[CONTRIBUTION FROM THE RESEARCH LABORATORY OF MERCK & CO., INC.]

A New Method for the Preparation of Aldehydo Sugar Acetates

BY ELMER W. COOK AND RANDOLPH T. MAJOR

Aldehydo sugar acetates have been prepared by acetylation of the aldehydo mercaptals[1] followed by removal of the thio-acetal groups and also by acetylation of the aldehydo semicarbazones or oximes[2] with the subsequent removal of the semicarbazone or oxime groups.

A new method based upon Rosenmund's[3] method for the reduction of acyl chlorides to aldehydes by means of hydrogen in the presence of palladiumized barium sulfate has been found. The acetyl derivatives of the sugar acid chloride may be reduced almost quantitatively to aldehydo sugar acetates.

Experimental

Aldehydo-*d*-glucose Pentaacetate.—Pentaacetyl-*d*-gluconyl chloride[4] (5 g.) in 25 cc. of anhydrous xylene (dried over sodium) was heated under reflux in the presence of 2 g. of 5% palladiumized barium sulfate. Hydrogen was passed in at such a rate that the catalyst was kept in a lively suspension. The reduction was complete within one and one-half hours as shown by the absence of ammonium chloride fumes when a rod moistened with ammonium hydroxide was held in the escaping gases. Complete reduction may also be determined by passing the exit gases through water and testing for chloride ion. After reduction the hot xylene solution was filtered. Upon cooling aldehydo-glucose pentaacetate[5] crystallized. It was recrystallized from xylene; yield was nearly quantitative; m. p. 117–118°; $[\alpha]^{20}\mathrm{D}$ $-3°$ (dry chloroform, *c*, 2); $[\alpha]^{20}\mathrm{D}$ $+10°$ (in methanol, 5 min., *c*, 2) changing slowly in the dextro direction.

Anal. Calcd. for $C_{16}H_{22}O_{11}$: C, 49.21; H, 5.68. Found: C, 49.52, 49.34; H, 5.85, 5.60.

Summary

Aldehydo-*d*-glucose pentaacetate has been prepared by the reduction of pentaacetyl-*d*-gluconyl chloride.

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[1] Wolfrom, THIS JOURNAL, **51**, 2188 (1929).

[2] Wolfrom, Georges and Soltzberg, *ibid.*, **56**, 1794 (1934).

[3] Rosenmund, *Ber.*, **51**, 585 (1917).

[4] Major and Cook, THIS JOURNAL, **58**, 2474 (1936).

[5] Wolfrom, *ibid.*, **51**, 2191 (1929).

RAHWAY, N. J. RECEIVED SEPTEMBER 25, 1936

[CONTRIBUTION FROM THE BAKER LABORATORY OF CHEMISTRY AT CORNELL UNIVERSITY]

Temperature–Concentration Equilibria in the Systems Chloroform–Chlorine and Chloroform–Bromine. The Chloroform Chlorinates[1]

BY J. ALLEN WHEAT, II, AND A. W. BROWNE

In view of the well-known fact that chlorine occupies a higher position than bromine in the activity series of electronegative elements and radicals[2] arranged in the descending order of electronegativity, it has seemed reasonable to suppose that dissolved chlorine should be removed from chloroform more readily than dissolved bromine on treatment with metallic sodium. Quite the opposite is true.

As the result of an extended series of experiments in which chloroform solutions containing free bromine and chlorine in molar ratios (Br_2: Cl_2) ranging from about 0.25 to 2.50 were subjected at room temperature to the action of metallic sodium in excess, it was found that a considerable amount of free chlorine remained in solution in every case after complete removal of the bromine had been effected.

This entirely unanticipated result might conceivably be attributable either (1) to chemical action of the chlorine upon the chloroform and lack of similar action on the part of the bromine, or (2) to formation of one or more coördination compounds between molecular chlorine and chloroform and either (a) non-formation of similar bromine compounds, or (b) formation of relatively less stable bromine compounds. The first explanation is clearly invalidated by the presence of "free" (though possibly coördinated) chlorine in the residual solutions, as already noted, and by

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[1] This article is based upon the thesis presented to the Faculty of the Graduate School of Cornell University by Joseph Allen Wheat, II, in partial fulfilment of the requirements for the degree of Master of Science.

