of insoluble salts. There were washed with hot benzene, and the filtrate and washings were evaporated to dryness under reduced pressure. The residue was dissolved in ether (100 ml.) and the solution was washed with dilute ammonium hydroxide and with water. Evaporation of the dried ether solution left 6.5 g. (97.5%) of thick oil which crystallized on standing. After two recrystallizations from a mixture of *n*-hexane and benzene, the desired pure *threo*-monoacetate VIII was obtained as white crystals, m.p. 86–88°.

Anal. Calcd. for $C_{16}H_{16}O_3$: C, 74.98; H, 6.29. Found: C, 74.93; H, 6.21.

***dl*-1,2-Di-*O*-acetyl-1,2-diphenylethylene Glycol.**—A pyridine solution (5 ml.) of the above *threo*-monoacetate VIII (0.45 g.) was treated with 5 ml. of acetic anhydride, and the resulting solution was allowed to stand at room temperature for a period of 12 hr. The mixture was then evaporated under reduced pressure, yielding 0.5 g. of solid residue, m.p. 100–105°. After two recrystallizations from a mixture of *n*-hexane and benzene, the pure *dl*-diacetate was obtained, m.p. 116–117°. The reported melting point is 114–116°.[26]

***erythro*-1-*O*-Acetyl-1,2-diphenylethylene Glycol (VII) and *meso*-1,2-Di-*O*-acetyl-1,2-diphenylethylene Glycol (IX).**—The starting material, *meso*-hydrobenzoin, was prepared by the sodium borohydride reduction of benzil after the procedure of Fieser.[15] One recrystallization of the crude product from dilute ethanol yielded sufficiently pure product, m.p. 135–136.5°.

A pyridine solution (10 ml.) of *meso*-hydrobenzoin (1.1 g.) and acetic anhydride (0.6 ml., 1.2 equiv.) was allowed to stand at room temperature for a period of 2 hr., whereupon sufficient water was added to engender cloudiness. On standing in the cold room for 12 hr., a white solid crystallized from the turbid solution. The crystals were collected and the filtrate was acidified with dilute hydrochloric acid and extracted three times with ether. The extracts were washed with water, dried, and evaporated, affording 0.5 g. of thick oil. The original white solid (0.3 g., m.p. 128–131°) was recrystallized from a mixture of *n*-hexane and benzene, yielding white needles, m.p. 135–136.5°. The reported melting point for *meso*-1,2-di-*O*-acetyl-1,2-diphenylethylene glycol is 136–138°.[24] The crude oil extracted from the above aqueous filtrate was chromatographed on 100 g. of silicic acid using benzene, gradually enriched in ether, as eluent. The first 600 ml. of eluent was discarded. Evaporation of the next 700 ml. of eluent left 0.39 g. of white solid. This was recrystallized from a mixture of *n*-hexane and benzene, affording the pure *erythro*-monoacetate VII, m.p. 90–92°. The infrared spectrum showed a strong O–H stretching band at 3380 cm.$^{-1}$ in addition to two typical ester bands at 1732 (C=O) and 1239 cm.$^{-1}$ (C–O).

Anal. Calcd. for $C_{16}H_{16}O_3$: C, 74.98; H, 6.29. Found: C, 75.27; H, 6.43.

1,2-Diphenyl-1-propyl Acetate (IX).—1,2-Diphenyl-1-propanol was prepared in the customary manner by the action of phenylmagnesium bromide (20% excess) on hydratropaldehyde. The thin layer chromatogram of the crude product displayed two spots, with no spot corresponding to starting aldehyde, and its infrared spectrum showed an O–H stretching band at 3420 cm.$^{-1}$, and no carbonyl bands. The crude 1,2-diphenyl-1-propanol (10 g.) was added to a mixture of pyridine (10 ml.) and acetic anhydride (10 ml.), and the resulting solution was stirred at room temperature for a period of 18 hr., then was treated with an excess of chilled dilute sulfuric acid, extracted with ether, and processed in the usual fashion. The crude acetylation product was a thick oil, 11.4 g., which partially crystallized on standing. It was recrystallized once from petroleum ether (b.p. 66–70°), affording sharp rectangular crystals, m.p. 103–105°. The reported melting point for *erythro*-1,2-diphenyl-1-propyl acetate is 109–110°, and that for the *threo*-epimer is 38–39°.[25]

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[26] D. Swern, G. Billen, T. Findley, and J. Scanlan, *J. Am. Chem. Soc.*, **67**, 1786, (1945).

