by the pyrolysis of an acetate may also. There is one feature concerning xanthates, however, which prevents such a conclusion. It has been reported[21,22] that some xanthates are converted to a "stable form" if they are distilled. Such "stable forms" are not the dithiocarbonates but they have the same composition, molecular weight and melting point as the xanthate from which they are derived. The *cis*-xanthate, it will be observed, had to be distilled in order to obtain a pure sample. We have no evidence of it, but if such a "stable form" resulted from the distillation of the *cis*-compound, data such as those shown in Fig. 1 might be obtained.

Concerning pyrolysis of the acetates, it is certainly clear that the *cis*-form is more stable than the *trans*-form. The fact that 2-methylnaphthalene, rather than 2-methyl-3,4-dihydronaphthalene, was isolated, however, may indicate that the acetic acid measured in the pyrolysis of the *cis*-acetate was formed by another path of reaction.

Acknowledgment.—We are indebted to Miss Rachel Kopel and Miss Emily Davis for the microanalyses reported in this paper.

Summary

Two isomers of 2-methyl-1-tetralol have been synthesized. One of these, which we believe to be the *trans*-isomer, was prepared by a sodium-ethanol reduction of 2-methyl-1-tetralone. The other, which we believe to be the *cis*-isomer, was prepared by hydrogenation of the same ketone in the presence of Raney nickel.

The thermal decomposition of *trans*-2-methyl-1-tetralyl acetate and methyl-*trans*-2-methyl-1-tetralylxanthate proceeds at considerably lower temperatures than does the decomposition of the corresponding *cis*-isomers. These results are in agreement with the point of view that the Chugaev reaction and the simple thermal decomposition of acetates involve the intermediate formation of a transitory six-membered ring with a *cis*-β-hydrogen atom.

URBANA, ILLINOIS RECEIVED DECEMBER 17, 1949

(21) McAlpine, *J. Chem. Soc.*, 1114 (1931); 906 (1932).

(22) Bulmer and Mann, *ibid.*, 666 (1945).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND THE DEFENSE RESEARCH LABORATORY, THE UNIVERSITY OF TEXAS]

Allylic Chlorides. XI. Cuprous Chloride Catalyzed Hydrolysis of Several Allylic Chlorides[1]

BY LEWIS F. HATCH, ALLEN N. BROWN AND HOWARD P. BAILEY

There have appeared in the literature several references[2,3,4] to the cuprous chloride catalyzed hydrolysis of allylic chlorides. The present paper presents an extension of these studies to include a number of compounds not heretofore investigated. From these data it has been possible to elucidate the influence on this reaction of certain substituents on both the number one and number two carbon atoms of allyl chloride and to assign geometrical configuration to the two isomers of 1,3-dichloro-2-methylpropene.

Experimental

Cuprous Oxide.—Baker C. P. Analyzed (98.8%) cuprous oxide was used without further purification.

Hydrochloric Acid.—The 1.5% hydrochloric acid used in this investigation was prepared by diluting 33 ml. of Reagent Grade concentrated hydrochloric acid to one liter with distilled water.

All other inorganic reagents were of Reagent Grade or its equivalent.

The following compounds were furnished for this investigation by Shell Chemical Co., San Francisco, California, and in each case the compound was distilled through a four-foot, glass-helix packed vacuum jacketed column before use.

Allyl Chloride.—Boiling point 44.4° (744 mm.).

Methallyl Chloride.—Boiling point 72.1° (742 mm.).

2,3-Dichloro-1-propene.—Boiling point 93.4° (746 mm.).

cis- and *trans*-**1,3-Dichloropropene.**—These isomers were separated using a Podbielniak Hypercal distillation column, then redistilled through a two-foot glass-helix packed column immediately before use.

cis-**1,3-Dichloropropene.**—Boiling point 104° (746 mm.); n^{25}_D 1.4650 (lit.[5] n^{25}_D 1.4652).

trans-**1,3-Dichloropropene.**—Boiling point 112° (745 mm.); n^{25}_D 1.4712 (lit.[5] n^{25}_D 1.4712).

2-Bromo-3-chloro-1-propene.—The 2-bromo-3-chloro-1-propene (Halogen Chemicals, Columbia, South Carolina) was distilled at a pressure of 50 mm. through a two-foot glass-helix packed column. The fraction used boiled at 45.7°; n^{25}_D 1.4968 (lit.[6] n^{25}_D 1.4968). This compound was not stable and it was necessary to use it immediately after fractionation.

