acetic ester method, was reduced to 1-hexene-5-ol with aluminum isopropoxide, ozonized and the ozonide reduced with zinc and acetic acid. The product had the following properties: b.p. 65–67° (10 mm.), n^{25}D 1.43295, *p*-bromophenylhydrazone m.p. 86–88°. *Anal.* Calcd. for $C_6H_{10}O_2$: C, 58.5; H, 9.8. Found: C, 58.68; H, 9.72.

The cyclic hemiacetal, 30 g. in 100 ml. of water, was oxidized with 20 g. of chromium trioxide dissolved in 30 ml. of water. The temperature rose to 70° but subsided within an hour after which the mixture was heated on the steam-bath for two hours. The reaction mixture was continuously extracted with ether, the ether extract dried over sodium sulfate, and distilled. The fraction boiling at 85–87° was identified as γ-*n*-valerolactone, n^{20}D 1.4320, phenylhydrazide m.p. 77–79°, yield 75%. Similar results were obtained when acetic acid was used as solvent in the oxidation.

Preparation and Oxidation of 2-Hydroxy-5-methyl-5-*t*-butyltetrahydrofuran.—Allylacetone (200 g., 2.7 mols) in 500 ml. of ether was added over a 24-hour period to the Grignard reagent prepared from 3.5 moles of *t*-butyl chloride. The product was decomposed with ice and ammonium chloride and worked up in the usual manner. A 22% yield of 5,6,6-trimethyl-1-heptene-5-ol, b.p. 85° (20 mm.), n^{20}D 1.4514, was obtained. This was ozonized and the ozonide decomposed with zinc and acetic acid to yield 79% of 2-hydroxy-5-*t*-butyltetrahydrofuran, b.p. 86° (7 mm.), n^{25}D 1.4535. *Anal.* Calcd. for $C_9H_{18}O_2$: C, 68.35; H, 11.39. Found: C, 68.40; H, 11.76.

Oxidation of 19 g. with 9 g. of chromium trioxide with acetic acid as solvent with ice cooling (temperature under 30°) and isolation as above yielded 18.1 g. (90%) of the lactone of 4-hydroxy-4,5,5-trimethylcaproic acid, n^{20}D 1.4531. *Anal.* Calcd. for $C_9H_{16}O_2$: C, 69.23; H, 10.26; sapn. equiv., 156. Found: C, 69.09; H, 10.53; sapn. equiv., 156.2.

Oxidation of Isovaleraldehyde and Isobutyl Alcohol Mixtures.—The two substances, 0.5 mol each, were dissolved in 75 ml. of 80% acetic acid, the mixture cooled to 0° with ice–salt mixture and a solution of 35 g. of chromium trioxide in 250 ml. of 80% acetic acid added over a period of 24 hours with stirring. Water was added, the mixture extracted with ether, the extracts washed with sodium carbonate solution until neutral, the product dried and fractionated through a column of 20 theoretical plates. The following fractions were obtained: (A) b.p. 60–80°, n^{20}D 1.3799, weight 2.5 g., yield 4.2%, identified as isobutyraldehyde, 2,4-dinitrophenylhydrazone m.p. and mixed m.p. 180°; (B) 88–100°, 1.3930, 10.5 g., 24.4%, recovered isovaleraldehyde, 2,4-dinitrophenylhydrazone m.p. and mixed m.p. 122°; (C) 100–115°, 1.3988, 9.6 g. 26%, recovered isobutyl alcohol, 3,5-dinitrobenzoate m.p. and mixed m.p. 85°; (D) 136–150°, 1.4010, 6.6 g., 9%, identified as isobutyl isobutyrate by the method of Hardy[12] to give isobutyrylanilide, m.p. and mixed m.p. 103–104°; hydrolysis with potassium hydroxide in diethyleneglycol gave isobutyl alcohol, m.p. and mixed m.p. of 3,5-dinitrobenzoate 84°; (E) 160–170°, 1.4060, 18.83 g., 23.6%, identified as above as isobutyl isovalerate, anilide of acid fraction m.p. and mixed m.p. 110°, 3,5-dinitrobenzoate of alcohol fraction 84°. From the alkaline washings of the ether extract was obtained a 16.6% recovery of isovaleric acid, anilide m.p. and mixed m.p. 109–110°.

