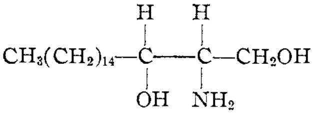
cluded that natural dihydrosphingosine has the *erythro* configuration. In conjunction with previous data on the configuration of the amino carbon of dihydrosphingosine[10] it would appear that dihydrosphingosine is *erythro*-D-1,3-dihydroxy-2-aminoöctadecane.



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

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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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).