

THE RING CLOSURE OF 5-METHYLCYCLOPENTA-1,3-DIEN-5-YLCARBENE TO 1-METHYLBENZVALENE.

AN INTRAMOLECULAR 1,4 CHELETROPIC CARBENE ADDITION

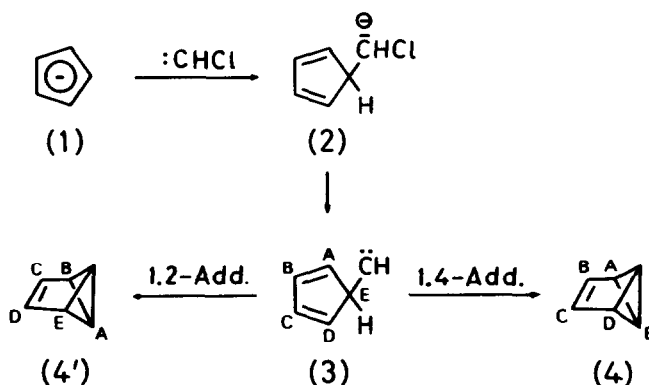
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Abstract. The title carbene (7) is shown to produce the benzvalene skeleton by stereospecific intramolecular 1,4 addition and not by classic cyclopropanation.

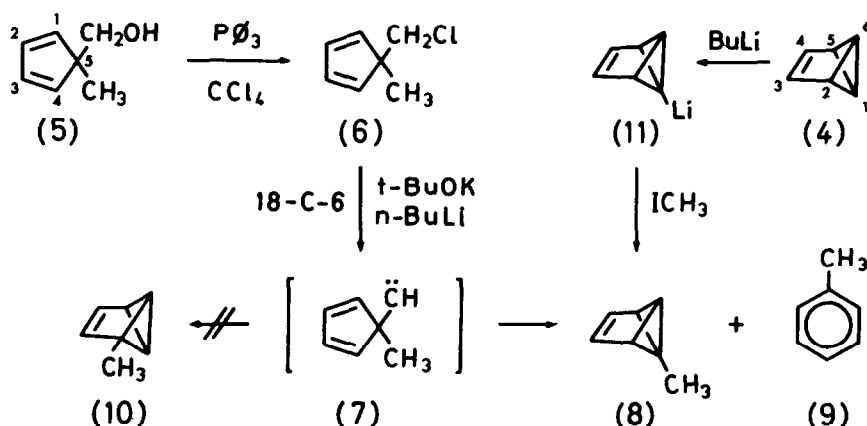
Cyclopentadienylianium (1) reacts with chlorocarbene generated from dichloromethane and methyl lithium to give benzvalene (4).¹ Analogous reactions have been reported for further carbo- and heteroaromatic anions.² Mechanistic studies in our laboratory suggest that the parent reaction proceeds *via* the cyclopentadienylcarbene (3).



However, an interesting question has not yet been answered: benzvalene may formally result from (3) by a classic cyclopropanation reaction, *i.e.* a 1,2 addition [(3)→(4')], or by 1,4 addition [(3)→(4)]. We now wish to show, by independent generation of a properly substituted cyclopentadienylcarbene, that indeed the abnormal pathway is followed, *i.e.* the benzvalene skeleton results from stereospecific intramolecular 1,4 addition of the carbene to the butadiene unit.⁴

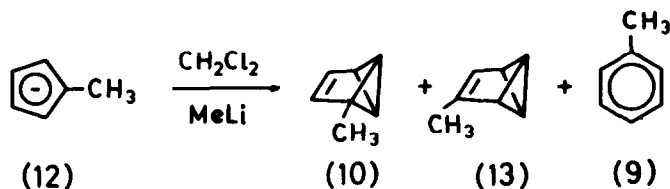
For this purpose, the cyclopentadienylcarbene (7) was generated with the C-5 hydrogen atom of (3) replaced by a methyl group. This group has a triple function. Firstly, the notoriously

fast 1,5 hydride shift of monosubstituted cyclopentadienes, which would scramble any peripheral label, is avoided.⁵ Secondly, in the absence of an acidic ring proton, carbene (7) can be generated directly by base-induced α -elimination⁶ from the chloromethyl group of (6). Finally, from the site of the methyl group in the resulting benzvalene [(8) or (10)] we discover the pathway by which the bicyclobutane unit is formed.