1,1,3-Trichloro-2-methyl-1-propene.—This trichloride (Halogen and Perfume Chemicals, Columbia, South Carolina) was distilled at 36 mm. pressure through a two-foot glass-helix packed column. The fraction used boiled at 71.5°; n^{25}_D 1.4932 (lit.[6] n^{25}_D 1.4933).

α and β-**1,3-Dichloro-2-methylpropene.**—The isomeric 1,3-dichloro-2-methylpropenes were prepared from methallyl chloride[7] which was chlorinated to 1,2,3-trichloro-2-methylpropane using sulfuryl chloride. The trichloride was dehydrochlorinated to a mixture of the 3-chloro-2-methyl-2-propen-1-ols which was separated by means of a

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(1) Presented in part at the Southwest Regional Meeting of the American Chemical Society, Shreveport, La., December 11, 1948.

(2) Williams, *Trans. Am. Inst. Chem. Engs.*, **37**, 157 (1941).

(3) Williams, *Chem. Met. Eng.*, **47**, 834 (1940).

(4) (a) Hatch and Estes, THIS JOURNAL, **67**, 1730 (1945); (b) Hatch and Roberts, *ibid.*, **68**, 1196 (1946); (c) Hatch and Ballin, *ibid.*, **71**, 1041 (1949); (d) Hatch and Gerhardt, *ibid.*, **71**, 1679 (1949).

(5) Hatch and Perry, *ibid.*, **71**, 3262 (1949).

(6) Hatch, Gordon and Russ, *ibid.*, **70**, 1093 (1948).

(7) Hatch, Russ and Gordon, *ibid.*, **69**, 2614 (1947).

Podbielniak Hypercal distillation column. The chloroalcohols were converted to the corresponding dichlorides using concentrated hydrochloric acid.

α-1,3-Dichloro-2-methylpropene.—Boiling point 80° (120 mm.); n^{25}_D 1.4699 (lit.[7] n^{25}_D 1.4698).

β-1,3-Dichloro-2-methylpropene.—Boiling point 82° (120 mm.), n^{25}_D 1.4742 (lit.[7] n^{25}_D 1.4740).

Cuprous Chloride Catalyzed Hydrolysis.—The various allylic chlorides were hydrolyzed using a procedure previously described.[4c] The method was modified only to the extent of varying the temperature at which the hydrolysis took place. The data obtained are given in Fig. 1 and in Table I.

TABLE I

CUPROUS CHLORIDE CATALYZED HYDROLYSIS OF VARIOUS ALLYLIC CHLORIDES

Compound	Time, min.	Temp., °C.	Reacted, %
$C(CH_3)_2=CHCH_2Cl$[a]	60	0	81.8
$CH_2=C(CH_3)CH_2Cl$	60	40	84.0
$CH_2=CHCH_2Cl$	60	40	77.6
$CH_2=CBrCH_2Cl$	60	70	15.1
$CH_2=CClCH_2Cl$	60	70	12.4
$CCl_2=C(CH_3)CH_2Cl$	120	70	5.0
β-$CCH_3(Cl)=CHCH_2Cl$[b]	60	40	42.7
α-$CCH_3(Cl)=CHCH_2Cl$	60	40	32.8
cis-$CHCl=CHCH_2Cl$	60	40	11.2
	60	70	73.4
trans-$CHCl=CHCH_2Cl$	30	70	95.9
α-$CHCl=C(CH_3)CH_2Cl$	60	70	13.0
β-$CHCl=C(CH_3)CH_2Cl$	60	70	53.6

[a] Hatch and Gerhardt, THIS JOURNAL, **71**, 1679 (1949).
[b] Hatch and Ballin, *ibid.*, **71**, 1041 (1949).

Discussion

Table I contains a list of various allylic chlorides which have been hydrolyzed under nearly comparable conditions. From these data it is clear that the electron attracting or releasing ability of the substituent on the number two carbon atom of allyl chloride has a marked influence on the ease of cuprous chloride catalyzed hydrolysis. The order of reactivity in respect to atoms and the methyl group is $CH_3 > H > Br > Cl$. This order does not hold, however, when there is a chlorine atom on the number one carbon atom for both isomers of 1,3-dichloropropene are more reactive than either isomer of 1,3-dichloro-2-methylpropene.

