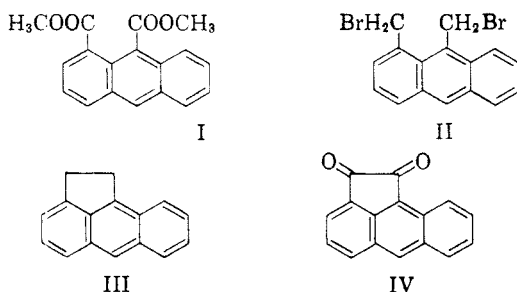


Dimethyl anthracene-1,9-dicarboxylate (I)³ was reduced by lithium aluminium hydride to the corresponding diol and the latter converted into the dibromide (II). Treatment of II with phenyllithium gave aceanthrene (III) in 84% yield, the overall yield being 60%, calculated on the acid corresponding to I.

Aceanthrene (III) was identified by its m.p. and that of its picrate as well as by the absorption spectrum which was practically identical with that reported by Deno.⁴

For the preparation of anthracene-1,9-dicarboxylic acid, the oxidation of aceanthrenequinone (IV) by means of hydrogen peroxide was employed for the sake of convenience. This method has been used for the oxidation of acenaphthenequinone⁵ and benzil.⁶



EXPERIMENTAL

Aceanthrenequinone (IV) was prepared according to Liebermann and Zsuffa⁷ from anthracene and oxalyl chloride in 58% yield. It was purified by sublimation and melted at 270°. The carbonyl absorption was observed at 1695 cm.⁻¹ (potassium bromide pellet).

Anthracene-1,9-dicarboxylic acid. When 6 ml. of 2*N* sodium hydroxide and 5 ml. of 30% hydrogen peroxide solution were added to a suspension of 1 g. of (IV) in 20 ml. of dioxane, an exothermic reaction set in which was kept under control by cooling with ice water. After 45 min., 50 ml. of water was added to the yellow solution and the acid precipitated by addition of dilute sulfuric acid. The yellow precipitate was filtered, washed with water, and dried. The yield was 1 g. (quantitative). The compound melted at 290° (this is probably the m.p. of the anhydride).³

Dimethyl anthracene-1,9-dicarboxylate (I). To a solution of 2.65 g. of the foregoing acid in 10 ml. of 2*N* sodium hydroxide, 2 ml. of dimethyl sulfate was added at 0° with stirring. After 1 hr., a yellow precipitate began to settle. With stirring, 1 ml. of dimethyl sulfate and 5 ml. of 2*N* sodium hydroxide and after a further hour, 0.5 ml. of dimethyl sulfate and 2.5 ml. of 2*N* sodium hydroxide were added, both at room temperature, and the stirring was continued for 1 further hour at room temperature and for 30 min. at 70°. The mass was cooled and the product filtered and recrystallized from isopropyl alcohol. The yellow needles of m.p. 149–150° were obtained in a yield of 2.5 g. (86%). The carbonyl absorption (potassium bromide pellet) was observed at 1700 cm.⁻¹

(3) M. Kordos, *Ber.*, **46**, 2086 (1913).

(4) N. C. Deno, Dissertation, University of Michigan, 1948.

(5) G. Charrier and A. Beretta, *Gazz. chim. ital.*, **54**, 993 (1924).

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1,9-Dihydroxymethylanthracene. The solution of 2.2 g. of (I) in 50 ml. of benzene and 150 ml. of anhydrous ether was added to 1 g. of lithium aluminum hydride in 200 ml. of ether at 0°. Then the mixture was refluxed for 2 hr., cooled and decomposed with ice and dilute sulfuric acid. The organic layer was washed with water, sodium bicarbonate solution and water, dried and concentrated. After recrystallization from isopropyl alcohol, the product formed needles of m.p. 181–182°. The yield was 1.7 g. (95%).

Anal. Calcd. for C₁₆H₁₄O₂: C, 80.7; H, 5.9. Found: C, 81.0; H, 5.7. IR spectrum (KBr pellet): 3200, 2900, 2800 cm.⁻¹.

1,9-Dibromomethylanthracene (II). At 60°, 2.4 g. of phosphorus tribromide was added to the solution of 1.5 g. of the foregoing compound in 150 ml. of benzene, to which 3 drops of pyridine had been added. After 2 hr. at 55° (stirring), the mass was cooled, and water and ether was added. The organic layer was washed with sodium bicarbonate solution and water, dried and concentrated. The oily residue was triturated with petroleum ether and the solid product recrystallized from a mixture of benzene and petroleum ether. The yield was 2.1 g. (87%), the m.p. 138–139°.

