Anal. Calcd. for $C_6H_6N_2$: N, 26.41. Found: N, 26.10, 26.22.

Saponification of (B).—A mixture of 5 g. of the solid (B) and 35 cc. of concentrated hydrochloric acid was heated on a steam-bath for two hours and then evaporated on the steam-bath to dryness. Five to six extractions of the residue with ether removed 2.4 g. of an acidic material (D) leaving a residue (E).

The Acidic Product (D).—The crude acid (m. p. 97–116°) was recrystallized three or four times from benzene, giving *cis*-β-methylglutaconic acid of m. p. 150–151°. A mixed melting point with a sample of this acid prepared from diethyl α-cyano-β-methyl-glutaconate[14] gave no depression.

A product of m. p. 112–115° was also obtained from the acidic material (D). It is probable that this consisted in large part of *trans*-β-methyl-glutaconic acid.

The Residue (E).—When the chloride salt (E) was extracted with ammonium hydroxide, the filtered extract treated with acetic acid and cooled in a refrigerator, 2.6 g. of crystalline solid separated. Recrystallization of this from absolute alcohol gave 2,6-dihydroxy-4-methylpyridine, m. p. 192–193°. A mixed melting point with a synthetic sample[14] showed no depression.

The Liquid Residue (C).—The liquid nitrile remaining after the separation of the solid was cooled in an ether–Dry Ice-bath, but very little solid separated from the sirup. Several distillations led to the separation of more of the solid (B). Eventually a liquid product b. p. 130–132° at 12 mm. was obtained; d^{20}_4 1.0498; $n^{20}D$ 1.4726; MR_D 29.61; d^{55}_4 0.9799; $n^{55}D$ 1.4590; MR_D 29.48. However, the analytical results were inconclusive.

The saponification of the liquid nitrile gave the same *cis*-β-methylglutaconic acid and 2,6-dihydroxy-4-methylpyridine obtained from the solid (B).

The saponification of the dinitrile with sodium hydroxide gave a product of m. p. 208°.

Anal. Calcd. for $C_6H_8N_2O$: N, 22.59. Found: N, 22.63, 22.69.

Quantitative Behavior of Unsaturated Compounds with Bromine.—On account of the inconclusive nature of the qualitative bromine tests for unsaturation, the quantitative method of McIlhiney[10] was used on several of our compounds. In our study of the chloronitrile (VI), a weighed amount of the compound dissolved in carbon tetrachloride was transferred to an iodine flask and treated with a known excess of *M*/3 bromine solution in the same solvent. The flask was stoppered, shaken and set in a dark place for eighteen hours. Water was then poured around the stopper of the flask and the flask was cooled in order to create a decrease in internal pressure, when the stopper was slightly loosened so that water was sucked into the flask without permitting the escape of hydrogen bromide. The excess of bromine was then determined by titration with thiosulfate after the addition of potassium iodide solution. The amount of substitution was then ascertained by the addition of potassium iodate followed by a second thiosulfate titration. Table II summarizes the results.

TABLE II

Compound	Solvent	% Addition		% Substitution	
ClCH=C(CH₃)CH₂CN	CCl_4	12.7	14.3	1.2	1.2
ClCH=C(CH₃)CH₂Cl	CCl_4	0	0	0	0
ClCH₂C(=CH₂)CH₂Cl	CCl_4	2.6	2.9	0	0
C₆H₅OCH₂C(CH₃)=CHCN	CCl_4	83.4	80.4 80.5	38.6	38.8 37.2
Solid dinitrile (B)	$CHCl_3$	38.6	40.7	0.3	0.3
Liquid dinitrile (C)	$CHCl_3$	11.5	11.6	0.5	0.5

Summary

1. Eastman Kodak Co. practical "1,3-dichloroisobutane" reacts with cuprous cyanide to give 4-chloro-3-methyl-3-butenonitrile, which originates from 1,3-dichloro-2-methyl-1-propene, a 20–30% admixture in the Eastman product, now discontinued. A method is given for the preparation of the 1,3-dichloro-2-methyl-1-propene by the action of quinoline on 1,2,3-trichloro-2-methylpropane, whose synthesis from methallyl chloride and sulfuryl chloride is also described.