[2] Birckenbach and Kellermann, *Ber.*, **58**, 786, 2377 (1925).

the absence of hydrogen chloride and carbon tetrachloride from these solutions, as well as from controls to which no sodium was added.

In order to test the validity of the second explanation an investigation of the temperature–concentration equilibria in the binary systems chloroform–chlorine and chloroform–bromine has been undertaken. The results of this investigation are presented herewith.

Experimental Procedure.—Freezing points in the systems under investigation were determined in the conventional manner with the aid of a calibrated pentane thermometer, and with liquid air or solid carbon dioxide as refrigerant. The mixtures of chloroform and chlorine were quantitatively synthesized either (1) by introducing successive measured volumes of chlorine gas into a known amount of chloroform, or (2) by adding successive measured volumes of chloroform to a known amount of liquid chlorine. The composition of the system was accurately determined at the end of each series of temperature measurements, by treatment with potassium iodide in excess, and titration of the liberated iodine against standard sodium thiosulfate. The absence of hydrogen chloride and carbon tetrachloride from the solutions justifies the conclusion that no *chloridation*[3] of the chloroform has taken place under the conditions prevailing in the experiments.

TABLE I

TEMPERATURE–CONCENTRATION OR SOLUBILITY DATA OF THE SYSTEM $CHCl_3$–Cl_2

Temp., °C.	Concn., mole. % Cl_2	Curve (Fig. 1)
− 63.5	0.0	A. (Solid $CHCl_3$, liq., vapor)
− 64.8	3.8	AB. (Solid $CHCl_3$, satd. soln., vapor)
− 67.5	7.5	
− 70.5	11.0	
− 74.0	14.3	
− 77.5	17.5	
− 81.0	20.3	
− 84.0	23.2	
(− 90.0)	25.0	B. (Eutectic: solid $CHCl_3$, solid $(CHCl_3)_2{\cdot}Cl_2$, satd. soln., vapor)
− 88.5	25.3	BCD. (Solid $(CHCl_3)_2{\cdot}Cl_2$, satd. soln., vapor)
− 84.5	25.8	
− 82.0	28.6	
− 81.0	30.6	
− 79.5	32.7	
− 80.5	32.9	
− 82.0	34.9	
− 84.5	37.9	
− 87.5	40.0	
− 91.0	42.7	
− 94.0	44.3	
− 97.5	45.5	
−102.0	47.5	D. (Eutectic: solid $(CHCl_3)_2{\cdot}Cl_2$, solid $CHCl_3{\cdot}Cl_2$, satd. soln., vapor)
−100.0	48.0	DEF. (Solid $CHCl_3{\cdot}Cl_2$, satd. soln., vapor)
− 98.0	48.6	
− 97.0	49.0	
− 99.0	51.8	
−101.5	54.1	
−105.0	56.6	
−107.5	58.5	
−111.0	60.5	
−112.0	61.6	
−114.5	63.0	
−117.0	64.0	
(−118.0)	64.7	F. (Eutectic: solid $CHCl_3{\cdot}Cl_2$, solid $CHCl_3{\cdot}2Cl_2$, satd. soln., vapor)
−116.0	65.3	FGH. (Solid $CHCl_3{\cdot}2Cl_2$, satd. soln., vapor)
−113.0	66.4	
−115.5	68.0	
−118.5	68.9	
(−121.0)	69.3	H. (Eutectic: solid $CHCl_3{\cdot}2Cl_2$, solid $CHCl_3{\cdot}3Cl_2$, satd. soln., vapor)
−118.0	70.8	HIJ. (Solid $CHCl_3{\cdot}3Cl_2$, satd. soln., vapor)
−116.0	72.9	
−116.0	76.0	
−118.5	78.0	
−121.0	79.0	
(−123.0)	79.1	J. (Eutectic: solid $CHCl_3{\cdot}3Cl_2$, solid Cl_2, satd. soln., vapor)
−121.7	81.0	JK. (Solid Cl_2, satd. soln., vapor)
−118.0	84.2	
−114.5	87.8	
−108.4	93.5	
−104.5	97.8	
−102.0	100.0	K. (Solid Cl_2, liquid, vapor)

