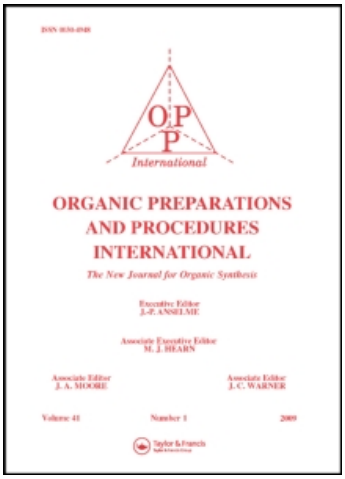


Organic Preparations and Procedures International
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t902189982

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

M. Vinatoru[a]; M. Elian[a]; Ecaterina Cioranescu[a]
[a] Organic Chemistry Research Center, Bucharest, Romania

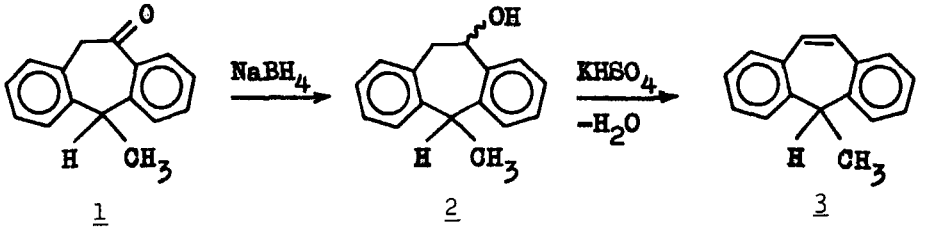
To cite this Article Vinatoru, M. , Elian, M. and Cioranescu, Ecaterina(1975) 'THE SYNTHESIS OF 5-METHYL- AND 5,5-DIMETHYL-5*H*-DIBENZO[*a*,*d*]CYCLOHEPTENE', Organic Preparations and Procedures International, 7: 2, 98 — 101
To link to this Article: DOI: 10.1080/00304947509355579
URL: http://dx.doi.org/10.1080/00304947509355579

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

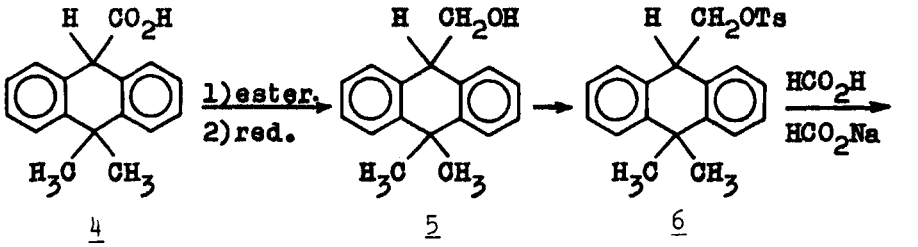
Submitted by M. Vinatoru, M. Elian and Ecaterina Cioranescu
(2/24/75)

Organic Chemistry Research Center
Spl. Independentei 202-B
Bucharest 15, Romania

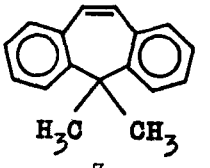
The title compounds were synthesized according to the following schemes.



1 2 3



4 5 6



7

EXPERIMENTAL[3]

5-Methyl-5H-10,11-dihydrodibenzo[a,d]cyclohepten-11-ol (2). - Ketone 1 (1 g, 4.50 mmoles) in CH_3OH (40 ml) was treated with a solution of $NaBH_4$ (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 (CCl_4, cm^{-1}): 1036 vs, 3200-3500 w, 3584 m. Nmr ($CDCl_3$, δ): 1.68 and 1.78 (two doublets J = 7.5; CH_3), 1.90 (s, OH), 3.00-3.80 (m, CH_2), 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 $KHSO_4$ (0.6 g, 4.41 mmoles) was heated at 150-60°/4 mm Hg. The product was recrystallized from CH_3OH to yield 0.3 g (54%) of 3, mp. 56-56.5°.

Anal. Calcd. for $C_{16}H_{14}$: C, 93.16; H, 6.84
Found: C, 92.9; H, 7.0

Nmr (CCl_4, δ, 40°): 1.31 (d, J = 7, axial CH_3), 1.86 (d, J = 7, equatorial CH_3), 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 4[2] and EtOH saturated with HCl) was reduced with $LiAlH_4$ (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).

REFERENCES

1. N. J. Leonard, A. J. Kresge and M. Oki, J. Am. Chem. Soc., 77, 5078 (1955).

2. M. A. Davis, S. O. Winthrop, R. A. Thomas, J. Med. Chem., 7, 88 (1964).

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).