2. The structure of the 4-chloro-3-methyl-3-butenonitrile, exclusive of stereochemical considerations, has been deduced from a study of the corresponding acid and amide, whose formation from the nitrile and related imido ester salt is described.

3. The action of cuprous cyanide on the Eastman "1,3-dichloroisobutane" gives a solid and a liquid dinitrile, both of which on saponification with hydrochloric acid give *cis*-β-methylglutaconic acid and 2,6-dihydroxy-4-methylpyridine.

TROY, N. Y. RECEIVED[22] JANUARY 3, 1946

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

Behavior of Nitro Alcohols toward Formic Acetic Anhydride

BY CHARLES D. HURD, STEVENS S. DRAKE AND OTIS FANCHER

The literature mentions only a few references to esterification of nitro alcohols. These esters are chiefly the acetates, propionates, butyrates and isobutyrates with no mention of formates. Pauwels[1] and Shaw[2] were the first to report in this field. They prepared 2-nitrobutyl acetate and 2-nitroisopentyl acetate by reaction of the corresponding nitro alcohols with acetic anhydride. Three 1-alkyl-2-nitroethyl acetates were synthesized, by Schmidt and Rutz,[3] alkyl representing methyl, ethyl and *n*-propyl. A few other acetates were added in 1940 by Vanderbilt and Hass and by Gloor.[4] The latest work on this subject was by Tindall[5] who reported the preparation of propionates, butyrates, and isobutyrates of twenty-five nitro alcohols. He found that the nitro primary alcohols could be esterified by interaction with the organic acid in the presence of a little sulfuric acid, whereas the nitro secondary alcohols required the use of the acid anhydride.

(1) Pauwels, *Rec. trav. chim.*, **17**, 27 (1898).

(2) Shaw, *ibid.*, **17**, 50 (1898).

(3) Schmidt and Rutz, *Ber.*, **61**, 2142 (1928).

(4) Vanderbilt and Hass, *Ind. Eng. Chem.*, **32**, 34 (1940); Gloor, U. S. Patent 2,185,297; *C. A.*, **34**, 2862 (1940).

(5) Tindall, *ibid.*, **33**, 65 (1941).

He found also that if the crude ester was treated with water or aqueous alkaline solutions to remove residual acid such a treatment brought about decomposition of the ester into a nitroölefin at the time of distillation.

The present study concerns itself with the behavior of a few nitro alcohols toward formic acetic anhydride. This reagent was discovered by Béhal,[6] who found that it reacted unidirectionally with simple alcohols to produce alkyl formates free from acetates. Work in this Laboratory[7] has shown that formic acetic anhydride is easily prepared by the reaction of anhydrous formic acid with ketene and that toward aniline it reacts quantitatively to give formanilide.

2-Nitro-1-butanol, 2-nitro-2-methyl-1-propanol and 2-nitro-2-methyl-1,3-propanediol were investigated with the finding that their formic esters could be prepared smoothly by maintaining a reaction temperature of 50–60° or lower. The use of ether as solvent met this requirement. At higher temperatures, or if sulfuric acid was added as a catalyst, a different reaction ensued giving rise to acetic esters. In other words, conditions which produce a vigorous reaction cause the formation of acetic esters, perhaps by way of preliminary decomposition of the mixed anhydride into acetic anhydride or acetic acid.

It is noteworthy that mixing of formic acetic anhydride and 2-nitro-2-methyl-1-propanol is accompanied by marked cooling. This endothermic effect was not noticed with the other nitro alcohols.

