with benzoyl chloride as recommended by King.[8] The results are summarized in Table III.

Photocyclization of Styrylpyridinium Salts (II).—The usual procedure was to dissolve 0.50 g of the styrylpyridinium salt (II) in 200 ml of 95% ethanol in a 250-ml beaker, and then 25 mg of iodine was added. The top of the beaker was closed with aluminum foil and the solution was stirred magnetically while the solution was irradiated by a 250-w mercury lamp placed 20 cm from the side of the beaker. Progress of the reaction was followed by observing the ultraviolet absorption spectra of samples withdrawn at regular intervals.

Preliminary experiments done with the 1-styrylpyridinium cation revealed that the purity of the product was decreased if stirring was omitted, that distilled water was not quite so satisfactory a solvent for the irradiation (low solubility of iodine) as ethanol, that the perchlorate anion was as satisfactory as the bromide, and that the optimum reaction time was about 24 hr. Omission of iodine, but not the stirring, reduced the yield from 60 to 40% and gave a less pure product. While quantum yields were not determined, it was noted that decrease in intensity of radiation (operation of lamp at lower voltage or at greater distance from the solution) resulted in a marked decrease in the rate of cyclization.

After the irradiation was complete, the solution was concentrated and the salt (if not a perchlorate) was taken up in about 25 ml of water, filtered, and converted to a perchlorate by addition of perchloric acid. Methanol and methanol–ethyl acetate were used as solvents for crystallization. The yields represented in Table I are not optimum and in most cases are the result of a single experiment. New phenanthridizinium salts obtained by the photocyclization method are listed in Table IV.

Acknowledgment.—The authors wish to express their appreciation to Drs. Peter Smith and James Crosthwaite for advice and encouragement.

Aldehyde Synthesis. A Study of the Preparation of 9,10-Anthracenedicarboxaldehyde and Other Aromatic Dialdehydes

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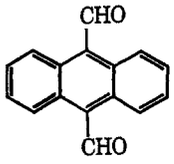
Received March 14, 1966

9,10-Anthracenedicarboxaldehyde can be conveniently prepared by the reaction of 9,10-bis(chloromethyl)-anthracene in dimethyl sulfoxide with the sodium salt of 2-nitropropane. The role of dimethyl sulfoxide is shown to be that of a solvent only. Other methods for the preparation of 9,10-anthracenedicarboxaldehyde have been examined and shown to be of no value or inferior in some way to the above method. An unexpected product, 10-methyl-9-anthraldehyde, was formed as one of the products in the reaction of 9,10-bis(chloromethyl)-anthracene with hot dimethyl sulfoxide. Tetramethylterephthaldialdehyde, 2,5-dimethylterephthaldialdehyde, and 1,5-naphthalenedicarboxaldehyde can also be easily prepared by the same procedure.

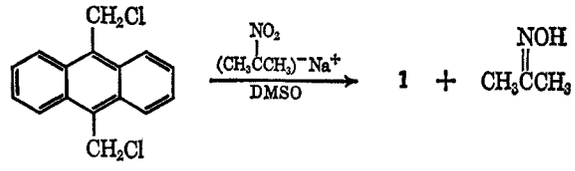
Aromatic dialdehydes, such as 9,10-anthracenedicarboxaldehyde (**1**), are potentially valuable synthetic intermediates. For the preparation of **1**, no convenient, simple, and economical procedure is available. Two methods for the synthesis of **1** have been reported.[1] One method involves a low-yield, multistep synthesis starting from anthraquinone and is obviously not practical. The other method employs the reaction of 9,10-dibromoanthracene with butyllithium to form the 9,10-dilithio derivative which gives aldehyde **1** upon treatment with dimethylformamide. This procedure is reasonable but is neither convenient nor economical.