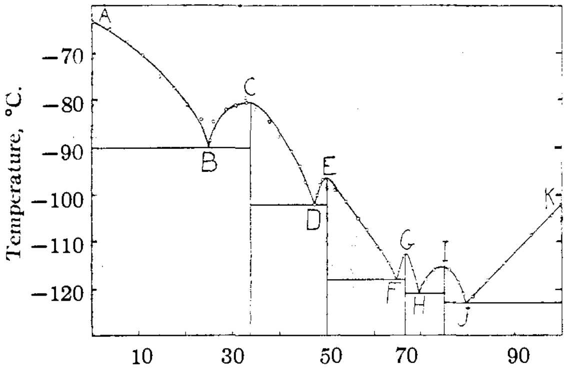

Fig. 1.—Freezing point *vs.* composition in system of $CHCl_3$–Cl_2.

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[3] Since the term chlorination seems appropriate as a means of designating the process by which solvates ("chlorinates") are formed in liquid chlorine solutions, it is suggested that *chloridation* be used for the process of chloride formation.

The mixtures of chloroform and bromine were prepared in each case by bringing together accurately measured volumes of the two liquid components.

Results Obtained.—Temperature–concentration data of the system chloroform–chlorine are presented in Table I and are plotted in Fig. 1.

Temperature–concentration data of the system chloroform–bromine are presented in Table II and are plotted in Fig. 2.

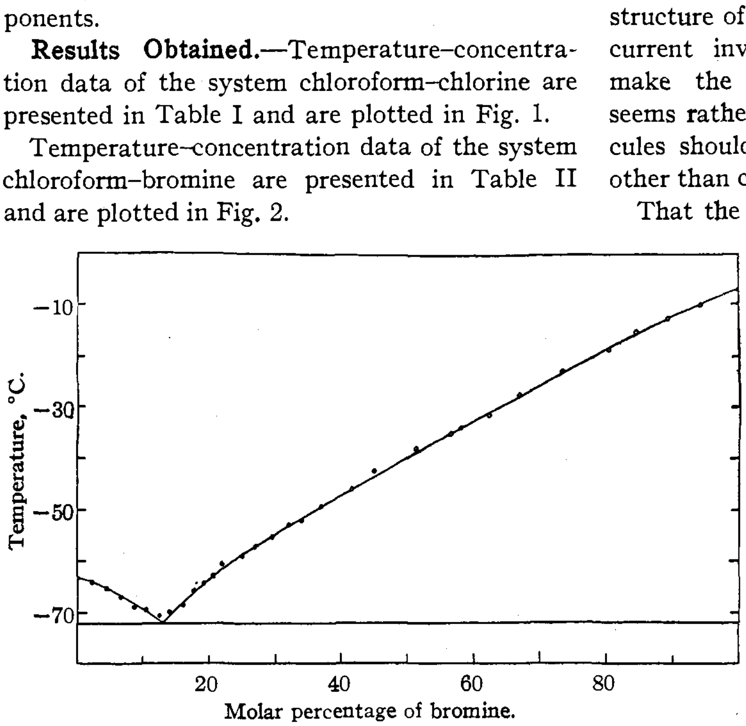


Fig. 2.—Temperature–concentration curves of system chloroform–bromine.

Table II

Temperature–Concentration or Solubility Data of the System $CHCl_3$–Br_2

Temp., °C.	Concn., mol. % Br_2	Temp., °C.	Concn., mol. % Br_2
−63.5	0.0	−53.0	32.0
−64.0	2.1	−52.0	34.0
−65.5	4.5	−49.5	37.1
−67.0	6.5	−46.0	41.5
−69.0	8.5	−42.5	45.1
−69.5	10.6	−38.0	51.5
−70.5	12.4	−35.0	56.4
−70.0	14.0	−34.0	58.0
−68.5	15.9	−31.5	62.2
−66.0	17.5	−27.5	67.5
−64.5	18.9	−23.0	73.4
−63.0	20.5	−18.5	80.6
−61.0	22.0	−15.0	84.6
−59.5	24.8	−12.5	89.4
−57.5	27.3	−10.0	94.4
−55.5	29.7	− 7.0	100.0