Experimental

The nitro alcohols used in this investigation were generously supplied by Commercial Solvents Corporation. One was a liquid and the rest were cream-colored, waxy solids: 2-nitro-1-butanol, b. p. 127–130° (25 mm.); 2-nitro-2-methyl-1-propanol, m. p. 85–86°; 2-nitro-2-methyl-1,3-propanediol, m. p. 144–145°; tris-(hydroxymethyl)-nitromethane, m. p. 149–150°.

Formic acetic anhydride[7] was prepared from ketene. It distilled at 36–38° (28 mm.) and its purity was checked by reaction with aniline to produce formanilide quantitatively: b. p. 135° (6 mm.); m. p. 47°. Kept in a glass stoppered bottle it still yielded formanilide quantitatively after a two-week period.

2-Nitroisobutyl Formate.—Six and four-tenths grams of formic acetic anhydride was added into an ice-cold mixture of 8.5 g. of 2-nitro-2-methyl-1-propanol and 75 ml. of absolute ether. The solution was refluxed for eight hours and distilled. The fraction, b. p. 59–60° (3 mm.), weighed 7.2 g. (61% yield). On redistillation through a 10-cm. Vigreux column a little unused nitro alcohol was separated in the first fraction (94–96° (13 mm.)). This fraction partially solidified. The pure formate was collected at 97.5–99° (16 mm.) or 86–87° (10 mm.); $n^{25.5}D$ 1.4327, d^{20}_{20} 1.145.

Anal. Calcd. for $C_5H_9O_4N$: N, 9.52. Found: N, 9.88.

The compound was also prepared by direct mixing of equivalent quantities of 2-nitro-2-methyl-1-propanol (15.6 g.) and formic acetic anhydride (10 ml.). There was a pronounced endothermic effect which left the flask quite cool. The mixture was warmed to 50–60° on a water-bath for thirty minutes, then set aside overnight. Vacuum distillation gave a forerun of 1.2 g. of unreacted nitro alcohol (m. p. 85–86°) and a main fraction which, on redistillation, yielded 7.8 g. (44% yield) of 2-nitroisobutyl formate, b. p. 65° (5 mm.).

Hydrolysis of this ester by refluxing with dilute sodium hydroxide solution yielded sodium formate, characterized by Duclaux constants, and by conversion to *p*-bromophenacyl formate.

Two modifications of the esterification without solvent were performed, both of which yielded the acetate rather than the formate. In one, the same equimolar reaction mixture was heated to boiling immediately after mixing. In the other, a drop of concentrated sulfuric acid was added to the cool endothermic mixture. After one minute a vigorous reaction took place with sufficient heat evolution to cause rapid solution of the solid alcohol. The reaction was largely completed at this stage, but the mixture was refluxed for an hour. After cooling, ether was added and the solution was extracted with sodium bicarbonate solution, dried over sodium sulfate, and distilled. Both runs yielded 75–80% of 2-nitroisobutyl acetate, b. p. 92–94° (10 mm.). Hydrolysis of both and derivatization yielded *p*-bromophenacyl acetate; m. p. and mixed m. p. 85–86°.

2-Nitrobutyl Formate.—Mixing of 15.6 g. of 2-nitro-1-butanol and 10 ml. of formic acetic anhydride was not accompanied by any appreciable temperature change. With general details as in the previous run, 17 g. (88% yield) of 2-nitrobutyl formate was collected at 72–76° (5 mm.), chiefly at 75–76°. Hydrolysis and conversion to the *p*-bromophenacyl derivative showed it to be the formate.

It was also prepared differently by refluxing for eight hours a mixture of 6.7 g. of formic acetic anhydride, 8.5 g. of 2-nitro-1-butanol and 75 ml. of dry ether. Five grams (48% yield) of product, b. p. 65–66° (2 mm.), was redistilled to give a pure sample which was collected at 98–98.5° (10 mm.); $n^{25.5}D$ 1.4345.

Anal. Calcd. for $C_5H_9O_4N$: N, 9.52. Found: N, 9.85.

