sequence of three transformations. Chloromethylation[4] of the hydrocarbon gave 12-chloromethyl[10]paracyclophane (73%); b.p. 150–152° (0.7 mm.), $n^{20}\mathrm{D}$ 1.5775, m.p. 75–76° (from 30–60° petr. ether at −70°). *Anal.* Calcd. for $C_{17}H_{25}Cl$: C, 77.09; H, 9.55; Cl, 13.39; mol. wt., 265. Found: C, 77.26; H, 9.32; Cl, 13.15; mol. wt., 259 (Rast). Reaction of the chloromethyl compound with sodium 2-nitropropanenitronate[5] produced [10]paracyclophane-12-carboxaldehyde (84%); b.p. 130° (0.15 mm.), $n^{20}\mathrm{D}$ 1.5803. *Anal.* Calcd. for $C_{17}H_{24}O$: C, 83.55; H, 9.90. Found: C, 83.76; H, 9.68. This aldehyde showed a typical carbonyl band in the infrared at 5.92 μ and formed a 2,4-dinitrophenylhydrazone derivative, m.p. 202–203°. Finally, neutral permanganate oxidation of the aldehyde in acetone gave the acid I (45%); m.p. 192–193° (from aqueous ethanol). *Anal.* Calcd. for $C_{17}H_{24}O_2$: C, 78.42; H, 9.29. Found: C, 78.56; H, 9.12. Decarboxylation of I produced known [10]paracyclophane and bichromic acid oxidation afforded trimellitic acid.

An acetone solution of (±)I and cinchonidine deposited the salt of the (+)acid(−)base which, after recrystallization from acetone, showed m.p. 154–155° and $[\alpha]^{27}\mathrm{D}$ + 22±2° (*c*, 10 in $CHCl_3$). *Anal.* Calcd. for $C_{36}H_{46}N_2O_3$: C, 77.93; H, 8.36; N, 5.06. Found: C, 78.15; H, 8.20; N, 5.03. Acidification of this salt with excess 5% hydrochloric acid precipitated pure (+)I; m.p. 160–161°, $[\alpha]^{24}\mathrm{D}$ + 80±2° (*c*, 0.77 in $CHCl_3$). *Anal.* Found: C, 78.50; H, 9.25. The combined mother liquor and crystallization filtrates from the isolation of the (+)acid(−)base salt were evaporated to dryness and treated with excess 5% hydrochloric acid. A *rapid* fractional crystallization of this partially racemized acid I from warm ethanol-water gave, as the most soluble fraction, pure (−)I; m.p. 159–160°, $[\alpha]^{28}\mathrm{D}$ −82±2° (*c*, 0.96 in $CHCl_3$). *Anal.* Found: C, 78.39; H, 9.31.

Observed changes in the m.p.'s of samples of pure (+) and (−) I on standing at different temperatures for varying lengths of time suggest that the optical antipodes racemize at an appreciable rate in the solid state. For example, (+)I, m.p. 160–161°, showed m.p. 158–162° after standing at −20° for five days. After additional standing for five days at 25° this (+)I had m.p. 155–167°. Complete racemization studies will be made when an adequate quantity of the acid I is at hand.

(4) "Organic Syntheses," Coll. Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1955, p. 195.

(5) H. B. Hass and M. L. Bender, THIS JOURNAL, 71, 1767 (1949).

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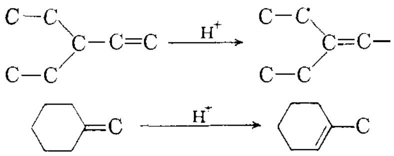
RECEIVED FEBRUARY 26, 1960

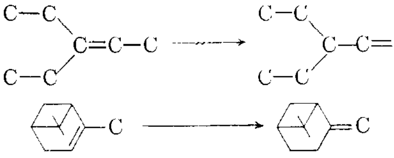
HYDROBORATION AS A CONVENIENT SYNTHETIC ROUTE FOR THE CONTRA-THERMODYNAMIC ISOMERIZATION OF OLEFINS

Sir:

The usual acid catalyzed isomerization of terminal olefins results in a preferential migration of the double bond into the chain or ring, with the final product being predominantly the more thermodynamically stable, most highly substituted olefin.[1]



We wish to report that hydroboration provides a convenient synthetic route from the more stable, highly substituted olefin to the less stable terminal products.



