently Grob and Jenny[7] resolved the DL-1,3-dihydroxy-2-aminoöctadecane melting at 100° and concluded that one of the enantiomorphic forms was identical with natural dihydrosphingosine. Unfortunately no acyl derivatives of the resolved base were reported. However in the light of our data it seems probable that the resolved base was actually a diastereoisomer of natural dihydrosphingosine.

Resolution of the *erythro* base is being investigated and the results of this study will be reported shortly.

[10] H. E. Carter and C. G. Humiston, *J. Biol. Chem.*, **191**, 727 (1951).

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RECEIVED JANUARY 10, 1953

THE REACTIVITY OF BRIDGEHEAD BROMIDES

Sir:

The peculiar situation existing in a bicyclic system with a bridgehead halide is pertinent to the hypothesis of hyperconjugation, planarity and degree of substitution as they are related to the energy of carbonium ions and to the hypothesis of solvation at the rear as it relates to rate of solvolysis. Encouraged by the implications of these theoretical considerations and dissuaded of the opinion that bicyclic halides are generally unreactive[1] by detection of reactivity in 4-chlorocamphane (I),[2] we have synthesized by various methods 1-bromobicyclo[2.2.1]heptane (II), 1-bromo-8,8-dimethylbicyclo[2.2.2]octane (III) and 1-bromobicyclo[2.2.2]octane (IV) and wish to report initial results of the investigation of their reactivities, which is continuing.

II reacts with aqueous silver nitrate at 150° for two days to give 1-hydroxybicyclo[2.2.1]heptane whereas III and IV react at room temperature in 4 hr. giving 1-hydroxy-8,8-dimethylbicyclo[2.2.2]octane and 1-hydroxybicyclo[2.2.2]octane, respectively. The rate of ethanolysis of III is first order in III and independent of ethoxide ion concentration and the product is 1-ethoxy-8,8-dimethylbicyclo[2.2.2]octane. The first order rate constants for hydrolysis in 70% (by vol.) aqueous dioxane at 100.0° and 131.2° are 1.49 and 19.8 $\times 10^{-5}$ sec.$^{-1}$ for III and 0.68 and 9.33 $\times 10^{-6}$ sec.$^{-1}$ for IV. By way of comparison, the calculated rate of hydrolysis of *t*-butyl bromide at 100° in 80% aqueous alcohol is 0.82 sec.$^{-1}$.[3]

The increased reactivity of 1-bromobicyclo[2.2.2]octane as compared with that of 1-bromobicyclo[2.2.1]heptane appears to us to be experimental evidence supporting the hypothesis that a tetrahedral (sp^3) carbonium ion is of higher energy than some other configuration, most probably the planar (sp^2).[4] Relative to the effect of substitution, the operation of hyperconjugation and the ability to become solvated, the carbonium ions derived from II and IV are comparable, but relative to the amount of energy required to deviate from the tetrahedral configuration, the highly constrained ion from II is at a disadvantage compared to the more flexible ion from IV.[5]

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[1] P. D. Bartlett and L. H. Knox, THIS JOURNAL, **61**, 3184 (1939); P. D. Bartlett and S. G. Cohen, *ibid.*, **62**, 1183 (1940); P. D. Bartlett and E. S. Lewis, *ibid.*, **72**, 1005 (1950).

[2] W. v. E. Doering and E. F. Schoenewaldt, *ibid.*, **73**, 2333 (1951).

[3] K. A. Cooper and E. D. Hughes, *J. Chem. Soc.*, 1183 (1937).

[4] Professor G. E. Kimball, Columbia University (private communication) has suggested that a tetrahedral carbonium ion in which only $^3/_4$ of the 2s orbital is occupied will be approximately 24 kcal. ($^1/_4$ of the energy required to promote a 2s electron of carbon to a 2p orbital [A.G. Shenstone, *Phys. Rev.*, **72**, 411 (1947)]) higher in energy than a planar carbonium ion in which the entire 2s orbital is occupied.

[5] The strain energy required to obtain a planar ion from IV is estimated to be 6 kcal. [G. E. Humphrey and R. Spitzer, *J. Chem. Phys.*, **18**, 902 (1950)].

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PENTAVALENT OSMIUM

Sir:

When ammonium hexabromoösmate (IV) is added slowly to anhydrous ethylenediamine at 10°, the exothermal reaction yields a red solution from which micaceous pink plates of (I) separated. This contained apparently three molecules of the base and two ionized bromine atoms per atom of osmium, and acted as a weak monoacid base when titrated with hydrobromic acid to yield green needles of (II). Substance (II) contained one atom of ionized bromine more than (I), into which it was changed by alkali. Both (I) and (II) were diamagnetic, and did not show the reducing properties to be expected of Os(II) or Os(III). On reduction with sodium hydrosulfite, colorless solutions resulted which, on addition of sodium iodide, gave bright yellow plates (III) of tris-ethylenediamineosmium(III) iodide. This is concluded from its similarity to the hexammine[1] $Os(NH_3)_6I_3$, its reduction of silver nitrate, and its paramagnetism, (1.6 B.M.). Found: Os, 24.3; N, 10.8; I, 48.5. Calcd. for $Os(en)_3I_3 \cdot 2H_2O$: Os, 24.20; N, 10.69; I, 48.46. Therefore (I) and (II) are Os(IV) complexes, two or one protons, respectively, having been lost from the ethylenediamine as in the gold complexes of Block and Bailar.[2] These magnetic moments are consistent with the usual experience of Os(IV) compounds, in which in conflict with Hund's rule all of the 5d electrons are paired leaving a vacant orbital.

[1] F. P. Dwyer and J. W. Hogarth, *J. Proc. Roy. Soc. N.S.W.*, **85**, 113 (1951).

[2] B. P. Block and J. C. Bailar, THIS JOURNAL, **73**, 4722 (1951).