single reduction observed is that of the ethyl or that of the phenyl radical. Further work on other phenylammonium ions should be carried out. It is probable that all these reductions result in the formation of an amine and a hydrocarbon in the case of the tetraalkylammonium ions, ethyl alcohol in the case of choline, ethyl acetate in the case of acetylcholine, etc.

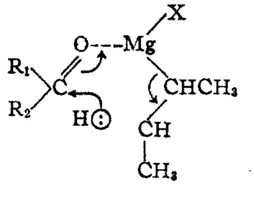
DEPARTMENT OF CHEMISTRY
UNIVERSITY OF OREGON
EUGENE, OREGON
RECEIVED APRIL 9, 1945

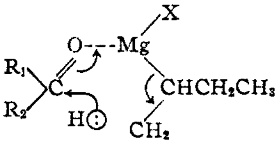
The Butenes from the Reduction of Isobutyraldehyde by *s*-Butylmagnesium Bromide

BY WILLIAM G. YOUNG AND JOHN D. ROBERTS[1]

Whitmore and George[2] have shown that the reduction of diisopropyl ketone by a Grignard reagent involves hydrogen atoms attached to the beta-carbon atom of the Grignard reagent. If the Grignard reagent had no hydrogen atoms on the β-carbon, as with neopentylmagnesium chloride, no reduction was detected. It was pointed out that a correlation exists between the extent of reduction of diisopropyl ketone and the number and primary, secondary or tertiary character of the β-hydrogens of the Grignard reagents. It is difficult, however, to determine the relative reduction rates of the different classes of β-hydrogen atoms from data obtained with several Grignard reagents because the competing reactions of addition and enolization are also markedly influenced by structure.

The relative reducing tendencies of primary and secondary β-hydrogens should be directly obtainable, independent of the addition and enolization reactions, from the ratios of 1- to 2-butene in the butenes resulting from the reduction of carbonyl compounds by *s*-butylmagnesium halides. The reduction reactions undoubtedly involve concerted cyclic processes[3] of the types





In the present work the butenes have been isolated from the reaction of *s*-butylmagnesium bromide with isobutyraldehyde. Infra-red spectroscopic analysis showed the butene mixture to consist of 1-butene (34%), *cis*-2-butene (8%) and *trans*-2-butene (58%). The 1- to 2-butene ratio was hence 34:66 or about 1:2. Since *s*-butylmagnesium bromide carries two secondary and three primary β-hydrogens, the relative tendency of primary and secondary β-hydrogens to be involved in reduction is thus about one to three.

Similar experiments with isopropylmethylcarbinylmagnesium bromide and isopropylethylcarbinylmagnesium bromide should give the relative rates of reduction of tertiary *vs.* primary and tertiary *vs.* secondary β-hydrogens, respectively.

Experimental

Isobutyraldehyde (54 g., 0.75 mole) dissolved in an equal volume of ether was added dropwise to a solution of *s*-butylmagnesium bromide prepared from 18 g. (0.75 gram atom) of magnesium, 102 g. (0.75 mole) of *s*-butyl bromide and 300 ml. of ether. The effluent gases were condensed in a Dry Ice cooled trap. The condensate was distilled into cold ether and the butenes converted to the dibromobutenes by treatment with bromine while cooling in an ice-hydrochloric acid bath. The ether was evaporated, the dibromides purified[4] and the butenes regenerated[4] and collected in an ampoule.

An infrared spectroscopic analysis was made of the butene mixture by Dr. O. Beeck of the Shell Development Company. An infrared analysis of a check sample was in satisfactory agreement with an analysis obtained by another method.[5] The Grignard complexes were decomposed with iced ammonium chloride solution and the higher-boiling products isolated in the usual way. Fractionation gave 12 g. (22%) of isobutyraldehyde, 19 g. (37%) of isobutyl alcohol, 31 g. (31%) of impure isopropyl-*s*-butylcarbinol and 12 g. of high-boiling residue. Refractionation of the addition product gave 23 g. (23%) of pure isopropyl-*s*-butylcarbinol, b. p. 81.9° (50 mm.), n^{20}_{D} 1.4325.

Anal. Calcd. for $C_8H_{18}O$: C, 73.78; H, 13.93. Found: C, 73.80; H, 14.2.

---

[1] Abbott Laboratories Research Fellow, 1943–1944.

[2] Whitmore and George, THIS JOURNAL, **64**, 1240 (1942).

[3] Whitmore and George, paper presented before the Division of Organic Chemistry at the Atlantic City Meeting of the American Chemical Society, September, 1941.

[4] Young, Winstein and Prater, THIS JOURNAL, **58**, 289 (1936).

[5] Dillon, Young and Lucas, *ibid.*, **52**, 1949 (1930).

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF CALIFORNIA AT LOS ANGELES
LOS ANGELES 24, CALIFORNIA
RECEIVED DECEMBER 5, 1944

Derivatives of N,N′-Dicyclohexyl-ethylenediamine

BY F. B. ZIENTY AND R. C. THIELKE[1]

Since certain diacyl derivatives of N,N′-dicyclohexyl-ethylenediamine[2,3] had been shown to possess good solvent power for polyvinyl acetal resins and other plastic compositions, it seemed desirable to extend the study of these acyl derivatives.[4]

N,N′-Dicyclohexyl-ethylenediamine (I), prepared in 90% yield from cyclohexylamine and ethylenedichloride,[2,5] was easily acylated by reaction with acid chlorides and acid anhydrides. In the case of the formyl derivatives, however, (I) reacted with formic acid and the formate was dehydrated to the amide. Depending on the conditions of reaction, either a mixture of the monoformyl (II) and diformyl (III) derivatives

---

[1] Present address: Emmett, Idaho.

[2] Kyrides, U. S. Patent 2,126,560 (Aug. 9, 1938).

[3] Kyrides, U. S. Patent 2,267,685 (Dec. 23, 1941).

[4] Lob, *Rec. trav. chim.*, **55**, 859 (1936), made a comprehensive investigation of the derivatives and reactions of a related amine, N,N′-dibenzyl-ethylenediamine.

[5] Clifford, U. S. Patent 2,126,620 (Aug. 9, 1938).