Tetrahedron Letters No. 36, pp 3143 - 3146, 1977. Pergamon Press. Printed in Great Britain.

DECAMETHYLANTHRACENE AND ITS 9,10-'DEWAR' ISOMER

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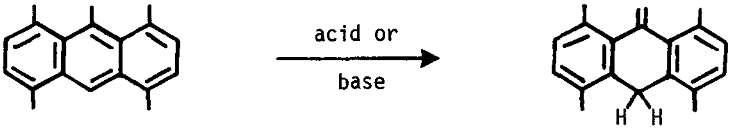
(Received in USA 20 June 1977; received in UK for publication 14 July 1977)

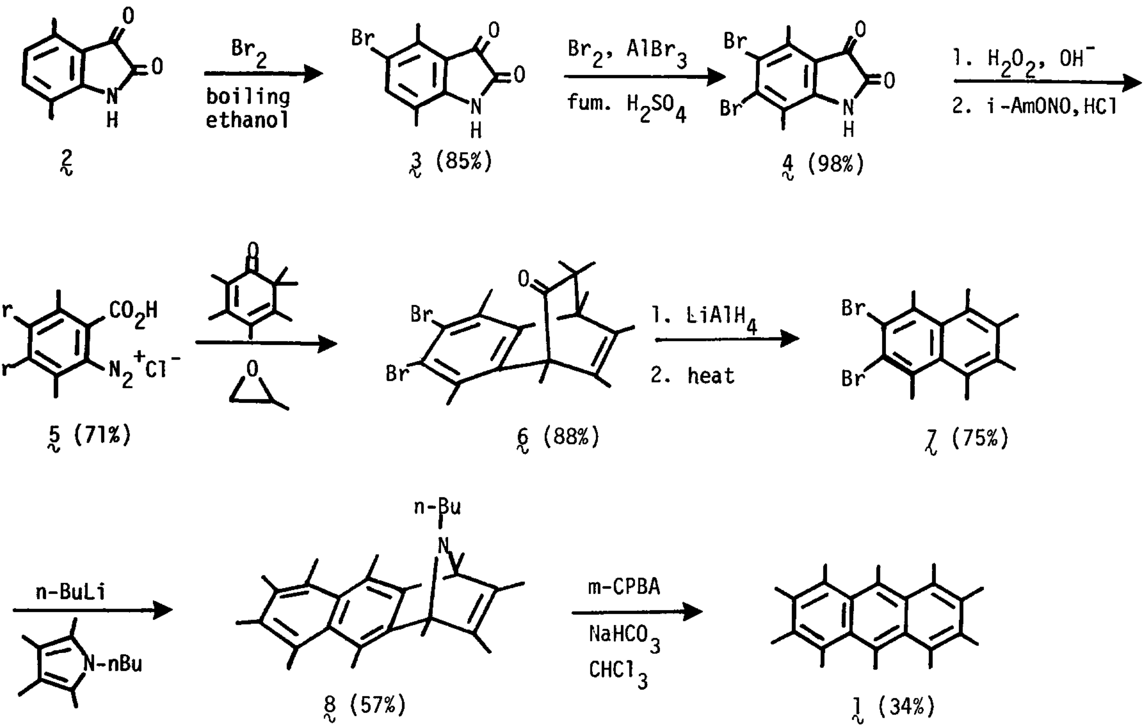
Peri interactions in naphthalenes and anthracenes cause molecular distortions which may result in unusual reactions.[1] Anthracenes with a double-peri interaction (i.e., substituents at C1, 8 and 9) or with two peri interactions (i.e., substituents at C1, 9 and either C4, 10 or C5, 10) may be unstable relative to the tautomeric form in which the central ring is not aromatic.[2] For example, 1,4,5,8,9-pentamethylanthracene,[3,4] which has a double-peri methyl interaction, rearranges in acid[2,4] or in base[5] to the 9-methylidene-9,10-dihydro tautomer. Consequently in the synthesis of the fully aromatic form of these compounds it is important to avoid if possible acidic or base reaction conditions at or after the point that the peri strain is introduced.[6]



We wish to describe here the first synthesis of decamethylanthracene (**1**).[7] Our route is general and can be extended to other highly substituted, strained aromatics. Decamethylanthracene has some unusual properties as a consequence of its strain.

