for 15 min, 0.233 mol of the appropriate ester was added in 75 ml of ether. The reaction mixture was stirred for 20 min; then an excess of ammonium chloride was added. The ammonia was evaporated on the steam bath as an equal volume of ether was added. The resulting ethereal suspension was stirred with water to dissolve the inorganic salts. The layers were separated, and the aqueous layer was extracted twice with small portions of ether. The combined ethereal solution was dried over anhydrous sodium sulfate and saturated with anhydrous hydrogen chloride. The resulting precipitate was collected and dried to give the crude hydrochloride salts of the aroyl N,N-dimethylglycinonoitriles 2a-c in yields of 80, 70, and 75%, respectively. The salts were neutralized with aqueous sodium bicarbonate to liberate the free base. Extraction of the aqueous mixture with ether, removal of the ether under reduced pressure, and recrystallization of the solid residue from hexane provided 2a-c in the yields given in Table I.

To a solution of the aryl N,N-dimethylglycinonitrile in ethanol was added an excess of aqueous copper acetate solution with stirring. The mixture was stirred for about 20 min; then the precipitate was collected and recrystallized from 95% ethanol to give the copper chelate (see Table I).

Benzoyl N,N-Dimethylglycinamide (6a).-Benzoyl N,N-dimethylglycinonitrile (2a) (1g) was dissolved in 5g of concentrated sulfuric acid and heated on the steam bath for 30 min. The reaction mixture was poured onto crushed ice and the solution was neutralized with solid sodium bicarbonate. The mixture was extracted several times with ether; the combined ethereal extract was dried over anhydrous potassium carbonate and the ether was removed under reduced pressure. The residue was recrystallized from a benzene-hexane mixture giving 0.9 g (85%) of the amide **6a**: mp 93–94°; ir, 3.0 (s), 3.15 (s), 3.5 (m), 3.55 (m), 5.9 (s), 6.1 (w), and 6.25 (m)  $\mu$ . Anal. Calcd for C<sub>11</sub>H<sub>14</sub>N<sub>2</sub>O<sub>2</sub>: C, 64.1; H, 6.84; N, 13.59.

Found: C, 64.38; H, 6.75; N, 13.33.

3-Dimethylamino-4-para-Substituted 6-Phenyl-2(1H)-pyridones (Table II) .-- The aroyl N,N-dimethylglycinonitrile was stirred into five times its weight of polyphosphoric acid, and then an equivalent of acetophenone was added. The reaction mixture was placed in an oil bath and heated at 80-90° until a homogeneous solution was obtained. An additional equivalent of acetophenone was added and the temperature was raised to 140° and maintained at this temperature for 25 min. Upon addition of the solution to crushed ice, a precipitate formed. The resulting mixture was made basic with ammonium hydroxide and the precipitate was collected. Recrystallization of the product from benzene-ethanol gave the pyridone.

In a similar manner,  $\hat{N}$ , N-dimethylbenzoylglycinamide (6a) was cyclized to give pyridone 5a in 35% yield.

Registry No.---1, 926-64-7; acetophenone, 98-86-2; 2a, 16607-55-9; 2b, 16607-56-0; 2c, 16607-57-1; 3a, 16591-65-4; 3b, 16591-66-5; 5a, 16607-58-2; 5b, 16607-18-4; 5c, 16607-19-5; 6a, 16622-18-7; 6b, 16607-20-8.

## **A** Convenient Preparation of Dimethyl Cyclohexa-1,3-diene-1,4-dicarboxylate. A Bicyclo[2.2.2]octane Precursor

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We wish to report a convenient synthesis of dimethyl cyclohexa-1,3-diene-1,4-dicarboxylate (5; see Chart I), a bicyclo[2.2.2]octane precursor. Bridgehead substituted bicyclo[2.2.2]octanes have been a subject of intensive study.1 A time-consuming synthesis of these



compounds was developed by Kauer and coworkers<sup>2</sup> which involves the dehydrohalogenation of dimethyl 1,4-dibromocyclohexane-1,4-dicarboxylate followed by addition of ethylene to the resulting 1,3-diene.