Chlorination of Furfural in Concentrated Hydrochloric Acid

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Treatment of furfural with manganese dioxide or chlorine in hydrochloric acid to produce mucochloric acid yielded two unknown crystalline materials, one as an intermediate of the reaction and the other as a by-product. The intermediate was identified as β-chloro-β-formylacrylic acid and the by-product as α-chlorocrotonolactone.

When furfural is treated with manganese dioxide or chlorine gas in concentrated hydrochloric acid, the major product is mucochloric acid (III) which is the raw material for the synthesis of dichloromaleic acid.

Mucochloric acid has been produced by a variety of methods,[1,2] such as by the action of chlorine on furoic acid, treatment of furoic acid in hydrochloric acid with manganese dioxide, treatment of β,γ-dichlorofuroic acid with an excess of bromine water or with nitric acid, and by reaction of furfural with the reagents mentioned in the first paragraph. The mechanisms of these reactions are very complex since the process involves chlorination, oxidation, and opening of the furan ring. In this article, two unknown crystalline compounds were isolated, one from the initial stage of the reaction of furfural with manganese dioxide in hydrochloric acid and the other from the reaction of furfural with manganese dioxide or chlorine, and their structures were determined.

The reaction of furfural with manganese dioxide in concentrated hydrochloric acid is the most convenient way to prepare mucochloric acid on a laboratory scale A yield of nearly 75% was obtained by the method of Yanagida.[3]

In this process, the reaction can be considered to take place in two steps, the first below and the second above 10°. If the reaction is interrupted after the first step and extracted with ether, and the ether extract is distilled at reduced pressure, colorless crystals of m.p. 53–55° are obtained (compound A). If the reaction is allowed to proceed to completion, the mucochloric acid is separated by filtration, and the mother liquors are ether extracted, evaporation of the ether and distillation of the residue (105–115° at 4 mm.) yields a colorless liquid that crystallizes on standing, m.p. 25–27° (compound B). However, treatment of furfural with chlorine in hydrochloric acid is more convenient to obtain compound B in high yield.

Elementary analysis of compound A agreed with formula $C_4H_3O_3Cl$. Its infrared spectrum resembled that of mucochloric acid which exists not as the open-chain α,β-dichloro-β-formylacrylic acid but in the ring structure (III). The spectrum had bands at 1625

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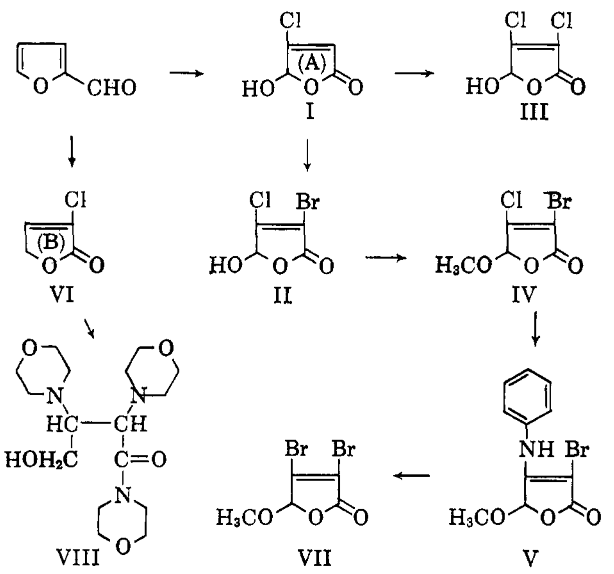
[1] D. T. Mowry, *J. Am. Chem. Soc.*, **72**, 2535 (1950).

[2] A. P. Dunlop and E. Sherman, U. S. Patent 2,821,553 (1958).

[3] M. Yanagida, *J. Pharm. Soc. Japan*, **72**, 1383 (1952).

SCHEME I



(C–C double bond), at 1760 (lactone carbonyl), and at 3290 cm.$^{-1}$ (hydroxyl). Carboxylic acid bands were absent. Compound A was converted to mucochloric acid with manganese dioxide in concentrated hydrochloric acid at 60–80°. From these results, the compound was presumed to be the ring form of α- or β-chloro-β-formylacrylic acid.