Anal. Calcd. for C₁₆H₁₂Br₂: C, 52.8; H, 3.3. Found: C, 52.9; H, 3.5.

Aceanthrene (III). During 15 min., a solution of 1.8 g. of II in 20 ml. of dry benzene was added to a solution of phenyllithium, prepared from 0.033 g. of lithium and 0.8 g. of bromobenzene in 30 ml. of ether. The operation was carried out in an atmosphere of nitrogen. After 1 hr. at room temperature, 20 ml. of benzene was added and the mixture refluxed for 1 hr. The usual work-up yielded 0.8 g. (84%) of aceanthrene (III), which, after recrystallization from ethanol, formed yellow leaflets of m.p. 113–114°. ^{8,9}

Anal. Calcd. for C₁₆H₁₂: C, 94.1; H, 5.9. Found: C, 93.8; H, 5.6.

The *picrate*,^{8,9} prepared in benzene solution and recrystallized from isopropanol, formed dark red needles of m.p. 120–121°.

Anal. Calcd. for C₂₂H₁₅N₃O₂: C, 61.0; H, 3.4. Found: C, 60.8; H, 3.4. Spectrum (in ethanol): 225 mμ (4.05); 256 mμ (4.14); 258 mμ (5.06); 355 mμ (3.50); 375 mμ (3.80); 395 mμ (3.56).

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Compounds Related to Podophyllotoxin. IX. 3,4-Methylenedioxyphenyllithium¹

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The present communication is concerned with the preparation of 3,4-methylenedioxyphenyllithium, a reagent of interest in connection with work on the synthesis of picropodophyllin.

(1) Previous papers of this series will be found in *J. Am. Chem. Soc.*, **72**, 3318 (1950); **73**, 5555 (1951); **74**, 2959 (1952); *J. Org. Chem.*, **18**, 9 (1953); *J. Am. Chem. Soc.*, **76**, 315, 5890 (1954); **77**, 3674 (1955); *J. Org. Chem.*, **21**, 261 (1956).

Metalation of aromatic ethers is known to occur ortho to the ether group.² However, no report on the behavior of methylenedioxybenzene (1,3-benzodioxole) could be found, and, with the possibility in mind of metalation taking place at the para position, the reaction of this compound with butyllithium was tried. An uncomplicated metalation was not observed. Carbonation after exposure of methylenedioxybenzene to butyllithium either at room temperature or at reduced temperatures gave only colored water-soluble tars, from which no pure material was isolated. When, in place of carbon dioxide, acetic anhydride was used to trap the organolithium compound, only 1,2-diacetoxybenzene was obtained. Evidently, under the conditions employed, the hetero ring in methylenedioxybenzene suffers cleavage.³

Another approach to the desired organometallic compound makes use of the corresponding bromo compound. The reaction of methylenedioxybenzene with *N*-bromosuccinimide⁴ provided a convenient source of 3,4-methylenedioxy-1-bromobenzene, in which the proper orientation was indicated by its conversion with cuprous cyanide to piperonylnitrile. Direct combination of 3,4-methylenedioxy-1-bromobenzene with metals failed, the compound reacting sluggishly if at all with magnesium⁵ or with lithium. Carbonation after exposing the bromo compound to the action of ethereal butyllithium⁶ at room temperature was also discouraging; a dark mixture was formed similar to that obtained in the metalation experiments. The same halogen-metal exchange at lower temperatures was more promising in that treatment with acetic anhydride led to a product provisionally considered to be 1,1 - bis(3',4' - methylenedioxyphenyl)ethylene. Eventually, halogen-metal interchange conditions giving 3,4-methylenedioxyphenyllithium in a practical manner were found. The results of carbonation

after reaction of the bromo compound with butyllithium for ten minutes at -35° showed that the aryllithium was formed in yields of at least 60%. It may be anticipated that 3,4-methylenedioxyphenyllithium will prove useful in synthesis of compounds containing the methylenedioxyphenyl grouping.

EXPERIMENTAL⁷

Methylenedioxybenzene treated with butyllithium followed by acetic anhydride. Methylenedioxybenzene⁸ (3.0 g. or 0.025 mole) in a flask fitted with a dropping funnel and an inlet through which nitrogen was passed was cooled by placing the flask in a -35° mixture of kerosene and solid carbon dioxide in a large Dewar flask. Fifty milliliters of an ethereal solution containing 0.025 mole of butyllithium⁹ was added over a short period, and the mixture after being shaken once or twice was allowed to stand at -35° for 3 days.

