[CONTRIBUTION FROM THE CENTRAL RESEARCH LABORATORIES, MONSANTO CHEMICAL COMPANY]

Mucochloric Acid. II. Reactions of the Aldehyde Group[1]

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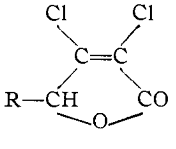
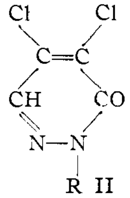
Mucochloric acid has been condensed with compounds containing a reactive methinyl hydrogen alpha to a carbonyl, nitro or cyano group in cold alkaline solution to form 3,4-dichloro-2(5)-furanones substituted in the 5-position. Reactive phenols under similar conditions, however, form α-aryloxy-β-chloro-β-formylacrylic acids. Reaction of mucochloric acid with hydrazine or a substituted hydrazine under appropriate conditions leads to 4,5-dichloro-3-pyridazones.

Dieckmann and Platz[2] have condensed mucochloric acid with acetophenone in the presence of cold alkali to give 3,4-dichloro-5-phenacyl-2(5)-furanone (I, R = $C_6H_5COCH_2$–).


I


II

These results have been confirmed and the reaction has been extended to the preparation of similar 5-substituted furanones by the use of nitromethane, nitroethane, 2-nitropropane, cyanoacetamide and phenylacetonitrile. Acetone condenses similarly with two moles of mucochloric acid. The yields in all cases were low, presumably because of a competing reaction involving degradation of mucochloric acid by aqueous alkali to α,β-dichloroacrylic acid.[3] The products are described in Table I. Attempts to effect a condensation of the aldehyde moiety of mucochloric acid with reactive methylene groups under less basic or acidic conditions have been unsuccessful. For example, the desired products were not obtained in the Doebner modification of the Perkin reaction using malonic acid and α-picoline or when mucochloric acid was refluxed in benzene solution with ethyl cyanoacetate in the presence of ammonium acetate or dimethylanilinium acetate catalysts.

TABLE I

2,3-DICHLORO-2(5)-FURANONES FROM MUCOCHLORIC ACID

2,3-Dichloro-2(5)-furanone	Yield, %	M.p., °C.	Formula	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Nitrogen, % Calcd.	Nitrogen, % Found
5-Phenacyl-[a]	45	118	$C_{12}H_8O_3Cl_2$	..	..	..	..	...	...
5-Nitromethyl-	38	102 dec.	$C_5H_3O_4NCl_2$	28.3	29.0	1.42	1.74	6.62	6.63
5-(α-Nitroethyl)-	10	124	$C_6H_5O_4NCl_2$	31.8	32.1	2.23	2.17	6.20	5.85
5-(2′-Nitro-2′-propyl)-	17	93	$C_7H_7O_4NCl_2$	35.0	35.1	2.94	2.95	5.84	5.46
5-(Carbamylcyanomethyl)-	17	163	$C_7H_4O_3N_2Cl_2$	35.7	36.0	1.72	1.86	11.92	11.32
5-(α-Cyanobenzyl)-	16	150	$C_{12}H_7O_2NCl_2$	53.8	53.8	2.63	2.65	5.23	5.00
2-Propanone-1,3-bis-(5,5′-	2	194 dec.	$C_{11}H_6O_5Cl_4$	36.8	36.9	1.67	1.66	...	...

[a] Dieckmann and Platz, ref. 2, report m.p. 121–122° (no yield given). Vinogradnova and Shemiakin, *J. Gen. Chem.* (*USSR*), 16, 716 (1946), report a yield of 42% for the analogous compound from mucobromic acid.

Mucochloric acid was reduced directly to 3,4-dichloro-2(5)-furanone (I, R = H) by the action of aluminum isopropoxide in 52% yield. This compound has been available previously only through reduction of mucochloryl bromide with tin and hydrochloric acid.[4]

Mucochloric acid formed a semicarbazone and phenylhydrazone in the expected fashion. On being heated in acetic acid solution, these products gave good yields of 4,5-dichloro-3-pyridazone (II, R = H) and 4,5-dichloro-2-phenyl-3-pyridazone (II, R = C_6H_5), respectively. The pyridazone was the only product isolated when an attempt was made to condense two moles of mucochloric acid with one mole of hydrazine to give an azine.

Although the aldehyde group has been condensed with benzene to form good yields of α,β-dichloro-γ,γ-diphenylcrotonic acid[5] in the presence of aluminum chloride, the use of sulfuric acid or benzenesulfonic acid catalysts gave only mucochloric acid anhydrides.[1] Reaction of mucochloric acid with caustic and phenol did not involve the aldehyde group, but replaced the α-chlorine atom with a phenoxy group.[6] This behavior was verified and extended to the use of other phenols, such as hydroquinone monomethyl ether, *p*-chlorophenol and β-naphthol.