The synthetic sequence is shown in the Scheme. The key intermediate is the dibromohexamethylnaphthalene **7**, used as an aryne precursor in the penultimate step. Unfortunately **7** was formed in only very low (∿5%) yield[8] from the readily available[9] 1,2,3,4,5,8-hexamethylnaphthalene and had to be approached obliquely. Addition of bromine (1.3 eq) to a boiling suspension of 4,7-dimethylisatin[10] gave a clear solution from which the monobromo derivative **3** quickly deposited as red crystals, mp 299-302°C (ethanol).[11] Further bromination of **3** required exceptionally severe conditions, but could be accomplished in excellent yield by stirring **3** with bromine (2 eq) and anhydrous $AlBr_3$ (0.16 eq) in fuming sulfuric acid (20% SO_3) at room temperature for 24 h (until aromatic protons were absent by NMR).[12] Dibromide **4**, mp 313-315°C (ethanol)[11] was converted by alkaline hydrogen peroxide to the corresponding anthranilic acid,[11a] mp 175°C, which on diazotization gave **5**, mp 129-130°C (explodes). Equivalent amounts of **5** and hexamethyl-2,4-cyclohexadienone[13] in 1,2-dichloroethane containing propylene oxide was heated at 70-80°C until N_2 evolution ceased, to give aryne adduct **6**, mp 110-112°C (ethanol).[11] Ketone **6** was rapidly[14] reduced

Scheme



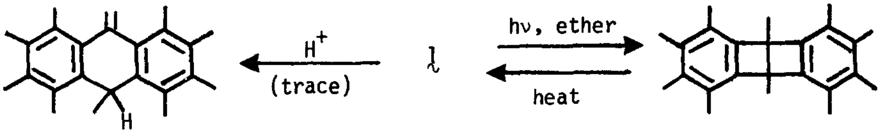
by $LiAlH_4$ in ether at 0°C to a mixture of epimeric alcohols which, when refluxed in mesitylene (under argon) for 44 h gave the desired **7**, mp 177-178°C (ethanol).[11]

In the final steps to **1**, n-butyllithium (in hexane) was added to equivalent amounts of **7** and N-*n*-butyl-tetramethylpyrrole[15] at room temperature (1 h) to give adduct **8**, mp 108-109°C (ethanol, -20°C).[11,16] Oxidation with *m*-chloroperbenzoic acid at 0° in chloroform and 10% aqueous sodium bicarbonate, followed by brief reflux and workup[17] gave **1** as yellow, fluorescent crystals, mp 210-212°C (methylene chloride/methanol).[11]

Decamethylanthracene showed three singlets in its proton NMR spectrum (C_6D_6) at δ1.62, 2.02 and 2.17, the last due to C9, 10 methyls. The ^{13}C NMR spectrum showed the expected seven peaks (δ17.27, 23.52, 29.29, 127.79, 128.46, 134.52, 136.86). The uv spectrum (hexane) had λ_{max} at 427 nm (log ε3.80), 405 (3.83), 390 (sh, 3.74) and 283 (5.05), and the fluorescence spectrum, measured at room temperature in the same solvent roughly mirrored the absorption spectrum, but with one broad maximum at 480 nm.

The strain inherent in **1** was evident from two experiments. A methylene chloride solution of **1** (60 mg in 10 ml) was treated with one drop of trifluoroacetic acid (violet color), then quenched on ice to give the colorless tautomer **9**, mp 246-248°C (methylene chloride/ethanol)[11]; NMR (CCl_4) δ1.20 (d, 3H, *J* = 7Hz), 2.18 (s, 12H), 2.28 and 2.43 (s, 6H each), 4.37 (q, 1H, *J* = 7Hz) and 5.24 (s, 2H).

Irradiation of a thoroughly degassed solution of 1 (benzene or ether) through Pyrex rapidly converted it to the 9,10-'Dewar' isomer 10.[11a] The proton and ^{13}C NMR spectra were consistent with the symmetry of this structure ['H(C_6D_6): δ1.78 (s, 6H), 1.95 (s, 12H), 2.15 (s, 12H);



9 10

^{13}C: 13.77, 15.28, 15.77, 59.23, 128.75, 133.14, 147.10].[18] Compound 10 can be obtained as a white solid by vacuum removal of the solvent from these irradiations. However it thermally rearranges to 1 (approx. 15% in benzene, 40°, 30 min).[19,20]

These studies are continuing.

Acknowledgement. We are indebted to the National Science Foundation (GP 43659X) for financial support of this research.

References and Notes

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11. a) Spectral data were in full accord with the assigned structure; b) a correct elemental analysis was obtained.
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of bromine, can occur and must be avoided.

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16. The N-benzyl adduct was also prepared, but gave poorer yields in the final step.
17. The procedure was based on that of G.W. Gribble, R.W. Allen, P.S. Anderson, M.E. Christy and C.D. Colton, Tetrahedron Lett., 3673 (1976).
18. The simplicity of the NMR spectra is also consistent with the symmetry of a 9,10-photodimer. This possibility was eliminated by a molecular weight determination (cryoscopic, benzene). We are indebted to Dr. Rodney Willer for this measurement.
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