Since (+)α-pinene is also available, the procedure makes it possible to obtain both of the optically active isomeric olefins.

Hydroboration of more than 50 mole per cent of a *dl* olefin with diisopinocampheylborane, should leave behind an olefin with increased optical purity. Indeed, when 150 mmoles of 3-methylcyclopentene was hydroborated with 120 mmoles of diisopinocampheylborane (derived from (−)α-pinene), it was found that the excess 3-methylcyclopentene was 65% optically pure with $[\alpha]^{26}_D$ −50.8°.

Acknowledgment.—We wish to acknowledge the assistance provided by the National Science Foundation (G 19878), and by Professor P. v. R. Schleyer for the sample of 2-methylnorbornene.

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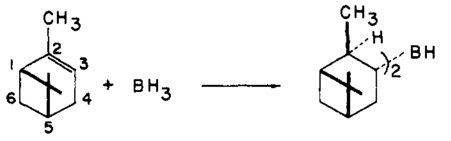
RECEIVED SEPTEMBER 20, 1962

HYDROBORATION AS A MEANS FOR THE ASSIGNMENT OF CONFIGURATIONS TO ALCOHOLS AND OLEFINS

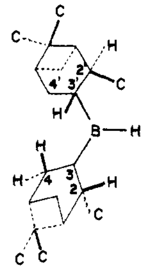
Sir:

We wish to report a new method for configurational assignment based on the hydroboration reaction. Thus, the configuration of alcohols and olefins derived from the hydroboration of a number of representative *cis*-olefins with diisopinocampheylborane can be successfully deduced by considering the steric course of the reaction.

Hydroboration of (+)α-pinene[1,2] (I) with diborane occurs *cis* and from the rear side of the olefin to yield (+) diisopinocampheylborane[3,4] (II). Inspection of models indicates that the most stable among the rotameric conformations for diisopinocampheylborane has (a) a diequatorial arrangement of the CH_3– and borane group in the pinane moiety, and (b) an *anti-* or nearly *anti-parallel* orientation of the CH_3– groups in the two pinane moieties. This leads to an unambiguous description of the model for (+) diisopinocampheylborane (III).

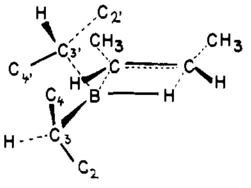


I II

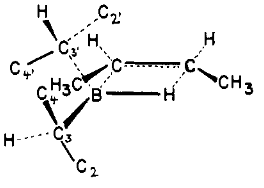


III

The addition of the boron–hydrogen bond to a double bond has been interpreted in terms of a four-center transition state.[3] The formation of such a highly rigid transition state should be strongly influenced by the steric factors of both the reagent and the olefin. Thus, the hydroboration of an olefin, such as *cis*-2-butene, with diisopinocampheylborane can be represented by transition states IV and V.



IV



V

The model (III) shows that the boron atom is bonded to carbon atoms (C_3 and C_3') carrying substituents of different size, namely, a bulky methylene group (C_4) and a hydrogen atom (at C_3'). The preferred transition state is therefore the one in which the methyl group of the olefin is positioned away from the bulky methylene group (C_4) and toward the smaller hydrogen atom (at C_3') of the diisopinocampheylborane reagent (IV). It is evident that the alternative transition state (V) will be much less favorable sterically with the bulky methyl group of the olefin and the methylene group at C_4 in close proximity. The 2-butanol obtained after oxidation, a reaction which occurs with retention of the configuration,[3] will have the R configuration.[2] *The same configuration is predicted for all alcohols derived from the hydroboration of acyclic cis-olefins.*

The addition of the boron–hydrogen bond to norbornene occurs from the *exo*-side.[3] In order to obtain an optimal steric fit, the norbornene has to be orientated on the model in the same way as *cis*-2-butene.

