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The Reaction of Decaborane with Carbonyl Compounds

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Synopsis. Decaborane formed adducts with cyclohexanones, 2-octanone, acetaldehyde, or acetone, which were cleft in the presence of water into alcohols, boric acid, and hydrogen. Olefins and boroxins as secondary products were identified.

Several addition compounds[1] of decaborane, $B_{10}H_{14}$,[2] have been studied since Stock's first observation[3] of $B_{10}H_{14}\cdot(NH_3)_6$, formed by the evaporation of a liquid ammonia solution of decaborane. In this study, new reactions of decaborane with carbonyl compounds, such as acetaldehyde, acetone, 2-octanone, cyclohexanone, 2-methylcyclohexanone, 3-methylcyclohexanone, and 4-methylcyclohexanone, were carried out.

When solid decaborane was treated with a carbonyl compound ($RCH_2R'CO$) in the range from room temperature to 120 °C, the 1 : 1 adduct from both reactants was formed in a pasty mass of the reaction mixture. Though the adduct could not be isolated because of its unstability for oxygen or moisture, its parent peak in the mass spectra and the lack of any absorption associated with the carbonyl group in IR observed in the adduct.

$$B_{10}H_{14} + RCH_2R'CO \longrightarrow RCH_2R'CO\cdot B_{10}H_{14}.$$

The addition of water as an additional reactant to decaborane and a carbonyl compound accelerated both adduct formation and their decomposition into alcohol, boric acid, and H_2. Based upon the measured molar yields of the products, the primary decomposition of the adduct may be stoichiometrically expressed as follows

$$RCH_2R'CO\cdot B_{10}H_{14} + 30\,H_2O \longrightarrow RCH_2R'CHOH + 10\,H_3BO_3 + 21\,H_2.$$

Beside the primary decomposition products, olefins and boroxin compounds were observed in the reaction. The formation of olefins may be brought about by the dehydration of the alcohols primarily yielded:

$$RCH_2R'CHOH \longrightarrow RCH{=}CHR' + H_2O.$$

Just after the reaction of decaborane with acetone in H_2O, three compounds, 2-propanol and boric acid in a pasty mass, and H_2, were found. Tri(isopropoxy)boroxin, however, was identified in the pasty mixture after the mixture was put aside without any treatment for 24 h. Thus, the boroxine may be formed by the condensation of alcohol and metaboric acid resulting from the dehydration of boric acid as the first product. No formation of boroxine from alcohol with boric acid was proven.

$$3\,H_3BO_3 \longrightarrow H_3B_3O_6 + 3\,H_2O,$$

$$3\,RCH_2R'CHOH + H_3B_3O_6 \longrightarrow (RCH_2R'CHO\text{-}\underset{|}{B}\text{-}O\text{-})_3 + 3\,H_2O.$$

The yields of the alcohols and olefins, together with their isomers as the main reaction products from decaborane with carbonyl compounds, are summarized in Table 1.

TABLE 1. ALCOHOL AND OLEFIN FROM THE REACTION OF DECABORANE WITH CARBONYL COMPOUNDS

Carbonyl compd	Alcohol,[a] %		Olefin,[a] %		Conditions
Cyclohexanone	Cyclohexanol	72.0	Cyclohexene	18.7	90 °C, in the absence of H_2O
Cyclohexanone	Cyclohexanol	15.4	Cyclohexene	80.0	Room temp, in the presence of H_2O
Cyclohexanone	Cyclohexanol	60.5	Cyclohexene	32.5	120 °C, in the absence of H_2O
2-Methylcyclohexanone	*cis*-2-Methylcyclohexanol *trans*-2-Methylcyclohexanol	4.0 7.8	1-Methylcyclohexene 3-Methylcyclohexene	4.7 44.2	The same as above
3-Methylcyclohexanone	*cis*-3-Methylcyclohexanol *trans*-3-Methylcyclohexanol	15.8 6.4	3-Methylcyclohexene 4-Methylcyclohexene	2.3 48.1	The same as above
4-Methylcyclohexanone	*cis*-4-Methylcyclohexanol *trans*-4-Methylcyclohexanol	4.8 25.8	4-Methylcyclohexene	49.7	The same as above
2-Octanone	2-Octanol	8.6	1-Octene *cis*-2-Octene *trans*-2-Octene	4.7 21.7 65.2	50 °C, in the absence of H_2O
2-Octanone	2-Octanol	26.0	Octenes	traces	Room temp, in the presence of H_2O
Acetaldehyde	Ethanol	26.0			The same as above
Acetone	2-Propanol	90.0			The same as above

a) The yields of alcohol and olefin were calcd based on decaborane.

