## An Extraordinarily Rapid [1,5] Benzyl Shift in a Molecule with a Ring System consisting Entirely of Fused Blocked Aromatic Rings

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Dehydrobromination of the dibromobicyclic ketone (4) at 0 °C resulted in the formation of ketone (5); the remarkably rapid [1,5] benzyl shift in this reaction is attributed to formation and rearrangement of ketone (2), a unique example of a molecule with a ring system consisting entirely of fused blocked aromatic rings.

Blocked aromatic molecules, in which a change in location of a single substituent can convert a nonaromatic ring into an aromatic one, undergo rapid and often unusual rearrangement processes.<sup>1,2</sup> Molecules with fused blocked aromatic rings, in which the migration of a substituent at a ring juncture could result in the simultaneous aromatization of two (or more) hydroaromatic rings, would be expected to exhibit still greater driving forces for rearrangement.

The synthesis of ketone (1), the first molecule to contain fused cyclohexadienone and semibenzene (methylenecyclohexadiene) rings, was recently reported.<sup>3</sup> However, the presence of the fused benzo ring in (1) greatly reduces the driving force for its rearrangement under thermal conditions, and results in aromatization of the semibenzene ring alone (*via* migration of the methyl group to C-10) being favoured over a 'double aromatization' process.<sup>3†</sup>

In this communication we report evidence for the formation and rearrangement of ketone (2), in which the ring system consists entirely of fused cyclohexadienone and semibenzene rings. Ketone (2) was chosen as a synthetic target because the benzyl substitutuent is capable of undergoing a variety of



Scheme 1. Reagents and conditions: i, Li, NH<sub>3</sub> (75% yield); ii, Bu<sup>n</sup>Li; iii, PhCH<sub>2</sub>Br, 25 °C, 19 h (20%); iv, Br<sub>2</sub>, NBS (0.1 mol) (45%); v, DBU, 0 °C.

<sup>+</sup> While ketone (1) is not exceptionally reactive under thermal conditions, it does undergo an exceptionally rapid and efficient photorearrangement (ref. 3).

exothermic rearrangement processes under thermal conditions, including [1,3] or [3,3] shifts [to either C-4 or the carbonyl oxygen of (2)] or a [1,5] shift to C-2. In addition, electrocyclic opening of the cyclohexadienone ring to form a ketene, possibly followed by recyclization at an unsubstituted position, might compete with rearrangement processes.

Ketone (3) (m.p. 89.5-90.5 °C) was prepared by a Claisen alkylation process as shown in Scheme 1. Attempts at allylic bromination of (3) employing N-bromosuccinimide (NBS) and dibenzoyl peroxide yielded intractable mixtures, so addition of bromine to the isolated double bond was employed instead. Our first attempts to add bromine to (3) in CCl<sub>4</sub> solution at 0 °C resulted in evolution of HBr and cleavage of the ketone to yield a mixture containing benzyl bromide, 2-t-butylnaphthol, and dihydronaphthols. Since it seemed probable that this unusual cleavage process was catalysed by acid, the addition of bromine was repeated under the same conditions, but employing 10–20 mol% of NBS as an acid scavenger. Under these conditions dibromide (4) was obtained in 45% yield after chromatography on Florisil.

A solution of (4) in carbon tetrachloride was stirred with four mol. equiv. of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) at 0 °C for 18 h to yield, after chromatography on silica gel, a bromine-free product identified as ketone (5) (70%).

The structure of (5) was established from its analytical and spectral data, $\ddagger$  as well as from its reaction with 0.01 m sulphuric acid in acetic acid to yield 2-benzylnaphthol. (Other 6-t-butylcyclohexa-2,4-dien-1-ones similarly lose isobutylene in acidic solutions.<sup>4</sup>)

No long wavelength u.v. peak corresponding to that expected for (2) could be detected during dehydrobromination of (4), nor could products from a Diels-Alder reaction with (2) be obtained when the dehydrobromination of (4) was



 $<sup>\</sup>ddagger$  I.r. (neat) 1660, 1601 cm<sup>-1</sup>; <sup>1</sup>H n.m.r. (CDCl<sub>3</sub>)  $\delta$  1.01 (s, 9H), 2.80 (d, J 13 Hz, 1H), 3.73 (d, J 13 Hz, 1H), 6.18 (d, J 10 Hz, 1H), 6.52 (d, J 10 Hz, 1H), 7.05–7.4 (including a large apparent singlet at 7.05, 8H), and 8.0 (dd, J 1.5, 7 Hz, 1H).

carried out in the presence of N-phenylmaleimide. Nonetheless, we believe that formation of (5) can only reasonably be explained as occurring by a [1,5] benzyl shift in the fused blocked aromatic ketone (2).

Thermal [1,5] benzyl shifts in cyclohexa-2,4-dien-1-ones have previously been observed.<sup>1</sup> However, rearrangement of ketone (6), for instance, proceeds with a half life of more than 3 h at 165 °C, while (2) rearranges so rapidly at 0 °C that it cannot be detected.

The remarkably rapid rearrangement of (2) can be attributed to its fused blocked aromatic structure, in which a concerted [1,5] benzyl migration results in the highly exothermic formation of a new aromatic ring. In contrast the [1,5] benzyl migration in (6) simply converts one nonaromatic ketone to another.

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