Excess acetic anhydride (15 ml.) was added and the mixture was allowed to stand cold for 5 min. and then at room temperature for 6 hr. The ethereal reaction mixture was washed several times with water, was dried over magnesium sulfate, and was then warmed on the steam bath under moderate vacuum to remove volatile materials. Two crystallizations of the residue afforded 3.2 g. (67%) of 1,2-diacetoxybenzene, m.p. $63.2-65^{\circ}$. The melting point after admixture with authentic 1,2-diacetoxybenzene¹⁰ having the same melting point was $64.0-65^{\circ}$.

To show that acetic anhydride alone has little effect, a solution of 3.0 g. of methylenedioxybenzene, 15 ml. of acetic anhydride, and 50 ml. of dry ether was allowed to stand at room temperature for 3 days. Distillation through a 6-inch Vigreux column permitted recovery of 2.7 g. (90%) of unchanged methylenedioxybenzene, b.p. $73-74^{\circ}$ (23 mm.).

3,4-Methylenedioxy-1-bromobenzene. A mixture of 12.2 g. (0.10 mole) of methylenedioxybenzene, 18.8 g. (0.105 mole) of *N*-bromosuccinimide, and 50 ml. of chloroform was boiled for three hours. Solids were removed from the cooled mixture by filtration, and were washed with two small portions of cold chloroform. The combined chloroform solutions, after contact with magnesium sulfate, were concentrated by distillation on the steam bath. The residual 3,4-methylenedioxy-1-bromobenzene,¹¹ distilled twice through a small Vigreux column, weighed 18.4 g. (91%), boiled at $85-86^{\circ}$ (1 mm.), and showed n_D^{25} 1.5778.

Anal. Calcd. for $C_7H_5O_2Br$: C, 41.82; H, 2.51. Found: C, 41.7; H, 2.5.

3,4-Methylenedioxybenzonitrile from 3,4-methylenedioxy-1-bromobenzene. A mixture of 2.01 g. (0.01 mole) of 3,4-methyl-

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(10) Cf. G. Heller, P. Lindner, and H. Georgi, *Ber.* **56**, 1868 (1923); J. J. Sudborough and W. Thomas, *J. Chem. Soc.*, **87**, 1752 (1905).

(11) Previously prepared by T. G. H. Jones and R. Robinson, *J. Chem. Soc.*, **111**, 903 (1917), and by E. Mameli with E. Boi, *Atti reale accad. Lincei*, **15**, 101 (1906) [*J. Chem. Soc. Abstracts* **90**, I, 743 (1906)].

enedioxy-1-bromobenzene, 1.1 g. (0.012 mole) of cuprous cyanide, and 1 ml. of anhydrous pyridine was heated under reflux for 15 hr. using an oil bath at 210–225°. The contents of the reaction flask were stirred thoroughly with dilute aqueous ammonia and then with 25 ml. of benzene, and the resulting mixture was filtered through a sintered glass funnel. After extracting the aqueous layer of the filtrate several times with benzene, all the benzene fractions were combined and were concentrated on the steam bath. Crystallization of the residue from aqueous alcohol gave slightly pink needles, which after drying, weighed 0.84 g. (57%).

Anal. Calcd. for $C_8H_5O_2N$: C, 65.30; H, 3.43. Found: C, 65.5; H, 3.5.

The melting point, 90–91°, of this product corresponds more closely to the reported m.p. 94–95° for 3,4-methylenedioxybenzoxonitrile (piperonylonitrile)¹² than to the m.p. 80° for 2,3-methylenedioxybenzoxonitrile.¹³

3,4-Methylenedioxy-1-bromobenzene treated with butyllithium followed by acetic anhydride. An ether solution (60 ml.) containing 0.064 mole of butyllithium was added over a 5-min. period to 12.8 g. (0.064 mole) of 3,4-methylenedioxy-1-bromobenzene. The reaction mixture was blanketed with nitrogen and was held at –35°. After swirling the mixture briefly it was allowed to stand at –35° for another 5 min. Acetic anhydride (15 ml.) was added rapidly to the cold solution, which was then allowed to come to room temperature and to stand at room temperature for 2 days. Volatile materials were removed by distillation on the steam bath at water-pump pressures. Distillation of the residual oil through a 6-inch Vigreux column furnished some starting material [1.2 g., b.p. 104–105° (9 mm.), n_D^{25} 1.5791], an intermediate fraction (2–3 ml.), and finally a viscous yellow oil, b.p. 170–175° (1 mm.). Decomposition was evident, especially during the last part of the distillation when the bath temperature was raised to 270°, and much residue remained in the flask. The yellow oil on standing deposited crystals (0.53 g.) with m.p. 90.5–101°. Chromatography of this material in benzene solution using an alumina column gave colorless crystals (0.33 g.), m.p. 91–93°. Recrystallization from absolute alcohol brought the melting point to 92–93°.

