[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE UNIVERSITY OF TEXAS]

Keto Ethers. VIII. Preparation of 3-Chloro-1-ethoxypropyl Alkyl Ketones[1]

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The synthesis of keto ethers has been the subject of several investigations in this Laboratory. Particularly useful as starting materials in the synthesis of such ketones are the α-chloro ethers which are conveniently prepared by the method of Henry.[3] Gauthier[4] has found that the chlorine atom in the α-position of the chloro ethers may be replaced by the nitrile grouping through the use of cuprous cyanide or mercuric cyanide. The discovery of Blaise[5] that nitriles are converted through the action of alkylmagnesium halides into ketones was followed by the conversion of alkoxy nitriles into ketones by the use of the Grignard reaction.[6]

amples of these two new types has been accomplished in the course of the study here reported.

1,3-Dichloropropyl Ethyl Ether.—Henry's[3] method was adopted for this preparation. From 45 g. (0.8 mole) of acrolein and 45 g. (25% excess) of ethanol saturated with dry hydrogen chloride there was obtained 82 g. (66% yield) of dichloro ether collected at 64–65° (18 mm.);[7] $n^{20}D$ 1.4478; d^{20}_4 1.1260; $MR\Sigma$ 36.67; MR found 37.31. This material was sufficiently pure for conversion into the nitrile.

3-Chloro-1-ethoxybutyronitrile.—This compound could not be obtained from interaction of the dichloro ether with cuprous cyanide, according to the general method of Gauthier,[4] but was obtained using silver cyanide; no evidence of formation of isonitrile was observed. From addition of 52 g. of 1,3-dichloropropyl ethyl ether, diluted

TABLE I

3-CHLORO-1-ETHOXYPROPYL ALKYL KETONES, $ClCH_2CH_2CH(-O-CH_2CH_3)COR$

—R	Yield, %	B. p. °C.	Mm.	d^{20}_4	$n^{20}D$	γ^{20} dynes/cm.	Chlorine, % Calcd.	Found
CH_3	48	68	4	1.0487	1.4340	31.54	21.54	21.78
C_2H_5	66	86–87	8	1.0301	1.4392	30.44	19.85	19.69
$n\text{-}C_3H_7$	75	95–96	6	1.0112	1.4403	30.23	18.40	18.51
$i\text{-}C_3H_7$	42	90–91	8	1.0070	1.4387	29.91	18.40	18.36
$n\text{-}C_4H_9$	69	96–98	4	0.9971	1.4424	30.93	17.15	17.03
$i\text{-}C_4H_9$	50	94–95.5	5	.9895	1.4400	29.71	17.15	16.91
$s\text{-}C_4H_9$	50	90–91	4	.9993	1.4416	29.57	17.15	17.08
$n\text{-}C_5H_{11}$	41	112–113	6	.9847	1.4438	29.42	16.06	15.84
$i\text{-}C_5H_{11}$	40	98–100	5	.9832	1.4435	28.37	16.06	15.75

—R	Molecular refraction Calcd.	Found	Parachor Calcd.	Found	Free surface energy, dynes/sq. cm.
CH_3	41.05	40.88	373.4	372.0	917.8
C_2H_5	45.64	45.64	412.4	407.4	946.7
$n\text{-}C_3H_7$	50.28	50.25	451.4	446.8	1001.0
$i\text{-}C_3H_7$	50.28	50.30	451.4	447.5	993.2
$n\text{-}C_4H_9$	54.90	54.90	490.4	488.9	1083.4
$i\text{-}C_4H_9$	54.90	55.06	490.4	487.4	1046.0
$s\text{-}C_4H_9$	54.90	54.69	490.4	482.4	1034.2
$n\text{-}C_5H_{11}$	59.52	59.53	529.4	522.1	1085.7
$i\text{-}C_5H_{11}$	59.52	59.58	529.4	518.2	1048.0

Prior to this investigation, chloroalkoxy nitriles have been synthesized but no examples of alkoxy chloronitriles have been prepared. Likewise, although a goodly number of chloroalkoxyalkyl alkyl ketones are known, the chemical literature contains no record of the production of an alkoxyalkyl chloroalkyl ketone. The synthesis of ex-

with 100 cc. of anhydrous ether, to 50 g. of silver cyanide, covered with an equal volume of dry ether, there was obtained 36 g. (70% yield) of nitrile boiling at 68–70° (3 mm.); $n^{20}D$ 1.4327; d^{20}_4 1.0546; γ^{20} 31.42 dynes/cm.; $MR\Sigma$ 36.24; MR found 36.24; P 333.2; P found 331.8; free surface energy 851.1 ergs.

Anal. Calcd. for $C_6H_{10}ClNO$: Cl, 24.02; N, 9.49. Found: Cl, 24.33; N, 9.29.

3-Chloro-1-ethoxypropyl Alkyl Ketones.—These ketones were synthesized by the method of Sommelet.[8] A Grignard reagent solution was prepared from 1.1 equivalent

(1) Preceding paper in this series, Lingo with Henze, THIS JOURNAL, **61**, 1574 (1939).

(2) From the Ph.D. dissertation of R. C. Wilson, June, 1941.

(3) Henry, *Bull. soc. chim.*, [2] **44**, 458 (1885).

(4) Gauthier, *Compt. rend.*, **143**, 831 (1906).

(5) Blaise, *ibid.*, **132**, 38 (1901).

(6) Béhal and Sommelet, *ibid.*, **138**, 89 (1904).

(7) Duliere [*Bull. soc. chim.*, **33**, 1647 (1923)] reported b. p. 56° (12 mm.); $n^{20}D$ 1.44235; d^{20}_4 1.122; MR 37.05.

(8) Sommelet, *Ann. chim. phys.*, [8] **9**, 484 (1906).

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.

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

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Previous communications from this Laboratory have shown that allylic rearrangements occur during the formation and hydrolysis of butenylmagnesium bromides in diethyl ether[1] 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 study[3] of butenylmagnesium bromides demonstrated that the coupling reaction, frequently encountered[4] 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 Lucas[5] in which the necessary corrections were applied[6,2b] or by distillation in a Frey–Hepp column[7] 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.*, **43**, 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).