

of magnesium turnings and 1.21 equivalent of the appropriate alkyl bromide in six to eight volumes of absolute ether. One equivalent of 3-chloro-1-ethoxybutyronitrile was diluted with an equal volume of anhydrous ether and added to the alkylmagnesium bromide. After being decomposed with cold, dilute hydrochloric acid and dried over calcium chloride, the ether was removed and the product fractionated under 4-9 mm. pressure. The yields reported are based upon the quantity of keto ether obtained from the first fractionation. The ketones were colorless when freshly distilled, but soon darkened upon standing in a sealed container. These compounds are sparingly soluble in water, but are miscible in the usual organic solvents. Certain data representing physical properties and analyses for these nine new keto ethers are listed in Table I.

Only two of the nine ketones, namely, the *n*-propyl and *n*-butyl members, formed semicarbazones, even when the ketones and reagents stood for several weeks.

Semicarbazone of 3-chloro-1-ethoxypropyl *n*-propyl ketone, m. p. 130° (cor.) with decomposition.

Anal. Calcd. for $C_{10}H_{20}ClN_3O_2$: N, 16.83. Found: N, 16.70.

Semicarbazone of 3-chloro-1-ethoxypropyl *n*-butyl ketone, m. p. 104° (cor.) with decomposition.

Anal. Calcd. for $C_{11}H_{22}ClN_3O_2$: N, 15.93. Found: N, 15.63.

Summary

Acrolein was converted into 1,3-dichloropropyl ether, and the latter, in turn, into 3-chloro-1-ethoxybutyronitrile by interaction with silver cyanide. From the nitrile, by means of the appropriate Grignard reagents, were prepared nine new 3-chloro-1-ethoxypropyl alkyl ketones.

AUSTIN, TEXAS

RECEIVED MAY 12, 1941

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF THE UNIVERSITY OF CALIFORNIA AT LOS ANGELES]

Allylic Rearrangements. XI. The Action of Magnesium and Zinc on Crotyl and Methylvinylcarbinyl Chlorides

BY WILLIAM G. YOUNG AND MORTON EISNER

Previous communications from this Laboratory have shown that allylic rearrangements occur during the formation and hydrolysis of butenylmagnesium bromides in diethyl ether¹ and during the reaction of several other metals with the butenyl bromides in boiling 80% ethanol.^{2a,b} In both solvents, diethyl ether and ethanol, the composition of the butene mixtures produced as a result of this rearrangement was independent of the nature of the butenyl (crotyl and methylvinylcarbinyl) bromide mixture, but was related to the molal electrode potential of the metal when the reaction was carried out in boiling 80% ethanol.

However, a complete understanding of the rearrangements requires a study of the effect of temperature, solvent, and halide as well as character of the metal. It is the purpose of this paper to present a preliminary report on such a study.

Experimental Part

Preparation and Hydrolysis of the Grignard Reagent.—

A series of experiments on small quantities of butenyl chlorides carried out in the apparatus used in the study³ of butenylmagnesium bromides demonstrated that the coupling reaction, frequently encountered⁴ with other allylic

halides, could be minimized by increasing the mole ratios of ether and magnesium turnings to butenyl chloride provided the chloride was added slowly accompanied by vigorous stirring. When the mole ratios were 30:15:1 the yield of Grignard reagent was 86%. The yield was only 40% when the ratios were 7.5:3:1. In order to conserve both materials and time in working with 0.3-0.7 mole quantities of the butenyl chloride mixtures, we chose an addition time of three to four hours and mole ratios of 19:10:1 for the ether, magnesium and chloride, respectively. The hydrolysis of the Grignard reagent and the recovery and purification of the butenes as dibromobutanes was carried out as described by Young, Winstein and Prater.¹

The Reaction of Butenyl Chlorides with Zinc.—Mixtures of crotyl and methylvinylcarbinyl chlorides containing different proportions of these primary and secondary butenyl chlorides were converted into butene mixture by the action of zinc in boiling 80% ethanol according to the method used by Young and Winstein.^{2a} However, it was found that the butenyl chlorides were sufficiently volatile to pass through the purification train along with the butenes and contaminate the final product. The addition of silver nitrate to the perchloric acid in the washing train proved an effective means of removing the volatile chloride without causing rearrangement of the butenes.

Analysis of the Butene Mixtures.—The composition of butene mixtures formed from the butenyl chlorides was determined either by the dibromobutane reaction rate method of Dillon, Young and Lucas⁵ in which the necessary corrections were applied^{6,2b} or by distillation in a Frey-Hepp column⁷ modeled after the one used by Hurd and Goldsby.⁸ In some cases both procedures were used as a

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

(2) (a) Young and Winstein, *ibid.*, **58**, 441 (1936); (b) Young, Kaufman, Loshokoff and Pressman, *ibid.*, **60**, 900 (1938).

(3) Young, Prater and Winstein, *ibid.*, **55**, 4908 (1933).