TABLE I

CORRELATION OF CONFIGURATIONS OF ALCOHOLS AND OLEFINS *via* HYDROBORATION WITH DIISOPINOCAMPHEYLBORANE

Olefin	Product formed	Configuration[a] Predicted	Found
cis-2-Butene	(−) 2-Butanol	R	R
cis-2-Pentene	(−) 2-Pentanol	R	R
cis-3-Hexene	(−) 3-Hexanol	R	R
cis-4-Methyl-2-pentene	(−) 4-Methyl-2-pentanol	R	R
Norbornene	(−) *exo*-Norbornenol	2S	2S
3-Methylcyclopentene	(+) 3-Methylcyclopentene	R	R
3-Ethylcyclopentene	(+) 3-Ethylcyclopentene	R	R
1-Methylnorbornene	(+) 1-Methylnorbornene	1S:4R	1S:4R

[a] Configuration predicted and found based on the use of (+)α-pinene with configuration 1R:5R. The opposite configurations are realized by the use of (−)α-pinene with configuration 1S:5S.

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[1] For a summary of the evidence (and references) dealing with the configuration of (+)α-pinene see: J. H. Brewster, *J. Am. Chem. Soc.*, **81**, 5493 (1959). Structure I shows (+)α-pinene with absolute configuration 1R:5R.

[2] For the R-S configurational nomenclature see, R. S. Cahn, C. K. Ingold and V. Prelog, *Experientia*, **12**, 81 (1956).

[3] H. C. Brown and G. Zweifel, *J. Am. Chem. Soc.*, **83**, 2544 (1961).

[4] Although it is not certain whether the monomer or the dimer (*sym*-tetraisopinocampheyldiborane) is the actual hydroborating agent, the following discussion is referred to the monomeric form. However, this is not a decisive factor for the interpretation of the results obtained in the present study.

As indicated in Table I the predicted configuration of a number of alcohols is in complete agreement with the experimental results.

It has been shown that hydroboration of a racemic olefin mixture with a deficient amount of diisopinocampheylborane yields optically active olefins.[5] However, in this case the enantiomer with the better steric fit reacts preferentially with the reagent, leaving behind an excess of the other enantiomer (Table I).

The hydroboration of *trans* olefins and slow reacting *cis*-olefins follows a different reaction path. Consequently, the rules outlined above do not apply to these olefins.[6]

Acknowledgment.—We wish to acknowledge the assistance provided by the National Science Foundation (G 19878).

(5) H. C. Brown, N. R. Ayyangar and G. Zweifel, *J. Am. Chem. Soc.*, **84**, 4341 (1962).

(6) The results obtained will be discussed in a forthcoming paper.

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RECEIVED SEPTEMBER 20, 1962

THE PROTONATION OF PHLOROGLUCINOL AND ITS ETHERS: AN EXCEPTION TO THE ACIDITY FUNCTION CONCEPT[1]

Sir:

For many years after Hammett introduced the acidity function, H_0,[2] this concept of a unique extension of the pH scale to concentrated acids remained a useful and satisfactory way of treating strongly acidic systems.[3] Recently, however, evidence has been accumulating which shows that a single scale does not exist even for indicator bases of the same charge type: large deviations from H_0 have been found.[4] These deviations appear to be uniform within a class of structurally similar bases, and the discrepancies have been handled by defining new acidity functions for each of the new classes of indicator base.[4a,b,d,f] This proliferation of acidity functions did not seriously impair the original concept. We wish, however, to report a phenomenon which may: we have discovered wide variations in the behavior of a group of structurally very similar bases.[5]

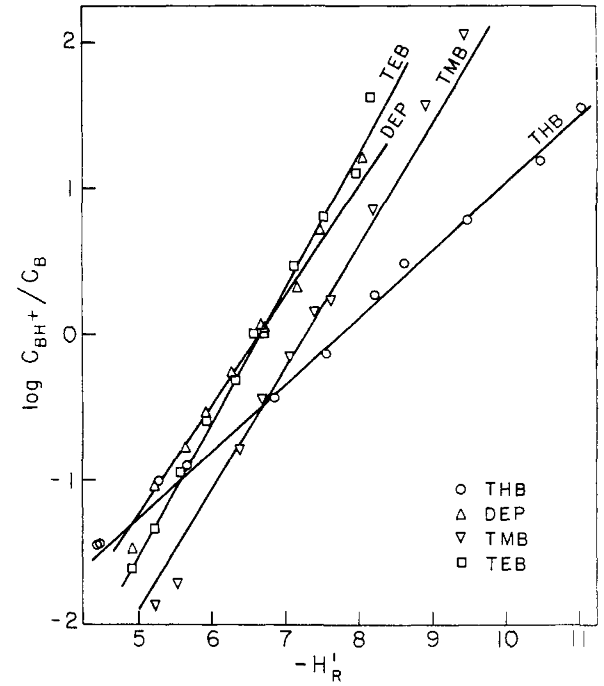
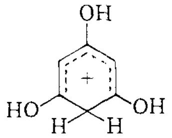


Fig. 1.—Indicator data for phloroglucinol (THB), 3,5-diethoxyphenol (DEP), 1,3,5-trimethoxybenzene (TMB), and 1,3,5-triethoxybenzene (TEB) in aqueous perchloric acid at 25°.

