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CARBENE-CARBENE REARRANGEMENTS. A SIMPLE ROUTE TO DI- AND TETRAHYDROPENTALENES

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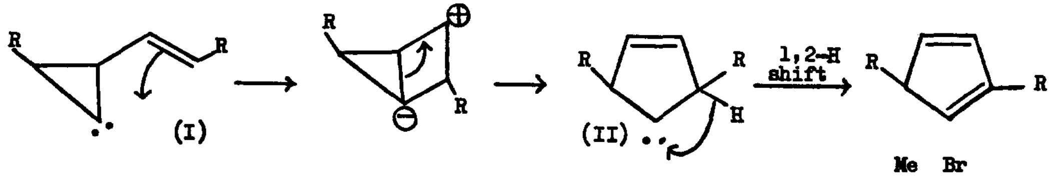
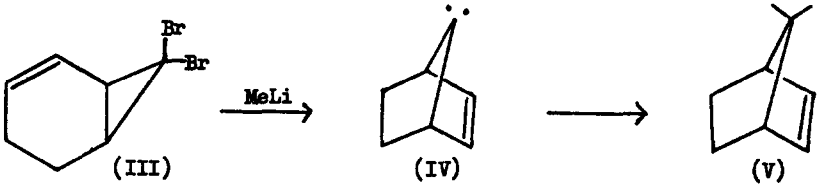
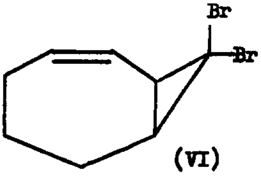
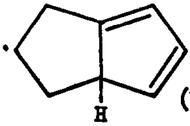
The reaction of vinyl-*gem*-dibromocyclopropanes with methyl lithium has been reported by Skattebøl to lead to cyclopentadienes, presumably *via* a rearrangement of the initially formed cyclopropylidene (I), or a related carbenoid, to the cyclopentenylidene (II), followed by a 1,2-hydrogen shift.[1] In the case of the bicyclic dibromide (III), the assumed rearranged carbene (IV), corresponding to (II), cannot readily undergo a 1,2-hydrogen shift, and is instead trapped as (V)[1] under the reaction conditions.

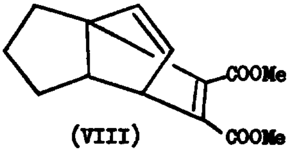


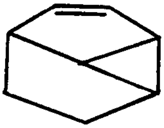


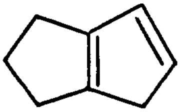
Reaction of 8,8-dibromobicyclo[5.1.0]oct-2-ene (VI)[2] with methyl lithium at -30° to -40°, followed by quenching with H_2O or D_2O at below -20°, led[3] to a single major product (VII) (65%) [n.m.r. spectrum (CCl_4): τ 3.8 (1H, dt, *J* = 5, 1.5 Hz), 4.0 (1H, br. dd, *J* = 5, 0.8 Hz), 4.2 (1H, br. s), 7.1 (1H, br.dd, *J* = 12, 8 Hz) and 7.6 - 8.0 (6H, m)]. This compound was unstable[4] and could not be purified by preparative g.l.c. However, addition of dimethyl acetylenedicarboxylate to the reaction mixture led to the formation of a single adduct (VIII). Analysis of the remaining volatile products showed only the presence of (IX) (*ca.* 5%).[5]

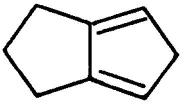

(VI)

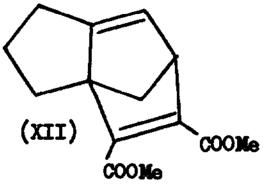

(VII)


(VIII)


(IX)

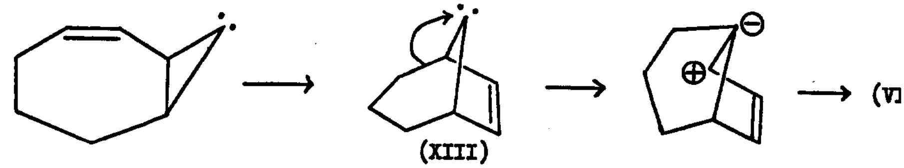

(X)


(XI)

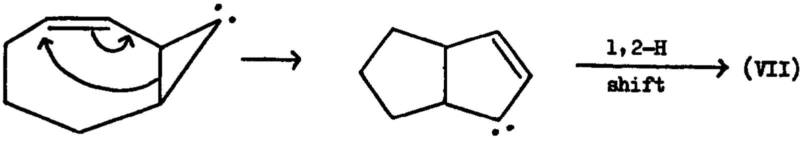

(XII)

When (VI) was treated with methyl lithium at 25-35° and then quenched with H_2O, (VII) was not obtained. Instead, analysis of the volatile products showed the preser of a ca. 4 : 1 mixture of (X) and (XI) (70%)[6] which, on hydrogenation, gave cis-bicyc [3.3.0]octane. Addition of dimethyl acetylenedicarboxylate to the crude reaction mi gave largely (XII), the adduct of (X). If the above reaction was quenched with D_2O instead of with H_2O, the dienes (X) and (XI) were each found to contain one deuteriu Presumably the initial product (VII) is converted at the higher temperature by the ex of MeLi to its conjugate base, protonation or deuteration of which then leads to the observed products.