1

Discussion

A simple, convenient, good-yield synthesis for aldehyde **1** has now been devised and shown to be general for three other aromatic dialdehydes. The reaction of a suspension of 9,10-bis(chloromethyl)anthracene (**2**) in dimethyl sulfoxide with an ethanolic solution of the sodium salt of 2-nitropropane leads to the formation of **1** in 70% yield. 9,10-Bis(chloromethyl)anthracene is readily prepared in good yield from anthracene *via* chloromethylation.[2-6]



2

Noteworthy features of this reaction are the following. (1) Dimethyl sulfoxide, as an additional solvent, is necessary for the reaction to occur. Aldehyde **1** cannot be prepared by the method of Hass and Bender[7] which utilizes conditions similar to those mentioned without the use of dimethyl sulfoxide. (2) Dimethylformamide may also be employed as the reaction solvent, but yields are not so satisfactory (52%). (3) 2-Nitropropane is necessary for the reaction to occur. An experiment carried out without 2-nitropropane resulted in formation of 9,10-bis(ethoxymethyl)anthracene which obviously was formed from the reaction of sodium ethoxide with chloride **2**. Furthermore, a vapor phase chromatographic analysis of a reaction mixture (using 2-nitropropane) confirmed

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the presence of the theoretical amount of acetone oxime as the other product. Thus, the anion of 2-nitropropane is the active species in this reaction, and dimethyl sulfoxide and dimethylformamide serve only as solvents. (4) A reaction was carried out without ethanol and with only the sodium salt of 2-nitropropane in dimethyl sulfoxide. In this case, aldehyde **1** was formed, but in a lower yield (52%); the presence of ethanol probably prevents undesirable side reactions.

The Sommelet reaction has been shown to be unsuccessful for the conversion of di-*ortho*-substituted benzylic-type halides (*via* hexamethylenetetramine) to aldehydes,[8,9] and a fused ring acts as an *ortho* substituent.[9] A number of other aldehyde syntheses[10-12] were also considered and shown to be of no value as is demonstrated in the Experimental Section. A noteworthy result was obtained in the case of the reaction of chloride **2** with hot dimethyl sulfoxide. 10-Methyl-9-anthraldehyde was isolated and characterized along with aldehyde **1**. The formation of 10-methyl-9-anthraldehyde is unusual in that it formally represents reduction of one of the chloromethyl groups to a methyl substituent and oxidation of the other chloromethyl group to an aldehydic function.

Tetramethylterephthaldialdehyde, 2,5-dimethylterephthaldialdehyde, and 1,5-naphthalenedicarboxaldehyde were prepared from the corresponding bis(chloromethyl) precursors in the same manner as for aldehyde **1**, and comparable yields were obtained.

Experimental Section

9,10-Anthracenedicarboxaldehyde (1).—To a stirred suspension of 25 g (0.091 mole) of 9,10-bis(chloromethyl)anthracene[2] (**2**) in 500 ml of dimethyl sulfoxide (dried over calcium hydride) under nitrogen at room temperature (20–25°) was added slowly (0.5 hr) a solution prepared by adding 30.0 g (0.34 mole) of 2-nitropropane to a solution of 5.0 g (0.22 g-atom) of sodium in 300 ml of absolute ethanol. The reaction mixture gradually changed from yellow to dark orange and became homogeneous. At this point (2.5–3.0 hr), the mixture was filtered into 2 l. of ice–water. The orange precipitate, which was filtered off, was dissolved in methylene chloride and extracted with water. The methylene chloride solution was dried with sodium sulfate and concentrated to dryness. The orange product weighed 6.45 g (30%), mp 241–244° dec (lit.[1] mp 244–245°). The original reaction filtrate in ice–water was refrigerated overnight, and the yellow-orange precipitate was filtered off, washed with water, and then dissolved in methylene chloride. The solution was extracted with dilute hydrochloric acid and dilute sodium bicarbonate solution. The methylene chloride solution was dried with sodium sulfate and concentrated to a very small volume (~50 ml) until crystallization became very heavy. After refrigeration, the orange crystals were removed by filtration and weighed 8.35 g (40%), mp 241–244° dec. The infrared spectrum (KBr) of the product showed strong absorption at 1680 cm^{-1} (C=O). A total yield of 70% was obtained.