(4) (a) Gilman and McGlumphy, *Bull. soc. chim.*, **48**, 1322 (1928); (b) Gilman and Kirby, *THIS JOURNAL*, **51**, 3475 (1929); (c) Gilman and Zoellner, *ibid.*, **52**, 3984 (1930); (d) Gilman and Harris, *Rec. trav. chim.*, **50**, 1052 (1931).

(5) Dillon, Young and Lucas, *THIS JOURNAL*, **52**, 1953 (1930).

(6) Young and Winstein, *ibid.*, **58**, 102 (1936).

(7) Frey and Hepp, *Ind. Eng. Chem.*, **25**, 441 (1933).

(8) Hurd and Goldsby, *THIS JOURNAL*, **56**, 1812 (1934).

check on each other. The results of the experiments with magnesium are listed in Table I and those with zinc in 80% ethanol in Table II.

Materials. Magnesium turnings were prepared as needed from bars of the commercial c. p. grade purchased from the Aluminum Corporation of America. The zinc was a mixture of equal parts of dust and 80-mesh which had been activated by the method of Marvel, Sample and Roy.⁹ Two types of butenyl chloride mixtures were prepared by fractional distillation of a commercial product¹⁰ containing equal quantities of the primary (crotyl) and secondary (methylvinylcarbonyl) chlorides. The two mixtures contained from 75–95% and 5–25% of primary chloride, respectively, the exact composition being determined before a given butenyl chloride mixture was used.

Discussion of Results

Reduction of Butenyl Chloride with Magnesium.—Two different mixtures of crotyl and methylvinylcarbonyl chlorides have been converted into butene mixtures by the action of magnesium in ether followed by hydrolysis and by the action of activated zinc in boiling 80% ethanol. The results using magnesium are shown in Table I. The composition of the butene mixtures obtained from both mixtures of butenyl chlorides agrees well with that previously found when butenyl bromides¹ were used. The discrepancy between runs I and II resulted from a

difference in density caused by a trace of impurity in sample II. This difficulty was overcome by reconverting sample II into a butene mixture which was analyzed in a Frey–Hepp column.⁷

Reduction of Butenyl Chlorides with Zinc.—The results obtained from reduction of different butenyl chloride mixtures by the action of activated zinc in boiling 80% ethanol are listed in Table II along with those obtained from the action of zinc on butenyl bromides.^{2a} They show that the butene mixtures are independent of the composition of the butenyl chloride mixtures used.

TABLE II

FREY-HEPP ANALYSIS OF BUTENE MIXTURES FROM THE ACTION OF ZINC ON BUTENYL CHLORIDE MIXTURES IN BOILING 80% ETHANOL

Expt. number.....	III	IV	V	Butenes from butenyl bromides ^c
n_D^{20} of butenyl chloride	1.4143	1.4127	1.4299	..
Crotyl chloride, %	16.0	8.0	93.5	..
Methylvinylcarbonyl chloride, %	84.0	92.0	6.5	..
1-Butene, %	69.2 ^a	67.4	67.4	62
<i>cis</i> -2-Butene, %	30.8	32.6	32.6	30
<i>trans</i> -2-Butene, %	... ^b	... ^b	... ^b	7

^a These results are of qualitative significance only since the gas sample contained some butenyl chloride which made it difficult to recover all of the 2-butene in the Frey–Hepp analysis. ^b The distillation curves indicate a trace of *trans*-2-butene, probably <2%. ^c Results obtained by Young and Winstein.^{2a}

TABLE I
ANALYSIS OF BUTENE MIXTURES FROM THE ACTION OF MAGNESIUM ON BUTENYL CHLORIDE MIXTURES IN DIETHYL ETHER

Run number.....	I	II	Butenes from butenyl bromide ^b	
n_D^{20} of butenyl chloride mixture	1.4277	1.4151		
Crotyl chloride, %	82.6	24.9		
Methylvinylcarbonyl chloride, %	17.4	75.1		
Reaction rate, K_2 , of $C_4H_7Br_2$ mixture	0.0605	0.0602		
d_{25}^4 of dibromide mixture	1.7836	1.7810 ^a		
Analytical method	Rate	Rate ^a	Frey-Hepp	
1,2-Dibromobutane (1-butene), %	54.7	41.6 ^a	54.2	56.4 = 2.0
<i>dl</i> -2,3-Dibromobutane (<i>cis</i> -2-butene), %	21.0	45.1	20.4	17.2 = 3.3
<i>meso</i> -2,3-Dibromobutane (<i>trans</i> -2-butene), %	24.3	13.4	25.4	25.5 = 1.4

^a A low density due to traces of impurities gives an erroneous analysis. This could be overcome by regeneration of the butenes. Since the sample was small we chose to check the analysis by the Frey–Hepp method after regenerating the butenes from the dibromobutane mixture. ^b Results obtained by Young, Winstein and Prater^{2b} from butenyl bromide mixtures.

