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## THE SYNTHESIS OF 2,7-DIMETHYLPHENANTHRENE<sup>1</sup>

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### ABSTRACT

The synthesis of 2,7-dimethylphenanthrene from dimethyl 4,4'-dimethyldiphenate is described. The ester groups were reduced to hydroxymethyl groups and the latter converted to bromomethyl groups. Cyclization of the latter with phenyllithium followed by dehydrogenation of the product over palladium-on-charcoal afforded 2,7-dimethylphenanthrene.

A quantity of 2,7-dimethylphenanthrene was needed as a non-strained isomer of 4,5-dimethylphenanthrene so that accurate heats of combustion (Frisch et al., 1963) could be used to measure strain energy.

2,7-Dimethylphenanthrene has been synthesized previously (Haworth et al., 1934). Our main synthesis proceeded from dimethyl 4,4'-dimethyldiphenate and followed the phenanthrene synthesis previously described (Hall et al., 1950). The required diphenic acid was prepared from p-toluidine via 5-methylisatin (Marvel et al., 1932), followed by oxidation to 5-methylanthranilic acid and coupling of the latter to 4,4'-dimethyldiphenic acid.

Alternately, a small amount of equally pure 2,7-dimethylphenanthrene was

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prepared from 2,7-dimethyl-9-hydroxymethylfluorene by a route similar to that used previously (Brown et al., 1940; Collins, 1948). This work was supported by research grant G-2757 from the National Science Foundation.

#### EXPERIMENTAL RESULTS

(All microanalyses were performed by Galbraith Laboratories, Knoxville, Tenn. The term "worked up in the usual manner" means that an ether-benzene solution of the products was washed with acid and/or alkali and saturated sodium chloride solution, then filtered through a quantity of anhydrous magnesium sulfate. Solvents were then removed and the product distilled or crystallized or both. All melting points are uncorrected.)

*4,4'*-Dimethyldiphenic Acid.—5-Methylisatin (Marvel et al., 1932) was oxidized with alkaline hydrogen peroxide (Schmidt, 1921) at 10 to 15 C to yield 82 per cent of 5-methylantranilic acid, mp 171 to 173 C. This was coupled (Atkinson et al., 1932) to 4,4'-dimethyldiphenic acid mp 260 to 261 C, in 87 per cent yield. Dimethyl-4,4'-dimethyldiphenate, bp 190 to 190 C at 2 mm, mp 92 to 93 C from Skellysolve B (petroleum ether, bp 65 to 70 C) was prepared by acid catalyzed treatment with methanol.

Anal. Calcd. for  $C_{18}H_{18}O_4$ : C, 72.5; H, 6.1.

Found: C, 72.4; H, 6.0.

*2,2'*-Hydroxymethyl-4,4'-dimethylbiphenyl.—Lithium aluminum hydride reduction at reflux in ether for 30 min followed by a conventional workup afforded the desired diol recrystallized from benzene as colorless crystals, mp 124 to 126 C, in 84 per cent yield, from the above dimethyl ester. A lower yield was obtained by reduction of the diphenic acid.

Anal. Calcd. for  $C_{16}H_{18}O_2$ : C, 79.3; H, 7.5.

Found: C, 79.6; H, 7.4.

*2,2'*-Dibromomethyl-4,4'-dimethylbiphenyl.—To a suspension of 9.0 g of the above diol in 300 ml of benzene containing a few drops of pyridine was added 28 g of phosphorus tribromide. The diol slowly dissolved and the reaction was completed by heating at 60 C for 2 hr. After working up in the usual way, crystallization from Skellysolve F (petroleum ether, bp 35 to 40 C) yielded 11.0 g (80 per cent) of dibromide, mp 102 to 103 C, pure enough for use in the next step. Recrystallization yielded the analytical sample, mp 106.5 to 107.0 C.

Anal. Calcd. for  $C_{16}H_{16}Br_2$ : Br, 43.5.

Found: Br, 43.7.

*9,10*-Dihydro-2,7-dimethylphenanthrene.—A solution of the phenyllithium prepared from 37 g of bromobenzene, 3 g of lithium and 350 ml of ether was added to a solution of 55 g of the above dibromide in 650 ml of ether. After 1 hr at ambient temperature and 1 hr at reflux, workup in the usual manner, followed by vacuum fractionation, yielded 27 g (87 per cent) of the dihydrophenanthrene, bp 185 to 188 C at 3 mm, mp 84 to 92 C, suitable for the next step. Recrystallization from Skellysolve B yielded the analytical sample, mp 98.5 to 100.0 C.

