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THE TRANSITION METAL INDUCED ISOMERIZATION OF BENZVALENE AND BENZOBENZVALENE

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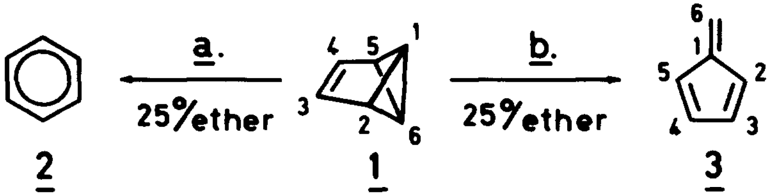
In recent years the isomerization of strained hydrocarbons by transition metals has been intensively studied with particular attention being paid to homogeneous catalysis by ionic or zerovalent metal complexes[1-6]. We wish to report on the zerovalent metal promoted isomerization of benzvalene (1) in which two different rearrangement courses are followed depending on the nature of the metal used.

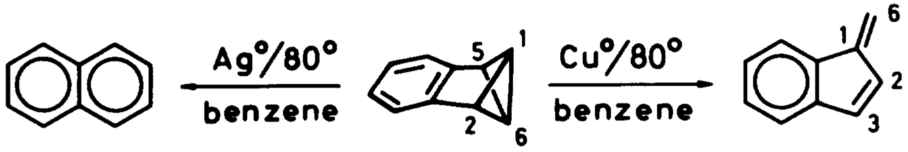
Benzvalene[7] on contact with splinters of silver or iron simply undergoes valence isomerization to benzene (2), whereas platinum, palladium, gold, nickel or copper bring about rapid rearrangement of 1 to fulvene (3) in high yield.



a. contact with Ag^o, Fe^o.

b. contact with Pt^o, Pd^o, Au^o, Ni^o, Cu^o.

Benzobenzvalene (4)[7] also undergoes similar rearrangement at slightly higher temperatures. A few minutes exposure of 4 to copper in boiling benzene gives benzofulvene (5). However, the action of silver converts 4 exclusively into naphthalene (6).



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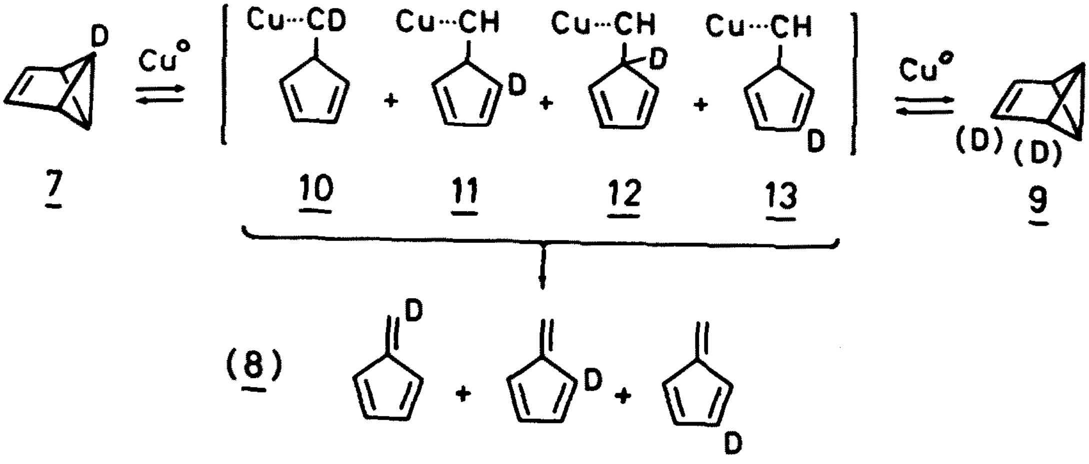
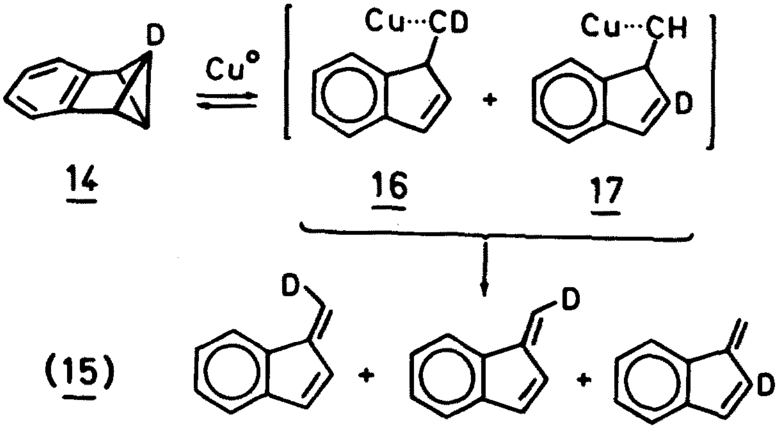
In order to learn more about the mechanism of these novel rearrangements, we have examined the behaviour of 1-deuterobenzvalene (7) and its benzo-annelated derivative (14). The surprising result is that 7 with copper gives fulvene (8) in which label is distributed over all possible positions[8]. The deuterium distribution was found to be 24%, 20% and 56% for the C-2, C-3 and C-6 positions respectively[9]. Still more surprising was the finding that benzvalene recovered from copper after some 80-120 sec reaction was shown to be labelled not only in the starting position C-1 (81%) but also in positions C-2 (12%) and C-3 (7%)[11]. In striking contrast 1-deuterobenzobenzvalene (14) afforded just three isotopomeric benzofulvenes (15) when treated with copper. Label distribution was found to be 25% at $C\text{-}6_{syn}$, 25% at $C\text{-}6_{anti}$ and 50% at C-2[12]. Silver catalysis however, produced only β-deuteronaphthalene.

