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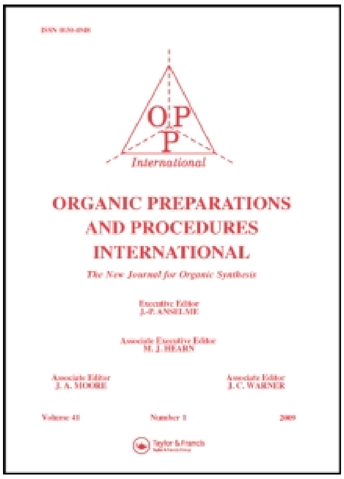

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# 1,6 - BIS (HYDROXYMETHYL) PYRENE AND 1 - BROMO - 6 - HYDROXYMETHYLPYRENE

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ORGANIC PREPARATIONS AND PROCEDURES INT. 5(1), 37-39 (1973)

# 1,6-BIS(HYDROXYMETHYL)PYRENE AND 1-BROMO-6-HYDROXYMETHYLPYRENE

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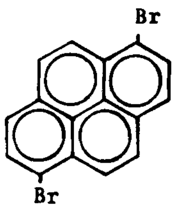
We wish to report improved synthetic routes to 1,6-bis(hydroxymethyl) pyrene III and 1-bromo-6-hydroxymethylpyrene II. Convenient routes to these derivatives are desirable in view of their possible use as intermediates in the syntheses of multilayered compounds of pyrene



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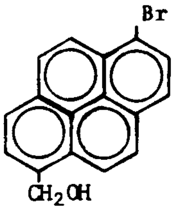

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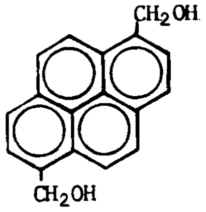

III

1,6-bis(hydroxymethyl)pyrene III has been synthesized previously by the conversion of 1,6-dibromopyrene I to its dicyano derivative followed by hydrolysis, esterification and reduction.[1] This series of reactions yielded the crude dialcohol III which was converted to its bis(bromomethyl) derivative.

We have found that the mono- or dilithio- derivatives of 1,6-dibromopyrene can be generated by the use of appropriate amounts of n-butyllithium in ether-benzene. In situ reaction of the mono- or dilithiopyrene with paraformaldehyde, followed by hydrolysis, provides the dialcohol III or monoalcohol II in good yield. Conversion of dialcohol III to 1,6-bis(acetoxymethyl)pyrene proceeds in high yield. A wide variety of substituted pyrene compounds can be prepared by the use of this method.

## EXPERIMENTAL

1-Bromo-6-hydroxymethylpyrene. - A 100 ml three-necked flask equipped with a condenser, magnetic stirrer and inlet tube for admission of dry nitrogen was flamed out and filled with dry argon. Throughout the reaction the apparatus was maintained under a slight positive argon pressure. Into the flask were placed 3.6 g (0.01 mole) of 1,6-dibromopyrene and 40 ml of a 3:1 mixture of dry benzene-ether. To the stirred slurry at room temperature was added a solution of 6.4 ml (0.01 mole) of *n*-butyllithium in hexane. After the slurry had been held at reflux for 1 hr, 1.5 g of dry paraformaldehyde and 20 ml of ether were added. The mixture was heated at reflux for 2 hrs and then cooled to room temperature and filtered to remove 2.3 g of a yellow solid, mp 183-190°. After washing with water and then dilute HCl the solid was recrystallized twice from methanol-chloroform, 2:1, to yield 1.8 g of yellow crystals of 1-bromo-6-hydroxymethylpyrene, mp 208-209°.

Anal Calcd for $C_{17}H_{11}BrO$: C, 65.61; H, 3.56; Br, 25.68. Found: C, 65.49; H, 3.50; Br, 25.61.

1,6-Bis(hydroxymethyl)pyrene. - To the stirred slurry formed by treatment of a solution of 5.6 g (0.015 mole) of 1,6-dibromopyrene [2] in 40 ml of 3:1 benzene:ether was added a solution of 20.5 ml (0.031 mole) of *n*-butyllithium in hexane. After this yellow mixture had been held at reflux for 1 hr, 3.2 g (0.1 mole) of dry paraformaldehyde and 20 ml of ether were added. The resulting mixture was heated at reflux for 2 hrs, cooled to room temperature and filtered to remove 6.0 g of a light orange solid. After washing with water and dilute HCl the product was recrystallized from methanol to afford 4.1 g of crude 1,6-bis(hydroxymethyl)pyrene, mp 203-210°. Recrystallization from methanol:chloroform, 3:1, provided 3.0 g of yellow crystals,mp 220-224°. For analysis, a sample was recrystallized twice from methanol:chloroform, 3:1, to afford pale yellow crystals, mp 225.5-227.0°; ir (KBr) 3350 cm$^{-1}$ (OH stretching).

Anal Calcd for $C_{18}H_{14}O_2$: C, 84.42; H, 5.37. Found: C, 81.96; H, 5.05.

1,6-Bis(acetoxymethyl)pyrene. - A 370 mg sample of 1,6-bis(hydroxymethyl)pyrene was dissolved in 20 ml of pyridine and to the solution was added 20 ml of acetic anhydride. The resulting solution was heated at 60° for 5 hrs and then allowed to stir at room temperature for 48 hrs. To the reaction mixture was added 60 ml of 20 percent HCl; the precipitated yellow solid was filtered, washed with water and air dried to afford 450 mg of 1,6-bis(acetoxymethyl)pyrene, mp 170-174°. Two recrystallizations from chloroform afforded 370 mg of yellow crystals, mp 175.2 - 176.2°; ir (KBr) 1760 cm$^{-1}$ (carbonyl stretching).

Anal Calcd for $C_{22}H_{18}O_4$: C, 76.28; H, 5.24. Found: C, 76.03; H, 5.48.

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