When one mole of iodine trichloride was added gradually to eleven moles of benzene with stirring, the initial reaction was almost explosive. After refluxing and working up by distillation and crystallization, 27% of pure *o*-dichlorobenzene, identified by its constants, analyses, and 4,5-dinitro derivative,[5] was obtained. *No p-dichlorobenzene was isolated!* In addition, 7% of monochlorobenzene, 6% of 1,2,4,5-tetrachlorobenzene, and 3% of hexachlorobenzene were isolated. When 0.1 mole of iodine trichloride was mixed with 0.1 mole of benzene in carbon tetrachloride, 61% of *o*-dichlorobenzene and 9% of monochlorobenzene were the only isolated products. When 0.4 mole of iodine trichloride and 0.1 mole of benzene were allowed to react in carbon tetrachloride, 67% of *o*-dichlorobenzene and 32% of 1,2,4,-5-tetrachlorobenzene were obtained. The 1,2,4,5-tetrachlorobenzene was apparently uncontaminated by other isomers, and was identified by melting point (139–40°) and mononitro-derivative (m. p. 94–96°).[6]

Similar results were obtained with anisole, which would be expected to yield 2,4-dichloro- or 2,4,6-trichloroanisole. When 0.1 mole of anisole was refluxed with 0.2 mole of iodine trichloride in carbon tetrachloride, 40% of 3,4-dichloroanisole, (b. p. 200–204°, m. p. −7°[7]) identified by conversion to 3,4-dichlorophenol (m. p. 64°) and its mononitro derivative, m. p. 72–74°,[8] was obtained. In addition 54% of unreacted anisole was recovered.

When aliphatic acid chlorides are chlorinated in the presence of iodine, light being absent, only alpha-substituted derivatives are obtained.[9] When 0.2 mole of *n*-butyryl chloride was refluxed with 0.4 mole of iodine trichloride in carbon tetrachloride, 16% of 2,3-dichlorobutyryl chloride, identified by analysis, conversion to 2,3-dichlorobutyric acid, m. p. 74–75°, and to 2,3-dichlorobutyramide, m. p. 122–124°, was obtained: 55% of unsubstituted butyryl chloride was recovered.

The above products indicate that iodine trichloride must bring about substitution of adjacent carbon atoms simultaneously. This adjacent disubstitution occurs apparently in aromatic and aliphatic compounds. We have tentatively termed this phenomenon "Simultaneous Vicinal Dichlorination." Geometrical considerations suggest that a transitory cyclic intermediate, perhaps I_2Cl_6, is involved.

We are now engaged in determining the extent and limitations of "simultaneous vicinal disubstitution," both in aliphatic and aromatic compounds. It will be interesting to know whether iodine tribromide, iodine trinitrate, etc., can take part in this reaction. These results may also throw some light on the nature of iodine trichloride.

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RECEIVED NOVEMBER 16, 1949

SUBSTITUTED CYCLOÖCTATETRAENES

Sir:

An attempt to prepare phenylcycloöctatriene by addition of phenyllithium to cycloöctatetraene has led to discovery of a direct route to substituted cycloöctatetraenes. The products isolated were phenylcycloöctatetraene and a mixture of 1,3,5- and 1,3,6-cycloöctatrienes, formed by a process equivalent to hydrogen transfer between the initial adduct and cycloöctatetraene. The mixture of cycloöctatrienes was identified by infrared and ultraviolet absorption spectra, and by preparation of a known maleic anhydride adduct of the 1,3,5-isomer, which was formed in larger amount.

Phenylcycloöctatetraene (I) was isolated in 14–19% yield as a yellow liquid, b. p. 92–93° (0.2 mm.); n^{25}D 1.6182; d^{25}_4 1.0335 (*Anal.* Calcd. for $C_{14}H_{12}$: C, 93.34; H, 6.66. Found: C, 93.24; H, 6.83). Treatment of I with one equivalent of powdered silver nitrate in boiling absolute ethanol yielded a yellow-green complex, m. p. 144.5° (dec.) (*Anal.* Calcd. for $C_{14}H_{12}\cdot AgNO_3$: C, 48.02; H, 3.46. Found: C, 48.11; H, 3.54). Hydrogenation of I in methanol in the presence of a palladium catalyst required 99% of four molar equivalents of hydrogen and formed phenylcycloöctane, n^{25}D 1.5300, m. p. 8.2–8.7°, which did not depress the m. p. of an authentic sample. Reaction of I with maleic anhydride in benzene yielded a colorless adduct, m. p. 173–174° (*Anal.* Calcd. for $C_{18}H_{14}O_3$: C, 77.67; H, 5.07. Found: C, 77.69; H, 5.42). Likewise a yellow benzoquinone adduct was obtained, m. p. 191.5–192° (*Anal.* Calcd. for $C_{20}H_{16}O_2$: C, 83.31; H, 5.59. Found: C, 83.41; H, 5.79).

Reaction of cycloöctatetraene with *p*-dimethylaminophenyllithium yielded *p*-dimethylaminophenylcycloöctatetraene (II) (13–25%), yellow-orange leaflets with m. p. 90–90.5° (*Anal.* Calcd. for $C_{16}H_{17}N$: C, 86.05; H, 7.68; N, 6.27. Found: C, 86.34; H, 7.75; N, 6.27). II absorbed 97–99% of four molar equivalents of hydrogen in the presence of palladium in methanol and formed *p*-dimethylaminophenylcycloöctane (III), a colorless liquid, b. p. 145–147° (0.3 mm.), n^{25}D 1.5520, which was characterized as the picrate, m. p. 149–150° (dec.) (*Anal.* Calcd. for $C_{22}H_{28}N_4O_7$: C, 57.38; H, 6.13; N, 12.17. Found: C, 57.20; H, 6.31; N, 12.32). III was identified by an independent synthesis. Coupling of 3-bromocycloöctene with *p*-dimethylaminophenyllithium yielded 3-(*p*-dimethylaminophenyl)-cycloöctene (IV) (34%), a colorless liquid, b. p. 134–

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[5] Huntress. "Organic Chlorine Compounds." John Wiley and Sons, Inc., New York, N. Y., 1948, pp. 794, 796, 1077, 1081.

[6] Reference 5, pp. 367, 471.

[7] Holleman, *Rec. trav. chim.*, 37, 102 (1918).

[8] Hodgson and Kershaw, *J. Chem. Soc.*, 2922 (1929).

[9] Ash and Brown, *Rec. Chem. Prog.*, 9, 85 (1948).

135° (0.1 mm.); n^{25}_{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*-dimethylaminophenylcycloöctane (III), b. p. 135–137° (0.1 mm.); n^{25}_{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 cycloöctatetraene with other organometallic compounds and investigation of the products, including attempted resolution of II, are in progress.

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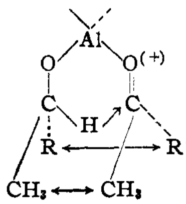
PARTIALLY ASYMMETRIC MEERWEIN–PONNDORF–VERLEY REDUCTIONS

Sir:

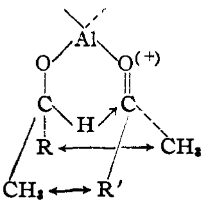
The hypothetical mechanisms of the aluminum alkoxide[1] and sodium alkoxide[2] catalyzed oxidation–reduction reaction of carbonyl–carbinol systems (*cf.* A and B) satisfy among others the condition that solvent deuterium does not participate[2] and, in consequence of the close approach of the components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

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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).