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A BICYCLO[2.1.0]PENTANE PHENONIUM ION

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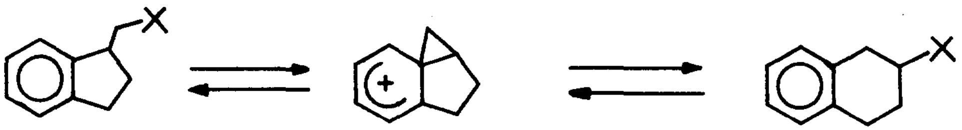
Huisgen and coworkers[1-8] and others[9] have addressed themselves to the question of solvolytic interconversion of benzocycloalken-3-methyl- and benzocycloalken-4-yl derivatives in a variety of normal and medium sized ring systems. Their general conclusions may be summarized, taking a particular ring system as example, in equation 1.



(1)

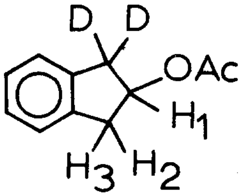
We have investigated the lowest member of this homologous series currently preparable and wish to report that exclusive aryl migration (equation 2) is also seen here.

(2)

Solvolysis of benzocyclobuten-3-ylcarbinyl toluenesulfonate[10,11] in refluxing buffered acetic acid proceeds at a rate ($k = 4 \times 10^{-4}$ sec^{-1}) approximately one half that calculated for the analogous indanylcarbinyl toluenesulfonate at this temperature.[7] The product is initially a 7:3 mixture of indan-2-yl acetate and indan-1-yl acetate. The latter product is not stable under the reaction conditions and goes over to indene (1) on prolonged reflux. Indan-2-yl acetate (2) is stable to the reaction conditions.

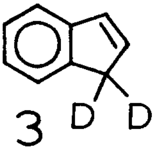
To distinguish between the various mechanistic possibilities, and particularly between aryl vs alkyl shifts, the solvolysis of benzocyclobuten-3-yldideuterocarbinyl toluenesulfonate[12] was investigated. The indan-2-yl acetate-d_2 formed was isomer **2**-d_2. That **2**-d_2 is dideuterated follows from

2-d_2



its mass spectrum:[13] m/e 178 (parent, weak), m/e 118 (indene-d_2) and m/e 117 (indene-d_1). The latter two were in the ratio of 2:1 as shown by a low voltage mass spectrum and result from pyrolytic elimination of acetic acid[14] from **2**-d_2. The NMR spectrum of **2**-d_2, when compared with that of **2**-d_0 required that the two deuterium atoms of **2**-d_2 reside on the same methylene, H_2 and H_3 appearing as a quartet of doublets as in **2**-d_0 and H_1 as a quartet, J_{13} = 6, J_{12} = 4 cps, in contrast to the complex multiplet of **2**-d_0.

The indene isolated from the solvolysis was a mixture of predominately **3** and **4**, as shown by: 1) its mass spectrum; **1**-d_2 (m/e 118):**1**-d_1 (m/e 117) = 2.5 with negligible intensity of peak m/e 116 (**1**-d_0). 2) its NMR spectrum:



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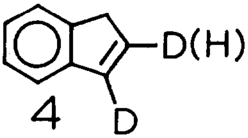

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the vinyl hydrogens appeared as an AB quartet, J_{AB} = 5.5 cps centered at δ 6.67 relative to TMS and the methylene hydrogen appeared as a broad singlet at δ 3.33 in equal intensity.

These results require the formal intermediacy of a bicyclo[2.1.0]pentylphenonium ion (aryl migration) in this rearrangement. Our thoughts as to the pathways are shown in figure 1.

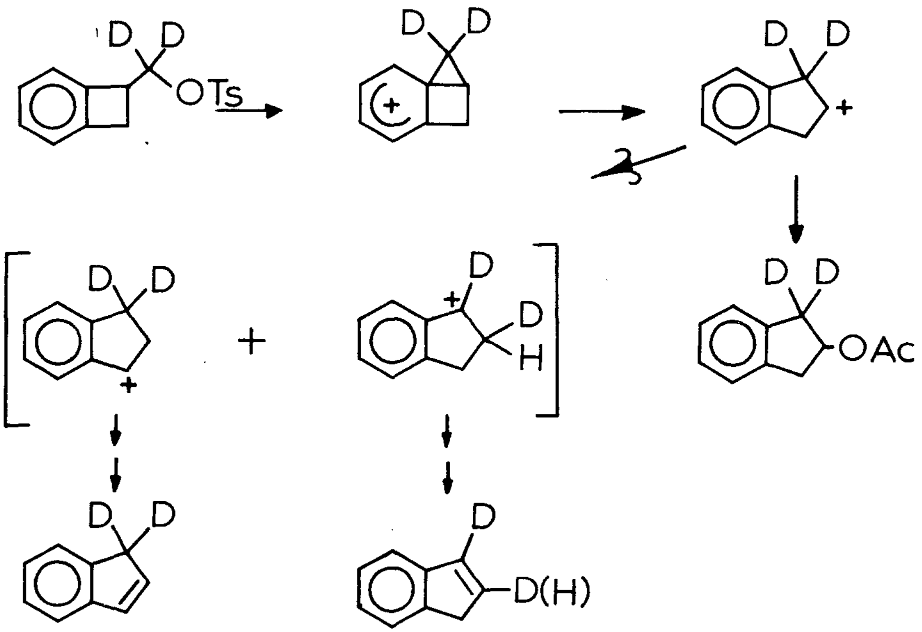

FIG. 1

Acknowledgment

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12. Prepared by lithium aluminum deuteride reduction of benzocyclobuten-3-yl carboxylic acid and subsequent tosylation.

13. Mass spectra were determined in a CEC-103C mass spectrometer with a heated glass inlet system held at 250°. Isotope analyses were corrected for the natural isotope level.

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