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THE SYNTHESIS OF 5-METHYL- AND 5,5-DIMETHYL-5H-DIBENZO[*a,d*]CYCLOHEPTENE

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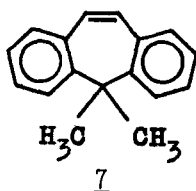
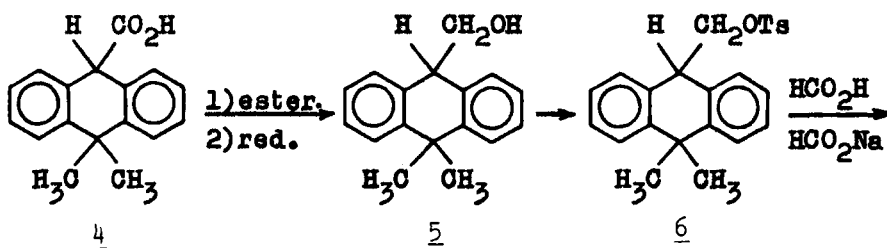
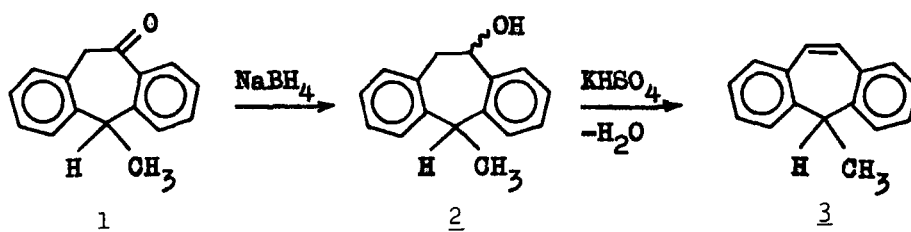
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THE SYNTHESIS OF 5-METHYL- AND
5,5-DIMETHYL-5H-DIBENZO[a,d]CYCLOHEPTENE

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The title compounds were synthesized according to the following schemes.



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EXPERIMENTAL³

5-Methyl-5H-10,11-dihydrodibenzo[a,d]cyclohepten-11-01 (2). - Ketone 1 (1 g, 4.50 mmoles) in CH₃OH (40 ml) was treated with a solution of NaBH₄ (0.12 g, 3.17 mmoles) in 0.33% NaOH (2.6 ml). After 48 hr. at room temperature, the solvent was removed and the residue was extracted with ether. The evaporation of ether gave 1 g (99%) of an oily mixture of the epimeric alcohols 2. IR (CCl₄, cm⁻¹): 1036 vs, 3200-3500 w, 3584 m. Nmr (CDCl₃, δ): 1.68 and 1.78 (two doublets J = 7.5; CH₃), 1.90 (s, OH), 3.00-3.80 (m, CH₂), 4.40 (m, CH), 5.15 (m, CH(OH)), 7.15-7.50 (m, aromatic H).

5-Methyl-5H-dibenzo[a,d]cycloheptene (3). - A mixture of crude alcohols 2 (0.6 g, 2.68 mmoles) and KHSO₄ (0.6 g, 4.41 mmoles) was heated at 150-60°/4 mm Hg. The product was recrystallized from CH₃OH to yield 0.3 g (54%) of 3, mp. 56-56.5°.

Anal. Calcd. for C₁₆H₁₄: C, 93.16; H, 6.84

Found: C, 92.9; H, 7.0

Nmr (CCl₄, δ, 40°): 1.31 (d, J = 7, axial CH₃), 1.86 (d, J = 7, equatorial CH₃), 3.47 (q, J = 7, axial CH), 4.19 (q, J = 7, equatorial CH), 6.76 and 6.96 (two singlets, CH=CH), 7.12 (s, aromatic H).

9,9-Dimethyl-10-hydroxymethyl-9,10-dihydroanthracene (5). - The ethyl ester of 4 (1.52 g, 5.42 mmoles) (from 4² and EtOH saturated with HCl) was reduced with LiAlH₄ (0.12 g, 3.16 mmoles) in ether. The usual work-up and recrystallization from n-hexane gave 1.13 g (87%) of 5, mp. 85-87°.

Anal. Calcd. for $C_{17}H_{18}O$: C, 85.67; H, 7.61

Found: C, 85.86; H, 7.88

IR (CCl_4 , cm^{-1}): 1044 vs, 3599 s. Nmr (CCl_4 , δ): 1.27 (1H, s, OH), 1.58 (3H, s, CH_3), 1.76 (3H, s, CH_3), 3.60 (2H, d, s, OH), 1.58 (3H, s, CH_3), 1.76 (3H, s, CH_3), 3.60 (2H, d, J = 6.5, CH_2), 4.05 (1H, t, J = 6.5, CH), 7.0-7.7 (8H, m, aromatic H).

9,9-Dimethyl-10-tosyloxymethyl-9,10-dihydroanthracene (6). -

The product with mp. 102-103° (CH_3OH), was obtained in 94% yield.

Anal. Calcd. for $C_{24}H_{24}O_3S$: C, 73.44; H, 6.16; S, 8.17

Found: C, 73.51; H, 6.33; S, 8.46

5,5-Dimethyl-5H-dibenzo[a,d]cycloheptene (3). - Tosylate 6

(0.32 g, 0.82 mmoles) and HCO_2Na (0.12 g, 1.76 mmoles) in HCO_2H 99% (6 ml) were heated for 24 hr. at 75°, then poured into water, neutralized with 10% Na_2CO_3 and extracted with ether. After solvent evaporation, the oily residue was chromatographed over Al_2O_3 with petroleum ether (bp. 30-40°), to yield 0.15 g (74%) of 3, mp. 47-48°.

Anal. Calcd. for $C_{17}H_{16}$: C, 92.68; H, 7.32

Found: C, 92.76; H, 7.56

Nmr (CCl_4 , δ , 40°): 1.65 (6H, s, CH_3), 6.90 (2H, s, $CH=CH$), 7.0-7.6 (8H, m, aromatic H).

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3. IR spectra were recorded on a Carl-Zeiss UR-20 spectrophotometer and nmr spectra with a Varian A-60A instrument (TMS as internal standard).