2-Nitro-2-methyl-1,3-propanediol Diformate.—With ether (75 ml.) as solvent as in the preparation of 2-nitroisobutyl formate, 3.7 g. (53%) of product, b. p. 101–103° (3 mm.), was obtained from 5 g. of 2-nitro-2-methyl-1,3-propanediol and 7.2 g. of formic acetic anhydride. This fraction possessed these constants: $n^{27.5}D$ 1.4520, d^{30}_{30} 1.297.

Anal. Calcd. for $C_6H_9O_6N$: N, 7.33. Found: N, 8.05.

Without the ether as diluent a vigorous exothermic reaction was observed. The quantities of reagents taken were 10 ml. of anhydride and 8.3 g. of the diol. Reaction was complete even before the contents of the flask could be cooled by an ice-bath. The resulting product was a pale yellow, viscous solution. Distillation at 2 mm. yielded 12 g. (89%) at 109–112°; $n^{20}D$ 1.4493; d^{20}_{20} 1.2379. This was chiefly 2-nitro-2-methyl-1,3-propanediol diacetate as judged by hydrolysis and conversion to *p*-bromophenacyl acetate, m. p. 85–86°. When mixed with an authentic specimen the m. p. was 86.5–87.5°.

Tris-(hydroxymethyl)-nitromethane.—Twenty ml. of formic acetic anhydride gradually brought 1.32 g. of tris-(hydroxymethyl)-nitromethane into solution with no temperature effect. No doubt, the formic ester was obtained but it could not be distilled without decomposition at 0.001 mm. and a bath temperature of 140°.

Acknowledgment.—Microanalyses were performed by W. Brandt and R. Pivan. Assistance in purifying some of the samples was given by W. A. Bonner.

Summary

Formic acetic anhydride mixes endothermically with 2-nitro-2-methyl-1-propanol, exothermically with 2-nitro-2-methyl-1,3-propanediol and dis-

(6) Béhal, *Compt. rend.*, **128**, 1400 (1900).

(7) Hurd and Roe, THIS JOURNAL, **61**, 3355 (1939).

plays no appreciable temperature effect with both 2-nitro-1-butanol and tris-(hydroxymethyl)-nitromethane. Formic esters are produced by avoiding high reaction temperatures and by not using sulfuric acid catalyst. Acetic esters are produced if vigorous conditions are maintained or if the sulfuric acid is present as catalyst.

EVANSTON, ILLINOIS RECEIVED JANUARY 25, 1946

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE OHIO STATE UNIVERSITY]

L-Fructose[1]

BY M. L. WOLFROM AND ALVA THOMPSON[2]

Although L-fructose was reported by Fischer[3] and characterized by its osazone (L-glucose phenylosazone), it was obtained only in solution and was never isolated. D,L-Glucose phenylosazone (α-acrosazone) had been isolated from the reaction mixture obtained by the action of alkali upon either dibromoacrolein[4] or "glycerose,"[5] an oxidation product of glycerol containing glyceraldehyde and dihydroxyacetone. Hydrolysis to the osone with subsequent reduction served to transform D,L-glucose phenylosazone into D,L-fructose.[3,6] Treatment of the latter with yeast removed the D-fructose, leaving a solution of L-fructose. Crystalline D,L-fructose was obtained later by Schmitz[7] through the action of very dilute alkali upon crystalline D,L-glyceraldehyde.

In the present work the synthesis of L-fructose was effected by the reaction sequence: L-arabonic acid tetraacetate → L-arabonyl chloride tetraacetate → 1-diazo-1-desoxy-*keto*-L-fructose tetraacetate → *keto*-L-fructose tetraacetate → L-fructose. This reaction series had been carried out in the D-configuration but new and improved details for these procedures are presently communicated. All of the products were isolated in crystalline form.