Experimental

The decaborane, supplied by the Callery Chem. Co., U.S.A., was purified by recrystallization from hexane. The other liquid reagents were distilled before the reaction. The experiments were performed in an atmosphere of dry nitrogen or of argon. The products were examined with an infrared spectrometer, a mass spectrometer, and by gas chromatography, In the gas-chromatographic analysis a Molecular sieve 5A column was used for H_2, with He as the carrier gas. A didecyl phthalate column was also used for the liquid products.

Reaction of Decaborane with Cyclohexanone. A solution of 1.227 g (0.01 mol) of decaborane and 0.980 g (0.01 mol) cyclohexanone in 17 g of cyclohexane was kept at 80—83 °C for 4 h. The subsequent removal of the solvent and the excess constituents *in vacuo* gave 2.11 g of a pasty solid; IR (in CS_2) 1338, 1360 cm^{-1} (B–O); mass spectrum *m/e* 222 (M^+ $B_{10}H_{14}COC_5H_{10}$).

The pasty solid product decomposes mainly into boric acid and cyclohexanol, upon filtration, drying, and so on.

Reaction of Decaborane with Cyclohexanone in the Presence of Water. The mixture from 0.086 g (0.71 mmol) of decaborane 1.3 g (13 mmol) of cyclohexanone and 0.3 g (17 mmol) of water was stirred at room temperature for 15 min. During the reaction, the 156-ml portion (760.8 mmHg, 17 °C) of gas evolved was put in a gas receiver and was analyzed by gas chromatography; the gas was found to be a mixture of H_2 (99.0%) and N_2(1.0%).

The liquid portion of the reaction mixture was distilled off under reduced pressure. The liquid distillate, which weighed 0.14 g, was then subjected to gas-chromatographic analysis. Four constituents—cyclohexanone recovered (35%), cyclohexanol (8%), cyclohexene (30%), and an unknown compound (10%)—were found.

The mixture remaining after evacuation was extracted with light petroleum, after which the solvent was evaporated; this gave a residue which, on recrystallization from benzene-light petroleum, yielded 0.02 g of tris(cyclohexyloxy)boroxin. The mp and mixed mp with an authentic sample[4] was 166—167 °C; IR 720, 735 cm^{-1} (out-of-plane boroxin skeletal vibration) 1338, 1360 cm^{-1} (stretch B–O); mass spectrum *m/e* 378.

Found: B, 8.58%. Calcd for $C_{18}H_{33}O_6B_3$: B, 8.58%.

The remainder after extraction with light petroleum gave 0.3 g boric acid. The mp and mixed mp with an authentic sample was 184—185 °C.

Found: B, 17.16%. Calcd for H_3BO_3: B, 17.48%.

Reaction of Decaborane with Acetone in the Presence of Water. To a mixture of 0.37 g (3 mmol) of decaborane and 3.48 g (60 mmol) of acetone we added 1.80 g (100 mmol) of H_2O. A reaction took place, and 1425 ml (776.5 mmHg, 20 °C) (60.5 mmol) of hydrogen were evolved. The rectification of the reaction mixture gave a liquid distillate which was determined by gas chromatography to contain 0.16 g (2.7 mmol) of 2-propanol. The recrystallization of the solid residue with aqueousethanol yielded 0.18 g (29 mmol) of boric acid, which was identical in its mp and IR spectrum with the authentic sample.

Boroxin Formation from Decaborane, Acetone, and Water. A mixture of 0.32 g (2.6 mmol) of decaborane, 2.6 g (45 mmol) of acetone, and 0.35 g (10.5 mmol) of H_2O was allowed to stand for 24 h at room temperature. The subsequent removal of the liquid portion and the recrystallization of the resulting solid residue by using light petroleum and benzene–petroleum gave 1.0 g of tris(isopropyl)boroxin, mp 45—46 °C; IR (in CS_2) 720, 735 cm^{-1} (B–O in boroxin skeleton); mass spectrum *m/e* 258 (M^+).

Found: B, 12.60%. Calcd for $C_9H_{21}B_6O_3$: B, 12.58%.

References

1) a) W. H. Hilland and M. S. Johnson, *Anal. Chem.*, **27**, 1300 (1955); b) S. J. Fitch and A. W. Laubengayer, *J. Am. Chem. Soc.*, **80**, 5911 (1958); c) H. C. Beachell and D. E. Hoffman, *ibid.*, **84**, 180 (1962).

2) a) A. Stock "Hydrides of Boron and Silicon," Cornell University Press, Ithaca, New York (1933); b) E. L. Muetterties "Boron Hydride Chemistry," Academic Press, New York (1975); c) W. N. Lipscomb, *Science*, **196**, 1047 (1977).

3) A. Stock and E. Pohland, *Ber.*, **62B**, 90 (1929).

4) K. G. O'Brien, *Aust. J. Chem.*, **16**, 915 (1963).