[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, PURDUE UNIVERSITY]

The Hydrolysis of 1,2-Dichloro-2-methylpropane Producing Isobutyraldehyde[1,2]

BY J. M. HERSH AND R. E. NELSON

Moderate quantities of 1,2-dichloro-2-methylpropane have been available from the thermal chlorination of isobutane.[3] The ready production of this material has made it desirable to study the possibility of its conversion into more desirable derivatives, such as isobutyraldehyde. The first study of this subject was that of Newlin,[4] who succeeded in showing that the hydrolysis of 1,2-dichloro-2-methylpropane resulted in the formation of a considerable amount of hydrochloric acid and an aldehyde accepted as isobutyraldehyde. This work was carried out in the liquid phase at temperatures below 100° using the 1,2-dichloride from the thermal chlorination of isobutane. In it there were several anomalies that called for further study and clarification. The present study of this reaction had as its objectives, (1) the preparation of pure 1,2-dichloro-2-methylpropane from some source other than isobutane, (2) the comparison of dichlorides from several sources in typical hydrolysis reactions, (3) the study of the hydrolysis reaction in the liquid phase and in the vapor phase in the presence of substances which might have a catalytic effect on the reaction, and (4) the separation and identification of isobutyraldehyde. Purified 1,2-dichloro-2-methylpropane prepared from *t*-butyl alcohol was hydrolyzed, mainly in the vapor phase in the presence of contact catalysts, to produce isobutyraldehyde.

Experimental

Preparation of 1,2-Dichloro-2-methylpropane.—The desired synthesis from some source other than isobutane led to the use of tertiary and isobutyl alcohols. The procedures followed in this preparation were: (a) dehydration to isobutene with subsequent chlorination,[5] (b) direct chlorination of *t*-butyl alcohol,[6] and (c) the low temperature chlorination of 2-chloro-2-methylpropane prepared from the alcohol by treatment with hydrochloric acid.[7] Of these methods, the last was markedly successful in producing 1,2-dichloro-2-methylpropane of desirable purity. This dichloride has a clean, mild, sweetish odor; even after six months' standing it is free of hydrogen chloride. No product of thermal chlorination has yet been prepared which compares with this synthesized material in stability, freedom from hydrogen chloride and mildness. The above preparation of 1,2-dichloro-2-methylpropane allowed a reasonable assumption that it was not contaminated with 1,1-dichloro-2-methylpropane, the only other dichloride which would be difficult to remove by distillation. Pure 1,2-dichloro-2-methylpropane has the following physical constants: b. p. 38.6–39.2° (70 mm.), 59–60° (150 mm.) and 106.5° (760 mm.) (corr.); n^{20}_{D} 1.4370 (Abbe); d_{20} 1.093 g./cc.

Aldehyde Analysis.—The titration of isobutyraldehyde by the hydroxylamine hydrochloride method was found to give unreliable results. The more reliable method of Seyervetz and Bardin[8] using a sodium sulfite solution was standardized against known isobutyraldehyde–water solutions. An analytical factor was established for use in the analysis of the products of hydrolysis of subsequent reactions, and the method was found to give concordant results.

Hydrolysis in Liquid Phase.—The first hydrolysis studies followed the simpler liquid phase procedure used by Newlin. The results of these studies indicated moderate hydrolysis with the formation of appreciable quantities of aldehyde, with yields obtainable as high as 33–35%. The effective conversion to aldehyde was improved with higher water to dichloride ratios, a ratio of 20:1 giving satisfactory yields.

Throughout these hydrolysis studies it was generally apparent that the hydrochloric acid capable of titration was far in excess of the aldehyde found by analysis. This condition was especially true in liquid phase hydrolysis where the tendency toward pyrolysis was at a minimum. It was evident then, that hydrochloric acid was evolved as several intermediate products were formed; these were then incompletely converted to isobutyraldehyde. Thus the acidity of the reaction products was bound to be high without the formation of an equivalent amount of isobutyraldehyde.

Catalytic Hydrolysis in Vapor Phase.—A hydrolysis unit was set up to operate at 300–450°. The apparatus designed for this purpose is shown diagrammatically in Fig. 1. Following the diagram, the apparatus was operated in the following manner: air under pressure (A) from an adjustable hydrostatic head, varied by the mercury pressure regulators (C), forced water from a graduated cylinder (G) and a constant flow (E) of dichloride from a reservoir (F) into the preheater (H). A line (B) to a vacuum pump permitted the dichloride reservoir to be filled readily. The preheater had concentric Pyrex coils so that the water

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(1) Abstracted from a thesis by J. M. Hersh, presented to the Faculty of Purdue University, in partial fulfilment of the requirements for the Ph.D. degree, June, 1935.

(2) Presented before the Division of Organic Chemistry at the 91st meeting of the American Chemical Society, Kansas City, Mo., April, 1936.

(3) Hass, McBee and Weber, *Ind. Eng. Chem.*, **27**, 1190 (1935); **28**, 333 (1936).

(4) Newlin, M. S. Thesis, Purdue University, 1932.

(5) Senderens, *Compt. rend.*, **154**, 778 (1912).