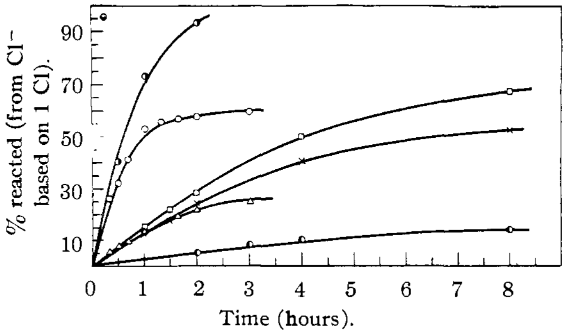


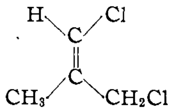
Fig. 1.—Cuprous chloride catalyzed hydrolysis of various allylic chlorides at 70°: ◒, *trans*-1,3-dichloropropene; ◑, *cis*-1,3-dichloropropene; ○, β-1,3-dichloro-2-methylpropene; □, 2-bromo-3-chloro-1-propene; ×, 2,3-dichloro-1-propene; △, α-1,3-dichloro-2-methylpropene; ◐, 1,1,3-trichloro-2-methyl-1-propene.

The situation in regard to substituents on the number one carbon atom of allyl chloride is in some cases complicated by the concomitant influence of geometrical isomerism and the possible removal of the vinyl chlorine atom. The two compounds with substituents on the number one carbon atom which do not exhibit geometrical isomerism are 1-chloro-3-methyl-2-butene and 1,1,3-trichloro-2-methyl-1-propene, and they clearly show the relationship between electron releasing ability and reactivity. The compound containing the two electron attracting chlorine atoms hydrolyzes only slightly more than would be expected by an S_N1 reaction in water. This lack of reactivity is in contrast to the enhanced reactivity of this same compound toward potassium iodide in acetone[6] and sodium ethoxide in ethanol.[8] This is also in contrast to the enhanced reactivity of the compound with two methyl groups on the number one carbon atom toward all three reactions.

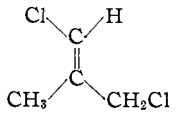
The replacement of a hydrogen atom on the number one carbon atom by a chlorine atom also results in a diminution in reactivity for both allyl chloride (1,3-dichloropropene) and methallyl chloride (1,3-dichloro-2-methyl-1-propene). When the remaining hydrogen atom on the number one carbon atom of 1,3-dichloropropene is replaced by a methyl group, there is the expected increase in reactivity at least when the chlorine atom and chloromethyl group are *cis* to one another.[9]

We believe that the catalytic effect of cuprous chloride is due to the formation of some type of coördination complex at the double bond, similar in character to those proposed by Keefer and Andrews[10] for allyl alcohol. The data show that the reactivity of the allylic chloride is sensitive to the release of electrons to the double bond.

When the vinyl chlorine and the chloromethyl group of 1,3-dichloropropene are in the *cis* position, the reactivity is less than when these groups are in the *trans* position. By analogy to these isomers, it follows that the alpha form of 1,3-dichloro-2-methylpropene has the *cis* (Cl, CH_2Cl) configuration and the beta isomer has the *trans* (Cl, CH_2Cl) configuration because α-1,3-dichloro-2-methylpropene is hydrolyzed less readily than the beta isomer. The



Alpha (*cis*)



Beta (*trans*)

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[8] Hatch and Alexander, THIS JOURNAL, **71**, 1037 (1949).

[9] For the configuration of the 1,3-dichloro-2-butenes, see Hatch and Hudson, *ibid.*, **72**, 2505 (1950).

[10] Keefer and Andrews, *ibid.*, **71**, 1723 (1949).

1,3-dichloro-2-butenes also show the same relationship between structure and reactivity, but in this case there is considerable removal of the vinyl chlorine atom during the reaction, thus the reactions may not be strictly analogous.

Acknowledgment.—The authors wish to thank both the Research Corporation, New York, and the Defense Research Laboratory, The University of Texas, for their financial assistance in support of these and related investigations.

Summary

Several allylic chlorides have been hydrolyzed using cuprous chloride as a catalyst to determine the effect of replacing one or more hydrogen atoms on the number one and number two carbon atoms of allyl chloride by a methyl group, a chlorine atom or a bromine atom.

When a hydrogen atom is replaced by a halogen atom in either position, the rate of hydrolysis is less than for allyl chloride.

The rates of hydrolysis of methyl substituted allyl chlorides are greater than for unsubstituted allyl chloride.

It is believed that the catalytic effect of cuprous chloride is due to the formation of some type of coördination complex at the double bond, similar in character to those previously proposed for allyl alcohol.

