Synthesis of *cis*-1,2,3,4,4a,5,8,8a-Octahydronaphthalene and of *cis-transoid-cis*-1,4,4a,5,8,8a,9,9a,10,10a-Decahydroanthracene

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The Diels-Alder $_{\pi}4_s + _{\pi}2_s$ reaction proceeds selectively: in the cycloadduct the new σ bonds are *cis* related and also the new π bond is precisely located. The removal without epimerization of the activating groups on the former $_{\pi}2_s$ component provides synthetically useful unsaturated cyclic compounds with a determined position of the double bond. We took advantage of the low basicity and good nucleophilicity of *p*-toluenesulfonyl hydrazide to prepare, with retention of *cis* geometry, the bis-tosylhydrazones (**2** and **5**) of the diketones **1** and **4**. Reduction of these with an excess of sodium borohydride[1] in dimethylformamide affords the title compounds **3** and **6** free of any epimeric contaminant. In previously described related reductions, substantial[2] or modest[3] epimerisation has been noted.

Our preparation has the following merits. Elimination reactions from 2-substituted *cis*-perhydronaphthalenes invariably give mixtures of **3** and its somewhat more stable 1,2-unsaturated isomer[4]. Admittedly, a stereospecific synthesis of **3** is already on record[5], but it is more elaborate than the one reported here. Hydrocarbon **6** has been obtained in a 6% yield by a classical alkaline Wolff-Kishner reduction of **4** (or isomers)[6]. We did not succeed in securing **6** by Wolff-Kishner reduction of **4** in dimethyl sulfoxide[7], nor by reduction of its bis-tosylhydrazone **5** with sodium borohydride in acetic acid[8].

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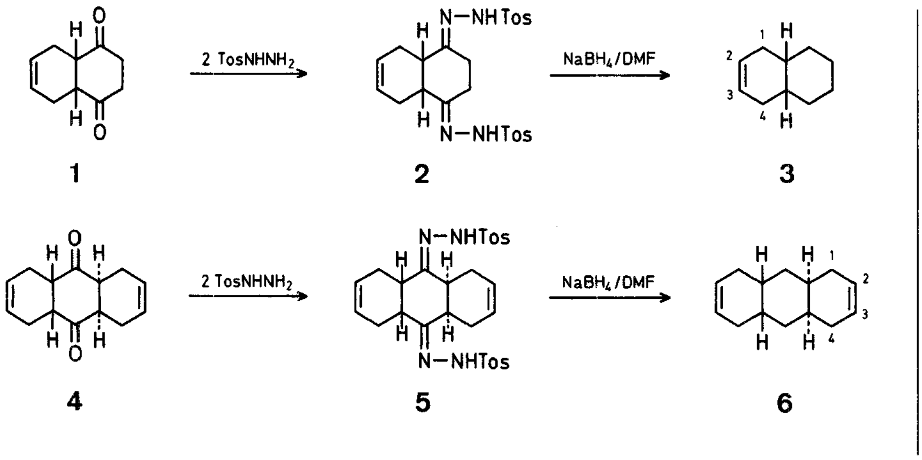
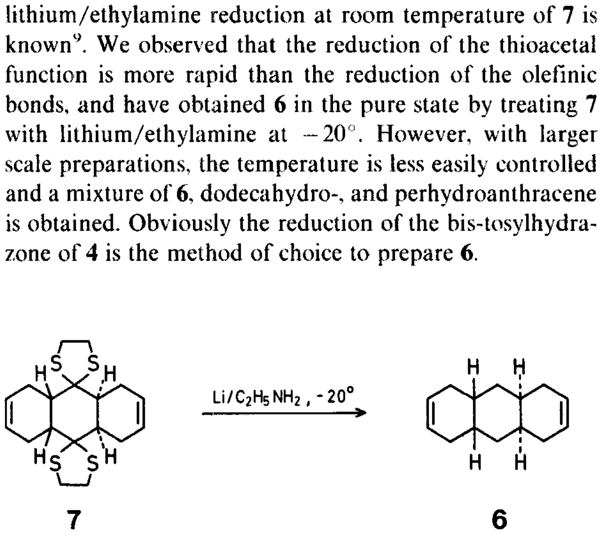


The preparation of *cis-transoid-cis*-perhydroanthracene by lithium/ethylamine reduction at room temperature of **7** is known[9]. We observed that the reduction of the thioacetal function is more rapid than the reduction of the olefinic bonds, and have obtained **6** in the pure state by treating **7** with lithium/ethylamine at −20°. However, with larger scale preparations, the temperature is less easily controlled and a mixture of **6**, dodecahydro-, and perhydroanthracene is obtained. Obviously the reduction of the bis-tosylhydrazone of **4** is the method of choice to prepare **6**.