Oxidation of Isovaleraldehyde in the Presence of Diisopropyl Ether.—Isovaleraldehyde (0.5 mol) and diisopropyl ether (1.0 mol) were dissolved in 125 ml. of glacial acetic acid and cooled to 0–5°. To this solution was added over a period of 12 hours 35 g. of chromium trioxide in 10 ml. of water and 200 ml. of acetic acid. When worked up as in the above reactions, 19.4% isopropyl isovalerate, anilide of acid portion m.p. and mixed m.p. 110°, 3,5-dinitrobenzoate of alcohol fraction m.p. and mixed m.p. 121–122°, was obtained. A 59% yield of isovaleric acid was isolated, anilide m.p. and mixed m.p. 110°. No isopropyl acetate was found.

Oxidation of Propionaldehyde in the Presence of Diisopropyl Ether and Isobutyl Alcohol.—The three substances to be oxidized were used in 1-mol amounts and oxidized as in the above experiment. A 34% yield of isobutyl propionate, a 6% of isobutyl isobutyrate and a 14% yield of propionic acid were obtained.

Oxidation Rate Studies.—The general procedure was as follows: 125 ml. of 0.0210 *M* chromium trioxide solution was placed in a 250-ml. flask with ground-glass stopper. The flask was clamped in an ice–water-bath (0°) and the contents agitated with a magnetic stirrer. The substance to be oxidized was weighed from a Lunge pipet and diluted with 85% acetic acid. When temperature equilibrium was reached the substance solution was added quickly to the oxidant solution. The total volume was 150 ml. At intervals, 5-ml. portions were withdrawn, quenched in excess potassium iodide solution and the liberated iodine titrated with thiosulfate in the usual manner. The results are summarized in Fig. 1.

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[12] D. V. N. Hardy, *J. Chem. Soc.*, 398 (1936).

NEWARK, DELAWARE

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE GEORGIA INSTITUTE OF TECHNOLOGY]

The Dehydration of Alcohols in the Presence of Haloforms and Alkali[1]

BY JACK HINE, E. L. POLLITZER AND HANS WAGNER

RECEIVED JULY 1, 1953

It is shown that the ethylene arising from the reaction of haloforms with ethanol and alkali is formed from the ethanol, since the analogous reaction of isopropyl alcohol yields propylene. Olefin is also found in the corresponding reactions of *n*-propanol, all of the butanols and *t*-amyl alcohol. The olefin formed from the latter alcohol is shown to be about 80% 2-methyl-1-butene. Bromoform yields about 30% more olefin from isopropyl alcohol than does either chloroform or bromodichloromethane.

In 1855 Hermann reported that the reaction of bromoform with potassium hydroxide in aqueous ethanol yielded a mixture of carbon monoxide and ethylene containing 25–29% of the latter.[2] The gas produced by the reaction of sodium ethoxide with chloroform was reported by Bassett to consist largely of carbon monoxide, but a "small" amount of an inflammable gas, presumed to be ethylene, remained after all of the carbon monoxide had been absorbed.[3] Long reported that the ethylene composition of the gaseous product of this reaction remained between 24 and 25% despite increases in the potassium hydroxide concentration from about 0.8 to 2.5 *N*, with a simultaneous increase in water concentration from about 8 to 40%.[4] Mossler found that the analogous reaction of chloroform yielded a gaseous mixture of 25 ± 0.5% ethylene and 75 ± 0.5% carbon monoxide regardless of whether the potassium hydroxide was 0.16, 0.8 or 3.2 *N*, whether the ethanol was absolute or mixed with an equal amount of water and whether the chloroform or alkali was in excess.[5] Although

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[1] From the M.S. Thesis of Hans Wagner (1951), and the Ph.D. Thesis of E. L. Pollitzer (1953).

