



A Publication  
of Reliable Methods  
for the Preparation  
of Organic Compounds

## Working with Hazardous Chemicals

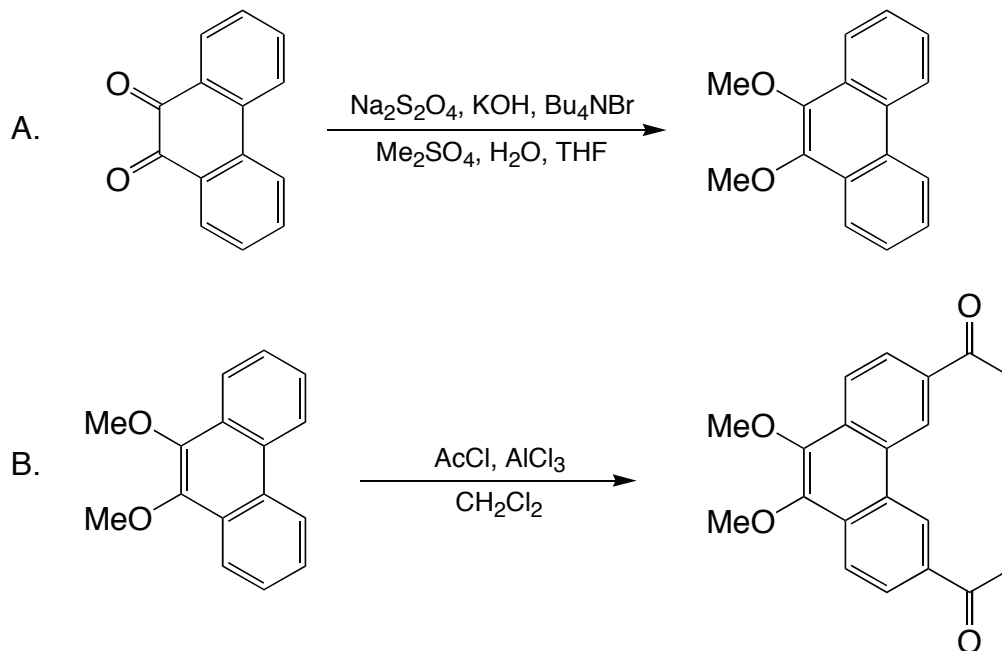
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*September 2014: The paragraphs above replace the section "Handling and Disposal of Hazardous Chemicals" in the originally published version of this article. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.*

**PREPARATION OF 9,10-DIMETHOXYPHENANTHRENE AND 3,6-DIACETYL-9,10-DIMETHOXYPHENANTHRENE**  
**[(Phenanthrene, 9,10-dimethoxy- and Ethanone, 1,1'-(9,10-dimethoxy-3,6-phenanthrenediyl)bis-)]**



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### 1. Procedure

*Caution: Dimethyl sulfate is highly toxic and a potential carcinogen. It should be handled with appropriate safeguards in a well-ventilated fume hood.*

*A. 9,10-Dimethoxyphenanthrene.* A mixture of 26 g (0.125 mol) of 9,10-phenanthrenequinone (Note 1), 13 g (0.04 mol) of tetrabutylammonium bromide ( $\text{Bu}_4\text{NBr}$ ), 65 g (0.37 mol) of sodium dithionite ( $\text{Na}_2\text{S}_2\text{O}_4$ ), 250 mL of tetrahydrofuran (THF), and 250 mL of water is shaken for 5 min in a 2-L separatory funnel. Dimethyl sulfate (62 mL, 0.65 mol) is added, followed by an aqueous solution of sodium hydroxide (64 g, 1.6 mol, in 125 mL of water) and 200 g of ice. The mixture is shaken for 5 min and, after another 200 g of ice has been added, shaken for another 10 min. Ethyl acetate

(EtOAc, 100 mL) is added and the mixture is shaken. The aqueous phase is separated and extracted with EtOAc ( $2 \times 100$  mL). The combined organic extracts are washed with water ( $3 \times 100$  mL), 15% aqueous ammonia ( $2 \times 100$  mL), water ( $3 \times 100$  mL), and finally brine (100 mL). The solution is dried over sodium sulfate ( $\text{Na}_2\text{SO}_4$ ) and filtered. The solvents are removed under vacuum (initially using a water aspirator, then at 0.5 torr). The residue, a thick brown oil, is dissolved in 80 mL of a ca. 2:1 mixture of dichloromethane ( $\text{CH}_2\text{Cl}_2$ ) and hexane and poured onto a plug of neutral alumina, from which it is eluted with a 170-mL portion of the solvent mixture. After the solvent has been removed, the residue is dried under vacuum (ca. 0.5 torr) to give 23.7 g (80%) of 9,10-dimethoxyphenanthrene as a yellow oil (Note 2).

