135° (0.1 mm.); $n^{25}\text{D}$ 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*-dimethylaminophenylcyclooöctane (III), b. p. 135–137° (0.1 mm.); $n^{25}\text{D}$ 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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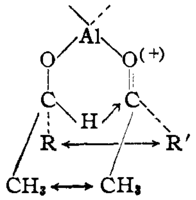
PARTIALLY ASYMMETRIC MEERWEIN-PONNDORF-VERLEY REDUCTIONS

Sir:

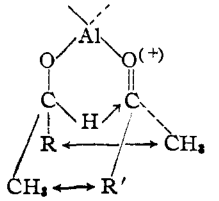
The hypothetical mechanisms of the aluminum alkoxide[1] and sodium alkoxide[2] catalyzed oxidation–reduction reaction of carbonyl–carbinol systems (*cf.* A and B) satisfy among others the condition that solvent deuterium does not participate[2] and, in consequence of the close approach of the components 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.; $[\alpha]^{26}\text{D}$ + 12.6°) and *rac.* aluminum-2-butoxide (5.0 g.) for eight hours at 36° affords (+)-6-methyl-2-heptanol (V, $[\alpha]^{28}\text{D}$ +0.56°; hydrogen phthalate, $[\alpha]^{26}\text{D}$ +2.8°; 5.9% asymmetric reduction) and I ($[\alpha]^{25}\text{D}$ + 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 ($[\alpha]^{30}\text{D}$ + 4.94°) and *rac.*-aluminum-3-methyl-2-butoxide to (+)-methylcyclohexylcarbinol (VI, $[\alpha]^{32}\text{D}$ + 1.03°; hydrogen phthalate, $[\alpha]^{31}\text{D}$ +12.1°; 21.8% asymmetric reduction), partially racemized (63%) III ($[\alpha]^{30}\text{D}$ + 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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[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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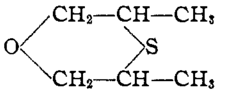
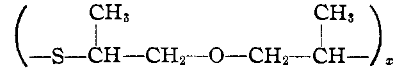
[1] Vaughan and Rust, *J. Org. Chem.*, **7**, 472 (1942).

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

sulfide to react with olefins in the presence of amines,[3] under which conditions an ionic "normal" addition occurs. In studies of the base-catalyzed reaction of hydrogen sulfide with diolefinic substances, we have observed the formation not only of oily, apparently essentially linear, adducts, but also of cyclic molecules. The yields are comparatively high and undoubtedly could be improved. Thus, from diallyl ether and hydrogen sulfide in the presence of di-*n*-butylamine, was obtained a 43% yield of 2,6-dimethyl-1,4-thioxane



as well as a linear polymer of the structure



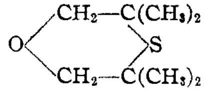
$$\left(-S-\overset{CH_3}{\overset{|}{CH}}-CH_2-O-CH_2-\overset{CH_3}{\overset{|}{CH}}-\right)_x$$

which is terminated either with allyl or mercapto groups or both. The relative amounts of the two products, as well as the magnitude of *x* in the second formula, can be varied by the operating conditions. Three illustrative examples are given in the following paragraphs.

2,6-Dimethyl-1,4-thioxane.—Diallyl ether (73.6 g., 0.75 mole), hydrogen sulfide (30 g., 0.88 mole) and di-*n*-butylamine (10 g., 0.078 mole) were heated together at 100° for eighty-nine hours in a 200-cc. 18-8 stainless steel bomb. By distillation the product was shown to contain 43% by weight of a water-white liquid boiling at 113–114° at 160 mm. pressure; $n^{20}\text{D}$ 1.4850. Analyses indicate that this liquid is 2,6-dimethyl-1,4-thioxane