From these findings it is seen that the copper-promoted reaction requires that the central and one of the lateral bonds in the bicyclobutane moiety be broken. Benzvalene gives the pair of exocyclic carbenoid species 10 and 11 and the benzo-derivative gives 16 and 17. Reclosure of 10 and 11 by internal 1,2 and/or 1,4 addition will account for the scrambling in benzvalene and its absence in benzobenzvalene. The remarkable difference of the label distribution observed in the fulvene products however, necessitates two different scrambling mechanisms. The first is the recycling process via benzvalene and the second involves [1,5] sigmatropic shifts of 11 to produce 12 and 13. Either hydride or group migration could be invoked. For reasons of geometry, the indenyl carbenoids (16 and 17) are incapable of undergoing such [1,5] shifts and accordingly the pattern of label distribution is different.





Clearly, the rearrangements by silver proceed by a fundamentally different mechanism as indicated by the exclusive formation of β-deuteronaphthalene from 14. It can be concluded that the two diagonally opposed bonds of the bicyclobutane moiety are broken with aromatization to naphthalene.

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7. T.J. Katz, E.J. Wang & N. Acton, J. Amer. Chem. Soc. 93, 3782 (1971).
8. Deuterium distribution was determined by ^{2}H-FT-NMR spectroscopy. See the accompanying letter by U. Burger & F. Mazenod.
9. 6.6-Dideuterofulvene was synthesized independently[10] and did not scramble its label on contact with copper.
10. D. Meuche, M. Neuenschwander, H. Schaltegger & H.U. Schlunegger, Helv. Chim. Acta 47, 1211 (1964).
11. cf. R.D. Suenram & M.D. Harmony, J. Amer. Chem. Soc. 95, 4506 (1973); R.D. Suenram & M.D. Harmony, J. Chem. Phys. 58, 5842 (1973).
12. The interpretation is based on the following ^{1}H-NMR shift assignement for the non-aromatic protons of 5 [values in δ [ppm] in CCl_4]: 6.70 (H-3), 6.32 (H-2), 5.88 (H-6$_{syn}$) and 5.55 (H-6$_{anti}$). See however ref.[13] for a differing tentative assignement.
13. R.F.C. Brown, G.E. Gream, D.E. Peters & R.K. Solly, Aust. J. Chem. 21, 2223 (1968).