Experimental[7]

2,3-Dichloro-2(5)-furanones (I).—The preparation of 5-phenacyl-2,3-dichloro-2(5)-furanone from acetophenone and mucochloric acid is typical of the preparations recorded in Table I.

Forty-two grams (0.25 mole) of mucochloric acid and 30 g. (0.25 mole) of acetophenone were dissolved in 150 ml. of methanol and cooled to 0°. A solution of 15 g. of sodium hydroxide in 150 ml. of water was then added slowly with stirring at 0–5°. The solution next was allowed to stand at room temperature for three hours before the slurry was poured into ice-water containing excess hydrochloric acid. The oily precipitate which formed was washed by decantation and dried to give 48 g. of crude product, m.p. 86–100°. Recrystallization from dilute ethanol gave 30 g. (45%) of nearly white plates, m.p. 117–118°. Another run which was allowed to stand for 20 hours before acidification gave the same yield.

3,4-Dichloro-2(5)-furanone (I, R = H).—A mixture of 338 g. (2 moles) of mucochloric acid, 500 g. (2.5 moles) of aluminum isopropoxide and 1500 ml. of isopropyl alcohol

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[1] Preceding paper, THIS JOURNAL, **72**, 2535 (1950).

[2] W. Dieckmann and L. Platz, *Ber.*, **37**, 4641 (1904).

[3] H. B. Hill, *Am. Chem. J.*, **3**, 165 (1881); **9**, 147 (1887).

[4] H. B. Hill and R. W. Cornelison, *ibid.*, **16**, 277 (1894).

[5] H. B. Hill and F. L. Dunlap, *ibid.*, **19**, 627 (1897).

[6] H. Sawyer, *Proc. Am. Acad. Arts Sci.*, **29**, 242 (1893–1894).

[7] All melting points are corrected.

was heated under a 100-cm. Vigreux column at reflux temperature until acetone stopped distilling. The excess alcohol was removed by distillation and the residue poured into a mixture of 2.5 kg. of ice and 800 ml. of concentrated hydrochloric acid. The resultant slurry was warmed to 50° and extracted with chloroform. After washing with water, sodium carbonate and hydrochloric acid solutions, the extract was distilled to give 150 g. of product boiling at 107–135° (13 mm.). The distillate solidified and was recrystallized from dilute ethanol to give 159 g. (52%) of the desired lactone, m.p. 51–52°. Hill and Cornelison[4] report m.p. 50-51°.

An attempt to prepare this compound from isopropyl mucochlorate using a smaller excess of aluminum isopropoxide gave only a 16% yield of lactone.

4,5-Dichloro-3-pyridazone (II, R = H).—Solutions of 126 g. (0.75 mole) of mucochloric acid, 84 g. (0.75 mole) of semicarbazide hydrochloride and 52 g. (0.375 mole) of potassium carbonate in 50% ethanol were mixed. The resultant precipitate was filtered after three hours and the product, 164 g. (89% yield), was recrystallized from ethanol. The semicarbazone melted at 183° with decomposition.

Anal. Calcd. for $C_5H_4O_3N_3Cl_2$: N, 18.74; Cl, 32.2. Found: N, 18.49; Cl, 32.13.

Eighty-four grams of this material was added slowly to 300 ml. of glacial acetic acid at 100–110° with stirring to facilitate evolution of carbon dioxide. The solution was diluted with water and cooled to give 42 g. (69% yield) of 4,5-dichloro-3-pyridazone, m.p. 202°.

Anal. Calcd. for $C_4H_2ON_2Cl_2$: C, 29.3; H, 1.22; N, 17.08; Cl, 43.2. Found: C, 29.28; H, 1.24; N, 16.90; Cl, 43.17.

This method is analogous to that used for the corresponding dibromo derivative prepared by Bistrzycki.[8] An attempt to prepare the azine from two moles of mucochloric acid and one mole of hydrazine using an adaptation of the method described by Hatt for benzalazine[9] gave the above pyridazone in 92% yield.

4,5-Dichloro-2-phenyl-3-pyridazone (II, R = C_6H_5).—A solution of 126 g. of mucochloric acid and 40 g. of anhydrous sodium carbonate in 1 l. of cold water was mixed with a cold solution of 108 g. of phenylhydrazine hydrochloride in 1 l. of water. After 1 hour, the yellow solid which formed in quantitative yield was filtered and recrystallized from dilute ethanol. The phenylhydrazone melted at 124–125° (dec.).

Anal. Calcd. for $C_{10}H_8O_2N_2Cl_2$: C, 46.4; H, 3.09; N, 10.80. Found: C, 46.31; H, 2.93; N, 10.81.

