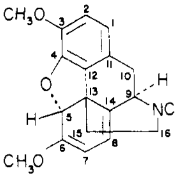
A STANDARD OF ABSOLUTE CONFIGURATION FOR OPTICALLY ACTIVE BIPHENYLS[1]

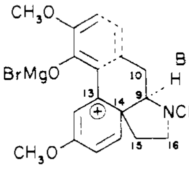
Sir:

The establishment of the absolute configuration of D-tartaric acid by the anomalous diffraction technique[2] provides the basis for the unique assignment of stereochemistry to any center of carbon atom asymmetry. Heretofore, no basis has existed for such assignments in the case of substances possessing axial asymmetry, *e.g.*, optically active biphenyls. We should like to point out that the configuration of the biphenyl system in phenyldihydrothebaine (III) can be related *operationally*[3] to the configuration of thebaine (I). Consequently, since the absolute configuration of the morphine thebaine group of alkaloids is now known,[5] the absolute configurations of the axially asymmetric systems in III, and in a series of its derivatives of the general formula IV, are established.

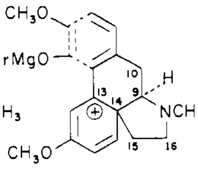
Thebaine (I) is converted by phenylmagnesium bromide to a mixture of two phenyldihydrothebaines (III) which differ only in the configuration at the asymmetric carbon atom.[6]



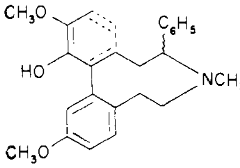
I



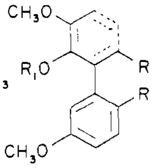
IIa



IIb



III



IV

Regardless of the details of the mechanism of this reaction, C.13 must become trigonal at or near the transition state for the migration of C.15 from C.13 to C.14. The two rings of the potential biphenyl system then approach coaxiality. This sets up two diastereomeric transition states,[7] and the configuration of the biphenyl becomes fixed when the reacting system chooses to employ one of them in thermodynamic preference to the other. For convenience, we discuss the choice between the metastable intermediates IIa and IIb, although the argument applies with at least equal force to the transition states. Models reveal that IIa is much more stable than IIb. In IIa, the angle between the plane defined by C.15–C.14–C.9 and that defined by C.14–C.9–*N* is close to 0°. In IIb, however, this angle is close to 60°. Thus if IIb were the intermediate, the five-atom ring (C.15, C.14, C.9, N, C.16) would have to be severely puckered. Even when the resultant release of non-bonded interaction is taken into consideration, an interplanar angle of 60° would be intolerable[8] when the system has available the Baeyer-strain-free alternative IIa. The biphenyl system of phenyldihydrothebaine therefore has the absolute configuration shown in III, and the simpler bicyclic derivatives (*e.g.*, the methines, isomethines, phenyltetrahydrothebaimine and the nitrogen-free degradation products[6]) all have the absolute configuration IV. The series provides a standard of absolute configuration for optically active biphenyls.

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(1) The support of this work by a grant from the National Science Foundation is gratefully acknowledged.

(2) J. M. Bijvoet, A. F. Peerdeman and A. J. van Bommel, *Nature*, **168**, 271 (1951).

(3) We recognize that because of the difference in symmetry orders between the asymmetric frames[4] (bisphenoid *vs.* regular tetrahedron), there is, in general, no *conceptual* way of relating an axially asymmetric configuration to that of a centrally asymmetric one.

(4) R. S. Cahn, C. K. Ingold and V. Prelog, *Experientia*, **12**, 81 (1956).

(5) (a) K. W. Bentley and H. M. E. Cardwell, *J. Chem. Soc.*, 3252 (1955); (b) J. Kalvoda, P. Buchsacher and O. Jeger, *Helv. Chim. Acta*, **38**, 1847 (1955).

(6) (a) M. Freund, *Ber.*, **38**, 3234 (1905). (b) L. Small, L. J. Sargent and J. A. Bralley, *J. Org. Chem.*, **12**, 1839 (1947). (c) R. Robinson, *Nature*, **160**, 815 (1947). (d) K. W. Bentley and R. Robinson, *J. Chem. Soc.*, 947 (1952).

(7) *Cf.* J. A. Berson and E. Brown, THIS JOURNAL, **77**, 450 (1955).

(8) Compare the interplanar angle of 17° in the pyrrolidine ring of hydroxyproline [J. Donohue and K. N. Trueblood, *Acta Cryst.*, **5**, 419 (1952)].

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INTERACTION OF DEUTERIUM WITH OLEFINS AND ALKANES ON CHROMIUM OXIDE GEL

Sir:

The background data for current interest in the mechanism of olefin hydrogenation are largely confined to platinum and nickel catalysts. It seemed important to investigate as different a catalyst as possible. Chromium oxide gel[1] was chosen because much is known about its behavior in other catalytic reactions. In reactions between hydrocarbons and deuterium we find that it yields products which are isotopically much simpler than those obtained with metallic catalysts. These reactions are of both mechanistic and preparative interest.

After dehydration above 400°, the gel[2] acquires hydrogenating activity at low temperatures. Table I presents isotopic distribution patterns of products of experiments with 2:1 mixtures of deuterium and hydrocarbon at space rates of about 1 cc. of liquid hydrocarbon per cc. of catalyst per hour. At 42°, the hexane from 1-hexene is largely hexane-d_2. Even at −78°, similar hydrogenation on nickel–kieselguhr gives broad distribution of exchanged species.[3]

At −20°, 1-butene yields butane-d_2 nearly exclusively. Cyclopentene behaves similarly at 27°. Mass spectrometric fragmentation patterns indicate that the butane is nearly all butane-1,2-d_2. The hexane prepared at 42° is mainly 1,2-d_2 with smaller amounts of other dideuterohexanes, principally 2,3-d_2.

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(1) W. A. Lazier and J. V. Vaughen, THIS JOURNAL, **54**, 3080 (1932).

(2) Prepared by the urea method, R. L. Burwell, Jr., *ibid.*, **59**, 1609 (1937).

(3) C. D. Wagner, J. N. Wilson, J. W. Otvos and D. P. Stevenson, *J. Chem. Phys.*, **20**, 338 (1952).