It was demonstrated previously that olefins of all types readily undergo hydroboration to form the corresponding organoborane[2] and that the boron atom readily migrates at temperatures of 100 to 150° from its original internal position in a chain or ring to a less hindered terminal position.[3] In order to achieve the desired contra-thermodynamic transformation from the more stable internal olefin to its less stable terminal isomer, it was necessary to demonstrate that the resulting organoborane could be converted into the desired olefin, *via* the displacement reaction,[4,5] without rearrangement.

Accordingly, 2-methyl-1-butene, 3-methyl-1-butene, 3-ethyl-1-pentene, 3-ethyl-2-pentene, 2,4,4-trimethyl-1-pentene, 2,4,4-trimethyl-2-pentene, and methylenecyclohexane were hydroborated in diglyme at 25° and the reaction products were treated for 3–6 hours with an excess of 1-decene at 160°. In each case the original olefin distilled out of the reaction mixture, with only negligible quantities of isomerized products.

It is noteworthy that even in the case of the organoboranes obtained from the labile, bicyclic systems, α- and β-pinene, displacement regenerates the original olefin without rearrangement. The hydroboration product from α-pinene (oxidizable to isopinocampheol in 90% yield) is isomerized readily to the organoborane from β-pinene (oxidized to *cis*-myrtanol in 70% yield).[6] Displacement of the isomerized product with 1-dodecene permits a simple conversion of α-pinene to β-pinene.

A typical procedure is given: 3-Ethyl-2-pentene, 9.8 g., 100 mmoles, was hydroborated under nitrogen in the usual manner in diglyme with 30 mmoles

(1) B. T. Brooks, *et al.*, ed., "The Chemistry of Petroleum Hydrocarbons," Reinhold Publishing Corp., New York, N. Y., 1955, Vol. 3, pp. 115–127.

(2) H. C. Brown and B. C. Subba Rao, THIS JOURNAL, **81**, 6428 (1959).

(3) H. C. Brown and G. Zweifel, *ibid.*, **82**, 1504 (1960).

(4) R. Köster, *Angew. Chem.*, **68**, 3831 (1956); R. Köster, *Ann.*, **618**, 31 (1958).

(5) H. C. Brown and B. C. Subba Rao, *J. Org. Chem.*, **22**, 1136 (1957); H. C. Brown and B. C. Subba Rao, THIS JOURNAL, **81**, 6434 (1959).

(6) R. Dulou and Y. Chrétien-Bessière, *Bull. soc. chim. France*, 1362 (1959), report that the hydroboration of β-pinene, then oxidation, produces *trans*-myrtanol.

of sodium borohydride and 40 mmoles of boron trifluoride (in diglyme). After heating under gentle reflux for one hour, 21 g. 150 mmoles, of 1-decene was added, and the reaction was heated under reflux in a Todd micro column, removing olefin as it appeared. Over six hours there was obtained 8.0 g., 82% yield, of olefin, 98% 3-ethyl-1-pentene and 2% 3-ethyl-2-pentene (v.p.c. analysis).

We are continuing to explore the influence of structure on the isomerization and displacement reactions of organoboranes.

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RECEIVED MARCH 7, 1960

X-RAY STRUCTURE OF BIS-TRICARBONYLCHROMIUM-BIPHENYL

Sir:

In connection with the studies carried out in our Institute by G. Natta, R. Ercoli and their coworkers on the synthesis and properties of tricarbonylchromium-arenes, we have undertaken the study of the X-ray structure of the new compound[1] bis-tricarbonylchromium-biphenyl (I). We have found two different crystal forms of (*I*), (a) and (b), with these unit cell constants:

(a) a = 10.68 ± 0.05 Å.; b = 10.83 ± 0.05 Å.; c = 7.24 ± 0.03 Å.; = 103°30′ ± 1°; $V \simeq 814$ Å.^{3}; sp. gr. $P2_1/c$; $N = 2$

(b) a = 7.29 ± 0.04 Å.; b = 6.98 ± 0.04 Å.; c = 8.44 ± 0.04 Å.; = 79°41′ ± 1°; = 76.39′ ± 1°; = 77°54′ ± 1°; V – 404 Å.^{30} sp. gr. P1 or $P\bar{1}$; $N = 1$

The space group of the (a) modification requires that the molecule be centrosymmetrical; consequently we have firstly supposed that the space group of the (b) modification, to which we have confined our study, be $P\bar{1}$.

