

form and other solvents gel in the presence of benzoyl peroxide or cobalt naphthenate. The fact that both these agents accelerate polymerization of glucose pentamethacrylate suggests that besides the addition polymerization, polymerization accompanied by oxidation takes place. This was further substantiated by the following experiments. After a month at room temperature, glucose pentamethacrylate crystals were still soluble in organic solvents, but combustion analysis showed only 57.8% carbon, which corresponds approximately to the original compound with one atom of oxygen added. After being heated for two hours at 100°, glucose pentamethacrylate became insoluble in all organic solvents. The carbon value was 54.2%, indicating the addition of approximately 3 atoms of oxygen.

Maltose octamethacrylate was prepared as an amorphous powder by the procedure used for glucose. It was soluble in the same solvents as glucose pentamethacrylate. Analysis showed 62.5% methacrylyl (calcd., 62.3%); specific rotation $[\alpha]_D^{25} +81.4^\circ$ in 4% solution in alcohol. A solution of maltose octamethacrylate (50% in chloroform) gelled in fifteen days at room temperature, in four in the presence of benzoyl peroxide, and in two in the presence of cobalt naphthenate. The amorphous powder became insoluble in one to two weeks at room temperature and in about two hours when heated at 100°.

Dextrin trimethacrylate was prepared in a similar manner (six hours at 95°). The amorphous powder was insoluble in alcohol and aliphatic hydrocarbons but soluble in most other usual solvents. It insolubilized on exposure to air.

Starch methacrylate (substitution 2.9) was prepared (seven hours at 95°) as an amorphous powder insoluble in most solvents but slightly soluble in pyridine and tetrachlorethane. It became entirely insoluble on exposure to air or after short heating.

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PHILADELPHIA, PA. RECEIVED MARCH 26, 1945

Polarographic Reduction Potentials of Quaternary Ammonium Ions

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The halides of tetra-substituted ammonium ions, particularly the tetramethylammonium ion, are used as supporting electrolytes in polarographic work whenever the reduction reactions to be studied occur at potentials more negative than those corresponding to the reduction of the ions of the alkali metals. In our polarographic researches¹ we have now been led to a study of the reduction of various quaternary ammonium ions in presence of the most difficultly reducible one of them all, the tetramethylammonium ion, $N(CH_3)_4^+$. A brief digest of the previous, and very fragmentary, work on some of these ions will be found in Kolthoff and Lingane's book.²

Materials.—Besides $N(CH_3)_4Br$, the other three tetraalkylammonium salts (tetraethylammonium bromide, tetra-*n*-propyl and *n*-butyl iodides) were also Eastman Kodak Co. white label products, ammonium chloride was Baker c. p. and trimethylammonium chloride was Kahlbaum c. p. Some of the choline hydrochloride used was Merck c. p. Choline isolated from the lecithin of egg yolks gave results identical with those obtained with the Merck product. The acetylcholine hydrochloride was

Merck c. p. The two other unsymmetrical ions were prepared by us according to standard methods.

Procedure.—The instrument was a Heyrovsky polarograph of the Sargent Company. Polarographic reduction curves of the supporting electrolyte alone (Eastman Kodak Co. white label tetramethylammonium bromide, carefully recrystallized from water-ethanol mixtures) were recorded as blanks for each case. The average of a large number of limiting tangent potentials for the reduction of this ion is -2.93 ± 0.03 volt referred to the saturated calomel electrode. Varying amounts of each one of the other salts were then added to the solution of the supporting electrolyte and their reduction waves recorded. The half-wave potentials could, in all cases, be determined without ambiguity. Several of the diffusion currents (but not those of the symmetrical ions) exhibited maxima before merging into the reduction wave of the supporting ion, but these maxima were always exactly reproducible. The crests of these maxima were used to determine the half-wave potential, since, in the case of choline, a detailed analysis showed that the heights of these crests were closely proportional to the concentration. The uncertainty on the various half-wave potentials is well within the general upper limit ≈ 0.03 volt. The temperature was not controlled but was in all cases close to 25°. No detectable variations could be observed in the reduction potentials for the cases which were repeated at intervals of several days.

Results.—In Table I we give for each quaternary ammonium ion the accompanying halide ion and the half-wave potential referred to the saturated calomel electrode. No striking regularity is apparent in Table I. It seems unlikely,

TABLE I
POLAROGRAPHIC HALF-WAVE REDUCTION POTENTIALS OF QUATERNARY AMMONIUM IONS

Positive ion	Negative ion	Half-wave potential, volts
NH_4^+	Cl^-	-2.21
$N(CH_3)_3H^+$	Cl^-	2.23
$N(C_2H_4OH)_3C_2H_5^+$	Br^-	2.38
$N(C_3H_7)_4^+$	I^-	2.52
$N(C_4H_9)_4^+$	I^-	2.57
$N(CH_3)_3C_2H_4OCOCH_3^+$	Cl^-	2.64
$N(C_2H_5)_4^+$	Br^-	2.67
$N(CH_3)_2C_2H_5C_4H_9^+$	Br^-	2.71
$N(CH_3)_3C_2H_4OH^+$	Cl^-	2.72
$N(CH_3)_4^+$	Br^-	2.93 (tangent potential)

however, that the reduction corresponding to the $N(CH_3)_4^+$ ion could be the decomposition of water,² since different potentials are observed with the other tetraalkylammonium ions. This is also indicated by some experiments in which these other tetraalkylammonium salts were used as supporting electrolytes. The inversion in the sequence $N(C_3H_7)_4^+$, $N(C_4H_9)_4^+$, $N(C_2H_5)_4^+$, $N(CH_3)_4^+$ is peculiar, but is again substantiated in the results obtained when using the corresponding salts as supporting electrolytes. In the case of the unsymmetrical ions it appears that the reduction potential of the most reducible group is affected by the nature of the other groups present, as is clear if one compares the relative positions of these ions in the table. In the only case where three different groups are present, $N(CH_3)_3C_2H_5C_4H_9^+$, it is impossible to decide whether the

(1) P. Van Ryselberghe and G. J. Alkire, THIS JOURNAL, 66, 1801 (1944).

(2) I. M. Kolthoff and J. J. Lingane, "Polarography," Interscience Publishers, Inc., New York, N. Y., 1941, p. 380.

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.

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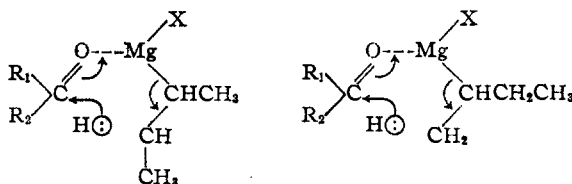
RECEIVED APRIL 9, 1945

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

BY WILLIAM G. YOUNG AND JOHN D. ROBERTS¹

Whitmore and George² 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 processes³ 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

(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.

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 purified⁴ and the butenes regenerated⁴ 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_D^{20} 1.4325.

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

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

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

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LOS ANGELES 24, CALIFORNIA RECEIVED DECEMBER 5, 1944

Derivatives of *N,N'*-Dicyclohexyl-ethylenediamine

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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.*, **66**, 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).