[2] M. Hermann, *Ann.*, **95**, 211 (1855).

[3] H. Bassett, *ibid.*, **132**, 54 (1864).

[4] H. Long, *ibid.*, **194**, 23 (1878).

[5] G. Mossler, *Monatsh.*, **29**, 373 (1903).

Hermann regarded the reaction as a dehydration of the ethanol, Nef has stated that the reaction of bromoform involves a dissociation to Br_2 and CHBr dimerization of the latter, and reduction of the $C_2H_2Br_2$ to ethylene.[6] We have demonstrated that the olefin does come from the alcohol used by isolating propylene bromide after adding bromine to the gaseous reaction product from sodium isopropoxide and chloroform and by isolating amylenes from a similar reaction of *t*-amyl alcohol.

We have therefore investigated this method of dehydrating alcohols with regard to its utility in preparing olefins and to the effect of changes in the structure of the haloform and the alcohol on the course of the reaction (including the nature of the olefin formed when more than one are possible). We have also made suggestions concerning the mechanism of the reaction based on data of the type described.

Discussion of Results

A number of variations in the reaction procedure were tested in an attempt to get the best possible yield of ethylene. A number of higher alcohols were then treated under the conditions found best for ethanol to give yields as shown in Table I. It should be noted that the yields given do not refer to the isolation of a pure product. In the case of gaseous olefins, for example, the yield was determined by an Orsat analysis. It may be noted from the table that the best yields were obtained in general from those alcohols most easily dehydrated by conventional methods.

TABLE I

YIELDS OF OLEFINS OBTAINED FROM VARIOUS ALCOHOLS[a]

Alcohol	Olefin yield, %	Alcohol	Olefin yield, %
Ethyl	7.5	*s*-Butyl	34
n-Propyl	8.3	Isobutyl	8–11
Isopropyl	28	*t*-Butyl	32–35
n-Butyl	8.9	Cyclohexyl[b]	14

[a] Procedure: 50 ml. of $CHCl_3$ dropped into 200 g. of KOH, 150 ml. of H_2O and 0.17 mole of alcohol. [b] Double quantities used.

Since it appears that this reaction would be a useful method of preparing olefins only in very unusual cases, no further work along this line was carried out. However, certain additional studies, such as determinations of optimum conditions for several alcohols, recovering unreacted alcohol and/or products reconvertible to alcohol, etc., are to be recommended as a basis for serious use of the method for synthetic purposes.

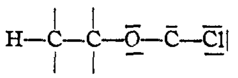
In order to determine the nature of the olefin formed from an alcohol which may yield more than one, the reaction of potassium *t*-amyloxide with chloroform was studied. The amylenes produced were found to consist of about 80% 2-methyl-1-butene and 20% 2-methyl-2-butene. This orientation in an elimination reaction (according to Hofmann's rule[7]) commonly occurs for *onium* ions only, although it has been reported in a few other cases.[8]

The effect of a change in the nature of the haloform upon the yield of olefin was tested by the reaction of potassium isopropoxide with chloroform bromodichloromethane and bromoform. Bromoform yielded about 30% more propylene than either of the other two haloforms which differed very little from each other. It is felt that little significance may be attached to the carbon monoxide yields, since calculations based on the data of Adickes and Schäfer and of Christiansen and Gjaldbaek[9] show that considerable amounts of fixation of carbon monoxide and its reverse (decarbonylation of alkyl formate) may have occurred thus

$$ROH + CO \overset{NaOR}{\rightleftharpoons} HCO_2R$$

so that the carbon monoxide observed may not be a primary product, and its yield may depend upon such variables as the length of time during which the reaction mixture remained strongly basic, etc.

