The reaction flask was then flushed with nitrogen, stoppered and shaken occasionally. In the course of 36 hours the originally orange solution became murky, changing in color to brown, then brown-green, gray-green and finally gray (colloidal suspension). After 7 days, separation in the centrifuge (or better, in the ultracentrifuge) resulted in a fine gray precipitate and a colorless methanolic solution. This solution was extracted with pentane, the pentane evaporated and the solvolysis product distilled (40° (7 mm.)) to give 0.6 g. (75%) of a liquid which on infrared examination proved to be pure, parent alcohol, 2,4-dimethyl-4-hexanol. The methyl ether of the carbinol, 4-methoxy-2,4-dimethylhexane, was not detected.

The dried gray solid had a chromium content of 33.29%. Duplicate experiments gave solid in which the chromium % was 32.32 and 35.45. These values compare favorably with the calculated chromium content of chromic methoxide, $Cr(OCH_3)_3$: 35.86%.

The chromate ester besides being insoluble in water is also relatively inert toward it, requiring about 2 weeks for complete decomposition. The product is a mixture of the parent alcohol, ketonic material (5.83 μ) and olefin(s) with peaks at 6.0, 6.1 and 11.26 μ (intense).

Repetition of the methanolysis of di-(2,4-dimethyl-4hexyl) chromate just described using optically active chromate diester prepared from 2,4-dimethyl-4-hexanol, $[\alpha]$ D +4.54° (α 0.27°, c 11.9 in CCl₄), was performed. The pure carbinol isolated from the methanolysis was also optically active: $[\alpha]$ D +4.35° (α 0.23°, c 10.58 in CCl₄). This represents 96% retention of configuration during reaction.

Reaction of Di-(2,4-dimethyl-4-hexyl) Chromate with Sodium Methoxide.—Fifty drops of the liquid diester (1.12

g.) was dropped into a solution of 10 g. of sodium in 100 ml. of methanol. After flushing with nitrogen the flask was stoppered and shaken. A yellow-green slurry formed at once which separated after 30 minutes as a deposit of yellow, crystalline sodium chromate in a green solution. An additional 50 ml. of methanol was now added, then 200 ml. of water, and the resultant green solution was extracted with four 50-ml. portions of pentane. After drying with sodium sulfate and removal of pentane by evaporation, the product was distilled (40° (7 mm.)) to give 0.65 g. (76%) of pure 2,4-dimethyl-4-hexanol (infrared comparison). The aqueous layer was shaken with dimedon solution (ρ H 4.6) from which the white crystalline derivative of formaldehyde was isolated. This solid was filtered, washed with water and dried; m.p. 190°.

In a side experiment the chromate diester of triphenylcarbinol was treated with sodium methoxide by the same procedure. Although the major product was the parent alcohol, a small amount of its corresponding methyl ether $(9.3 \ \mu)$ was detected.

Reaction between sodium methoxide and optically active chromate ester taken from the same source as that used in the solvolysis work above resulted in the formation of optically active parent alcohol, $[\alpha] p + 4.27^{\circ} (\alpha 0.25^{\circ}, c \, 11.7 \, \text{in}$ CCl_4). This amounts to 94% retention of configuration.

Optically active di-(2,4-dimethyl-4-hexrl) chromate was also prepared from 2,4-dimethyl-4-hexrl) chromate was and chromyl chloride. Reaction of this ester with sodium methoxide in methanol gave pure carbinol, $[\alpha]D + 4.33^{\circ}$ $(\alpha \ 0.26^{\circ}, c \ 12.0 \text{ in CCl}_4)$, with 95% retention of configuration.

DAYTON 7, OHIO

[Contribution from the Departments of Chemistry, Virginia Polytechnic Institute and the Washington and Lee University]

Branched-chained Tertiary Alcohols. I. Diisobutylethylcarbinol

By Robert C. Krug, Warren L. Choate, Joseph T. Walbert and Robert C. Leedy Received September 6, 1955

The reaction of ethylmagnesium bromide with diisobutyl ketone yields diisobutylethylcarbinol accompanied by considerable reduction and enolization. The structure of the alcohol is confirmed through dehydration and the ozonolysis on the resulting olefins.