Bis-Tosylhydrazones 5 and 2; General Procedure:
Ketone **4** (4.32 g, 20 mmol) and 4-toluenesulfonyl hydrazide (7.44 g, 40 mmol) are dissolved in hot chloroform (100 ml). The solvent is evaporated on a rotary evaporator. The residual liquid is heated under evaporation for 2 min at 100°. The mixture becomes viscous and then foam-like. Methanol (100 ml) is added and the mixture is boiled. On cooling, white crystals are deposited (6.7 g). A second quantity of 2.2 g is obtained by evaporating the methanol, heating the residue again for 2 min on the steam bath, and crystallizing from methanol (50 ml); yield: 8.9 g (80%); m.p. 195° (with decomposition). The mono-tosylhydrazone is a minor contaminant (~5%).

$C_{28}H_{32}N_4O_4S_2$	calc.	C 60.85	H 5.84	N 10.14	S 11.60
(552.7)	found	61.15	5.52	9.65	11.80

^{1}H-N.M.R. (DMSO-d_6): $\delta = 10.15$ and 10.31 ppm (two N NH Tos signals of about equal intensity, due to *Z/E*-isomerism).

The bis-tosylhydrazone[10] of **1**[11] is similarly prepared in 78% yield, m.p. 230°; Lit. [10] m.p. 181°.

Caution: The tosylhydrazide[12] must be pure – otherwise epimeric end products are obtained. Commercial samples were often unsatisfactory.

Reduction of Tosylhydrazones 5 and 2; General Procedure:
The bis-tosylhydrazone of **4** (25 g, 40 mmol) is dissolved in dimethylformamide (300 ml). The temperature is raised to 80°. Sodium borohydride (25 g, 650 mmol) is added in portions of 5 g over 1 h. The yellow colour of the solution disappears gradually, and in the beginning nitrogen is evolved vigorously. The mixture is kept at 80° for 3 h. After cooling, water (100 ml) is added. The mixture is extracted with pentane. The pentane is evaporated and the residue is separated from minor impurities by chromatography over a short silica gel column. The eluent pentane is evaporated to give *cis-transoid-cis*-1,4,4a,5,8,8a,9,9a,10,10a-decahydroanthracene (**6**); yield: 2.33 g (31%); m.p. 98°; Lit. [6] m.p. 95–96.5°.

^{1}H-N.M.R. (360 MHz, $CDCl_3$): $\delta = 5.63$ (4H); 2.06 (12H); 1.42 ppm (4H).

The known[5] hydrocarbon **3** was obtained in the same fashion in 42.5% yield; b.p. 192°/770 torr; Lit. [5] b.p. 68°/14 torr.

Lithium/Ethylamine Reduction of 7:
Dithioacetal **7** (5 g, 13.5 mmol)[6,9] is suspended at −20° in anhydrous ethylamine (200 ml) and treated gradually under stirring with lithium (1 g, 145 mmol). The blue color persists, and stirring is continued for an additional 30 min. Ethanol (2 ml) and then solid ammonium chloride is added. The ethylamine is distilled off, the residue is acidified with 6 normal hydrochloric acid, and the aqueous layer extracted with pentane. Evaporation of the pentane layer and crystallization from acetone give a first and second crop of **6**; yield: 900 mg (35%); m.p. 98°.

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[1] L. Caglioti, P. Grasseli, *Chem. Ind. (London)* **1964**, 153.
[2] R. O. Hutchins, C. A. Molewski, B. E. Maryanoff, *J. Am. Chem. Soc.* **95**, 3662 (1973).
[3] A. Van der Gen, K. Wiedhaup, J. J. Swoboda, H. C. Dunathan, W. S. Johnson, *J. Am. Chem. Soc.* **95**, 2656 (1973).
[4] R. Bucourt in *Topics in Stereochemistry*, Vol. 8, E. L. Eliel, N. L. Allinger, Eds., Interscience, New York, 1974, p. 207.
[5] H. J. Bestmann, H. Pfüller, *Angew. Chem.* **84**, 528 (1972); *Angew. Chem. Int. Ed. Engl.* **11,** 508 (1972).
[6] R. K. Hill, J. G. Martin, W. H. Stouch, *J. Am. Chem. Soc.* **83**, 4006 (1961).
[7] (a) D. J. Cram, M. R. V. Sahyun, G. R. Knox, *J. Am. Chem. Soc.* **84**, 1734 (1962);
(b) H. H. Szmant, M. N. Roman, *J. Am. Chem. Soc.* **88**, 4034 (1966).
[8] R. O. Ruthins, N. R. Natale, *J. Org. Chem.* **43**, 2299 (1978).
[9] N. S. Crossley, H. B. Henbest, *J. Chem. Soc.* **1960**, 4413.
[10] B. M. Jacobson, *J. Am. Chem. Soc.* **95**, 2579 (1973).
[11] P. A. Robins, J. Walker, *J. Chem. Soc.* **1958**, 409.
[12] L. Friedman, R. L. Little, W. R. Reichle, *Org. Synth.* **40**, 93 (1960).