Anal. Calcd for $C_{16}H_{10}O_2$: C, 82.0; H, 4.3. Found: C, 81.7; H, 4.5.

In a similar experiment (with dimethyl sulfoxide), no product was filtered from the original reaction mixture, but a comparable total yield was obtained.

Dimethylformamide was employed as the reaction solvent by the same procedure except that 6–8 hr were required for the reaction mixture to become homogeneous. The product was obtained in this manner in 52% yield.

One run was carried out in which the solvent was removed from the ethanolic solution of the sodium salt of 2-nitropropane, and the dry salt was added to the reaction mixture. Only 1 hr was needed for the reaction mixture to become homogeneous and a 52% yield was obtained.

An experiment carried out after the method of Hass and Bender[7] (without dimethyl sulfoxide) for 17 hr at room temperature yielded only traces of a carbonyl compound as well as starting material.

In one run, a sample of the reaction mixture was removed before the reaction mixture was added to ice–water. A vapor phase chromatographic analysis (8-ft Carbowax 20M column at 139°) showed that this sample contained the theoretical amount of acetone oxime.

9,10-Bis(ethoxymethyl)anthracene.—To a stirred suspension of 25 g (0.091 mole) of chloride **2** in 500 ml of dimethyl sulfoxide (dried over calcium hydride) at room temperature under nitrogen was added slowly (0.5 hr) a solution of 5.0 g (0.22 g-atom) of sodium in 300 ml of absolute ethanol. The solution was stirred for a total of 2 hr and became dark orange-brown. The homogeneous reaction mixture was added to 2 l. of ice–water and refrigerated. The yellow precipitate was filtered off and dissolved in methylene chloride. This solution was extracted with water, dried with sodium sulfate, and concentrated to dryness. The yellow residue was recrystallized from ethyl acetate. The first crop weighed 15.5 g, mp 139–141° (lit.[2] mp 139–141°), and the second crop weighed 2.5 g, mp 136–139°, to give a total yield of 68%.

N,N'-Anthracene-9,10-dimethylenebis(pyridinium chloride) (3).—A mixture of 10.0 g (0.036 mole) of **2** in 500 ml of pyridine was refluxed for 2.5 hr. After cooling, the yellow precipitate was removed by filtration and washed well with acetone. The product weighed 15.0 g (95%), mp >350°.

Anal. Calcd for $C_{26}H_{22}N_2Cl_2$: C, 72.1; H, 5.2; N, 6.6; Cl, 16.4. Found: C, 72.1; H, 5.1; N, 6.5; Cl, 16.4.

Aldehyde 1 from 3.—To a cooled solution (0°) of 0.50 g (0.00115 mole) of **3** and 0.35 g (0.00233 mole) of N,N-dimethyl-*p*-nitrosoaniline in 25.0 ml of ethanol was added 10 ml of cold 0.5 *N* NaOH. The reaction mixture became dark, and 10 min later a solution of 1 ml of concentrated sulfuric acid in 10 ml of ice–water was added. The reaction solution was allowed to stand at room temperature for 3 hr, heated on a steam bath for 1 hr, and then filtered to remove a dark orange-brown precipitate which had formed. This material was treated with methylene chloride and water, and the organic layer was extracted with dilute sodium bicarbonate solution, dried with sodium sulfate, and concentrated to dryness. A few milligrams of yellow-orange material was obtained which vapor phase chromatographic analysis indicated to be aldehyde **1** in about 75% purity. Attempts to characterize the intermediate bisnitrone were unsuccessful.