Although 1,4-cyclohexanedione is available by other routes,<sup>3</sup> we found the oxidation of 1,4-cyclohexanediol with chromium trioxide to be a convenient source of this dione. Compound 1 reacts readily with acetone cyanohydrin to yield compound 2. This material, in turn, is then converted in two steps into dimethyl 1,4-diacetoxy-1,4-dicarboxylate (4). Pyrolysis of this diacetate at 400° affords the desired diene (5) in 75%yield. The other major product, formed in 18% yield, is dimethyl terephthalate. The crude pyrolysate reacted readily with maleic anhydride to give 1,4-bis-(methoxycarbonyl)bicyclo[2.2.2]oct-5-ene-endo-2,3-dicarboxylic anhydride (6). It is of interest to note the remarkable selectivity of the pyrolysis reaction under the conditions studied, especially since previous work strongly suggests that dimethyl cyclohexa-1,4-diene-1-4-dicarboxylate is the most stable of the methyl esters of the dihydroterephthalic acids.<sup>4</sup>

### Experimental Section<sup>5</sup>

1,4-Cyclohexanediol.-This alcohol was prepared in 93% yield by the hydrogenation of hydroquinone according to the procedure of Owen and Robins.6

1,4-Cyclohexanedione  $(1)^{8,7}$  was prepared by adding a solution of  $CrO_3$  (9.1 g) and concentrated sulfuric acid (7.7 ml) in water  $(33.8-ml total volume)^{8}$  to 1,4-cyclohexanediol (5.0 g, 0.043 mol) in acetone (300 ml) at 10°. After addition was completed (1 hr, voluminous precipitate), stirring for 0.5 hr, pouring into ice water, neutralizing with  $Na_2CO_3$ , continuous extraction with CH<sub>2</sub>Cl<sub>2</sub>, drying (MgSO<sub>4</sub>), evaporating, and sublimation of the residue gave 4.1 g (84%) of 1.

1,4-Dihydroxy-1,4-dicyanocyclohexane (2).-1,4-Cyclohexanedione (56 g, 0.5 mol) was mixed with acetone cyanohydrin<sup>9</sup> (750 ml, Matheson Coleman and Bell, practical grade) and heated to

(2) J. C. Kauer, R. E. Benson, and G. W. Parshall, J. Org. Chem., 30, 1431 (1965). These authors discuss the synthetic difficulties of previously reported approaches toward these compounds.

(3) A. T. Nielsen and W. R. Carpenter, Org. Syn., 45, 25 (1965).

(4) See ref 2, footnote 17.

(5) Melting points are corrected and were recorded on a Fisher-Johns apparatus. Microanalyses were done by H. C. Jones of this laboratory. Ultraviolet spectra were recorded on a Perkin-Elmer Spectracord Model 4000A. Infrared spectra were taken as KBr pellets using a Perkin-Elmer Infracord Model 137 spectrophotometer. Gas chromatographic analyses were done using an F & M Model 700 chromatograph. Recrystallizations were done in ethyl acetate.

(6) L. N. Owen and P. A. Robins, J. Chem. Soc., 320 (1949).

(7) J. R. Vincent, A. F. Thompson, Jr., and L. I. Smith, J. Org. Chem., **3**, 603 (1939).

(8) C. Djerassi, R. R. Engle, and A. Bowers, ibid., 21, 1547 (1956). (9) H. J. Ringold, J. Amer. Chem. Soc., 82, 961 (1960).

40°: 10% NaOH (20 ml) was added; and this temperature was kept for 0.5 hr. The mixture was cooled and poured into 1500 ml of ice water containing 10 ml of glacial HOAc. The white precipitate after drying and recrystallizing weighed 56 g (67%), mp 167-168°. The yield of cyanohydrin can be raised to 85% of theoretical by running the reaction overnight at room temperature. An infrared spectrum of this solid exhibited absorptions inter alia at 3400 (OH stretching vibration) and at 2265  $\rm cm^{-1}$  (C=N stretching vibration).

Anal. Calcd for C<sub>6</sub>H<sub>10</sub>O<sub>2</sub>N<sub>2</sub>: C, 57.85; H, 6.07; N, 16.85. Found: C, 57.54; H, 6.14; N, 16.97.

