Summary

Asymmetric condensation of glycolaldehyde to optically active sugars, through the decomposition of active salts of dihydroxymaleic acid to glycolaldehyde and carbonates, was not obtained on account of the precedence of the rate of decomposition over the rate of subsequent condensation. Choice of a condensation catalyst disclosed an unexpected stability in disodium dihydroxymaleate and necessitated the study of the decomposition mechanism. It is concluded from a consideration of reaction rates that the rate of decomposition of dihydroxymaleates is proportional: (1) to the concentration of non-ionized dihydroxymaleate molecules present, (2) to the degree of solvation of these molecules, and (3) to the oxidizing tension of the cations produced by dissociation of the dihydroxymaleate.

CARMEL-BY-THE-SEA, CALIFORNIA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF COLORADO]

THE ADDITION PRODUCTS OF METHYLETHYL KETONE WITH CHLOROFORM, BROMOFORM AND IODOFORM

BY JOHN B. EKELEY AND CARL J. KLEMME

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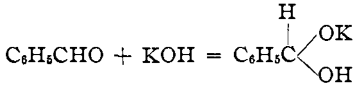
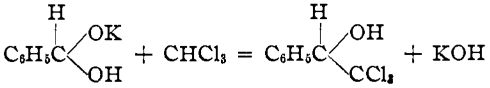
The course of the reaction between methylethyl ketone and chloroform, bromoform or iodoform in the presence of powdered potassium hydroxide may be inferred from the experiments of Willgerodt[1] and of Guedras.[2] When these investigators allowed acetone to react with the same reagents, trihalogen-*tertiary*-butyl alcohols were produced, $(CH_3)_2C(OH)CX_3$. The chlorine and bromine derivatives possess some therapeutic value; during the world war, the British Government used the chlorine compound mixed with desiccated antitetanic serum as an anodyne and as a mild antiseptic to dust wounds.

Jocicz[3] studied the behavior of benzaldehyde under similar conditions; he claims that the reaction may be described by the following equations.



$$C_6H_5CHO + KOH = C_6H_5\overset{H}{C}\begin{matrix}OK\\OH\end{matrix} \qquad (1)$$



$$C_6H_5\overset{H}{C}\begin{matrix}OK\\OH\end{matrix} + CHCl_3 = C_6H_5\overset{H}{C}\begin{matrix}OH\\CCl_3\end{matrix} + KOH \qquad (2)$$

It is evident that potassium hydroxide will react with chloroform simultaneously to produce potassium chloride and potassium formate; the solid residue gave tests for both of these compounds.

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[1] Willgerodt, *Ber.*, **14,** 2451 (1881); **15,** 2305 (1882); **16,** 1585 (1883).

[2] Guedras, *Compt. rend.*, **133,** 1011 (1901).

[3] Jocicz, *Chem. Centr.*, [5] **1,** 1013 (1897).

Our investigations show that methylethyl ketone does react with chloroform, with bromoform, and with iodoform in an analogous manner; the addition products, trihalogen-*tertiary*-amyl alcohols, are described below.

Experimental Part

Trihalogen-tertiary-amyl Alcohols.—Two molecular proportions each of chloroform, bromoform, and iodoform were mixed with one molecular proportion of methylethyl ketone in large Erlenmeyer flasks. Addition of finely powdered dry potassium hydroxide equal to one-fifth to one-eighth of the weight of the mixture caused vigorous reactions, so that the flasks were fitted with reflux condensers and the contents cooled. After the reactions had subsided, the flasks were allowed to stand for 24 hours until equilibrium was reached. The contents were then filtered, the excess reagents distilled, and the distillate was again treated with dry powdered potassium hydroxide. This was repeated several times until as much of the reaction products as possible had been secured from the original mixtures. The red-brown liquids thus obtained were in each case combined and distilled with steam. The compound obtained from chloroform, after being dried over anhydrous sodium sulfate, was purified by distillation under diminished pressure until the distillates showed a constant index of refraction. This could not be done in the case of the compounds from bromoform and iodoform, since they suffered considerable decomposition even on distillation under diminished pressure. These distillates were therefore repeatedly distilled with steam until on drying over anhydrous sodium sulfate they showed constant indices of refraction. The yields obtained from 25 g. of methylethyl ketone were, with chloroform 8–10 g., with bromoform 6–7 g., and with iodoform 5–6 g.