Our interest in the general problem of the synthesis of branched-chain tertiary alcohols was stimulated by the discovery that in a preparation involving the condensation of ethylmagnesium bromide with diisobutyl ketone the yield of the expected alcohol I was almost zero. This was a striking result in view of the fact that ethylmagnesium bromide with diisopropyl ketone is reported to give a 77%yield of the addition product.1 Whitmore and George studied a series of ketone-Grignard reagent reactions and determined the extent of addition, reduction and enolization obtained in each case. With branched-chained ketones where the branching occurred on the α -carbon atoms the addition reaction of n-propyl and higher Grignard reagents ceased to be the main reaction. Whitmore and Lewis² found that the degree of enolization of the carbonyl compound in the presence of methylmagnesium bromide depends upon the nature of the substituents on the carbon atom adjacent to the carbonyl group, and that substitution on the β carbon atom had less effect on the reaction of the carbonyl group.

(1) F. C. Whitmore and R. S. George, This Journal, $\boldsymbol{64},\ 1239$ (1942).

In order to obtain an appreciable yield of the addition product, an excess of Grignard reagent to ketone was employed. The replacement of ethyl ether by benzene in the Grignard reagent solution and the subsequent higher temperature used during the addition of the ketone had little effect upon the product distribution. Only a trace of I was obtained from the two runs in which an approximate 1:1 mole ratio of Grignard reagent to ketone was employed.

The reaction of an excess of ethylmagnesium bromide with diisobutyl ketone gave 20% enolization and reduction, 40% unreacted diisobutyl ketone and 40% I. The large amount of unreacted ketone differs from the results of Whitmore and George¹ in the study of the reaction of ethylmagnesium bromide and diisopropyl ketone.

The alcohol was easily dehydrated in the presence of oxalic acid. Ozonolysis of the olefinic material gave diisobutyl ketone and ethyl isobutyl ketone. The ketones were identified by conversion to the corresponding 2,4-dinitrophenylhydrazones. Thus, the dehydration of I gave a mixture of two new isomeric olefins, 4-ethyl-2,6-dimethyl-3-heptene and 3-isobutyl-5-methyl-2-hexene. The structure of the alcohol is established.

⁽²⁾ F. C. Whitmore and C. E. Lewis, *ibid.*, **64**, 2964 (1942).

Diisobutylethylcarbinol (I).—A solution of ethylmagnesium bromide in ether prepared from 218 g. (2.0 moles) of ethyl bromide and 48.6 g. (2.0 moles)of magnesium turnings in a total of 500 ml. of anhydrous ether was refluxed 30 minutes, and treated with a 1:1 ether solution of 142 g. (1.0) mole of diisobutyl ketone added over a period of 1.5 hours. A total of 5.2 l. (S.T.P.) of gas was evolved during this addition. This volume represented a total of approximately 0.2 mole of ethane and ethene. The reaction mixture was slowly hydrolyzed with 600 ml. of 4 N HCl during 3.5 hours, 33.5 l. (S.T.P.) of gas being collected. This volume represented 1.5 moles of ethane. The ether and water layers were separated and the aqueous phase extracted three times with 150-ml. portions of ether. The original ether layer and the extracts were combined and dried over anhydrous sodium sulfate. The ether was removed on a water-bath leaving 158 g. of higher boiling material. This liquid was distilled at 16 mm. pressure using a modified Vigreux column, and the following were obtained: (a) unreacted diisobutyl ketone, b.p. 61-67°, d²⁵₄ 0.7576, n^{25} D 1.4254, 36.5 g., identified by its 2,4-dinitrophenylhydrazone melting at 92°; (b) diisobutylcarbinol and diisobutyl ketone, b.p. 78-88°, n²⁵D 1.4286-1.4330, 32.5 g., and (c) the tertiary alcohol I, b. 88–93°, n^{25} _D 1.4330–1.4353, 65.0 g. A small amount of olefinic material also was detected in a. The physical constants of a selected fraction of the new alcohol I are b.p. 91–93° (16 mm.), d²⁵₄ 0.8252 and n^{25} D 1.4347. The gas evolved during hydrolysis of the reaction mixture represented unreacted Grignard reagent, and approximately 0.4 mole of ketone failed to react.