This investigation was not aimed at the determination of the reaction mechanism and the data obtained do not warrant a complete discussion of this subject,[10] but it might be mentioned that there is good evidence that the reaction involves the intermediate formation of CCl_2.[11] Much of our (and other) experimental data may be explained by assuming the intermediacy of a compound of the type



$$H-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-\overline{\underline{O}}-\overline{C}-\overline{\underline{Cl}}|$$

which may (a) combine, at the divalent carbon atom, with other alkoxide or hydroxide ions to yield the orthoformate, formate or carbon monoxide, (b) undergo a β-elimination reaction to form olefin and the *OCCl* anion, or (c) undergo a nucleophilic replacement by alkoxide or hydroxide ion to give ether or alcohol and the *OCCl* anion. The *OCCl* anion may decompose to CO and Cl^- simultaneously or subsequently or may yield derivatives of formic acid.

Experimental

Formation of Propylene from Chloroform and Sodium Isopropoxide.—To 900 ml. of 99% isopropyl alcohol was added 34 g. (1.47 moles) of sodium, and when this had dissolved, 60 g. (0.50 mole) of chloroform was added slowly, and the 7 l. of gas evolved was collected under saturated salt solution. The gas was shaken with a slight excess of a concentrated Br_2–KBr solution, forming a separate oily layer which was taken up in ether, dried over calcium chloride and distilled. Between 130 and 142°, 13 g. of material was collected, which upon redistillation boiled largely between 139 and 141° to give a fraction $n^{25.5}D$ 1.5155, d^{22}_4

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(6) J. U. Nef, *Ann.*, **298**, 367 (1897).

(7) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., Section 31.

(8) R. L. Letsinger, A. W. Schnizer and E. Bobko, THIS JOURNAL, **73**, 5708 (1951).

NOTE ADDED IN PROOF: An almost identical olefin mixture has been found in the reaction of *t*-amyl bromide with potassium *t*-amyl oxide [H. C. Brown and I. Moritani, THIS JOURNAL, **75**, 4112 (1953)], assuming the authors mean "2-methyl-1-butene" where "3-methyl-1-butene" is written.

(9) F. Adickes and G. Schäfer, *Ber.*, **65B**, 950 (1932); J. A. Christiansen and J. C. Gjaldbaek, *Kgl. Danske Videnskab., Math.-fys. Medd.*, **20**, No. 3 (1942); *C. A.*, **38**, 3898^6 (1944).

(10) The mechanism is discussed in the theses mentioned in ref. 1.

(11) J. Hine, THIS JOURNAL, **72**, 2936 (1950).

1.925, in reasonable agreement with data listed for propylene bromide.

Reactions of Ethanol with Chloroform and Alkali.—In all cases the effluent gas from the reaction was passed through a condenser maintained at −78° into the gas collection system over saturated sodium chloride. When the reaction was completed the volume of gas was noted and that remaining in the reaction vessel was swept into the collecting system with nitrogen. The gas was analyzed in an Orsat apparatus, according to procedures described by Altieri[12] using mercuric sulfate in sulfuric acid to absorb ethylene and an acidic cuprous chloride solution for carbon monoxide.

In about twenty-five different runs, the ratios of reactants and reaction conditions were varied, seeking an optimum yield of ethylene (based on ethanol). Ultraviolet light was found to have no effect and use of pyridine, methanol and ether as co-solvents decreased the yield in each case. The best results were obtained by dropping chloroform into a solution of KOH in H_2O–EtOH. As the ratio of potassium hydroxide and chloroform to ethanol was increased, the percentage of ethylene in the gaseous product decreased, but the per cent. yield increased. However, increasing the ratio significantly past 20 g. of potassium hydroxide and 7.5 g. of chloroform per gram of ethanol so decreased the ethylene content of the effluent gases (and the accuracy of the analysis) that it was not thought practical. The optimum aqueous ethanol solution contained about 10% ethanol with higher and lower concentrations giving diminished yields. The best yield was obtained in the following run.

To a refluxing solution of 200 g. (3.0 moles) of 85% potassium hydroxide in 150 ml. of water and 0.17 mole of ethanol was added 50 ml. (0.63 mole) of chloroform. The gas produced contained 0.216 mole of carbon monoxide and 0.0127 mole of ethylene (7.5% yield).