(6) Whitmore, THIS JOURNAL, **55**, 1136 (1933).

(7) Adams and Adkins, "Organic Syntheses," Vol. VIII, John Wiley and Sons, Inc., New York, 1928, p. 50.

(8) Seyervetz and Bardin, *J. Soc. Chem. Ind.*, **25**, 202 (1906); Adams and Adkins, THIS JOURNAL, **47**, 1358 (1925).

and dichloride were vaporized individually in the desired ratio, preheated to 200°, and sent into the adjoining reaction tube (I), which was a 22-mm. Pyrex tube 60 cm. long packed with a contact mass and held at a fixed temperature by a Hoskins electric heating unit (K). A thermocouple (J) extending into the reaction zone permitted temperature recording and regulation by a recording pyrometer and thermal regulator. The products of the reaction were condensed (L) and collected in flasks (M).

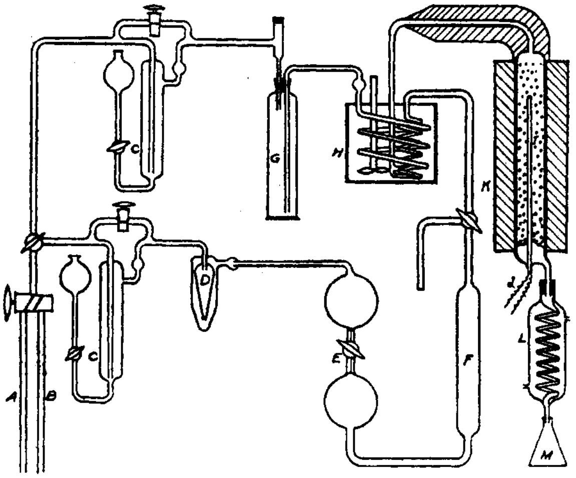

Fig. 1.

The procedure in each reaction carried out was to maintain a ratio of approximately 20:1 of water to dichloride, and to use generally 10 cc. of dichloride in each run. All the hydrolysis products were measured in volume, and the aqueous fraction containing aldehyde and hydrochloric acid was separated from the oily fraction consisting largely of unconverted dichloride. From each run two 10-cc. samples were taken from the aqueous portion and titrated for total acidity to determine the degree of conversion. The resulting neutral solution was analyzed for isobutyraldehyde by the method described. A 3-cc. sample from the aqueous portion was treated with fuchsin-aldehyde reagent for a color test of the aldehyde.

The first group of vapor phase hydrolysis studies made use of a series of fifteen catalyst filled reaction tubes. Subsequent studies made use of a series of sixteen reaction tubes in which a unit weight (10 g.) of a catalyst was mixed with a large amount of granular pumice filler. While the first reaction tubes required replacement before any large number of runs were completed, the reactors beginning with number six held up well, and ten or more runs were completed on each tube. Though fifteen catalyst filled reaction tubes were studied, at temperatures between 350 and 450°, a summary is presented in Table I of only typical catalysts, with a comparison based on the first ten hydrolysis runs completed on the reactor at 350°. The series of reaction tubes in which unit weights of catalyst were mixed with pumice is similarly summarized and presented in Table I. The average yields are given for

Table I

Comparison of Typical Catalysts[a]

No.	Catalyst Description	% Conversion	% Aldehyde	% DiCl Consumed	Criterion value
	A. Reaction tubes filled with catalyst (Approx. 50 cc.)				
1	Alumina, Weston, 4–16 mesh	66.4	29.2	51.9	44.2
2	Alumina, ALCOA, 8–16 mesh	56.6	35.3	41.4	42.2
3	Alumina, ALCOA, 4–8 mesh	52.5	21.9	49.0	36.3
4	Silica gel, granular, 8–16 mesh	31.2	20.9	33.6	26.7
5	Act. carbon, granular, finer than 10 mesh	39.9	13.4	37.7	26.1
6	Act. carbon, granular, 8–10 mesh	32.7	11.7	36.9	24.2
7	Silica gel + copper shreds	22.7	17.2	19.4	18.9
8	Pumice, granular	1.9	4.6	6.7	4.5
	B. Reaction tubes using 10.0 g. of catalyst				
1	Activated alumina, 8–16 mesh	38.1	24.0	24.1	27.6
2	Activated alumina, powdered	33.5	19.0	23.4	23.8
3	Titanium oxide, hydrated, pwd. and reduced	23.4	15.4	21.0	18.8
4	Zinc hydroxide, pptd., dried and powdered	20.0	15.0	23.0	18.3
5	Zinc chloride, deliquescent powder	16.3	16.8	21.5	17.9
6	Silica gel, granular, 8–16 mesh	18.7	16.3	20.0	17.9
7	Activated carbon, finer than 10 mesh	12.2	13.8	24.8	16.2
8	Vanadium pentoxide, powdered	16.4	15.7	17.0	16.2
9	Titanium oxide, hydrate, powdered	12.1	14.6	21.0	15.6
10	Tungstic oxide, yellow, powdered	7.2	19.3	15.0	15.2
11	Ceric oxide, yellow, powdered and reduced	12.0	15.6	13.7	14.2
12	Thorium oxide, from sintered nitrate	5.1	11.1	20.0	14.0
13	Ceric oxide, yellow, powdered	13.2	13.9	18.4	13.4
14	Thorium oxide, pptd. hydrate dried, powdered	13.3	11.2	15.4	12.9
15	Tungstic oxide, yellow powder reduced to blue	5.9	14.3	13.8	12.1
16	Thorium oxide, nitrate sintered and reduced	5.1	11.1	20.0	11.9

[a] Based upon first ten hydrolysis runs completed, using approximately 10 cc. of dichloride and 20 volumes of water.

each type of catalyst in order to give a measure of the degree of conversion, and the completeness of reaction.