Dimethyl 1,4-dihydroxy-1,4-cyclohexanedicarboxylate (3) was prepared by slowly adding HCl (Matheson, reagent grade) to a solution of 2 (8.4 g, 0.05 mol) in methanol (100 ml) until no more gas was absorbed. The mixture was stirred for an additional 2 hr and the resulting precipitate was collected and reacted with water (200 ml) overnight. The recrystallized white solid weighed 9.1 g (81% yield), mp 162-175°. An infrared spectrum of this material exhibited absorptions inter alia at 3510 (OH stretching vibration) and at 1730 cm<sup>-1</sup> (C=O stretching vibra-The diester (2.0 g) was saponified under usual condition). tions<sup>10</sup> and the white crystals collected after acidification were recrystallized to obtain 1.5 g of 1,4-dihydroxy-1,4-cyclohexanedicarboxylic acid, mp 224-237°. An infrared spectrum of this solid (KBr pellet) exhibited absorptions inter alia at 3415 and  $1720 \text{ cm}^{-1}$ 

Anal. Calcd for C<sub>8</sub>H<sub>12</sub>O<sub>6</sub>: C, 47.06; H, 5.93. Found: C, 46.92; H, 5.81.

Dimethyl 1,4-Diacetoxy-1,4-cyclohexanedicarboxylate (4).--To acetic anhydride (16.4 g, 0.16 mol) at 80° was slowly added a solution of compound 3 (9.2 g, 0.04 mol) in HOAc (80 ml). The reaction mixture was refluxed overnight, cooled, and poured into ice water. After drying and recrystallization 11.4 g (90% yield) of a white solid was obtained, mp 168-182°.

An infrared spectrum of this solid exhibited an absorption, inter alia, at 1750 cm<sup>-1</sup> (acetate C=O stretching vibration).

Anal. Calcd for C14H20O8: C, 53.16; H, 6.38. Found: C, 53.14; H, 6.27.

Dimethyl Cyclohexa-1,3-diene-1,4-dicarboxylate (5).--Pyrolyses<sup>11</sup> were conducted in a  $0.75 \times 18$  in. quartz column, filled with 0.25-in.-diameter glass beads, mounted vertically and surrounded by an electric heating oven. A slow stream of nitrogen was passed through the column during the pyrolysis. The temperature was controlled by means of a "Pyro-O-Vane" temperature controller. The temperature inside the column was measured with a thermocouple inserted in a well near the center of the column. The pyrolysate was collected in two traps connected in series and immersed in a Dry Ice-perchloroethylene mixture.

In a typical run, 5.0 g of dimethyl 1,4-diacetoxy-1,4-cyclohexanedicarboxylate was dissolved in 300 ml of methyl acetate at 50°, maintained at this temperature throughout the reaction by means of flexible heating tape, and was dropped through the column at 400° and at a rate of ca. 2.5 ml/min. When the addition was complete, the column was allowed to cool and was washed with additional methyl acetate.

Removal of the solvent afforded 3.8 g of a slightly yellow product. Vapor phase chromatographic analysis12 revealed that 95% of the starting material had been converted into two major products with retention times of 5.8 and 6.2 min. The first peak accounted for 18% of the pyrolysate, whereas the latter represented a 75% yield. Samples of both materials were collected from the gas chromatograph. The product with a retention time of 5.8 min melted at 139-141°, identical with the melting point of dimethyl terephthalate.<sup>13</sup> Comparison of the infrared spectrum and vpc retention time with an authentic sample<sup>14</sup> completed the identification. The 6.2-min product melted at  $83.5-84.2^{\circ}$  (lit.<sup>2</sup> mp  $83.1-84.6^{\circ}$ ). Comparison of the infrared and ultraviolet spectra with those of authentic samples

helped confirm the identification.<sup>15</sup> To complete the identification, the adduct of the pyrolysate with maleic anhydride was prepared by a previously described procedure.<sup>16</sup> The adduct melted at 185-192° (lit. mp 188.0-188.6°,<sup>16</sup> 191.5°<sup>17</sup>) and its infrared spectrum, as a KBr pellet, exhibited absorptions at 1865, 1780, 1745, and 1620 cm<sup>-1</sup> identical with the published spectrum<sup>17</sup> of 1,4-bis(methoxycarbonyl)bicyclo[2.2.2]oct-5-ene-endo-2,3-dicarboxylic anhydride.

