135° (0.1 mm.); $n^{25}\mathrm{D}$ 1.5662 (*Anal.* Calcd. for $C_{16}H_{23}N$: C, 83.79; H, 10.11; N, 6.10. Found: C, 83.97; H, 10.20; N, 6.18). Hydrogenation of IV in the presence of palladium in methanol yielded *p*-dimethylaminophenylcyclooötane (III), b. p. 135–137° (0.1 mm.); $n^{25}\mathrm{D}$ 1.5519 (*Anal.* Calcd. for $C_{16}H_{25}N$: C, 83.05; H, 10.89; N, 6.06. Found: C, 82.95; H, 11.03; N, 6.23). The picrate of III prepared in this way had m. p. 149–150° (dec.) and did not depress the m. p. of III picrate derived from II. The identity of III from the two sources was confirmed by comparison of their infrared spectra.

Extension of the synthesis of substituted cyclooctatetraenes by reaction of cyclooöctatetraene with other organometallic compounds and investigation of the products, including attempted resolution of II, are in progress.

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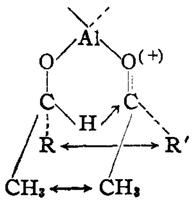
## PARTIALLY ASYMMETRIC MEERWEIN-PONNDORF-VERLEY REDUCTIONS

*Sir:*

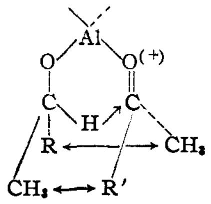
The hypothetical mechanisms of the aluminum alkoxide[1] and sodium alkoxide[2] catalyzed oxidation–reduction reaction of carbonyl–carbinol systems (*cf.* A and B) satisfy among others the condition that solvent deuterium does not participate[2] and, in consequence of the close approach of the components in the transition state, imply the stereochemical condition that partial asymmetry should be observed in the reduction of unsymmetrical ketones with optically active carbinols. Although Doering and Aschner[2] observed 2% asymmetry in the reduction of isobutyrophenone with (−)-2-methyl-1-butanol catalyzed by sodium alkoxide, Baker and Linn[3] were unable to detect any asymmetry in the reduction of acetophenone or *p*-chlorobenzophenone with (−)-2-methyl-1-butanol catalyzed by aluminum alkoxide.

Taking the experimental precautions indicated from related work on the stereochemical equilibration of alcohols[4] of effecting the reduction of the ketone with a large excess of highly active carbinol for a minimal time, we have observed partially asymmetric reductions in two systems, (+)-2-butanol (I) *vs.* 6-methyl-2-heptanone (II) and (+)-3-methyl-2-butanol (III) *vs.* methyl cyclohexyl ketone (IV) pairs in which the configurational relationships of the alcohols involved seem to be established.[5] The reduction of II (5.0 g.) with (+)-I (30.0 g.; $[\alpha]^{26}\mathrm{D}$ + 12.6°) and *rac.* aluminum-2-butoxide (5.0 g.) for eight hours at 36° affords (+)-6-methyl-2-heptanol (V, $[\alpha]^{28}\mathrm{D}$ +0.56°; hydrogen phthalate, $[\alpha]^{26}\mathrm{D}$ +2.8°; 5.9% asymmetric reduction) and I ($[\alpha]^{25}\mathrm{D}$ + 10.3°; 17% racemization), this separation as well as that of completely inactive V from a mixture of *rac.*-V and (+)-I being effected by distillation. In a similar way IV is reduced with (+)-III ($[\alpha]^{30}\mathrm{D}$ + 4.94°) and *rac.*-aluminum-3-methyl-2-butoxide to (+)-methylcyclohexylcarbinol (VI, $[\alpha]^{32}\mathrm{D}$ + 1.03°; hydrogen phthalate, $[\alpha]^{31}\mathrm{D}$ +12.1°; 21.8% asymmetric reduction), partially racemized (63%) III ($[\alpha]^{30}\mathrm{D}$ + 1.80°) being recovered.

These experiments are considered to support both the gross stereochemical consequence and the experimentally less accessible pseudo-six membered character of the mechanism. The reasonable hypothesis that steric interference between R–R′ and $CH_3$—$CH_3$ (A) will exceed that between R–$CH_3$ and R′–$CH_3$ (B) must be coupled with the pseudocyclic hypothesis (A and B) in order to accommodate the fact that the configurations of the reducing alcohol and the predominating enantiomer (B) of the reduced alcohol are the same.



A



B

This type of experiment on which work continues offers a unique method of measuring small differences in free energy of activation of purely steric origin. Thus $\Delta\Delta F^{\ddagger}(\Delta F^{\ddagger}_{A} - \Delta F^{\ddagger}_{B})$ in the present cases are at least 0.24 *T* and 0.88 *T*, respectively.

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RECEIVED DECEMBER 19, 1949

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(1) Woodward, Wendler and Brutschy, THIS JOURNAL, **67**, 1425 (1945).

(2) Doering and Aschner, Abstracts of Papers, 112th Meeting, American Chemical Society, New York, September 17, 1947, p. 21L.

(3) Baker and Linn, THIS JOURNAL, **71**, 1399 (1949).

(4) Doering and Aschner, *ibid.*, **71**, 838 (1949).

(5) Levene and Haller, *J. Biol. Chem.*, **69**, 165, 569 (1926); Levene, Walti and Haller, *ibid.*, **71**, 465 (1926); Levene and Harris, *ibid.*, **113**, 55 (1936); Stevens, THIS JOURNAL, **54**, 3732 (1932).

* Harvard University Ph.D. 1943.

## SULFUR-CONTAINING HETEROCYCLIC RINGS

*Sir:*

Hydrogen sulfide can be added to olefinic linkages by photolysis[1] or peroxide sensitization,[2] in which cases the reaction undoubtedly proceeds *via* a free-radical mechanism of so-called "abnormal" addition. It is also possible for hydrogen

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(1) Vaughan and Rust, *J. Org. Chem.*, **7**, 472 (1942).

(2) Hoeffelman and Berkenbosch, U. S. Patent 2,352,435 (June 27, 1944).