Tetrahedron Letters No. 31, pp 2811 - 2814.
©Pergamon Press Ltd. 1978. Printed in Great Britain.

0040-4039/78/0729-2811$02.00/0

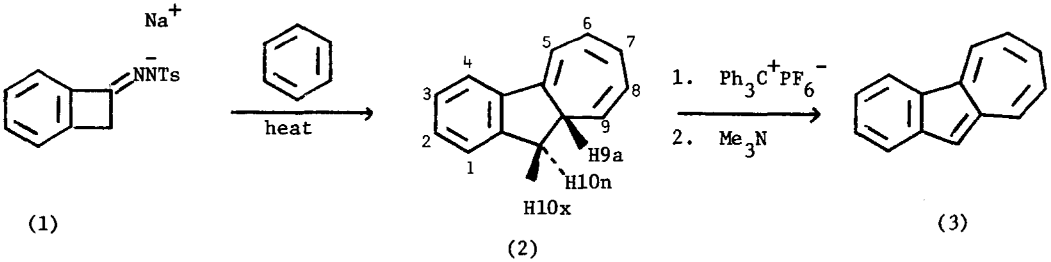
THE ADDITION OF BENZOCYCLOBUTENYLIDENE TO BENZENE. A NOVEL ROUTE TO BENZ[a]AZULENE.

Margaret A. O'Leary and Dieter Wege

Department of Organic Chemistry, University of Western Australia, Nedlands, Western Australia, 6009.

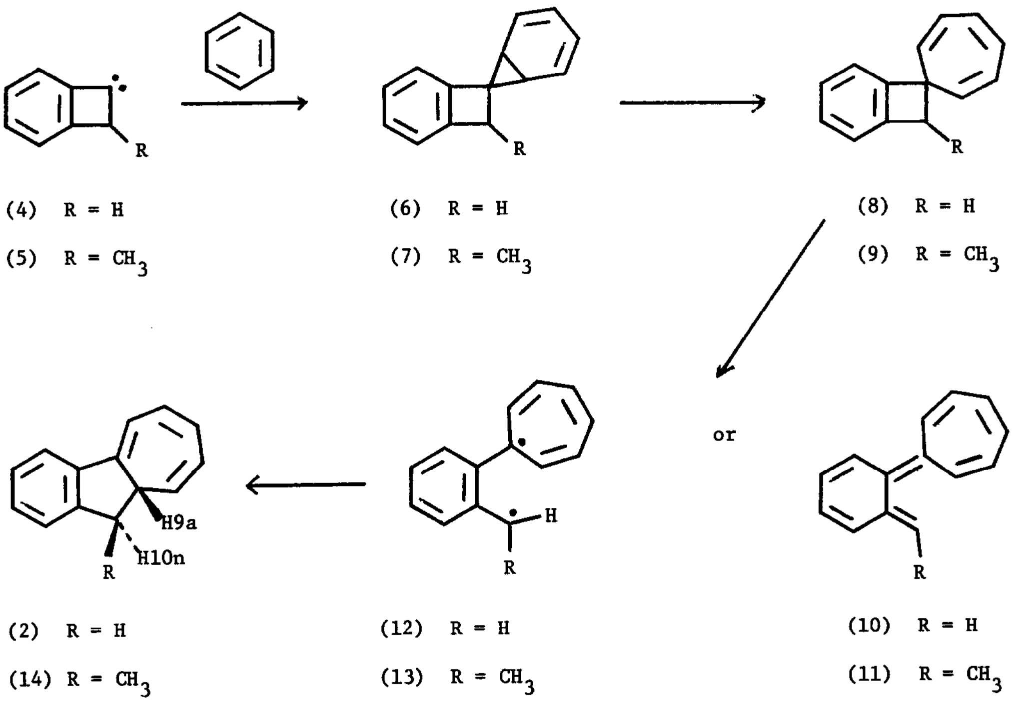
(Received in UK 8 May 1978; accepted for publication 2 June 1978)

