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THE MECHANISM OF THE SYNTHESIS OF BENZVALENE

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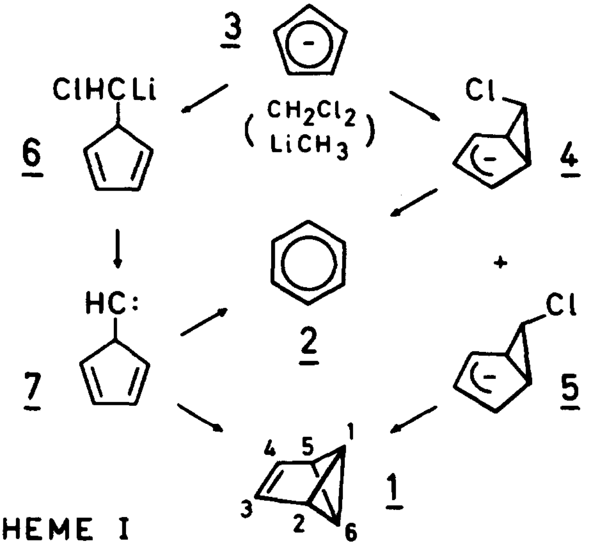
Benzvalene, one of the more interesting, but scarce isomers of benzene, has recently become available on a preparative scale. The method of synthesis consists of allowing cyclopentadienyllithium to react with dichloromethane in the presence of methyllithium. Benzvalene (1) is formed in some 45% yield, but always accompanied by benzene (2) as sole side-product[1]. At the moment the precise details of this reaction are not known, although a number of plausible mechanisms can be written. We now present evidence and arguments which reveal the correct pathway followed by this apparently simple homologation reaction.

Two closely related possibilities need to be considered (scheme 1). The first involves cyclopropanation of the cyclopentadienyl anion (3) to give the *syn* and *anti* adducts 4 and 5. Disrotatory rupture of the cyclopropane ring of the former adduct should occur to eliminate chloride ion with formation of benzene. However, the *anti* isomer 5 would be expected to undergo an internal nucleophilic attack on the cyclopropyl carbon expelling chloride ion to give benzvalene. The second possibility is that the cyclopentadienyl anion initially reacts with dichloromethyllithium to replace one of the chlorine atoms furnishing 6. This lithium salt subsequently will generate the carbene 7, which on internal 1,2 or 1,4 addition, forms benzvalene. Competitive ring enlargement gives benzene.

It has been previously reported that preparations carried out with dichloromethane labelled with ^{13}C or ^{2}H gave 1 with the label distributed increa-

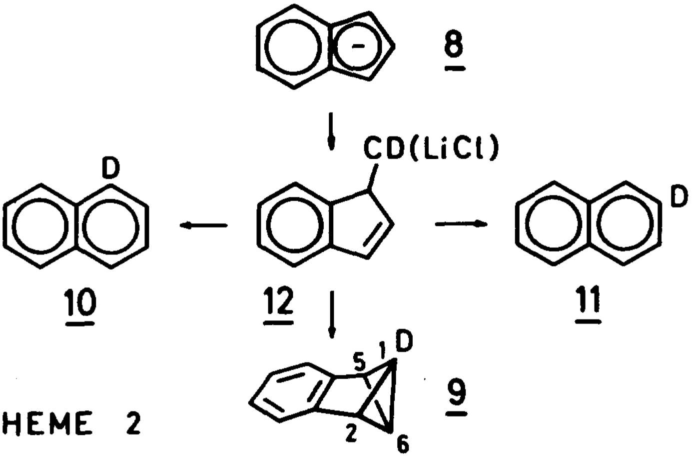


SCHEME I

singly in the C-3, C-2 and C-1 positions[2]. We have now carefully repeated the synthesis using dideuterodichloromethane; the resultant benzvalene was examined by the ^{2}H-FT-NMR-technique[3,5]. Deuterium label was found stereospecifically located at C-1 (97 ± 3%). Clearly the previously reported scrambling is an event entirely unconnected with the construction of the benzvalene skeleton. Of course, this finding is compatible with both possibilities of scheme 1. However, more information is forthcoming from the same reaction performed with indenyllithium(8).

Once again the use of dideuterodichloromethane yields benzobenzvalene (9) exclusively labelled at C-1. However, α and β-monodeuteronaphthalene (10 and 11) are also formed in a 0.6 : 1 ratio. These products can only be explained by invoking the intermediacy of the carbene precursor, namely the indenylchloromethyllithium (12). Ring enlargement can occur in just two ways which accounts for the distribution of deuterium label between the α and β-positions[6]. Internal 1,2 cheletropic addition gives benzobenzvalene uniquely labelled at C-1 (scheme 2). Finally it should be mentioned that benzobenzvalene on heating does not give rise to naphthalene, but furnishes benzofulvene instead[1,7].

On the basis of these findings, it can be safely concluded that the mechanism for the formation of benzvalene involves the initial formation of <u>one</u> new



SCHEME 2

C-C bond in a substitution reaction producing the carbene precursor. Further reaction and internal cheletropic addition gives benzvalene.

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2. R.D. Suenram & M.D. Harmony, J. Amer. Chem. Soc. 95, 4506 (1973); R.D. Suenram, ibid. 97, 4869 (1975).
3. Though it has been known for more than a decade, direct NMR spectroscopic observation of deuterium has not found wide application in organic chemistry. ^{2}H Spectra are easy to assign thanks to the 1:1 relation between ^{2}H and ^{1}H chemical shifts[4].
4. P. Diehl in "Nuclear Magnetic Resonance Spectroscopy of Nuclei other than

Protons". Editors T. Axenrod & G.A. Webb. John Wiley & Sons (1974), Chap. 18, page 275.

5. Proton noise-decoupled ^2H-NMR-spectra were obtained at 15.4 MHz on a *Varian XL-100* spectrometer by accumulation and *Fourier* transformation of 500 to 1000 free-induction decays. Complete deuterium relaxation was ensured by a 15 sec repetition interval of the 45° pulses. The ^{19}F resonance of external hexafluorobenzene was used for field/frequency stabilization.
6. See however: I. Murata & K. Nakasuji, Tetrahedron Letters 47 (1973).
7. U. Burger & F. Mazenod, see accompanying letter.