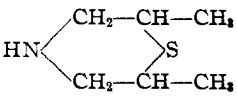
	Found	Calculated
S, %w	23.5, 23.6	23.3
SH, as S, %w	<0.01	0
Mol. wt. (cryo-benzene)	147	132
Mol. wt. (cryo-dioxane)	120	

2,2,6,6-Tetramethyl-1,4-thioxane.–Dimethallyl ether (94 g., 0.75 mole), hydrogen sulfide (30 g., 0.88 mole) and *n*-butylamine (3.6 g., 0.05 mole) were heated together in a stainless steel bomb for twenty-three hours at 110°. The product upon distillation yielded 22% of a colorless liquid: b. p. 130–132° at 190 mm., $n^{20}\text{D}$ 1.4748. This liquid appears to be 2,2,6,6-tetramethyl-1,4-thioxane



	Found	Calculated
S, %w	19.7	20.2
SH, as S, %w	0.29	0
Mol. wt., (cryo-benzene)	150	158

2,6-Dimethyl-1,4-thiazane.—Diallylamine (14.6 g., 0.15 mole) and hydrogen sulfide (5.1 g., 0.15 mole) were heated in a Pyrex bomb tube for thirty hours at 100°. Upon distillation 49% of the product boiled between 44 and 62°, mainly at 60°, at 0.2–0.5 mm.; $n^{20}\text{D}$ 1.5882. Analyses of this fraction indicate that it is 2,6-dimethyl-1,4-thiazane



	Found	Calculated
S, %w	24.5	24.4
SH, as S, %w	0.14	0
Mol. wt. (cryo-benzene)	129	131
N, %w (Dumas)	10.4	10.7

This synthesis is undoubtedly applicable to the formation of other heterocyclic rings such as 2,4-dimethyl-1,3-oxathiolane from allyl vinyl ether and 2,6-dimethyl-1,4-dithiane from diallyl sulfide. Davis and Fettes[4] have recently reported the production of related heterocyclics by treating dichloro compounds with sodium disulfide.

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RECEIVED SEPTEMBER 6, 1949

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[3] German Patent 669,961, to I. G. Farben.; also Keyssner, U. S. Patent 2,163,176 (June 20, 1939).

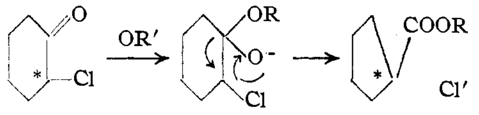
[4] Davis and Fettes, THIS JOURNAL, **70**, 2611 (1948).

* Harvard University Postdoctoral Fellow 1933–1937.

ON THE MECHANISM OF THE FAWORSKII[1] REARRANGEMENT OF α-HALO KETONES

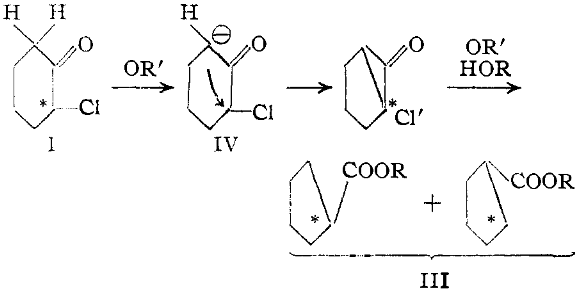
Sir:

There has been considerable effort to establish the mechanism of the base-catalyzed rearrangement of α-halo ketones. The mechanism which has received most support is one closely related to that of the benzilic acid rearrangement[2]



I II III

An alternative involves a cyclopropanone intermediate[3]



III

It will be observed that the fate of the chlorine-

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[1] Faworskii, *J. Russ. Phys. Chem. Soc.*, **46**, 1097 (1914); **50**, 582 (1920); *C. A.*, **9**, 1900 (1915); **18**, 1476 (1915).

[2] Tchoubar, *Compt. rend.*, **228**, 580 (1949).

[3] Wallach, *Ann.*, **414**, 294 (1918); Faworskii, *J. Russ. Chem. Soc.*, **26**, 559 (1894).