## 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<sup>1</sup> and the rearrangements of 6-allylcyclohexa-2,5-dien-1-ones to aryl ethers.<sup>2</sup>) 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.

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).



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

When (1) was heated on Pyrex beads at  $375 \,^{\circ}$ 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

† <sup>1</sup>H 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, 16055), 277 (21 330), 289 (16 742), 377 (16 350), and 390 (sh, 9175); *m/z* 206 (100%) and 191 (95).

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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,  $\alpha$ -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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