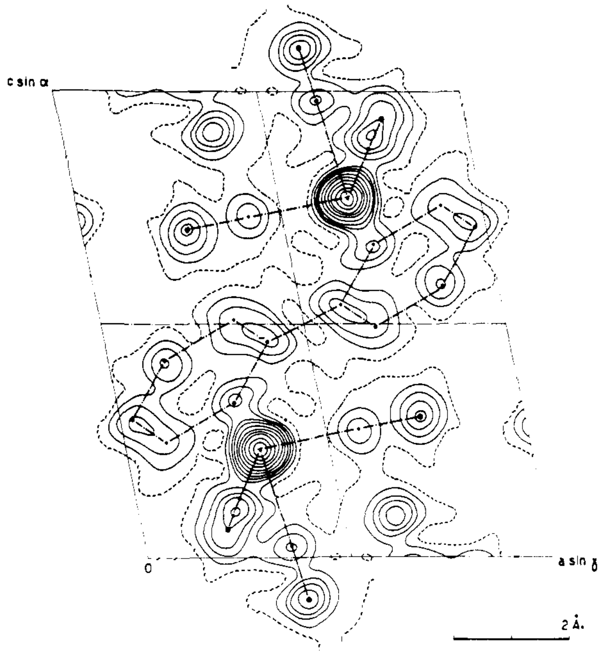

Fig. 1.—Fourier projection of the electron density on the *ac* plane; contours drawn at 2, 4, 6, 8, . . ., e/Å.^{2}, except around the Cr atom (. . . , 8, 10, 15, 20, . . . , e/Å.^{2}).

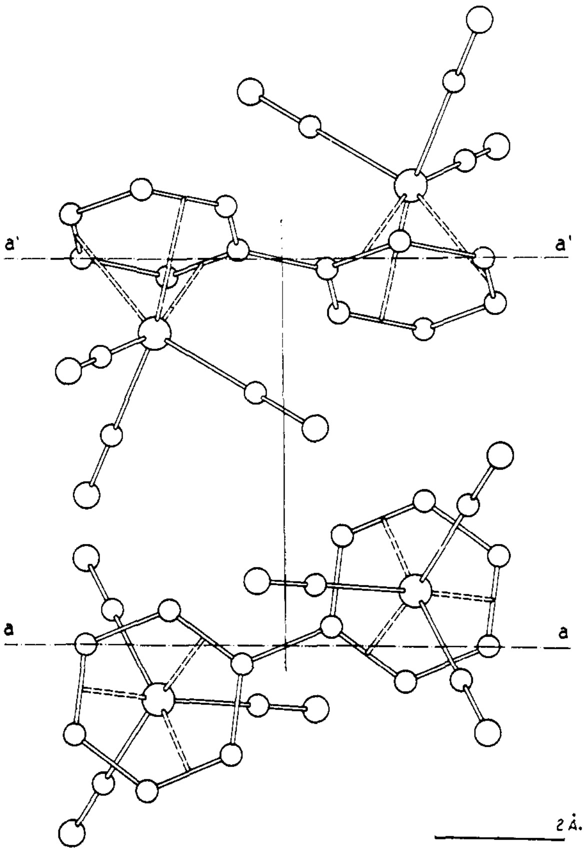

Fig. 2.—Model of the molecule of I: (aa) viewed in a direction perpendicular to the biphenyl plane; (a′,a′) the same rotated around the aa line, in order to be superposable to the Fourier image of Fig. 1.

From the 0*kl* and *h*0*l* Patterson projections, the coördinates of the chromium atoms have been obtained (x = 0.330; y = 0.269; z = 0.237), and the structure has been successively refined through the corresponding Fourier projections of the electron density. The assigned $P\bar{1}$ space group has been confirmed; at the present stage of refinement of the structure (R = 0.17) the (*h*0*l*) Fourier projection we have obtained is shown, as an example, in Fig. 1. The outcoming model of the molecule is shown in Fig. 2.

Characteristic features of the model are: (1) the two phenyl groups of biphenyl are coplanar,[2] the two chromium atoms being on *trans* sites at the same distance (d = 2.20 ± 0.03 Å.) from the six carbon atoms of each rings; (2) the angle between the colinear Cr–C–O groups is 89° ± 2°, and the plane defined by the O atoms is parallel within experimental errors to the benzene ring; the O atoms being at the same distance (3.02 ± 0.04 Å.) from the chromium atoms; (3) the Cr–C–O directions are approximately staggered (exp. deviation, 4 ± 1°) in respect of the phenyl ring to which the Cr(CO)$_3$ group is bonded. These data are in complete accordance with those found

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[1] R. Ercoli, F. Calderazzo, and A. Alberola, *La Chimica e l'Industria*, ottobre 975, (1959).

[2] J. Dhar, *Indian J. Physics*, **7**, 43–60 (1932).