L-Fructose crystallized in long, fine needles emanating from a center and forming a spherical cluster. D-Fructose is described[8] as crystallizing in the orthorhombic system and exhibiting prismatic or pyramidal habits of rather massive appearance. It is interesting to note that Jungfleisch and Lefranc,[9] who first crystallized D-fructose, described it as crystallizing in the anhydrous form as long, fine needles emanating from a center to form a spherical cluster. The material measured by Schuster[8] was furnished by Hönig and co-workers and consisted in large part of clear, individual crystals (maximum size 2 × 1.5 mm.) obtained by slow evaporation from ethanol of repeatedly crystallized material. Hönig also furnished Schuster with samples of the first lot of D-fructose that had crystallized in his laboratory. These were spherical clusters of fine needles. Schuster states[10] that their appearance was identical with that cited by Jungfleisch and Lefranc[9] for their preparation but that they were too small for measurement (by the methods then available). Hönig and Jesser[11] considered that this needle form was a hemihydrate but their evidence for such a conclusion was meager.

That the crystalline structure of the L-fructose herein reported is not enantiomorphous with that of the usual form of D-fructose is shown by comparative X-ray powder diagrams (Fig. 1) and by the tabulation of interplanar spacings and relative intensities of the X-ray diffraction lines (Table I).[12] Crystals that are enantiomorphous would exhibit identical X-ray powder diagrams. Single crystal diffraction photographs on D-fructose had been made and examined previously by Hengstenberg and Mark.[13]

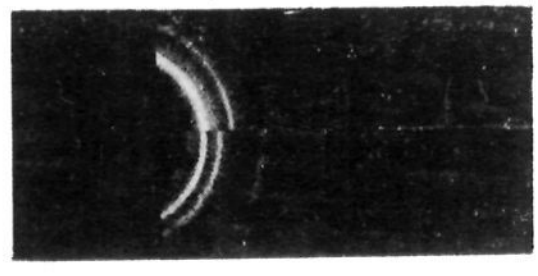

Fig. 1.—Comparative X-ray powder diagrams of L-fructose (upper) and D-fructose (lower) (*cf.* ref. 12 and Table I).

Analysis indicated that our preparation of L-fructose was anhydrous. The polarimetric and mutarotatory properties of this crystalline form of L-fructose, while not in exact numerical agreement with these difficultly determinable constants of D-fructose, are nevertheless sufficiently close to the accepted values to indicate that in

(1) Paper No. 8 in the series entitled "The Action of Diazomethane upon Acyclic Sugar Derivatives." Previous communication: M. L. Wolfrom, A. Thompson and E. F. Evans, THIS JOURNAL, **67**, 1793 (1945).

(2) Research Foundation Associate of the Graduate School.

(3) E. Fischer, *Ber.*, **23**, 389 (1890).

(4) E. Fischer and J. Tafel, *ibid.*, **20**, 1093, 2566, 3388 (1887).

(5) E. Fischer and J. Tafel, *ibid.*, **20**, 3384 (1887).

(6) E. Fischer and J. Tafel, *ibid.*, **22**, 97 (1889).

(7) E. Schmitz, *ibid.*, **46**, 2327 (1913).

(8) (a) M. Schuster, *Tschermak's mineralog. petrog. Mitt.*, **9**, 216 (1888); (b) M. Hönig, St. Schubert (and M. Schuster), *Monatsh.*, **8**, 555 (1887); (c) *cf.* F. J. Bates and Associates, National Bureau of Standards Circular C440, "Polarimetry, Saccharimetry and the Sugars," 541 (1942).

(9) Jungfleisch and Lefranc, *Compt. rend.*, **93**, 547 (1881).

(10) Ref. 8a, p. 222.

(11) M. Hönig and L. Jesser, *Monatsh.*, **9**, 563 (1888).

(12) For the X-ray photographs and measurements we are indebted to Professor P. M. Harris of this Laboratory.

(13) J. Hengstenberg and H. Mark, *Z. Krist.*, **72**, 301 (1929).