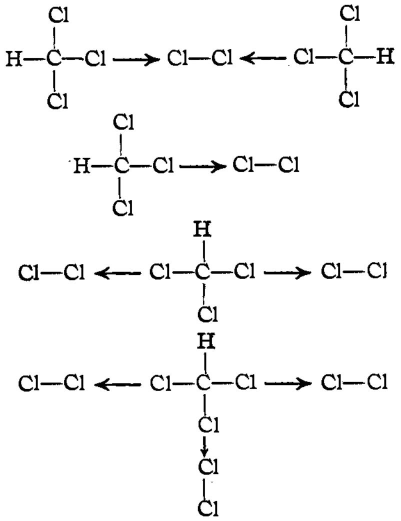
Discussion of Results.—It is obvious from the foregoing that bromine forms no solvates with chloroform, while chlorine forms four solvates, with congruent melting points, as follows:

(1) chloroform hemichlorinate, $(CHCl_3)_2 \cdot Cl_2$, −80.0°
(2) chloroform monochlorinate, $CHCl_3 \cdot Cl_2$, −96.5°
(3) chloroform dichlorinate, $CHCl_3 \cdot 2Cl_2$, −112.5°
(4) chloroform trichlorinate, $CHCl_3 \cdot 3Cl_2$, −115.0°

While no evidence whatsoever concerning the structure of these compounds is furnished by the current investigation, the authors venture to make the following tentative statement. It seems rather improbable that the chlorine molecules should be attached to the chloroform by other than coördinate links.

That the chlorine does not coördinate through the hydrogen of the chloroform is attested (1) by the paucity of evidence, up to the present time, that coördination through hydrogen attached to carbon is likely to occur;[4] (2) by the failure of the authors to obtain a chloroform tetrachlorinate; and (3) by the existence of a carbon tetrachloride tetrachlorinate.[5]

On the assumption that coördination takes place through the chlorine of the chloroform it is conceivable that this chlorine might serve either (1) as the acceptor, or (2) as the donor. For reasons that may be reserved for later discussion it seems that the latter alternative is preferable. The following tentative formulas are therefore suggested as the best present means of indicating the structure of the four chlorinates of chloroform



$$\mathrm{H{-}\underset{\underset{Cl}{|}}{\overset{\overset{Cl}{|}}{C}}{-}Cl \longrightarrow Cl{-}Cl \longleftarrow Cl{-}\underset{\underset{Cl}{|}}{\overset{\overset{Cl}{|}}{C}}{-}H}$$

$$\mathrm{H{-}\underset{\underset{Cl}{|}}{\overset{\overset{Cl}{|}}{C}}{-}Cl \longrightarrow Cl{-}Cl}$$

$$\mathrm{Cl{-}Cl \longleftarrow Cl{-}\underset{\underset{Cl}{|}}{\overset{\overset{H}{|}}{C}}{-}Cl \longrightarrow Cl{-}Cl}$$

$$\mathrm{Cl{-}Cl \longleftarrow Cl{-}\underset{\underset{\underset{\underset{\underset{Cl}{|}}{Cl}}{\downarrow}}{Cl}}{|}}{\overset{\overset{H}{|}}{C}}{-}Cl \longrightarrow Cl{-}Cl}$$

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[4] See N. V. Sidgwick, "The Electronic Theory of Valency," Oxford University Press, Oxford, England, 1927, p. 117.

[5] It has been established by a series of preliminary experiments performed in this Laboratory that carbon tetrachloride forms a tetrachlorinate, $CCl_4 \cdot 4Cl_2$, which shows a congruent melting point at −113°. Investigation of this system, and of various binary systems containing inorganic and organic halides is now in progress in this Laboratory, and results will be communicated in later articles.