Deterioration of Catalysts.—On reviewing any series of hydrolysis runs it was apparent that the catalyst was generally rapidly deactivated. This effect was first apparent with reactor number six using silica gel. The same effect was observed with each subsequent reactor and was apparent in the maximal to minimal change in conversion shown between the first and subsequent runs. This deterioration of catalysts was more pronounced at elevated temperatures where pyrolysis and carbonization were more evident, and varied also with the specific catalyst studied.

Separation of Hydrolysis Products.—The major part of the dichloride fed into the system was returned with the products of reaction as an oily, insoluble material, which was separated, filtered, dried and distilled. From 66–68% of this fraction appeared as crude dichloride which distilled over at 102–110°. It was further purified and fractionated to produce an additional quantity of 1,2-dichloro-2-methylpropane. Each batch of aqueous hydrolysis product containing isobutyraldehyde was distilled to remove an aldehyde-rich aqueous fraction. These aldehyde–water concentrates were further fractionated through a small column of the type described by Weston,[9] and the isobutyraldehyde was stripped from the large amount of water accompanying it. The crude aldehyde was purified and compared with Eastman isobutyraldehyde and with its known physical constants. Thus it was shown that the aldehyde isolated was the aldehyde expected in the reaction.

On reviewing the comparison of catalysts it was apparent that there was a pronounced difference in the catalytic influence of the several substances tested. The high value shown was that of activated alumina, and the lowest value that of granular pumice. Calculating the criterion value of these catalysts as dependent mainly (50%) on the percentage of aldehyde found by analysis, with additional consideration (25%) given to each the percentage of conversion and the percentage of dichloride consumed, the two series of catalysts were evaluated and arranged in the order of decreasing activity in Table I.

Summary

1. Pure 1,2-dichloro-2-methylpropane was prepared by the low temperature chlorination of 2-chloro-2-methylpropane. This compound was compared in hydrolysis with the dichloride from other sources; in each case isobutyraldehyde was produced in comparable yields.

2. The hydrolysis of 1,2-dichloro-2-methylpropane was quite effective in the vapor phase at 350°, with a ratio of 20:1 of water to dichloride, especially in the presence of catalysts. Yields of isobutyraldehyde were obtained as high as 33–35% per pass, or 90–100% based upon the dichloride consumed in the reaction.

3. Of the catalysts investigated, activated alumina showed a marked superiority, being especially resistant to deactivation at 350° as contrasted with catalysts such as silica gel.

4. The products of the hydrolysis of 1,2-dichloro-2-methylpropane were separated and the aldehyde produced was identified as isobutyraldehyde.

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[9] Weston, *Ind. Eng. Chem., Anal. Ed.*, **5**, 179 (1933).

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Tetraalkyl Barbituric Acids

BY ARTHUR W. DOX

For the preparation of 1,5,5-trialkylbarbituric acids two methods are available: (1) condensation of the dialkylmalonic ester with an alkylurea, and (2) direct alkylation of the 5,5-dialkylbarbituric acid. The first of these procedures was used by Fischer and Dilthey[1] and subsequently extended by Dox and Hjort.[2] The second method was studied by Dox and Jones[3] in the case of the more reactive halides such as benzyl chloride and allyl bromide, and by Lyons and Dox[4] with the still more reactive *p*-nitrobenzyl chloride.

Although the 5,5-dialkylbarbituric acids exist theoretically in two tautomeric forms, so that both N-alkyl and O-alkyl derivatives might be expected to result from direct alkylation of the sodium salt, only the former have actually been obtained and identified. The 1-benzyl-5,5-diethylbarbituric acid obtained by Dox and Jones[3] by direct alkylation of sodium barbital was identical with that prepared by them from ethyl diethylmalonate and benzylurea.

Marotta and Rosanova[5] recently claim to have obtained both tautomeric forms in the methylation of barbital by diazomethane. Their N-methyl derivative melted at 154° and was obviously identical with that which Fischer and

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[1] Fischer and Dilthey, *Ann.*, **335**, 334 (1904).

[2] Dox and Hjort, *J. Pharmacol.*, **31**, 455 (1927).

[3] Dox and Jones, THIS JOURNAL, **51**, 316 (1929).

[4] Lyons and Dox, *ibid.*, **51**, 288 (1929).

[5] Marotta and Rosanova, *Atti accad. Lincei*, **15**, 753 (1932).