Registry No.-2, 16273-48-6; 3, 16273-49-7; 3, free acid, 16273-50-0; 4, 16273-51-1; 5, 1659-95-6.

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(15) The author is grateful to Dr. J. C. Kauer for supplying these spectra. (16) J. C. Kauer, U. S. Patent 3,071,597 (Jan 1, 1963). (17) G. Smith, C. L. Warren, and W. R. Vaughan, J. Org. Chem., 28, 3323 (1963)

# Synthesis of $\alpha$ -Hydroxyarylacetic Acids from Bromoform, Arylaldehydes, and Potassium Hydroxide, with Lithium Chloride Catalyst

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A one-step preparation of  $\alpha$ -methoxyarylacetic acids from arylaldehydes, bromoform (or chloroform), and potassium hydroxide in methanol has been described.<sup>1</sup> The preparative method for the  $\alpha$ -hydroxyarylacetic acids given here is a modification of that procedure, differing in that lithium chloride serves as an additional catalyst along with the potassium hydroxide,<sup>2</sup> and a 50:50 mixture of water and 1,4-dioxane acts as solvent, instead of methanol. The yields in these  $\alpha$ -hydroxy compound syntheses (quantitative) are decidedly better than those obtained in the preparations of  $\alpha$ -methoxy compounds (1-80%).

There are a number of articles in the literature wherein others have reported preparation of trihalomethyl carbinols (a proposed intermediate in this reaction) in heterogeneous media, and/or treated trihalomethylcarbinols with nucleophilic reagents to obtain  $\alpha$ substituted acids, but none of these procedures<sup>2,3</sup> produces a quantitative yield of product.

In some of these cases<sup>2</sup> the yields are less because side reactions, such as the Cannizzaro, are occurring simultaneously or exclusively. In fact, when the preparations of the  $\alpha$ -hydroxyarylacetic acids were attempted in pure 1,4-dioxane and with lithium hydroxide as a base catalyst (a heterogeneous mixture), with six different aryl aldehydes only the corresponding arylcarboxylic acids were isolated.

<sup>(10)</sup> J. Cason and H. Rapoport, "Laboratory Text in Organic Chemistry," Prentice-Hall, Inc., Englewood Cliffs, N. J., 1950, p 83. (11) W. J. Bailey, R. Barclay, and R. A. Baylouney, J. Org. Chem., 27,

<sup>1851 (1962)</sup> 

<sup>(12)</sup> A 6 ft.  $\times$  0.25 in. diameter 10% XE-60 on 60/80 mesh Chromosorb W column was used. No corrections were made for differences in thermal conductivities

<sup>(13)</sup> I. Heilbron, "Dictionary of Organic Compounds," Vol. 5, Oxford University Press, New York, N. Y., 1965, p 2,949.

<sup>(14)</sup> Du Pont dimethyl terephthalate, refined grade.

<sup>(1)</sup> W. Reeve and C. W. Woods, J. Amer. Chem. Soc., 82, 4062 (1960); W. Reeve and E. L. Compere, Jr., ibid., 83, 2755 (1961).

<sup>(2)</sup> The potassium hydroxide is a reagent as well as a catalyst; see E. D. Bergmann, D. Ginsburg, and D. Lavie, *ibid.*, **72**, 5012 (1950).
(3) (a) P. Hebert, Bul. Soc. Chim. Fr., **27**, 45 (1920); (b) J. W. Howard, J. Amer. Chem. Soc., **47**, 455 (1925); (c) J. W. Howard, *ibid.*, **52**, 5059 (1930); (d) J. Jocicz, Zh. Russ. Fiz. Khim. Obshchest., 29, 100 (1897); Chem. Zentr., 1. 1013 (1897).