Summary

The formation of four chlorinates of chloroform has been demonstrated during an investigation of the temperature–concentration relations of the system chloroform–chlorine:

(1) *chloroform hemichlorinate*, $(CHCl_3)_2\cdot Cl_2$ (m. p. −80.0°)
(2) *chloroform monochlorinate*, $CHCl_3\cdot Cl_2$ (m. p. −96.5°)
(3) *chloroform dichlorinate*, $CHCl_3\cdot 2Cl_2$ (m. p. −112.5°)
(4) *chloroform trichlorinate*, $CHCl_3\cdot 3Cl_2$ (m. p. −115°)

The five eutectic points are located, respectively, at −90, −102, −118, −121 and −123°.

On the assumption that one or more atoms of chlorine in the chloroform may act as donor to the free chlorine, tentative structural formulas for the chlorinates have been suggested.

Bromine forms no coördination compounds with chloroform. The eutectic point of the system chloroform–bromine is located at −72°.

ITHACA, N. Y. RECEIVED JUNE 22, 1936

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY]

Temperature Dependence of the Energy of Activation in the Rearrangement of N-Chloroacetanilide

BY JOHN O. PERCIVAL AND VICTOR K. LA MER

Introduction

Until recently it has been an almost universal assumption to consider the energy of activation, defined as $E_{\text{act}} = RT^2(\mathrm{d}\ln k/\mathrm{d}T)$, as independent of the temperature. In 1933 La Mer[1,2] showed that Tolman's statistical development[3] demanded in general that E_{act} must be a function of temperature. He pointed out the importance of considering not only the energy but also the entropy and consequently the free energy of activation as concepts important for the interpretation of reaction velocity. A similar treatment involving a more explicit use of statistical formulas,[4,5] or the concept of an energy surface[6] for the calculation of the properties of the state and the reactivity of the intermediate complex for gaseous reactions[7] has proved useful in the hands of the authors cited.[8]

The reluctance in many quarters toward accepting E_{act} as a function of temperature arises from the fact that the precision obtainable in the study of the kinetics of gaseous reactions is rarely sufficient to establish small variations. On the other hand, the situation is quite different for reactions in solution.

A reinvestigation of the depolymerization of diacetone alcohol in the presence of dilute sodium hydroxide has established that $\mathrm{d}E_{\text{act}}/\mathrm{d}T$ not only may be surprisingly large, but that E_{act} reaches a maximum at about 35°.[9]

Since further information regarding the behavior of the E_{act} for different types of reaction is of importance for the elucidation of chemical kinetics, we have studied the rearrangement of N-chloroacetanilide to C-chloroacetanilide in 0.2 molal hydrochloric acid, a reaction which requires simultaneous catalysis by H^+ and Cl^- ions. Harned and Seltz[10] found that E_{act} increases with temperature, but their E_{act} values do not agree with those which we calculate from Rivett's[11] earlier work, as shown in Fig. 1. The length of the arrows indicates the probable experimental error.

A preliminary study disclosed disturbing factors which had not been considered previously: *e. g.* (a) the possibility of interfering side reactions which might invalidate conclusions regarding E_{act}; (b) the unreliability of certified thermometers as temperature standards. We will present evidence that side reactions are insignificant, and will submit more precise values for E_{act} over a carefully selected set of temperatures, using an improved analytical technique.

Mechanism

The mechanism of the conversion has received

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(1) V. K. La Mer, *J. Chem. Phys.*, **1**, 289 (1933).

(2) V. K. La Mer, THIS JOURNAL, **55**, 1739 (1933).

(3) R. C. Tolman, "Statistical Mechanics," Chemical Catalog Co., New York, 1927, pp. 259–269.

(4) W. H. Rodebush, *J. Chem. Phys.*, **1**, 440 (1933).

(5) O. K. Rice and H. Gershinowitz, *ibid.*, **2**, 853 (1934).

(6) H. Eyring and N. Polanyi, *Z. physik. Chem.*, **12B**, 279 (1931).

(7) H. Eyring, *J. Chem. Phys.*, **3**, 107 (1935).

(8) Wynne-Jones and Eyring, *ibid.*, **3**, 492 (1935).

(9) V. K. La Mer and M. L. Miller, THIS JOURNAL, **57**, 2674 (1935).

(10) H. S. Harned and H. Seltz, *ibid.*, **44**, 1475 (1922).

(11) A. C. D. Rivett, *Z. physik. Chem.*, **82**, 201 (1913).