The Observation of a Thermal 'Double Aromatization' Process in a Hydrocarbon with Fused Blocked Aromatic Rings

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On heating above 150 °C, compound (**1**), the first reported example of a hydrocarbon with fused blocked aromatic rings, rearranges to form 9-ethylanthracene, with simultaneous aromatization of two non-aromatic rings.

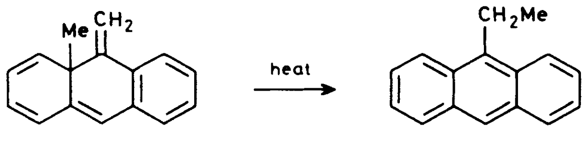
Rearrangements which result in the immediate conversion of non-aromatic rings into aromatic isomers are well known. (Typical examples include the 'semibenzene rearrangements' of methylenecyclohexadienes[1] and the rearrangements of 6-allylcyclohexa-2,5-dien-1-ones to aryl ethers.[2]) These reactions normally proceed at far more rapid rates than do analogous reactions which do not result in formation of new aromatic rings.

Rearrangements in which the migration of a single substituent would result in the simultaneous aromatization of two (or more) non-aromatic rings should proceed with exceptional ease, but no examples of such processes have previously been reported.

We now report the thermal conversion of the polyene (**1**) into 9-ethylanthracene: the first observation of a rearrangement resulting in the 'double aromatization' of two carbocyclic rings. Compound (**1**) represents the first reported example of a hydrocarbon with fused blocked aromatic rings.

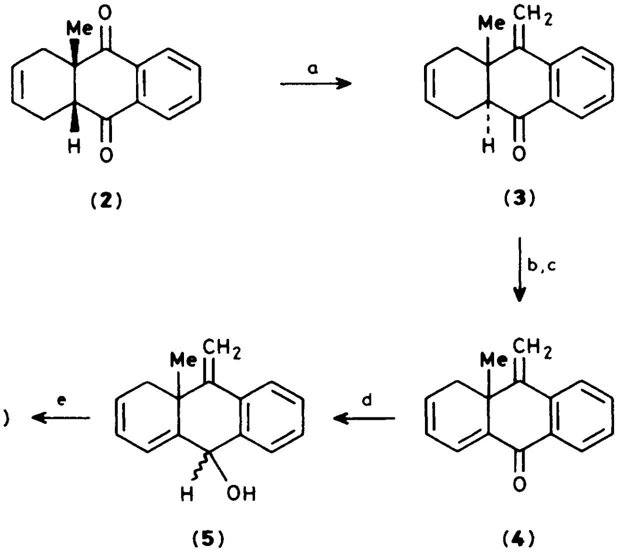
Compound (**1**) was synthesised in five steps from the diketone (**2**)[3] as shown in Scheme 1.

An initial attempt to prepare (**1**) proceeded by reduction of the ketone (**3**) to the alcohol and dehydration to form the triene (**6**). It was expected that allylic bromination of (**6**) with *N*-bromosuccinimide (NBS) and dibenzoyl peroxide followed by dehydrobromination would yield (**1**). However, reaction of (**6**) with NBS yielded none of the expected allylic bromination products. Instead, the bromide (**7**) was obtained, in what appears to be a unique example of vinylic bromination under free radical conditions.

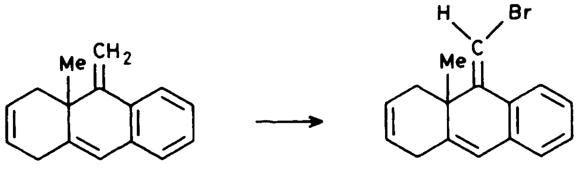


(**1**)

Hydrocarbon (**1**) is an air-sensitive yellow oil which polymerizes on prolonged standing even at 0 °C. It was freshly prepared from the alcohol (**5**) and purified by chromatography on alumina each day before use. Its structure was established



Scheme 1. *Reagents and conditions:* a, $Ph_3P{=}CHLi$, 70% (ref. 4); b, $LiN(C_6H_{11})_2$, tetrahydrofuran; PhSeBr, 73%; c, $NaIO_4$, 59%; d, $NaBH_4$, $CeCl_3$, MeOH; e, $ZnCl_2$, C_6H_6, heat for 20 min, 55% from (**4**).



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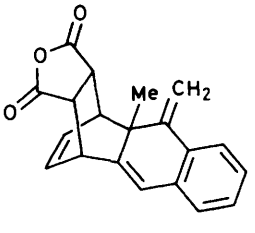

(8)

from its elemental analysis, its reaction with maleic anhydride in refluxing toluene to form adduct (**8**), m.p. 178—180 °C, and its spectra.†

When (**1**) was heated on Pyrex beads at 375 °C (contact time *ca.* 1 s) it was converted into a mixture of 9-ethylanthracene (40% yield) and 9-methylanthracene (8%), together with high molecular weight materials. Rearrangements in *N*,*N*-dimethylaniline or diphenyl ether solutions at temperatures between 150 and 190 °C also yielded 9-ethylanthracene (*ca.* 32%) and 9-methylanthracene (2%). In no instance was formation of any 9,10-dimethylanthracene observed. Addition of free radical inhibitors (including dicyclohexylphosphine, benzoquinone, α-naphthol, and hydroquinone) did not affect the product compositions or apparent reaction rates from thermolysis of (**1**) at 175 °C in diphenyl ether or at 375 °C, arguing against rearrangements *via* free radical chain mechanisms.

Although a concerted rearrangement cannot be ruled out, we suggest that (**1**) rearranges to 9-ethylanthracene *via* a radical dissociation–recombination process. The low temperatures required for this process indicate an exceptionally low bond energy for the methyl–carbon bond, reflecting the large gain in aromatic stabilization on conversion of (**1**) into a 9-anthracenylmethyl radical.

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† ^1H N.m.r. (300 MHz): δ 1.1 (s, 3H), 5.35 (s, 1H), 5.65 (s, 1H), 5.92—6.0 (m, 1H), 6.08—6.16 (m, 1H), 6.22—6.30 (m, 2H), 6.40 (s, 1H), 7.05—7.10 (m, 1H), 7.14—7.28 (m, 2H), and 7.56—7.6 (m, 1H); $\lambda_{max.}$ (hexane) 238 (ε 29 820), 247 (28 670), 253 (sh, 22 435), 268 (sh, 16 055), 277 (21 330), 289 (16 742), 377 (16 350), and 390 (sh, 9175); *m/z* 206 (100%) and 191 (95).

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