Reactions of Propanols and Butanols with Chloroform and Alkali.—The results shown in Table I were obtained when these alcohols were subject to reaction conditions which were the same as those described above for ethanol, except for the following modifications. In the case of the butanols, the reflux condenser through which the evolved gases passed was kept at −10°. In the Orsat analysis, the propylene and *n*-butylenes were absorbed by 87% sulfuric acid and the isobutylene by 64% sulfuric acid.

Reaction of Cyclohexanol with Chloroform and Alkali.—The reaction was run by the procedure described for ethanol above but with double portions of reagents (0.34 mole cyclohexanol). When the reaction was complete, 250 ml. of olefin-free isoöctane was added to the flask and the material was distilled. From the distillate, 150 ml. of organic layer was separated, dried over sodium sulfate and fractionated. The first 75-ml. fraction (b.p. up to 97°) was analyzed for olefin by a bromometric method found satisfactory for a blank sample of cyclohexene and resembling that of Stanerson and Levin.[13] The material was found to contain 0.047 mole of cyclohexene (14% yield).

Reaction of Potassium *t*-Amyloxide with Chloroform.—Into a refluxing solution of 2.32 moles of potassium in 1,250 ml. of *t*-amyl alcohol, was dropped 0.73 mole of chloroform. The resultant gas was passed through a trap cooled to −78° and thence to a gas collection system in which 0.237 mole of carbon monoxide was found when the reaction was completed. The reaction mixture was distilled and the material condensing below 90° was combined with the very little material in the trap, and fractionated through a 30″ column, $^1/_2$ in. in diameter, packed with glass helices. Since infrared measurement showed the presence of *t*-amyl alcohol, the distillate was warmed with metallic potassium and redistilled. The resultant material was found by an infrared analysis to contain 78% 2-methyl-1-butene, 19% 2-methyl-2-butene and 2% chloroform. In reasonable agreement with this result, an olefin determination[14] showed the presence of 92% amylenes (assuming these to be the only olefins present). The total yield of amylenes was 0.15 mole.

The infrared analysis was carried out on the liquid material in isoöctane (2,2,4-trimethylpentane) solution using a 0.1-mm. cell in a Beckman IR-2 spectrophotometer. Use was made of the absorption maxima of 2-methyl-1-butene, 2-methyl-2-butene and chloroform at 11.24, 12.23 and 13.10 microns, respectively, at which the respective extinction coefficients in isoöctane solution were 134, 38 and 781. These data for the 2-methylbutenes were determined on pure samples obtained from the National Bureau of Standards. Beer's law was shown to be followed and synthetic mixtures were analyzed successfully by the method developed.

Reaction of Potassium Isopropoxide with Chloroform, Bromodichloromethane and Bromoform.—Potassium (1.06 moles) was dissolved in 1,100 ml. of isopropyl alcohol and 0.35 mole of chloroform in 30 ml. of isopropyl alcohol was added. The gases produced contained 0.107 mole of propylene and 0.147 mole of carbon monoxide. From 1.09 moles of potassium and 0.35 mole of bromodichloromethane, 0.111 mole of propylene and 0.163 mole of carbon monoxide were obtained similarly, while 1.08 moles of potassium and 0.36 mole of bromoform yielded 0.148 mole of propylene and 0.168 mole of carbon monoxide.

Acknowledgments.—We should like to express our thanks to the Georgia Tech World Student Fund for a fellowship to H. L. W. and to the Dow Chemical Company for the gift of the bromodichloromethane used in this investigation.

ATLANTA, GEORGIA

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[12] V. J. Altieri, "Gas Analysis—Testing of Gaseous Materials," American Gas Association, Inc., New York, N. Y., 1945.

[13] B. R. Stanerson and H. Levin, *Ind. Eng. Chem., Anal. Ed.*, **14**, 782 (1942).

[14] H. J. Lucas and D. Pressman, *ibid.*, **10**, 140 (1938).