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.

LAFAYETTE, INDIANA RECEIVED MAY 20, 1936

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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).

Barbituric acid	Formula	M. p., °C.	Nitrogen, % Found	Nitrogen, % Calcd.
1,3,5-Triethyl-5-phenyl	$C_{16}H_{20}O_3N_2$	129	9.73	9.72
1-Methyl-3-phenyl-5-ethyl-5-propyl	$C_{16}H_{20}O_3N_2$	78	9.35	9.72
1-Methyl-3-benzyl-5,5-diethyl	$C_{16}H_{20}O_3N_2$	73	9.34	9.72
1,5,5-Triethyl-3-benzyl	$C_{17}H_{22}O_3N_2$	[a]	9.02	9.27
1,3-Dimethyl-5-ethyl-5-hexyl	$C_{14}H_{24}O_3N_2$	[b]	10.40	10.45
1,3-Dimethyl-5-ethyl-5-isoamyl	$C_{13}H_{22}O_3N_2$	[a]	10.75	11.02
1,3-Dimethyl-5-ethyl-5-(1-methylbutyl)	$C_{13}H_{22}O_3N_2$	[a]	10.72	11.02

[a] Liquid. [b] B. p. 165–170° at 12 mm.

Dilthey[1] had obtained from ethyl diethylmalonate and methylurea. In addition to this crystalline product Marotta and Rosanova obtained a non-crystallizing sirup which they assume to be the tautomeric O-methyl barbital having the isourea structure. Mention is made of methoxyl determinations but no analytical data are given. They make no mention whatever of the possibility that *both* nitrogens may have been methylated. As will be shown presently this is undoubtedly what occurred, and the non-crystallizing sirup which they assume to be the tautomeric monomethylbarbital was in reality an impure preparation of the low-melting dimethylbarbital.[6]

Experimental

Methylation was performed by dissolving the di- or trialkylbarbituric acid in a dry ether solution of diazomethane prepared by distilling ethyl N-nitroso-N-methylcarbamate with alcoholic potassium hydroxide in ether. Except in one instance where it was desired to obtain the monomethyl barbital, an excess of diazomethane was used. At room temperature the evolution of nitrogen began almost immediately and the reaction was complete in about an hour. Evaporation of the ether left a sirup which in a few instances crystallized readily, but more often required cooling or seeding, and occasionally did not crystallize at all. In two instances diazoethane, prepared similarly from the nitrosoethylurethan, was used for ethylation.

In the first experiment barbital was methylated with one equivalent of diazomethane. Evaporation of the solvent gave a crystalline product which on recrystallization from alcohol formed large prisms melting at 154°. Mixed with authentic methylbarbital the melting point showed no depression. A sirupy mother liquor failed to crystallize. This corresponds to the supposed O-methylbarbital of Marotta and Rosanova.

1,3-Dimethyl-5,5-diethylbarbituric Acid. (Dimethylbarbital.)—When barbital was treated with an excess of diazomethane, as shown by persistence of the yellow color after the evolution of nitrogen had ceased, evaporation gave only the sirup. This did not crystallize on cooling and stirring, but when seeded with a small crystal that had formed on the stem of the funnel through which the ether solution had been filtered, the sirup crystallized promptly and completely. The crystals melted at 32–34°, and recrystallization from ether raised the melting point to 37°. A peculiar property of the substance is its tendency to form a super-cooled sirup which immediately crystallizes when seeded with a crystal of the same substance. The yield was practically quantitative. The substance is readily volatile with steam, and is soluble in the usual organic solvents including petroleum ether, but insoluble in sodium hydroxide. It separates as an oil when the alcohol or acetone solution is diluted with water.

Anal. Calcd. for $C_{10}H_{16}O_3N_2$: C, 56.60; H, 7.55; N, 13.21. Found: C, 56.29; H, 7.37; N, 13.41.

The identity of the substance was corroborated by another method of synthesis. Diethylmalonyl chloride was condensed with symmetrical dimethylurea[7] by heating the mixture in an oil-bath for twelve hours at 135–140°, finally raising the temperature to 150°. The reaction product was dissolved in ether and shaken successively with water, *N* sodium hydroxide, *N* sulfuric acid, water, and finally dried with calcium sulfate. Evaporation of the ether left a sirup which immediately crystallized when seeded with a crystal of the product described above. The melting point was 37°, and mixed melting point showed no depression.

1,3-Dimethyl-5-ethyl-5-phenylbarbituric Acid. (Dimethyl-phenobarbital.)—Phenobarbital was methylated in the same manner. In contrast to the corresponding barbital derivative it crystallized spontaneously, possibly because of its higher melting point, 88–89°.

Anal. Calcd. for $C_{14}H_{16}O_3N_2$: C, 64.61; H, 6.15; N, 10.77. Found: C, 64.27; H, 6.57; N, 10.67.

These tetraalkyl barbituric acids, like the following homologs prepared from other 5,5-dialkylbarbituric acids and diazomethane or diazoethane, contain no replaceable hydrogen and hence are insoluble in sodium hydroxide. The yields were practically quantitative. Several of these products have failed to crystallize, but from the peculiar behavior of the dimethyl-barbital it may be assumed that crystallization will readily occur when once a crystal for seeding has been obtained. In three instances a 1,5,5-trialkylbarbituric acid was alkylated on the second nitrogen by the diazoalkane method.