*B. 3,6-Diacetyl-9,10-dimethoxyphenanthrene.* A 1-L, three-necked, round-bottomed flask, fitted with an addition funnel, mechanical stirrer, and hydrogen chloride trap, is charged with 23.7 g of 9,10-dimethoxyphenanthrene and 120 mL of  $\text{CH}_2\text{Cl}_2$  (Note 3). The solution is cooled in an ice-bath, and acetyl chloride (120 mL, (Note 4)) is added slowly. The cooling bath is removed, and over the course of 5 min, 44 g (0.33 mol) of aluminum chloride (Note 5) is added in portions to the stirred solution. The mixture is stirred for 15 min at ambient temperature and then carefully poured onto 1 L of crushed ice. The organic phase is separated, and the aqueous phase is extracted three times with 120-mL portions of  $\text{CH}_2\text{Cl}_2$ . The combined organic phases are washed with 120 mL of water, then with 120 mL of saturated aqueous sodium bicarbonate ( $\text{NaHCO}_3$ ). The solution is dried over  $\text{Na}_2\text{SO}_4$  and filtered. The solvent is removed, and the residual solid is suspended in 120 mL of methanol (MeOH), filtered, washed with an additional 120 mL of MeOH, and then dried (80 °C/ca. 0.5 torr) to afford 24.8 g (77% yield based on dimethoxyphenanthrene, 62% yield based on phenanthrenequinone) of 3,6-diacetyl-9,10-dimethoxyphenanthrene as a slightly pale yellow solid (Note 6).

## 2. Notes

1. 9,10-Phenanthrenequinone (95%), purchased from Acros, was used as received. The checkers purchased it from Tokyo Chemical Industry.

2. In two runs, the checkers obtained 27.0 and 25.7 g (91% and 90% yields). IR (neat film between NaCl plates)  $\text{cm}^{-1}$ : 2936, 1602, 1327, 1070.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz in accord with the literature<sup>2</sup>)  $\delta$ : 4.10 (s, 6H), 7.59-7.65 (m, 4H), 8.24 (dd,  $J = 8.0$ ,  $J = 1.5$ , 2H), 8.64 (dd,  $J = 7.0$ ,  $J = 1.5$ , 2H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz)  $\delta$ : 60.9, 122.1, 122.6, 125.8, 126.8, 128.6, 129.1, 143.9. HRMS (FAB)  $m/z$  calcd for  $\text{C}_{16}\text{H}_{14}\text{O}_2$ :  $[\text{M}]^+$  238.0994; found 238.1003.

3. Dichloromethane was distilled from  $\text{CaH}_2$ .

4. Acetyl chloride (98%), purchased from Aldrich Chemical Company, Inc., was used as received. The checkers purchased it from Tokyo Chemical Industry.

5. Aluminum chloride (98%), purchased from Aldrich Chemical Company, Inc., was used as received. The checkers purchased it from Wako Pure Chemical Industry.

6. In two runs, the checkers obtained 26.6 and 28.8 g (82% and 83% yields). Samples can be purified further by crystallization from MeOH, but no significant amounts of impurities are detected when the material is analyzed before crystallization by means of  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectroscopy and HPLC (reverse phase, 5  $\mu\text{m}$  LiChrospher<sup>(r)</sup> 100 from Hewlett-Packard, acetonitrile- $\text{H}_2\text{O}$  gradients varying from 80:20 to 100:0). The pure product is a white solid, mp 160-161  $^\circ\text{C}$ . IR ( $\text{CCl}_4$ )  $\text{cm}^{-1}$ : 2939, 1687, 1611, 1318, 1059.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz)  $\delta$ : 2.82 (s, 6 H), 4.13 (s, 6 H), 8.20 (dd,  $J = 8.5$ , 1.3, 2 H), 8.32 (d,  $J = 8.5$ , 2 H), 9.31 (d,  $J = 1.3$ , 2 H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz)  $\delta$ : 27.0, 61.1, 122.8, 123.6, 126.3, 128.5, 132.6, 134.7, 145.5, 198.0. UV-vis ( $\text{CH}_3\text{CN}$ ,  $c = 1.81 \times 10^{-4}$  M):  $\lambda_{\text{max}}$  (log  $\epsilon$ ) 266 (4.05), 325 nm (4.06). Anal. Calcd for  $\text{C}_{20}\text{H}_{18}\text{O}_4$ : C, 74.52; H, 5.63. Found: C, 74.52; H, 5.66.