Hill[4] and Prins[5] reported the oximes (m.p. 150°) which may be derived from α- or β-chloro-β-formylacrylic acid; however, their proof of the position of the chlorine atom may be questionable.

To determine the position of the chlorine atom, the compound was brominated to yield colorless crystals, m.p. 122–123°. The chloro–bromo compound gave a pseudo methyl ester, m.p. 37–38°. The ester was treated with aniline by the method of Wasserman[6] to form a monoanilino derivative, m.p. 115–117°, which gave no depression in melting point upon admixture with an authentic specimen of α-bromo-β-anilino-γ-methoxycrotonolactone[6] (V), and whose carbon–hydrogen analysis agreed with formula V. From these results, the structure of compound A was determined to be the cyclic form of β-chloro-β-formylacrylic acid (I). According to Kuh and Shepard,[7] β-bromo-α-chloro-β-formylacrylic acid is obtained by bromination of furfural followed by chlorination, which shows that the β-position of β-formylacrylic acid is more reactive toward halogenation than the α-position. These results are confirmed by the present work.

The elementary analysis of compound B, which was obtained as a by-product in the reaction of furfural with manganese dioxide or chlorine in concentrated hydrochloric acid to produce mucochloric acid, agreed with that calculated for $C_4H_3O_2Cl$. Its infrared spectrum showed bands at 1625 (C–C double bond) and 1775 cm.$^{-1}$ (carbonyl group) and had no hydroxyl bands. The spectrum corresponded to that of α-chlorocrotonolactone over the whole wave-length range. Compound B reacted with morpholine to produce the trimorpholino derivative (VIII), which was also produced from authentic α-chlorocrotonolactone.[8] From this evidence, the structure of compound B is deduced to be that of α-chlorocrotonolactone (VI).

Experimental

β-Chloro-β-formylacrylic Acid (I).—A round-bottom four-necked flask fitted with an efficient agitator, a dropping funnel, and a thermometer was charged with 1 l. of concentrated hydrochloric acid (35%) and cooled to 0° in a salt–ice mixture. A mixture of 80 g. of freshly distilled furfural and 320 g. of finely powdered manganese dioxide was added in small portions over a period of 3 hr. while the temperature was maintained below 10°. The reaction mixture was stirred at room temperature for 0.5 hr. and then was extracted with ether in a continuous extractor. After drying (sodium sulfate) and removal of the ether, 92 g. of a light yellow liquid was obtained. This was distilled *in vacuo* (120–150° at 1 mm.) and recrystallized from benzene yielding colorless crystals (85 g.) of m.p. 53–55°. Its molecular weight was 135 by cryoscopy in dioxane.

Anal. Calcd. for $C_4H_3O_3Cl$: C; 35.7; H, 2.23; Cl, 26.4; mol. wt., 134.5. Found: C, 35.84; H, 2.39; Cl, 26.22; mol. wt., 135.

Preparation of Mucochloric Acid (Yanagida's Method).—In the preceding procedure, after the reaction mixture attained room temperature and was stirred for 0.5 hr., it was heated with stirring to 60° in a water bath and an additional 140 g. of manganese dioxide was added in small portions while the temperature was raised to 80°. After the final addition, the reaction temperature was raised to 100° and was held there until the black color of the mixture changed to a red-brown. The reaction mixture was decanted while hot into a beaker and was allowed to cool. The crystals that formed were filtered and recrystallized from water to yield colorless crystals of mucochloric acid, m.p. 125°.

Mucochloric Acid (III) from I.—Five grams of I was suspended in 50 ml. of concentrated hydrochloric acid and 5 g. of manganese dioxide was added at room temperature. The reaction flask was heated slowly to 60° with stirring while an additional 20 g. of manganese dioxide was added over a period of an hour. The mixture then was heated at 95° for 0.5 hr., decanted into a beaker, and allowed to cool. Colorless crystals (2 g.), m.p. 125–126.5°, were obtained after recrystallization from water. They did not depress the melting point of an authentic sample of mucochloric acid.