Several of these substances possess asymmetric structure and should be separable into optical isomers. This was not attempted because the substances have neither acidic nor basic properties and cannot form salts with optically active bases or acids.

The action of diazomethane on barbituric acids containing only one alkyl in the 5-position has been studied

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(6) Marotta and Rosanova state that their work will be more fully described in the *Gazzetta chimica Italiana*. The proposed paper has not appeared after the lapse of four years.

(7) The dimethylurea was kindly supplied by Dr. Henry Gilman of Iowa State College.

by Biltz and Wittek.[8] They obtained the same trimethylbarbituric acid by diazomethane treatment of barbituric, 1-methylbarbituric and 1,3-dimethylbarbituric acids. Both nitrogens are thus amenable to methylation by diazomethane, but only one of the methylene hydrogens. To obtain a tetraalkylbarbituric acid with this reagent both of the methylene hydrogens must be previously substituted. The other method in which a symmetrical dialkylurea is used requires a condensation with the acid chloride instead of the ester of the dialkylmalonic acid. Fischer and Dilthey thus prepared the tetraethylbarbituric acid but failed to crystallize it, possibly because of its low melting point. Otherwise its properties were similar to those of the 1,3-dimethyl-5,5-diethylbarbituric acid prepared by both methods and described above.

Summary

Treatment of 5,5-dialkyl- or 1,5,5-trialkylbarbituric acid with diazomethane in ether solution gives practically quantitative yields of tetraalkylbarbituric acids in which both nitrogens have been methylated. A similar reaction occurs with diazoethane.

The statement of Marotta and Rosanova that the two tautomeric monomethyldialkylbarbituric acids are thus formed is erroneous. The supposed O-methylbarbital which they obtained as a sirup is in reality the low melting di-N-methyl derivative.

DETROIT, MICH. RECEIVED JUNE 17, 1936

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(8) Biltz and Wittek, *Ber.*, **54**, 1035 (1921).

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

Absorption Edges in the X-Ray Patterns of Native and Mercerized Cellulose

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In addition to the spacings of the currently accepted unit cell of cellulose,[3] numerous reports of other long spacings have appeared from time to time in the literature. Spacings of 16.0 and 35.3 Å.;[4] 7.9 or 8.3 Å.;[5] 50.0 Å.;[6,7] 274, 168, 156 and 85 Å.;[8,9] 42.2, 44.9, 66.5 and 83.5 Å.;[10] and 40 to 50 Å.,[11] have been interpreted as being due either to micellar dimensions, or to periodicities larger than the usual diffracting planes of the cellulose unit cell.

The authors[12] recently reported three new "interferences:" two (10.1 and 13.4 Å.) in native cellulose and one (14.2 Å.) in mercerized cellulose, which appear most intense in the pattern when the x-ray beam (Cu K) is parallel to the fiber axis. Regardless of the fibers used, these "spacings" were found to be constant, which indicated that they were not due to non-cellulosic constituents.

With other radiations (Mo, Fe and Cr), the "spacings" were found to vary, while the usual cellulose diffraction lines remained constant, as can be seen by comparing the original negatives of Figs. 1 and 2. The "spacings" were parallel to the 101 and 002 planes in native and the $10\bar{1}$ plane in mercerized cellulose. They were very weak with molybdenum radiation, but increased in intensity with larger values of λ, until with chromium radiation they are almost as intense as the usual diffraction lines. It is the purpose of the present paper to show that these new "spacings" are absorption edges.

It is well known that any element placed in an x-ray beam will absorb to a greater extent those wave lengths just shorter than that element's absorption edges, and on the long wave length side of this edge the x-ray beam will be less affected. If the planes in cellulose diffract general as well as characteristic radiation, definite bromine and silver absorption edges for each plane will appear on the x-ray film which would be similar to and might be mistaken for true diffraction lines.

Since the 002 (3.98 Å.) and 101 (6.10 Å.) planes in native and the $10\bar{1}$ (4.40 Å.) plane in mercerized cellulose diffract characteristic radiation to the greatest degree, they should behave likewise

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(3) K. R. Andress, *Z. physik. Chem.*, **B2**, 380 (1929); **B4**, 190 (1929).

(4) R. O. Herzog and W. Jancke, *Naturwissenschaften*, **16**, 618 (1928).

(5) U. Yoshida and C. Park, *Mem. Coll. Sci. Kyoto Imp. Univ.*, **A17**, 443 (1934).

(6) H. Mark, *Trans. Faraday Soc.*, **25**, 387 (1929).

(7) G. L. Clark, *Ind. Eng. Chem.*, **22**, 474 (1930).

(8) G. L. Clark and K. E. Corrigan, *Radiology*, **15**, 117 (1930).

(9) G. L. Clark and K. E. Corrigan, *Ind. Eng. Chem.*, **23**, 815 (1931).

(10) K. E. Corrigan, Thesis, University of Illinois, 1932.

(11) W. A. Sisson, *Textile Research*, **5**, 119 (1935).

(12) G. L. Clark and W. A. Sisson, Cellulose Symposium, Am. Chem. Soc., Div. Cellulose Chem., N. Y., 1935.