The thermal or photochemical decomposition of the salts of tosylhydrazones of aldehydes and ketones is a well established procedure for the generation of carbenes.[1] We find that thermolysis of the sodium salt of benzocyclobutenone tosylhydrazone (1) in benzene (70 hr at reflux, or 3.5 hr at 140°) gives 9a,10-dihydrobenz[a]azulene (2) in 20-30% yield. The structure of (2) follows from its spectroscopic properties: ^{1}H n.m.r. (90 MHz, $CDCl_3$) δ 7.56-7.06 (m, 4H aromatic), 6.55-6.30 (m, 3H, vinyl), 6.22-6.00 (m , 1H, vinyl), 5.24 (d of d, $J_{9,9a}$ = 4 Hz, $J_{9,8}$ = 9.5 Hz, 1H, H9), 3.60 (d of d, $J_{10x,10n}$ = 18 Hz, $J_{10x,9a}$ = 10 Hz, 1H, H10x) and 3.18-2.78 (m, 2H, H10n and H9a); mass spectrum m/e 180 (M^+, 100%), 179 (100), 178 (60), 165 (55), 152 (17), 89 (25), 76 (25), 63 (15), 51 (10); electronic spectrum λ_{max}^{EtOH} 217 (log ε 4.53), 250 sh (3.91), 330 (3.94) nm, and from the conversion of (2) into the known[2] benz[a]azulene in 51% yield by hydride ion abstraction followed by deprotonation (Scheme 1).



SCHEME 1

The formation of (2) can be rationalised (Scheme 2) in terms of addition of benzocyclobutenylidene (4) to benzene to give the spironorcaradiene (6), which can isomerise to the spirocycloheptatriene (8). Electrocyclic ring opening of the benzocyclobutene moiety of (8) would afford the o-quinodimethane derivative (10), or the equivalent diradical (12), which on ring closure gives the observed product (2).



(4) R = H

(5) R = CH_3

(6) R = H

(7) R = CH_3

(8) R = H

(9) R = CH_3

(2) R = H

(14) R = CH_3

(12) R = H

(13) R = CH_3

(10) R = H

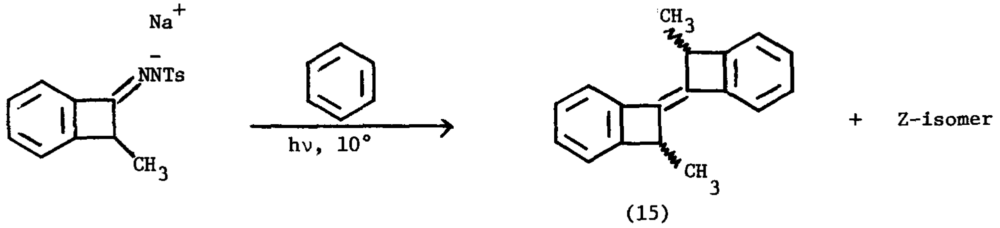
(11) R = CH_3

SCHEME 2

Generation of 2-methylbenzocyclobutenylidene (5) from the sodium salt of 2-methylbenzocyclobutenone tosylhydrazone[3] in refluxing benzene gave a single stereoisomer of 9a,10-dihydro-10-methylbenz[a]azulene (14) (31%), ^1H n.m.r. (90 MHz, $CDCl_3$) δ 7.55-7.00 (m, 4H, aromatic), 6.72-5.94 (m, 4H, vinyl), 5.30 (d of d, $J_{9,8}$ = 10 Hz, $J_{9,9a}$ = 4 Hz, 1H, H9), 3.31 (d of q, $J_{10,9a}$ = 4 Hz, J_{10,CH_3} = 7 Hz, 1H, H10), 2.54 (7 line m, 1H, H9a), 1.36 (d, J = 7 Hz, 3H, CH_3), mass spectrum m/e 194 (M^+, 30%), 180 (15), 179 (100), 178 (45), 165 (10), 152 (8), 89 (18), 76 (10). Molecular models reveal that the 9a,10-dihydrobenz[a]azulene ring system is conformationally rather rigid and that the C10-H10x: C9a-H9a and C10-C10n: C9a-H9a dihedral bond angles are _ca_ 0° and 110° respectively. Hence $J_{10x,9a}$ should be substantially larger in magnitude than $J_{10n,9a}$.[4] In the spectrum of (2), one of the H10 methylene proton resonances overlaps with that of H9a, but the other H10 resonance at δ 3.60 shows coupling to H9a, with J = 10 Hz. We therefore assign the signal at δ 3.60 to H10x, the _exo_-proton which is _cis_ to H9a. In the methyl substituted compound (14), $J_{10,9a}$ = 4 Hz, which is consistent with H10 and H9a being in a _trans_ orientation.