Forty grams of mucochloric acid phenylhydrazone was dissolved in 300 cc. of glacial acetic acid and heated to boiling for 15 minutes. A small amount of water was then added to the hot solution. On cooling this deposited 34 g. (90% yield) of crystals of the nearly pure pyridazone. After recrystallization from 90% ethanol, the glistening white prisms melted at 163–164°.

Anal. Calcd. for $C_{10}H_6ON_2Cl_2$: C, 49.8; H, 2.49; N, 11.61. Found: C, 49.65; H, 2.55; N, 11.60.

α-Aryloxy-β-chloro-β-formylacrylic Acids.—To a solution of 31 g. (0.25 mole) of hydroquinone monomethyl ether and 30 g. (0.55 mole) of potassium hydroxide at 5° was added 42 g. (0.25 mole) of mucochloric acid. The solution was stirred and cooled by the addition of crushed ice. After standing at 5–15° for one hour, the solution was poured into a cold solution of 70 ml. of concentrated hydrochloric acid in 100 ml. of water. The oil which precipitated was washed with water and crystallized on standing. Recrystallization from a mixture of benzene and hexane gave 40 g. (62%) of β-chloro-β-formyl-α-(*p*-methoxyphenyl)-acrylic acid, m.p. 105°.

Anal. Calcd. for $C_{11}H_9O_5Cl$: C, 51.5; H, 3.53. Found: C, 51.41; H, 3.54.

By a similar method using *p*-chlorophenol there was obtained a 69% yield of β-chloro-α-(*p*-chlorophenyl)-β-formylacrylic acid, m.p. 55°.

Anal. Calcd. for $C_{10}H_6O_4Cl_2 \cdot H_2O$: C, 43.1; H, 2.89. Found: C, 43.17; H, 2.89.

In analogous fashion, β-naphthol was converted in 44% yield to β-chloro-β-formyl-α-(2-naphthoxy)-acrylic acid, m.p. 156–157°.

Anal. Calcd. for $C_{14}H_9O_4Cl$: C, 60.8; H, 3.28. Found: C, 61.04; H, 3.55.

DAYTON, OHIO

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(8) A. Bistrzycki and C. Herbst, *Ber.*, **34**, 1014 (1901).

(9) H. H. Hatt, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 395.

[CONTRIBUTION FROM THE WALKER LABORATORY, DEPARTMENT OF CHEMISTRY, RENSSELAER POLYTECHNIC INSTITUTE]

The Reaction of Cyanogen and Related Nitriles with 1,3-Dienes. IV. Propionitrile and Butadiene[1]

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In the presence of a chromium oxide catalyst at 420° and atmospheric pressure, propionitrile and butadiene react to form 2-ethylpyridine and aniline. Using a catalyst containing 4% Cr_2O_3, and 4 seconds reaction time, 34 mole per cent. of the nitrile converted is accounted for as a basic product, containing ethylpyridine and aniline in nearly equimolar ratio. The reactivity of propionitrile in the pyridinic synthesis is found to be the same order as that previously found for acetonitrile, hydrogen cyanide and benzonitrile.

This communication reports an investigation of the reactions of propionitrile and butadiene over a chromium oxide–aluminum oxide catalyst at atmospheric pressure in the temperature range of 400°. The reaction conditions were selected to gain results comparable with those reported for butadiene and organic nitriles in Parts I and II of this series.[2] The addition of propionitrile to butadiene at somewhat higher temperatures (600°) and in the homogeneous gas phase has been reported in a recent paper.[3] As well as ethylpyridine in small amounts, larger amounts of aniline were obtained under these reaction conditions. As a guide to the present investigation the thermodynamics for the formation of ethylpyridine and aniline from these reactants were considered. The free energy changes were calculated at 700° and 900°K., respectively (*i.e.*, approx. 400° and 600°C.), using conventional methods.[4] At 700°K., the free energy changes were −13 and −21 kcal./mole, and at 900°K., −6

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(1) Abstracted in part from the thesis submitted by R. E. Myers in partial fulfillment of the requirements for the degree of Bachelor of Science (Chemical Engineering) at Rensselaer Polytechnic Institute, Troy, N. Y.

(2) G. J. Janz and P. J. Hawkins, *Nature*, **162**, 28 (1948); *J. Chem. Soc.*, 1479, 1485 (1949).

(3) C. S. Marvel and J. C. H. Hwa, *J. Org. Chem.*, **15**, 525 (1950).

(4) O. A. Hougen and K. M. Watson, "Chemical Process Principles," Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1948; J. E. Kilpatrick, H. G. Werner, C. W. Beckett, K. S. Pitzer and F. D. Rossini, *J. Research Natl. Bur. Standards*, **39**, 523 (1947); J. G. M. Bremner and G. D. Thomas, *Trans. Faraday Soc.*, **43**, 779 (1947).