Anal. Calcd. for $C_{16}H_{12}O_4$: C, 71.63; H, 4.51. Found: C, 70.5; H, 4.3.

This compound, tentatively considered to be 1,1-bis-(3',4'-methylenedioxyphenyl)ethylene, absorbed bromine rapidly from a chloroform solution, contained no halogen, and showed absorption peaks at 299 $m\mu$ ($\log \epsilon$ 3.85) and 269 $m\mu$ ($\log \epsilon$ 3.83) in a 1×10^{-4} M alcoholic solution.

3,4-Methylenedioxy-1-bromobenzene treated with butyllithium followed by carbon dioxide. 3,4-Methylenedioxy-1-bromobenzene (14.1 g. or 0.070 mole) was treated as described above with 148 ml. of an ethereal solution containing 0.0705 mole of butyllithium. After a maximum exchange time of 10 minutes, the mixture was poured over a slurry of approximately 20 g. of crushed solid carbon dioxide in ether. The mixture was acidified with dilute hydrochloric acid, the ether layer was removed, and the aqueous layer extracted twice with ether. The combined ether solutions were dried over magnesium sulfate and then were warmed to remove solvent. Two crystallizations of the residual solid from 95% alcohol resulted in 7.0 g. (60%) of piperonylic acid, m.p. 226–227°. The melting point of this carbonation product admixed with authentic piperonylic acid was 225.8–227°.

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Some Derivatives of Biphenyl as Liquid Scintillator Solutes

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Previous studies of liquid scintillator solutes¹ have indicated the general principle that efficient solutes must contain three, and preferably four, aromatic rings linked to one another in chainlike fashion. We have screened a variety of compounds which may be regarded as derivatives of biphenyl in that each has only two distinct benzene rings joined directly (although some have fused rings as well). A few of these compounds have high relative pulse height values for such "small" molecules.

TABLE I
PRIMARY-SOLUTE RELATIVE PULSE HEIGHTS

No.	Compound	Relative Pulse Heights	Ref.
1.	2-Aminobiphenyl	0.16	^a
2.	4-Benzylbiphenyl	<0.10	^b
3.	2,2'-Dimethoxybiphenyl	0.14	^c
4.	4,4'-Dimethoxybiphenyl	0.20	^d
5.	2,2'-Dimethoxy-3,3'-dimethylbiphenyl	<0.10	^c
6.	3,4-Benzocoumarin	<0.10	^a
7.	N,N,N',N'-Tetramethylbenzidine	0.28	^a
8.	4,4'-Bistrimethylsilylbiphenyl	0.30	^e
9.	N-(4-Biphenyl)-aniline	0.63	^f
10.	N-(<i>o</i> -Phenyldiphenylmethyl)-aniline	0.13	^g
11.	2,3-Dimethoxyphenanthrene	0.14	^h
12.	2-Aminophenanthrene	0.23	ⁱ
13.	3-Aminophenanthrene	0.20	^j
14.	1,1'-Binaphthyl	0.87	^k
15.	2,2'-Binaphthyl	0.25	^l
16.	Perylene	0.24	^m

^a Commercially available. ^b K. Goldschiedt, *Monatsh.*, **2**, 433 (1881). ^c H. Gilman, J. Swiss, and L. C. Cheney, *J. Am. Chem. Soc.*, **62**, 1963 (1940). ^d F. Ullman and O. Lowenthal, *Ann.*, **332**, 67 (1904). ^e H. A. Cook (Dow Corning Ltd.), Brit. Patent **671,553** (1952); *Chem. Abstr.*, **47**, 4909 (1953). ^f J. Piccard, *Helv. Chim. Acta*, **7**, 789 (1924). ^g H. Gilman, J. E. Kirby, and C. R. Kinney, *J. Am. Chem. Soc.*, **51**, 2252 (1929). ^h H. Gilman and T. H. Cook, *J. Am. Chem. Soc.*, **62**, 2813 (1940). ⁱ W. E. Bachmann and C. H. Boatner, *J. Am. Chem. Soc.*, **58**, 857 (1936). ^j J. Schmidt, *Ber.*, **34**, 3553 (1901). ^k H. Gilman and C. G. Brannen, *J. Am. Chem. Soc.*, **71**, 658 (1949). ^l F. Ullman and R. Gilli, *Ann.*, **332**, 50 (1904). ^m J. Weitzenbock and R. Seer, *Ber.*, **46**, 1996 (1913).

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