### Waste Disposal Information

All toxic materials were disposed of in accordance with "Prudent Practices in the Laboratory"; National Academy Press; Washington, DC, 1995.

### 3. Discussion

Almost no 9,10-dialkoxyphenanthrenes are known, and the quantities of those few made by other methods are either small or unstated.<sup>2,3</sup> The best alternative procedure gave 9,10-dimethoxyphenanthrene when 9,10-phenanthrenequinone was combined first with sodium in diglyme and then with dimethyl sulfate, but the yield after two chromatographic purifications was 51%.<sup>2b</sup> The only other reported alkylations of phenanthrene-9,10-diol are by 1-chloro-2-diethylaminoethane in 10% yield,<sup>3f</sup> and by 1,2-di(bromomethyl)benzene in 22% yield.<sup>3g</sup> Unlike the procedure recorded here, none of these employ two-phase alkylations catalyzed by phase transfer agents.<sup>4</sup>

3,6-Diacetyl-9,10-dimethoxyphenanthrene has not been prepared by any other method. However, two related compounds, 9,10-di-TBDMSO- and 9,10-diphenyl-methylenedioxyphenanthrene, have been prepared by brominating phenanthrene-9,10-dione, converting the diones to the ethers, coupling the dibromides with tributyl(1-ethoxyethenyl)stannane by the Stille method, and hydrolyzing the enol ethers.<sup>5</sup> The procedure described here circumvents three disadvantages of the tin reagents used in the Stille procedure: expense, toxicity, and the need for chromatography to remove side products, mainly  $\text{Bu}_3\text{SnBr}$ . 3,6-Diacetyl-9,10-dialkoxyphenanthrene, like the 9,10-di-TBDMSO- and 9,10-diphenylmethylenedioxy-derivatives, combines with 1,4-benzoquinone to give a [7]helicenebisquinone.<sup>6</sup>

There are no reported alternatives to the current procedure for the acylation of a phenanthrene using the Friedel-Crafts reaction.<sup>7,8</sup> Indeed, alternative methods to cleanly prepare 3,6-disubstituted derivatives of phenanthrene by means of electrophilic substitution are not known,<sup>9,10,11</sup> nor is there a precedent for the electrophilic substitution of any 9,10-dialkoxyphenanthrene.

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8. The only diacylations are by phthalic anhydride with aluminum chloride in "tetrachloroethane" and by benzoyl chloride with AlCl<sub>3</sub> in the absence of additional solvent. The diketones were isolated in 15% and unspecified yields, respectively, and their structures were not determined. Clar, E.; Kelly, W. *J. Am. Chem. Soc.* **1954**, *76*, 3502.
9. Upon sulfonation, phenanthrene-3-sulfonic acid gives mainly (but not exclusively) the 3,6-disulfonic acid (Fieser, L. F. *J. Am. Chem. Soc.* **1929**, *51*, 2471), but the starting phenanthrene-3-sulfonic acid can be obtained from phenanthrene in only ca. 25% yield, and then isolated only from a mixture including a comparable amount of the 2-sulfonic acid (Fieser, L. F. *Org. Synth., Coll. Vol. II* **1943**, 482).
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**Appendix**  
**Chemical Abstracts Nomenclature (Collective Index Number);**  
**(Registry Number)**

- 3,6-Diacetyl-9,10-dimethoxyphenanthrene: Ethanone, 1,1'-(9,10-dimethoxy-3,6-phenanthrenediyl)bis- (9); (310899-08-2)
- 3,6-Bis[1-(triisopropylsiloxy)ethenyl]-9,10-dimethoxyphenanthrene: Silane,[(9,10-dimethoxy-3,6-phenanthrenediyl)bis(ethenylideneoxy)]tris(1-methylethyl)- (9); (310899-13-9)
- Triisopropyl triflate: Methanesulfonic acid, trifluoro-, tris(1-methylethyl)silyl ester (9); (80522-42-5)
- Triethylamine: Ethanamine, *N,N*-diethyl- (9); (121-44-8)
- 1,4-Benzoquinone: 2,5-Cyclohexadiene-1,4-dione (9); (106-51-4)
- 6,13-Bis(triisopropylsiloxy)-9,10-dimethoxy[7]helicenebisquinone : Dinaphtho [2,1-c:1',2'-g]phenanthrene-1,4,15,18-tetrone, 9,10-dimethoxy-6,13-bis[[tris(1-methylethyl)silyl]oxy]- (9); (310899-14-0)