Phloroglucinol and its alkyl ethers are weakly basic: they protonate in 35 to 65% $HClO_4$. Three lines of evidence indicate that proton addition occurs on aromatic carbon. (1) The proton n.m.r spectrum of phloroglucinol in 70% $HClO_4$ consists of two lines of equal area at 3.88 and 5.85τ. These can be attributed to ring hydrogens and methylene hydrogens, respectively, in the phenonium ion



Similar lines are present in the spectra of 1,3,5-trimethoxybenzene and 1,3,5-triethoxybenzene. These lines disappear gradually in D_2SO_4. For phloroglucinol in perchloric acid less concentrated than 70%, the lines broaden, and an estimate of the rate of exchange based on this broadening is consistent with exchange rates determined by a tracer method in dilute acid.[6] (2) The ultraviolet spectra of phloroglucinol and its ethers in concentrated acids consists of two strong bands in the regions 2500 and 3650 Å. both with molar extinction coefficients of the order of 10^4. These spectra are very different from those of phenol and its ethers in concentrated acids (λ_{max} = 2650 Å., $\epsilon \sim 1.5 \times 10^3$) which are known to protonate on oxygen,[7] and they are consistent with predicted[8] and observed[9] spectra for carbon-protonated phenonium ions. (3) Phloroglucinol and its ethers are stronger bases

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(1) Work supported in part by the Atomic Energy Commission under USAEC Contract AT(11-1)-1025.

(2) L. P. Hammett and A. J. Deyrup, *J. Am. Chem. Soc.*, **54**, 2721 (1932).

(3) M. A. Paul and F. A. Long, *Chem. Revs.*, **57**, 1 (1957).

(4) (a) N. C. Deno, J. Jaruzelski and A. Schriesheim, *J. Am. Chem. Soc.*, **77**, 3044 (1955); N. C. Deno, P. Groves and G. Saines, *ibid.*, **81**, 5790 (1959); N. C. Deno, P. Groves, J. Jaruzelski and M. Lugasch, *ibid.*, **82**, 4719 (1960); N. C. Deno, unpublished work. (b) R. L. Hinman and J. Lang, *Tetrahedron Letters*, **21**, 12 (1960); A.C.S. Meeting Abstracts, Sept., 1961, p. 58Q; unpublished work. (c) R. W. Taft, Jr., *J. Am. Chem. Soc.*, **82**, 2965 (1960). (d) A. J. Kresge and Y. Chiang, *Proc. Chem. Soc.*, 81 (1961). (e) F. A. Long and J. Schulze, *J. Am. Chem. Soc.*, **83**, 3340 (1961); F. A. Long, unpublished work. (f) Y. Chiang and E. B. Whipple, unpublished work on pyrroles. (g) N. C. Deno and C. H. Spink, unpublished work on benzoic acid.

(5) Similar exceptional behavior for some of the same bases as well as several related substances was discovered simultaneously by W. M. Schubert and R. M. Quacchia (*J. Am. Chem. Soc.*, **84**, 3778 (1962)).

(6) A. J. Kresge, to be published.

(7) E. M. Arnett and C. Y. Wu, *J. Am. Chem. Soc.*, **82**, 5660 (1960); C. Y. Wu, Ph.D. Thesis, University of Pittsburg, 1961.

(8) A. A. Verrijn Stuart and E. L. Mackor, *J. Chem. Phys.*, **27**, 826 (1957); G. Dallinga, E. L. Mackor and A. A. Verrijn Stuart, *Mol. Phys.*, **1**, 123 (1958).

(9) C. Reid, *J. Am. Chem. Soc.*, **76**, 3264 (1954); H. Köhler and G. Scheibe, *Z. anorg. allgem. Chem.*, **285**, 221 (1956); M. Kilpatrick and H. H. Hyman, *J. Am. Chem. Soc.*, **80**, 77 (1958).