Dehydration of Diisobutylethylcarbinol (I).—The alcohol was heated under reflux in the presence of oxalic acid, and the hydrocarbon layer so obtained was then heated for 2.5 hours over sodium. That portion distilling at $159-162^{\circ}$ at 710 mm. had the following properties: d^{25}_{4} 0.7504, n^{25}_{5} 1.4248.

Anal. Calcd. for $C_{11}H_{22}$: C, 85.25; H, 14.58. Found: C, 85.49; H, 14.51.

Ozonolysis of the Olefins $C_{11}H_{22}$.—The ozone oxidation apparatus was similar to that employed by Henne and Hill.³ Using the procedure for the preparation of ketones as described by Henne and Hill,⁴ a fraction boiling over the range 70–90° was obtained which upon treatment with 2,4-dinitrophenylhydrazine reagent gave a solid melting at 73–74° (uncor.) from ethanol. The 2,4-dinitrophenylhydrazone from ethyl isobutyl ketone melts at 75°.⁴ Treatment of the fraction which distilled at 147° with the 2,4-dinitrophenylhydrazine reagent gave a solid which melted at 91–92° (uncor.) from ethanol. A mixed melting point of this compound with a sample of the 2,4-dinitrophenylhydrazone from diisobutyl ketone showed no depression.

(3) A. L. Henne and P. Hill, THIS JOURNAL, 65, 752 (1943).
(4) C. F. H. Allen, *ibid.*, 52, 2955 (1930).

Blacksburg, Virginia, and Lexington, Virginia

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, ILLINOIS INSTITUTE OF TECHNOLOGY]

The Reactions of Silver Nitrate with Some Substituted Neopentyl Bromides

By Myron L. Bender and Harry Robbins¹

RECEIVED APRIL 27, 1955

The reactions of silver nitrate with 2,2-dimethyl-1,3-dibromopropane, 2,2-dimethyl-3-bromo-1-propanol and 2,2-dimethyl-3-acetoxy-1-bromopropane in 70% aqueous ethanol produced 2-methylbutanal in each case. Kinetic studies indicated that the rate of each reaction was proportional to the halide concentration and to the silver ion concentration. Energies of activation for these reactions have been determined. On the basis of the product analyses and kinetics, mechanisms involving molecular rearrangement and, in one case, an allylic rearrangement are postulated. It appears that no neighboring group reactions take place in these 1,3-systems under the conditions described.

Introduction

The neighboring group reaction, in which an atom or group of atoms is postulated to participate in the reaction of a second functional group on an adjacent carbon atom, has been useful in explaining a number of stereochemical and kinetic results.² The neighboring group reaction has been postulated to proceed through cyclic, usually positively charged, intermediates arising from the participation of the neighboring group in the displacement of the leaving group. Such a mechanism ade-

(1) Abstracted from the M.S. thesis of H. R.

(2) (a) Much of the stereochemical work is summarized by S. Winstein, H. V. Hess and R. E. Buckles, THIS JOURNAL, **64**, 2796 (1942); (b) much of the kinetic results is summarized by S. Winstein and co-workers, *ibid.*, **70**, 812, 816, 821 and 828 (1948); (c) see also C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell Univ. Press, Ithaca, N. Y., 1953, pp. 381-395, and P. D. Bartlett in H. Gilman, "Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1953, Vol. III, pp. 37-41.

quately explains the stereochemical result of overall retention of configuration in certain reactions^{2a} and also explains the fact that some of the more powerful neighboring groups provide substantial driving forces to the reaction, resulting in enhanced rates of reaction.^{2b}

The participation of the neighboring groups cited above pertains to those groups situated on the carbon atom adjacent to the carbon atom containing the displaced group. Several reactions which can be interpreted as involving neighboring groups in the 3-position with respect to the displaced group have been reported with neopentyl derivatives. The neighboring groups in these cases may be the oxide ion,³ the hydroxyl group,^{4,7} the halogen

(3) F. Govaert and M. Beyaert, *Natuurw. Tijdschr.*, **22**, 73 (1940) (*C. A.*, **37**, 3054 (1943)); S. Searles, R. G. Nickerson and W. K. Witsiepe, Abstracts of the 123rd Meeting of the A.C.S., p. 31M (1953).

(4) J. Barbiere and J. Matti, Bull. soc. chim., [5] 5, 1565 (1938).