5-Chloromethyl-5-methylcyclopenta-1,3-diene (6) was obtained by reaction of alcohol (5)⁷ with a twofold excess of triphenylphosphine in carbon tetrachloride in 32% yield.⁸ When a 0.5 M solution of (6) in ether was allowed to react at 25°C in the presence of two equivalents each of potassium tertiary butoxide, *n*-butyl lithium and [18]-crown-[6] (18-C-6) for 3 hours, 1-methylbenzvalene (8) was formed stereospecifically in 38% yield, accompanied by toluene (9) [18%]. After the addition of 2 equivalents of water at 0°C, (8) could be isolated in ethereal solution by flash distillation. 23% of chloride (6) was recovered. The structure of (8) was unambiguously established from the ¹H-NMR spectrum.⁹ In addition, (8) was synthesized independently by the reaction sequence (4)→(11)¹⁰→(8).

In order to prove that no 2-methylbenzvalene (10) is formed besides (8), in the α -elimination of (6), we have also synthesized the former. Compound (10) was obtained in an analogous



manner to (4)¹ in 38.4% yield by reacting methylcyclopentadienyllithium (12) with dichloromethane

and methyllithium in dimethyl ether at -70°C ; 3-methylbenzvalene (13) [18.5%] and (9) [7%] are also formed, but remarkably no (8). The structures of (10) and (13) follow without difficulty from the $^1\text{H-NMR}$ spectrum of the mixture. (10) is characterized particularly by the presence of two chemically non-equivalent olefinic protons, whereas (13) displays a single olefinic proton now coupled to the methyl group.¹¹

Benzvalenes (8), (10) and (13) undergo thermal rearrangement to (9). At 30°C in ether the half-lives are respectively *ca.* 7, 13 and 35 hours. Thus all methylbenzvalenes are less stable than the parent compound (4) for which, under identical conditions, a half-life of 48 hours is observed. Apart from partial thermal decomposition, (10) and (13) are found to be stable under the conditions of the α -elimination (6) \rightarrow (8).

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- 3) U. Burger & F. Mazenod, *Tetrahedron Letters* 1976, 2881.
- 4) Concerning the problem of linear cheletropic carbene reactions see: H. Fujimoto & R. Hoffmann, *J. Phys. Chem.* 78, 1167 (1974); W.W. Schoeller, E. Yurtsever, *J. Am. Chem. Soc.* 100, 7548 (1978); C.W. Jefford, J. Mareda, J.C.E. Gehret, nT. Kabengele, W.D. Graham & U. Burger, *J. Am. Chem. Soc.* 98, 2585 (1976); W. Lilienblum, R.W. Hoffmann, *Chem. Ber.* 100, 3405 (1977), and the discussion by R.A. Moss & M. Jones, Jr., in "Reactive Intermediates", editors M. Jones, Jr., & R.A. Moss, Wiley Interscience, Vol. 1, 69 (1978).
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- 6) *cf.* R.A. Moss & F.G. Pilkiewicz, *J. Am. Chem. Soc.* 96, 5632 (1974); T. Sasaki, S. Eguchi & F. Nakata, *Tetrahedron Letters* 1978, 1999.
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- 8) (6): Bp. $48^{\circ}/12$ Torr, $^1\text{H-NMR}$ ($\text{CCl}_4/60$ MHz); $\delta = 6.30$ (s, 4H), 3.40 (s, 2H) and 1.25 (s, 3H)

- 9) (8): $^1\text{H-NMR}$, AA'EMM'-spin system of the protons directly bound to the benzvalene skeleton: (ether + 10% $|\text{D}_6|$ -benzene/100 MHz) $\delta = 5.80$ (t, 2H), 3.61 (m, 1H), 1.83 (m, 2H); methyl group: $\delta = 1.60$ (s).
- 10) R.J. Roth & T.J. Katz, J. Am. Chem. Soc. 94, 4770 (1972).
- 11) (10) + (13): $^1\text{H-NMR}$ of (10) (ether + 10% $|\text{D}_6|$ -benzene/100 MHz) ABE_2M -spin system of the protons directly bound to the benzvalene skeleton: $\delta = 5.99$ (m, 1H, $^3\text{J} = 5.3$ Hz), 5.80 (m, 1H, $^3\text{J} = 5.3$ Hz), 3.55 (d, 2H), 1.85 (m, 1H, owing to overlap with resonances of (13) determined by INDOR); methyl group (in $|\text{D}_8|$ -THF) $\delta = 1.17$ (s). $^1\text{H-NMR}$ of (13) (ether + 10% $|\text{D}_6|$ -benzene/100 MHz): $\delta = 5.49$ (m, 1H, couples with the methyl group $^4\text{J} = 1.8$ Hz), 3.64 (t, 2H), 1.8-1.9 (m, 2H), 1.78 (d, methyl group, $^4\text{J} = 1.8$ Hz).

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