All were more or less yellow liquids with pungent odors and produced a numbing sensation when placed upon the tongue. They are not so stable as the corresponding compounds from acetone. The chloroform and bromoform derivatives are fairly stable in the dark, but the compound from iodoform decomposes perceptibly even when protected from the light. The instability of this compound presented some difficulties in obtaining and checking analytical results and it became necessary to analyze the sample as soon as possible.

The most interesting fact concerning these compounds is that the experimental molecular-refraction data obtained on the pure compounds are considerably greater than the theoretical values as calculated according to Eisenlohr, in the case of the iodoform compound the difference being 4.165 units. In this case the discrepancy might be referred to impurities in the substance due to decomposition but, in the case of the more stable bromoform compound, the discrepancy of three units can hardly be explained in this way. The striking fact is observed that the discrepancies increase with the atomic weight of the halogen.

Attempts to prepare analogous compounds from acetophenone proved unsuccessful.

Trichloro-*tert.*-amyl Alcohol.—B. p., 110–113°, with decomposition, at 620 mm. (atm. press. Boulder); d_4^{20}, 1.2128; n_D^{20}, 1.4460; M_D, calc. 41.479, found 42.107.

Analysis. Calc. for $C_5H_9OCl_3$: C, 31.34; H, 4.69; Cl, 55.61. Found: C, 31.20; H, 4.75; Cl, 55.69.

Tribromo-*tert.*-amyl Alcohol.—B. p., 130–135° (40 mm.), with decomposition; d_4^{20}, 1.8788; n_D^{20}, 1.5130; M_D, calc. 50.226, found 53.23.

Analysis. Calc. for $C_5H_9OBr_3$: C, 18.46; H, 2.76; Br, 73.84. Found: C, 18.86; H, 2.71; Br, 73.15.

Tri-iodo-*tert.*-amyl Alcohol decomposes before the boiling point is reached even under diminished pressure; d_4^{20}, 2.1438; n_D^{20}, 1.5680; M_D, calc. 65.845, found 71.11.

Analysis. Calc. for $C_5H_9OI_3$: C, 12.88; H, 1.93; I, 81.76. Found: C, 12.99; H, 2.08; I, 79.12.

Summary

1. Three compounds, trichloro-*tertiary*-amyl alcohol, tribromo-*tertiary*-amyl alcohol, and tri-iodo-*tertiary*-amyl alcohol, homologs of the corresponding derivatives of acetone, have been prepared. This reaction is apparently a general one for the simple aliphatic ketones. The chloroform and bromoform derivatives are fairly stable in the dark, decomposing under the influence of light and heat.
2. The molecular refractions of the compounds as experimentally determined are considerably greater than those calculated from Eisenlohr's values, and the discrepancies increase with the increasing atomic weight of the halogens.

BOULDER, COLORADO

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

THE IRREVERSIBLE REDUCTION OF ORGANIC COMPOUNDS.

I. THE RELATION BETWEEN APPARENT REDUCTION POTENTIAL AND HYDROGEN-ION CONCENTRATION

BY JAMES B. CONANT AND ROBERT E. LUTZ

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The irreversible reduction of organic substances has been often expressed in terms of a qualitative scheme of oxidation-reduction potentials of the various reagents employed, but except in the case of electrolytic reduction no attempt has been made to treat the subject quantitatively. The interpretations of the reduction processes which take place at the cathode during electrolysis are complicated by the two-phase system which is necessarily present and similar difficulties are encountered in considering the reducing action of metals and metallic combinations. In order to avoid these complications we have turned our attention at first to the development of a quantitative theory of those cases of reduction which