Anal. Calcd. for  $C_{16}H_{16}$ : C, 92.3; H, 7.7.

Found: C, 92.3, 92.2; H, 7.8, 7.7.

*2,7*-Dimethylphenanthrene.—A mixture of 25 g of the above crude dihydrophenanthrene and 1 g of 10 per cent palladium-on-charcoal was heated for 1 hr at 200 C and 1 hr at 300 C. The reaction product in Skellysolve F was filtered through a column of activated alumina. Removal of solvent and recrystallization from methanol afforded 23 g (92 per cent) of pure (VPC) 2,7-dimethylphenanthrene (Haworth et al., 1934) mp 101.0 to 102.0 C. The trinitrofluorenone derivative (Orchin et al., 1946), mp 204 to 206 C, was obtained as pale orange crystals from alcohol-benzene.

Anal. Calcd. for  $C_{29}H_{19}N_3O_7$ : N, 8.1.

Found: N, 8.1.

*4,4'-Dimethyldiphenic Acid Anhydride*.—A solution of 10.0 g of 4,4'-dimethyldiphenic acid in 50 ml of acetic anhydride was refluxed for 30 min. On cooling, filtration and concentration of the mother liquors, 8.0 g (82 per cent) of the anhydride, mp 163 to 166 C, was obtained in two crops. The analytical sample, mp 165 to 166 C, was obtained on crystallization from toluene.

Anal. Calcd. for  $C_{16}H_{12}O_3$ : C, 76.2; H, 4.8.

Found: C, 76.2; H, 4.7.

*2,7-Dimethylfluorenone*.—A mixture of 3 g of copper powder and 9.5 g of the anhydride was heated at 360 C for 3 hr. Vacuum distillation afforded 5.0 g (66 per cent) of the fluorenone (Bergmann et al., 1951) mp 115 to 126 C, suitable for the next step. (Note that Bergmann et al. give a mp of 157 C. Our ketone was evidently a mixture composed of polymorphic forms as high yields derivatives were obtained from the low melting substance.) The oxime, mp 218 to 221 C (from ethanol-benzene) and the phenylhydrazone, mp 170 to 171 C (from ethanol) were prepared.

Anal. Calcd. for  $C_{15}H_{13}NO$ : N, 6.3.

Found: N, 6.4.

Anal. Calcd. for  $C_{21}H_{18}N_2$ : N, 9.4.

Found: N, 9.5.

*2,7-Dimethylfluorenicarboxylic Acid*.—By a typical Huang-Minlon modified Wolf-Kishner reduction, 10.0 g of the fluorenone was converted into 8.0 g (90 per cent) of crude 2,7-dimethylfluorene (Mascarelli et al., 1941) mp 108 to 114 C. When a solution of 13.5 g of similar material in 80 ml of ether was treated with a solution of the phenyllithium prepared from 1.4 g of lithium and 11.7 g of bromobenzene in 170 ml of ether, a dark green solution was obtained. After heating at reflux for 1 hr, the solution was poured into a slurry of dry ice and ether. A conventional workup afforded 13.5 g (81 per cent) of 2,7-dimethylfluorenicarboxylic acid, mp 218 to 220 C, pure enough for further use.

Anal. Calcd. for  $C_{16}H_{14}O_2$ : C, 80.6; H, 5.9.

Found: C, 80.3; H, 5.9.

On acid catalyzed esterification methyl 2,7-dimethylfluorenicarboxylate, mp 123 to 124 C (from methanol) was obtained in high yield.

Anal. Calcd. for  $C_{17}H_{16}O_2$ : C, 80.9; H, 6.4.

Found: C, 80.9; H, 6.2.

*2,7-Dimethyl-9-hydroxymethylfluorene*. Reduction of the above methyl ester with lithium aluminum hydride afforded the alcohol, mp 112.5 to 113.5 C (recrystallized from Skellysolve B) in high yield.

Anal. Calcd. for  $C_{16}H_{16}O$ : C, 85.7; H, 7.2.

Found: C, 85.5; H, 7.0.

On cyclization (Brown et al., 1940) the above alcohol (in crude form) was converted into 2,7-dimethylphenanthrene, mp 100 to 101 C, in 75 per cent yield.

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