# 9-Methylene-9,10-dihydrophenanthrene

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A degassed solution of 9-(2-anilinoethyl)phenanthrene gave 9-methylene-9,10-dihydrophenanthrene upon irradiation.

We report the first preparation of 9-methylene-9,10-dihydrophenanthrene (**2**), a nonaromatic isomer of 9-methylphenanthrene (**3**).

Irradiation by a high-pressure mercury lamp through a Pyrex filter on a degassed solution ($1.7 \times 10^{-2}$ mol/l) of 9-(2-anilinoethyl)phenanthrene (**1**)† gave a colourless viscous oil as the main product (50—60%) which was isolated by column chromatography. This compound was assigned the structure (**2**) on the basis of the following spectral data: i.r., $\nu_{\max}$ (liq. film) 3060, 3030, 2945, 1635, 1605, 1500, 1490, 1455, 895, 770, and 745 cm$^{-1}$; u.v., $\lambda_{\max}$ (hexane) 216 (log $\epsilon$ 4.42), 247 (4.46), and 278 nm (4.14); n.m.r., $\delta$ (CDCl$_3$) 7.8—7.0 (8H, m, aromatic), 5.26 (1H, d, $J$ 1.5 Hz, $>\mathrm{C{=}CH_2}$), 5.06 (1H, d, $J$ 1.5 Hz, $>\mathrm{C{=}CH_2}$), and 3.65 (2H, s, $>\mathrm{CH_2}$).

Irradiation of a solution of (**1**) in D$_2$O-saturated benzene gave a monodeuteriated compound in the n.m.r. spectrum of

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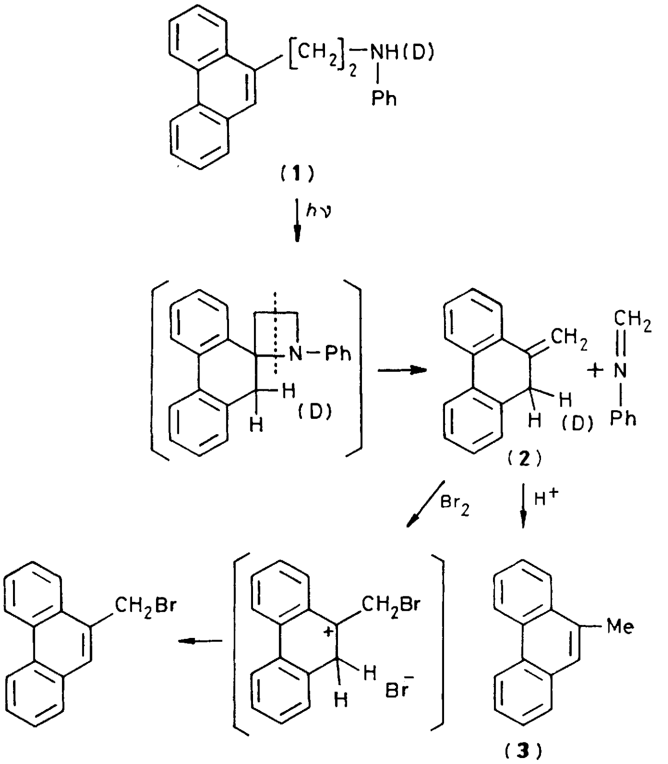
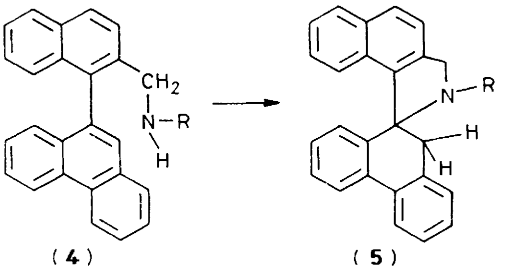
† Compound (**1**) was prepared by the reduction of the anilide obtained by the reaction of aniline with 9-phenanthrylacetyl chloride, and identified by spectral data (i.r. and n.m.r.) and elemental analyses.



Scheme 1

which the relative intensity of the n.m.r. signal at $\delta$ 3.65 (broad s) was reduced.

The assigned structure (**2**) was chemically confirmed by the following observations: (a) acid treatment led to aromatisation to afford (**3**) which was identified by comparison of the i.r. and n.m.r. spectra with those of an authentic sample; (b) bromination of (**2**) did not give 9-bromo-9-bromomethyl-9,10-dihydrophenanthrene but gave 9-bromomethylphenanthrene, presumably owing to stabilisation by aromatisation, as shown in Scheme 1.



**a**; R = Ph
**b**; R = Me
**c**; R = Cyclohexyl
**d**; R = Bu$^t$

Scheme 2

The suggested mechanism of the formation of (**2**) (Scheme 1) is based on our previous study,[1] in which irradiation of the phenanthrenes (**4a**—**d**) in degassed benzene resulted in the formation of the spiro compounds (**5a**—**d**) respectively in high yields, as shown in Scheme 2.

Since compound (**2**) is a nonaromatic isomer of (**3**) the difference in stability between (**2**) and (**3**) is expected. Accordingly, with acid treatment aromatisation of (**2**) to (**3**) easily occurs. The detailed physical and chemical properties of compound (**2**) are under further investigation.

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## References

1 A. Sugimoto, R. Sumida, N. Tamai, H. Inoue, and Y. Otsuji, *Bull. Chem. Soc. Jpn.*, 1981, **54**, 3500.