(9) Marvel, Sample and Roy, THIS JOURNAL, **61**, 3241 (1939).

(10) This product was kindly furnished to us by the Shell Development Company, Emeryville, California, through the courtesy of Dr. E. C. Williams.

The last column in the table gives the results reported^{2a} for butene mixtures obtained from the action of zinc on butenyl bromide mixtures. Although the mixtures from the chlorides and bromides are qualitatively the same, nevertheless the chlorides yield from 3–5% more 1-butene and 5–8% less *trans*-2-butene. These differences cannot be attributed to experimental error. Our experience with the two methods of analysis employed indicates a maximum error 2–3%.

The fact that both halides give the same results with the Grignard reaction and slightly different results under the action of zinc in alcohol is probably due to the different conditions of hydrolysis. In the boiling ethanol there is a serious question as to whether or not the butenylmetallic halide is actually formed. The activated complex involving the metal and the resonating butenyl halide (see previous discussion of the mechanism^{2b}) may be the species which is hydrolyzed rather than the organometallic compound itself, hence the character of the halide involved in the complex

may partially determine the composition of the hydrolysis products.

Effect of Solvent on the Reaction of Zinc with Butenyl Bromides.¹¹—In order to determine whether or not the composition of the butene mixtures prepared by the action of zinc on butenyl bromide mixtures^{2a} in 80% ethanol was independent of the character of the solvent, we have allowed zinc to react with a butenyl bromide mixture rich in primary bromide and with one rich in secondary bromide using absolute ethanol and absolute isopropanol as solvents. The four dibromobutane mixtures obtained from the butene mixtures were analyzed by the reaction rate method. The average analysis for the four samples was 60.3% 1-butene, 31.8% *cis*-2-butene and 7.9% *trans*-2-butene compared with 62.1, 30.5 and 7.5% found with the 80% ethanol. Hence we see that the change in solvent has had little or no effect.

(11) We were aided in this work by Mr. Abe Lasher and Mr. Norman Kaufman.

Summary

Optimum conditions are reported for obtaining excellent yields of butenylmagnesium chloride.

Butene mixtures have been prepared from the reaction of different mixtures of butenyl (crotyl and methylvinylcarbonyl) chlorides with (1) magnesium in diethyl ether followed by hydrolysis, and (2) zinc in boiling 80% ethanol. Allylic rearrangements during the reactions led to butene mixtures which are independent of the composition of the butenyl chloride mixtures but dependent on the character of the metal and solvent.

Magnesium gives the same butene mixture from butenyl chloride as from the corresponding bromide.

Zinc gives a butene mixture from butenyl chloride which is similar to but definitely different than the butene mixture from butenyl bromides.

Absolute ethanol and isopropanol give the same results as 80% ethanol when used as a solvent for the reaction of zinc with butenyl bromides.

LOS ANGELES, CALIF.

RECEIVED MARCH 21, 1941

[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

Inorganic Oxychlorides as Hydrogen Bonding Solvents

BY L. F. AUDRIETH AND R. STEINMAN

The present investigation was undertaken to determine if inorganic acid chlorides containing oxygen atoms of potential donor ability are capable of bonding with compounds containing an acceptor hydrogen to form the C—H←O linkage. In order to evaluate the influence of the highly negative chlorine atoms in the acid chlorides, it also became necessary to compare the observed effects with those of certain related organic compounds whose behavior has not been ascertained heretofore. The experimental study involved specifically the determination of the heats of mixing of phosphorus oxychloride, sulfuryl chloride, thionyl chloride, diethyl carbonate, diethyl sulfite, diethyl sulfate, and propionyl chloride with chloroform and with carbon tetrachloride.

Experimental

The calorimeter and method employed in carrying out the heat of mixing measurements were those described and employed previously by Zellhoefer and Copley.¹

All compounds were purified by fractional distillation.

(1) Zellhoefer and Copley, *THIS JOURNAL*, **60**, 1343 (1938).

Constancy of boiling point as well as of refractive index, where possible, were taken as a measure of purity. Care was taken to ensure pure, dry samples by storing them in a dark cupboard in glass-stoppered bottles over chemically inert drying agents. The refractive indices were frequently rechecked and the compounds redistilled when they began to deteriorate.

Propionyl chloride was prepared from benzoyl chloride and propionic acid.² Commercial samples were invariably found to contain thionyl chloride which could not be removed successfully by fractional distillation. Thionyl chloride boils at 78.8°, propionyl chloride at 80°.

Discussion of Results

The high heats of mixing of inorganic acid chlorides with chloroform as acceptor solvent give definite evidence of hydrogen bonding. This conclusion is verified by the fact that solution of these same compounds in carbon tetrachloride is accompanied by only a small temperature change—slight heat effect with phosphorus oxytrichloride and a barely observable cooling effect with thionyl chloride and sulfuryl chloride. The

(2) H. C. Brown, *ibid.*, **60**, 1325 (1938).