Bromination of I.—A four-neck round-bottom flask fitted with an efficient agitator, a dropping funnel, and a thermometer was charged with 12 g. of I and 50 ml. of water and was heated to 60–70°; 16 g. of bromine was added over a period of an hour. After cooling, filtration, and recrystallization from water, 16 g. of α-bromo-β-chloro-β-formylacrylic acid (II), m.p. 122–123°, was obtained.

Methylation of II.—The esterification was carried out by heating 11.5 g. of II with 60 ml. of methanol and 10 drops of 98% sulfuric acid. Lachrymatory crystals (8 g.) of the pseudo methyl ester, α-bromo-β-chloro-γ-methoxycrotonolactone (IV), were obtained, m.p. 37–38°, after recrystallization from petroleum ether (b.p. 35–70°).

α-Bromo-β-anilino-γ-methoxycrotonolactone (V).—A cold solution of 1.74 g. of aniline in 4 ml. of methanol was added to 2 g. of IV in 4 ml. of methanol, and the resulting solution was placed in the refrigerator overnight. The dropwise addition of water with stirring to the cold solution caused an oil to separate which gradually solidified to a light yellow solid. After several recrystallizations from methanol, colorless crystals were obtained, m.p. 115–117°.

Anal. Calcd. for $C_{11}H_{10}O_3BrN$: C, 46.41; H, 3.64. Found: C, 46.48; H, 3.55.

In a similar manner, mucobromic acid was converted to the pseudo methyl ester (VII), m.p. 48.5–49.5°, and then to the β-anilino derivative (V) which was identical in melting point with the one derived from IV and gave no depression upon admixture with it.

α-Chlorocrotonolactone (VI).—The reaction was run in a five-neck 300-ml. round-bottom flask fitted with an efficient agitator,

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(4) Hill and Allen, *Am. Chem. J.*, **19**, 665 (1897).

(5) H. J. Prins and H. G. Haring, *Rec. trav. chim.*, **73**, 479 (1954).

(6) H. H. Wasserman and F. M. Precopio, *J. Am. Chem. Soc.*, **76**, 1242 (1954).

(7) E. Kuh and L. Shepard, *ibid.*, **75**, 4597 (1953).

(8) Y. Hata, *J. Chem. Soc. Japan*, **79**, 1531 (1958).

reflux condenser, dropping funnel with a capillary stem, gas feed tube, and a thermometer. It is important that the capillary of the dropping funnel always remains below the surface of the reaction mixture.

The flask was charged with 250 ml. of 35% hydrochloric acid and cooled to 0°. A 1:2 mixture of chlorine and air (v./v.) was passed through the liquid at a rate of 2 l./min. Forty grams of furfural was added dropwise below 5° from the dropping funnel. After the addition, the reaction mixture was colorless. It was then heated slowly with stirring to 85° over a period of 2 hr. and kept at this temperature for 1.5 hr. The mixture then was cooled to room temperature to yield 14 g. of crystalline mucochloric acid. The mother liquors were extracted with ether, and the ether extract was vacuum distilled to yield 21 g. of a colorless liquid, b.p. 105–115° (4 mm.). This crystallized on standing and had a melting point of 25–27° after recrystallization from water.

Anal. Calcd. for $C_4H_3O_2Cl$: C, 40.50; H, 2.53; Cl, 29.92. Found: C, 40.96; H, 2.55, Cl, 29.94.

Trimorpholino Derivative of VI (VIII).—A mixture of 4 ml. morpholine and 0.8 g. of VI in 40 ml. of dry ether was refluxed for 6 hr. and allowed to stand overnight. The resulting white precipitate was separated and extracted with 50 ml. of dry acetone. Concentration of the acetone extract yielded 500 mg. of white crystals, m.p. 157–158°, after recrystallization from acetone and benzene.

Anal. Calcd. for $C_{16}H_{29}O_5N_3$: C, 55.96; H, 8.51; N, 12.24. Found: C, 55.38; H, 8.58; N, 11.96.

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Some New Reactions and Derivatives of Azulene[1]

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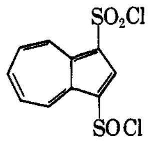
In the course of our studies on the chemistry of azulene[4] a number of new reactions and derivatives of azulene have been found which did not prove pertinent to subsequent papers. These collected results are reported.