Reaction of Dimethyl Sulfoxide with Chloride 2 or a Derivative of 2. A.—A mixture of 10.0 g (0.036 mole) of **2** and 20.3 g (0.073 mole) of *p*-toluenesulfonic acid silver salt in 200 ml of acetonitrile (protected from light) was stirred at 10° for 1 hr and then at room temperature for 22 hr. The reaction mixture was added to ice–water and the precipitate was extracted with methylene chloride. A red-orange residue was recovered from the methylene chloride, dissolved in 100 ml of dimethyl sulfoxide, and added to a mixture of 40.0 g of sodium bicarbonate in 200 ml of dimethyl sulfoxide at 95°. After 10 min the reaction mixture was added to ice–water. The orange precipitate which formed did not yield any aldehyde **1**. Infrared spectra indicated that small amounts of aldehyde **1** may have been formed.

B.—A mixture of 2.0 g (0.007 mole) of **2**, 4.0 g (0.048 mole) of sodium bicarbonate, and 40 ml of dimethyl sulfoxide (dried over calcium hydride) was heated on a steam bath for 8 hr, added to 400 ml of water, and refrigerated. The orange precipitate which formed was shown by thin layer chromatography to contain some aldehyde **1** in addition to a number of other products.

C.—A mixture of 25.0 g (0.091 mole) of chloride **2** and 250 ml of dimethyl sulfoxide was heated for 15 hr on a steam bath, added to 2 l. of ice–water, and refrigerated. The precipitate was removed by filtration, chromatographed first on a Florisil column packed in petroleum ether (bp 35–60°), and eluted with petroleum ether, benzene, and methylene chloride. The fractions containing a product which vapor phase chromatography in-

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dicated to be different from aldehyde **1** were combined and rechromatographed on an alumina (acid-washed) column packed in petroleum ether and eluted with various mixtures of petroleum ether and methylene chloride. The first component to be eluted was recrystallized from ethyl acetate to give yellow crystals of 10-methyl-9-anthraldehyde, mp 170–172° (lit.[13] mp 170–171.4°).

Anal. Calcd for $C_{16}H_{12}O$: C, 87.2; H, 5.5. Found: C, 86.9; H, 5.2.

The nmr spectrum (deuteriochloroform) showed absorption at τ −1.28 (CHO), 1.08–1.31, 1.70–1.95, 2.34–2.82 (ArH), and 7.04 (CH_3) with relative peak areas of 1:2:2:4:3; the mass spectrum exhibited a peak corresponding to the molecular ion.

The second component to be eluted was aldehyde **1**.

A vapor phase chromatographic analysis (2-ft SE-30 silicone rubber on Diatoport W column at 235°) of a similar reaction mixture indicated that 16% aldehyde **1** and 23% aldehyde **4** were formed.

Reaction times of 8 and 65 hr were also tried; in the former case the reaction had not proceeded far enough, and in the latter case a tarry mass was obtained.

Reaction of 1,4-Bis(chloromethyl)benzene with Dimethyl Sulfoxide.—A solution of 25.0 g (0.14 mole) of 1,4-bis(chloromethyl)benzene in 100 ml of dimethyl sulfoxide (dried over calcium hydride) was heated on a steam bath for 100 hr. White material sublimed to the top of the flask and was shown by infrared and elemental analyses to be paraformaldehyde.

Anal. Calcd for $(CH_2O)_x$: C, 40.0; H, 6.7. Found: C, 39.6; H, 6.8; S, <1; Cl, <1.

The reaction mixture was poured into ice–water and extracted with methylene chloride. The solvent was removed and the residue was shown by vapor phase chromatography to contain, at most, a trace of *p*-tolualdehyde in addition to a number of other products.