By analogy to the reactivity of the isomers of 1,3-dichloropropene, the low boiling (alpha) isomer of 1,3-dichloro-2-methylpropene has been assigned the geometrical configuration with the chlorine atom and the chloromethyl group in the *cis* position; the beta isomer has been assigned the structure with the chlorine atom and the chloromethyl group in the *trans* position.

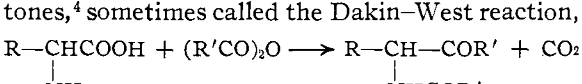
AUSTIN, TEXAS RECEIVED OCTOBER 14, 1949

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

A Study of the Basic Catalysis of the Acylation of α-Acylamino Acids[1,2]

BY SCOTT SEARLES[3] AND GEORGE J. CVEJANOVICH

The base-catalyzed reaction of α-amino acids with acid anhydrides to form α-acylaminoketones,[4] sometimes called the Dakin–West reaction,



$$\underset{\displaystyle NH_2}{R\text{—}CHCOOH} + (R'CO)_2O \longrightarrow \underset{\displaystyle NHCOR'}{R\text{—}CH\text{—}COR'} + CO_2$$

is of value in the synthesis of oxazoles. Recent work by Wiley and Borum[5] and by Cleland and Niemann[6] has extended its useful scope, but several phases of the mechanism remain somewhat obscure.

The report[4] that the reaction seems to be catalyzed by only pyridine and its homologs appeared surprising, but qualitative experiments carried out in this Laboratory indicated that certain tertiary amines also are effective catalysts, whereas certain pyridine homologs are quite ineffective. Since the reaction lends itself readily to quantitative measurements, a kinetic study of the catalysis by different bases has been made.

Acylamino acids were used as starting materials rather than the corresponding amino acids, since the former were completely soluble in the reaction mixture and gave simpler kinetic data. The reaction is followed conveniently by measuring the amount of carbon dioxide evolved, which is formed as a reaction product in equimolar amounts with the α-acetylaminoketone. Except in unfavorable cases, this is the only significant reaction and high yields of the ketone are well-known.[7] We found that the yield of carbon dioxide usually is practically the theoretical for the amount of amino acid used and that side reactions leading to the formation of resinous products do not appear to give rise to carbon dioxide.

Experimental

Materials.—α-Acetamidophenylacetic acid was prepared by slow addition of twice the theoretical amount of acetic anhydride to a solution of α-aminophenylacetic acid in sodium hydroxide at 5° and recrystallized from water; yield, 50%; m. p. 199°. Benzoylalanine was prepared by the method of Carter and Stevens[8]; m. p. 162–163°. Benzoylphenylalanine and α-benzamidophenylacetic acid were prepared also by this method; m. p. 185–186° and 174°, respectively.

Acetic anhydride was purified by fractional distillation over sodium acetate, the 139–140° fraction being used. Benzoic anhydride and 4,4′-dinitrobenzoic anhydride were recrystallized from benzene and petroleum ether and from acetone, respectively; m. p. 42° and 189–190°, respectively. The amines used as catalysts were purified by fractional distillation after drying over barium oxide, except 3- and 4-picoline, which were purified by means of their oxalate salts.[9] Dioxane, which was used as the solvent for much of this work, was purified by the methods of Hess and Frohm.[10]

Procedure.—The reactions were carried out in a 50 ml. flask placed in a steam jacket and equipped with a mercury-sealed stirrer and a water-cooled gas outlet tube. The temperature was 99.5–99.8°, constant to 0.05° in each run. Two standard types of reaction mixtures were used: (1) a solution of 0.01 mole of acylamino acid or azlactone, 20 ml. of pyridine and 10 ml. of acetic anhydride, used for

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(1) Much of this material is abstracted from the B.S. thesis of George J. Cvejanovich, University of Illinois, June, 1948.

(2) Presented before the 116th meeting of the American Chemical Society, Atlantic City, N. J., September, 1949.

(3) Department of Chemistry, Northwestern University, Evanston, Illinois.

(4) Dakin and West, *J. Biol. Chem.*, **78**, 91, 745 (1928).

(5) Wiley and Borum, THIS JOURNAL, **70**, 2005 (1948).

(6) Cleland and Niemann, *ibid.*, **71**, 841 (1949).

(7) Wiley, *J. Org. Chem.*, **12**, 43 (1947).

(8) Carter and Stevens, *J. Biol. Chem.*, **138**, 627 (1941).

(9) Lindstrom, *J. Chem. Soc.*, 242 (1940).

(10) Hess and Frohm, *Ber.*, **71**, 2627 (1938).