The facile reaction of azulene with mercuric chloride to form a bis(chloromercuri)azulene had been observed earlier,[5] but the derivative was very insoluble in organic solvents and attempts to establish the positions occupied by the chloromercuri groups through displacement reactions were unsuccessful (except for the formation of 1-acetylazulene in low yield). The analogous reaction with mercuric acetate has been found to give a diacetoxymercuri derivative (1) in high yield. Treatment of an acetic acid solution of **1** with iodine gave 1,3-diiodoazulene and provided evidence that the dimercuri compounds were, as expected, 1,3 substituted. Reaction of **1** with bromine or nitryl chloride, however, resulted in oxidative decomposition, and treatment with N-bromosuccinimide or N,N-dibromomethylhydantoin gave an unstable red oil which was not characterized. Warming a mixture of acetic anhydride and **1** in acetic acid formed 1-acetylazulene in 34% yield but no 1,3-diacetylazulene. This was unexpected, as no azulene was obtained when **1** was exposed to 85% phosphoric acid for several hours.[6]

Reaction of azulene with sulfur trioxide–dioxane adduct and then basification gave a red solid. That this material, which was not obtained analytically pure, was sodium 1-azulenesulfonate was indicated by the absorptions at 8.5, 8.95, 9.37, and 9.57 μ[7] in its infrared spectrum; its reaction with nitric acid and acetic anhydride to give 1,3-dinitroazulene[8a]; and the formation of azulene-1-sulfonyl-3-sulfinyl dichloride (2) from the reaction of the free acid with excess thionyl chloride. Attempts to isolate the free 1-azulenesulfonic acid afforded hygroscopic maroon needles. These results are similar to those obtained by Treibs and Schroth[8b] in the analogous sulfonation of guaiazulene and the preparation of a number of derivatives of the guaiazulenesulfonic acid.



2

The direct introduction of a cyano group onto benzenoid aromatic nuclei by Lewis acid-catalyzed reactions with cyanogen bromide is well known.[9] It has been found, however, that uncatalyzed reactions with thiophene[10] and furan[11] gave the α-bromo rather than the cyano substitution products. We have examined the stannic chloride-catalyzed reaction of cyanogen bromide with azulene, and the results obtained differ appreciably from those reported by Treibs[12] while our studies were in progress. The addition of azulene to one equivalent of preformed cyanogen bromide–stannic chloride complex in ether gave a 36% (94% net) yield of 1-cyanoazulene. When the same procedure was used but with a tenfold excess of cyanogen bromide–stannic chloride, there were obtained two different products: 1,3-dibromoazulene (16%) and a new substance which showed absorption at 567 mμ and a sharp band at 4.54

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[1] Supported in part by grants from the Office of Ordnance Research, U. S. Army, and from the National Science Foundation.

[2] National Science Foundation Predoctoral Fellow, summer, 1959; National Institutes of Health Fellow, 1959–1961.

[3] National Institutes of Health Fellow, 1961–1963.

[4] (a) A. G. Anderson, Jr., and L. L. Replogle, *J. Org. Chem.*, **28**, 262 (1963); (b) A. G. Anderson, Jr., R. G. Anderson, and T. S. Fujita, *ibid.*, **27**, 4535 (1962), and preceding papers.

[5] A. G. Anderson, Jr., E. J. Cowles, J. J. Tazuma, and J. A. Nelson, *J. Am. Chem. Soc.*, **77**, 6321 (1955).

[6] The 1,3-bis(chloromercuri)azulene was readily converted to azulene (66%) by this reagent.[5]

[7] N. B. Colthup, *J. Opt. Soc. Am.*, **40**, 397 (1950).

[8] (a) The electrophilic displacement of groups from the 1-position of azulene is well known [see, for example, A. G. Anderson, Jr., and R. N. McDonald, *J. Am. Chem. Soc.*, **81**, 5669 (1959)]; (b) W. Treibs and W. Schroth, *Ann.*, **586**, 202 (1954).

[9] P. Karrer and E. Zeller, *Helv. Chim. Acta*, **2**, 482 (1919); **3**, 261 (1920).

[10] W. Steinkopf, *Ann.*, **430**, 78 (1923).

[11] A. H. Klopp and G. F. Wright, *J. Org. Chem.*, **4**, 142 (1939).

[12] W. Treibs, *Ber.*, **92**, 606 (1959).