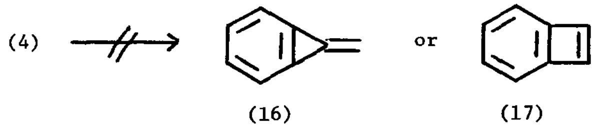
The finding that (14) has the trans stereochemistry shown raises an interesting mechanistic point. If the ring opening of the benzocyclobutene derivative (9) takes place in a controtatory fashion to give the o-quinodimethane derivative (11) having the methyl group in the less crowded "outer" environment, then the predicted disrotatory ring closure of (11) should yield cis-9a,10-dihydro-10-methylbenz[a]azulene. The fact that the trans isomer (14) is formed suggests that the spirocycloheptatriene to dihydrobenz[a]azulene rearrangement proceeds via diradicals (12) and (13), in which steric constraints prevent the attainment of the planar π-electron systems of (10) and (11). Carbon-carbon bond rotation in the diradical (13) can compete with ring closure to give the more stable trans product (14).[5]

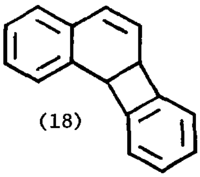
Attempts to isolate the spirocycloheptatriene intermediates (8) and (9) by carrying out the carbene addition to benzene at a lower temperature have so far been unsuccessful. Thus photochemical generation of the carbene (5) in benzene at 10° gives only the dimer (15) (56%) as a mixture of diastereomers (Scheme 3).[6]



SCHEME 3

In general, only those carbenes which are incapable of undergoing intramolecular reactions give appreciable yields of addition products with benzene or other aromatic substrates.[1] In the case of benzocyclobutenylidene (4) (and its methyl derivative) addition to benzene occurs readily presumably because intramolecular rearrangement processes are energetically unfavourable




(18)

Thus methylenebenzocyclopropene (16), the product expected[7] from ring contraction of (4), would be highly strained, and benzocyclobutadiene (17), the expected[7] product of insertion into the α C-H bond, possesses antiaromatic character. While we cannot rule out the possibility that (16) and (17) are formed and consumed in our reactions, the angular dimer (18) which is usually formed when (17) is generated,[8] was not detected in the thermolysis of (1).[9]

References and Footnotes

1. W. Kirmse, "Carbene Chemistry", 2nd Edition (Academic Press: New York and London 1971).
2. J.R. Nunn and W.S. Rapson, J. Chem. Soc., 825 (1949).
3. 2-Methylbenzocyclobutenone was prepared by silver ion-assisted hydrolysis of 1,1-dichloro-2-methylbenzocyclobutene, which in turn was obtained by the 2 + 2 cycloaddition of benzyne to 1,1-dichloropropene.
4. L.M. Jackman and S. Sternhell "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry", 2nd Edition, Chapter 4.2 (Pergamon Press: Oxford 1969).
5. The (8) → (2) and (9) → (14) transformations may also be regarded as [1,7] sigmatropic shifts. A full discussion of the possible mechanism must await the actual isolation of the spirocycloheptatrienes, and a more detailed study of their thermal rearrangement.
6. An analogous dimer is also formed in the photolysis of the sodium salt of 4,6-dimethylbenzocyclobutene tosylhydrazone: A.T. Blomquist and C.F. Heins, J. Org. Chem., 34. 2906 (1969).
7. Cyclobutylidene gives methylenecyclopropane and cyclobutene as the chief products: L. Friedman and H. Shechter, J. Amer. Chem. Soc., 82, 1002 (1960).
8. M.P. Cava and D.R. Napier, J. Amer. Chem. Soc., 79, 1701 (1957); C.D. Nenitzescu, M. Avram and D. Dinu, Chem. Ber., 90, 2541 (1957).
9. It has recently been reported that cyclobutenylidene undergoes ring opening to give vinylacetylene: S.F. Dyer, S. Kammula and P.B. Shevlin, J. Amer. Chem. Soc., 99, 8104 (1977).

As in the case of benzocyclobutenylidene, insertion into the α C-H bond or ring contraction do not appear to be important reaction pathways.