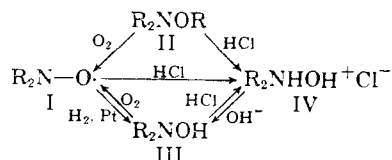


III oxidizes rapidly in air to I and reacts with hydrogen chloride to form *N,N*-di-*t*-butylhydroxylammonium chloride (IV) (Calcd. for $C_8H_{20}NOCl$: C, 52.88; H, 11.09; N, 7.71; Cl, 19.51. Found C, 52.58; H, 10.82; N, 7.75; Cl, 19.01; n.m.r. one peak at $\tau = 8.38$ for the two *t*-butyl groups and two broader peaks at $\tau = -1.37$ and -0.8). The intensity ratio of the peaks is 18:1:1, respectively, and the two low field peaks vanish in D_2O as expected for exchangeable hydrogens. IV also is formed by reaction of either I or II with anhydrous hydrogen chloride. This reaction of I is accompanied by the formation of *t*-nitrosobutane. Neutralization of IV with aqueous alkali reforms III. These transformations are summarized in the diagram.



Further examination of this reaction and its products is being pursued and will be reported upon in the future. The authors wish to thank Dr. N. Elliot, Brookhaven National Laboratories, for magnetic susceptibility determinations, and Dr. J. H. Deonarine and his group, of these Laboratories, for microanalyses.

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RECEIVED SEPTEMBER 15, 1961

HOMOGENEOUS HYDROGENATION CATALYZED BY BORANES

Sir:

Addition of molecular hydrogen to organic molecules with homogeneous catalysis has been reported for only a small fraction of the compounds which may be reduced by heterogeneous catalysis. Reduction of olefinic bonds has been observed frequently in the studies of hydroformylation. However, the utility of this method is limited since conditions have not been found which separate the reduction and hydroformylation reactions.¹

More recently Halpern² and co-workers have reported the reduction of maleic acid catalyzed by a water soluble ruthenium(III). Walling and Bollyky³ have reported the reduction of benzophenone and nitrobenzene in *t*-butyl alcohol catalyzed by potassium *t*-butoxide.

The facile addition reaction of boron hydrides to olefins has been developed by Brown⁴ and co-workers. This has been shown to be a general reaction for olefinic bonds. The uncatalyzed hydrogenolysis of a number of carbon to metal bonds also has been reported.⁵⁻⁸ In particular, Köster⁷ has

(1) For a review and discussion, cf. M. Orchin, *Advances in Catalysis*, **5**, 385 (1953).

(2) J. Halpern, J. F. Harrod and B. R. James, *J. Am. Chem. Soc.*, **83**, 753 (1961).

(3) C. Walling and L. Bollyky, *ibid.*, **83**, 2968 (1961).

(4) H. C. Brown, *Tetrahedron*, **12**, 117 (1961).

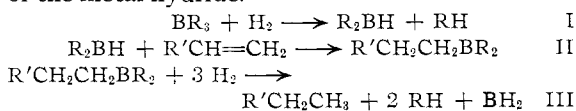
(5) H. Gilman, A. L. Jacoby and H. Ludeman, *J. Am. Chem. Soc.*, **60**, 2336 (1938).

reported the hydrogenolysis of a trialkyl borane to give a dialkyl boron hydride and a saturated hydrocarbon. These observations indicated that boranes might be effective homogeneous catalysts for the hydrogenation of olefins.

We now report on this very effective method of reduction. Cyclohexene or caprylene containing 3.8 mole % tri-*n*-butylborane is quantitatively hydrogenated in three hours at 220° under 1000 lb./in.² hydrogen pressure. The products were identified by gas chromatography and infrared spectroscopy. The reaction rate is highly temperature dependent (essentially no reaction below 200°) but is not markedly influenced by hydrogen pressures. The high temperature required has been identified with the hydrogenolysis of the carbon-boron bond. Very recently Köster⁸ has published preliminary results on olefin reduction catalyzed by an amine-borane complex.

This reaction is particularly valuable when applied to the reduction of high polymers in solution. Such polymers are reduced only with great difficulty and under very special conditions, using heterogeneous catalysis. Usually only incomplete hydrogenation is realized. The borane catalyzed, reduction of *cis*-1,4-polybutadiene gave a crystalline polymer. The infrared spectra and melt characteristics were those of a high density polyethylene of moderate molecular weight. Polypiperylene and polyisoprene, prepared by Ziegler type catalysis, yielded identical spectra (essentially that of the random copolymer of ethylene and propylene). Emulsion polybutadiene and SBR also were reduced in a similar fashion to give complete saturation of the aliphatic double bonds.

The essential steps are: (1) the hydrogenolysis of the metal to carbon bond forming an alkyl metal hydride, and (2) the addition of the resulting hydride to an olefinic bond. Reaction III completes the sequence giving hydrocarbon and some form of the metal hydride.



We also have evidence that the elimination reaction to give a dialkyl boron hydride and an olefin is also taking place, but this does not contribute to the over-all hydrogenation process.

(6) W. Ipatieff, G. Razuwajeff and I. F. Bogdanow, *Ber.*, **63**, 335 (1930).

(7) R. Köster, *Angew. Chem.*, **68**, 383 (1956).

(8) R. Köster, B. Gunter and B. Paul, *Ann.*, **644**, 1 (1961).

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RECEIVED OCTOBER 7, 1961

HCL CATALYZED FREE RADICAL FORMATION OF ISOPROPYL CHLORIDE DURING THE RADIOLYSIS AND PHOTOLYSIS OF *n*-PROPYL CHLORIDE

Sir:

This communication reports evidence that the isomerization of *n*- C_3H_7Cl to *i*- C_3H_7Cl observed in both the Co^{60} radiolysis and the photolysis of degassed liquid *n*- C_3H_7Cl occurs by a hydrogen chlo-