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Tetramethylterephthaldialdehyde.—To 42 g (0.182 mole) of 3,6-bis(chloromethyl)durene in 1 l. of dimethyl sulfoxide at room temperature (20–25°) under nitrogen was added slowly (30 min) a solution prepared by adding 60 g (0.68 mole) of 2-nitropropane to a solution of 10 g (0.44 g-atom) of sodium in 600 ml of ethanol. The reaction mixture gradually became homogeneous and then heterogeneous as it was stirred for 6 hr at room temperature. Then the reaction mixture was added to *ca.* 6 l. of ice–water and allowed to stand overnight. The precipitate was removed by filtration and dissolved in methylene chloride. This solution was extracted with dilute hydrochloric acid and sodium bicarbonate solution, dried with sodium sulfate, and concentrated to dryness to give 30.5 g, mp 180–185°, of off-white product. Recrystallization from benzene–cyclohexane gave 25.5 g (74%), mp 181–185°, of white product (lit.[14,15] mp 165°, 187°).

Anal. Calcd for $C_{12}H_{14}O_2$: C, 75.8; H, 7.4. Found: C, 75.5; H, 7.6.

2,5-Dimethylterephthaldialdehyde.—By using the same procedure as for tetramethylterephthaldialdehyde, the product was obtained in 56% yield, mp 96–101°.

Anal. Calcd for $C_{10}H_{10}O_2$: C, 74.1; H, 6.2. Found: C, 74.0; H, 6.1.

1,5-Naphthalenedicarboxaldehyde.—By using the same procedure as for tetramethylterephthaldialdehyde, the product was obtained in 65% yield, mp 192–194° (lit.[16] mp 192°).

Acknowledgment.—The author wishes to thank Mr. W. C. Perkins for technical assistance, Dr. T. H. Regan for nmr spectra, and Mr. G. P. Happ and Mr. D. P. Maier for mass spectra.

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The Base-Catalyzed Reaction of Pinacolone with Formaldehyde[1]

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Received February 9, 1966

The aldol reaction of pinacolone with formaldehyde has been carried out in water–dioxane and in methanol, giving products resulting from the addition of 2 moles of formaldehyde. Acetylation of the products gives the acetates which are shown to saponify in alkaline mercaptan solution without consuming mercaptan. This unexpected result is interpreted as a consequence of the molecular stereochemistry of these hindered compounds.

Although the aldol reaction of ketones with aldehydes forms an extensive body of knowledge[2] the specific reactions of pinacolone (methyl *t*-butyl ketone) have received scant attention. Base-catalyzed condensations of pinacolone with furfural[3] and piperonal[4] give the expected benzylidene derivatives. Pinacolone also undergoes a Mannich reaction with paraformaldehyde and piperidine[5] or dimethylamine[6] giving the normal base **1**. Colonge[7] has recorded the chloromethylation of pinacolone with paraformaldehyde, hydrogen chloride, and zinc chloride giving 1-chloro-4,4-dimethyl-3-pentanone **2**. No simple ketol has been reported from a reaction of formaldehyde with pinacolone. Dubois[2] was unable to isolate an identifiable ketol when pinacolone was treated with alcoholic formaldehyde catalyzed by sodium carbonate. In a kinetic study, Kangas[8] demonstrated that pinacolone gives no reaction with aqueous alcoholic formaldehyde catalyzed with lithium hydroxide in 24 hr at 25° or 5 hr at 35°. It is the purpose of this paper to report the successful reaction of pinacolone with formaldehyde and to record some interesting observations regarding the reactivities of the products obtained.

$$(CH_3)_3CCOCH_3 + ArCHO \longrightarrow (CH_3)_3CCOCH{=}CHAr$$

$$(CH_3)_3CCOCH_3 + CH_2O + R_2NH \longrightarrow \underset{\mathbf{1}}{(CH_3)_3CCOCH_2CH_2NR_2}$$

$$(CH_3)_3CCOCH_3 + CH_2O + HCl \xrightarrow{ZnCl_2} \underset{\mathbf{2}}{(CH_3)_3CCOCH_2CH_2Cl}$$

Pinacolone fails to react with excess, 37% aqueous formaldehyde at pH 1 or 9 even after heating under reflux for 50 hr. It has been found that reaction at pH 12 under reflux for 40 hr affords a crystalline

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