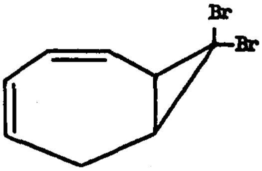
Scheme 1



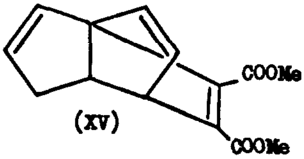
Scheme 2



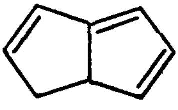
The formation of (VII) from (VI) can be explained (Scheme 1) in terms of an init carbene-carbene rearrangement to (XIII), followed by a second rearrangement. Such rearrangements have been described for a variety of bridged systems.[7] An alternative route (Scheme 2) for the conversion of (VI) to (VII) would appear to be less feasible Indeed, support for the mechanism indicated in Scheme 1 is provided by the reaction o 8,8-dibromobicyclo[5.1.0]octa-2,4-diene (XIV) with methyl lithium.[8,9] When this reac was carried out at -30° to -40° with H_2O or D_2O quenching, and the products treated w dimethyl acetylenedicarboxylate, a single major adduct (XV) was obtained [n.m.r. spectrum (C_6D_6):[10] τ 3.19 (1H, d, *J* = 5 Hz), 3.32 (1H, dd, *J* = 5, 3 Hz), 3.69 (1H, br.ddd, *J* = 6, 3, 1.5 Hz), 4.34 (1H, ddd, *J* = 6, 3, 2Hz), 6.21 (1H, br. s), 6.64 (6H, s), 7.39 (1H, br.dd, *J* = 9, 6.5 Hz), 8.0 – 8.15 (2H complex)].



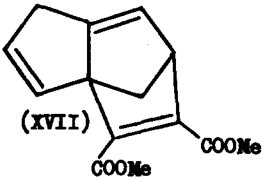
(XIV)



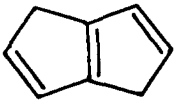
(XV)



(XVI)



(XVII)

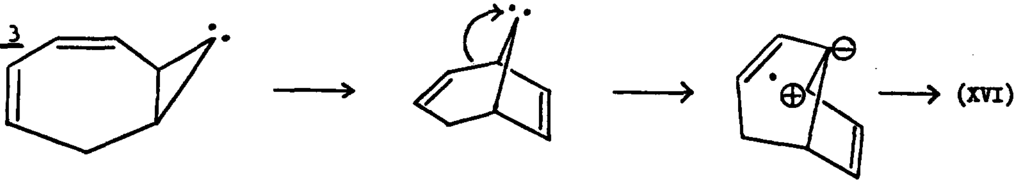


(XVIII)

Compound (XV) is an adduct of the dihydropentalene (XVI), and dimethyl acetylenedicarboxylate. When the latter compound was omitted from the reaction mixture, the presence of (XVI) could be detected by n.m.r. at -30°.[11] Although isolation of (XVI) was not possible, hydrogenation of the crude reaction mixture gave *cis*-bicyclo[3.3.0]octane (38%).

When (XIV) was treated with MeLi at 25-35°, the products quenched with water and then treated with dimethyl acetylenedicarboxylate, another adduct (XVII) was obtained [n.m.r. spectrum (C_6D_6):[12] τ 3.82 (1H, m), 3.95 (1H, m), 4.2 (1H, m), 4.2 (1H, m), 6.0 (1H, m), 6.53 (3H, s), 6.62 (3H, s), 7.27 (2H, complex), 7.66 (1H, dd, *J* = 1.5, 6 Hz) 8.1 (1H, dd, *J* = 6, 1.5 Hz)]. Compound (XVII) is an adduct of the dihydropentalene (XVIII) and dimethyl acetylenedicarboxylate. When the latter was omitted from the reaction mixture, a dihydropentalene,[13] which could once again be hydrogenated to *cis*-bicyclo[3.3.0]octane (32%), was obtained. When (XIV) was treated with MeLi at 25-35°, the products quenched with D_2O and then allowed to react with dimethyl acetylenedicarboxylate, an adduct containing one deuterium atom was obtained. Presumably the initially formed triene (XVI) is converted at the higher temperature, *via* a cyclopentadienide ion to the second triene (XVIII). A possible mechanism for the formation of (XVI) is outlined in Scheme 3.

Scheme 3



REFERENCES AND FOOTNOTES

1. L. Skattebøl, *Tetrahedron* **23**, 1107 (1967).
2. M.S. Baird and C.B. Reese, *Tetrahedron Letters* 4637 (1971); *J.C.S.Chem.Comm.* 784 (1968).
3. This reaction has been briefly reported to yield a mixture of C_8H_{10} hydrocarbons. [M.S. Baird, *Ph.D. Thesis*, Cambridge University, 1968; C.N. Blakesley, *Dissertation Abstracts* **31B**, 6492 (1971)].
4. On standing in CCl_4 at 40°, (VII) rearranged ($t_{\frac{1}{2}} \sim 1$ hr) to (X);[6] further heating at 60° resulted in the formation of an equilibrium mixture of (X) and (XI). Such thermal rearrangements of cyclopentadienes are well known: for example, 5-methylcyclopentadiene rearranges in 3 hr at 25-30° largely to 1-methylcyclopentadiene which, on further standing, is converted to a mixture of 1- and 2-methyl isomers [V.A. Mironov, E.V. Sobelov, and A.N. Elizarova, *Tetrahedron* **19**, 1939 (1963)].
5. O.L. Chapman, G.W. Borden, R.W. King, and B. Winkler, *J.Amer.Chem.Soc.* **86**, 2600 (1964).
6. A. DeMeijere and L. Meyer, *Angew.Chem.Internat.Edit.* **12**, 858 (1973).
7. See R.A. Moss and J.R. Whittle, *J.C.S.Chem.Comm.* 341 (1969); R.A. Moss, U.-H. Dolling, and J.R. Whittle, *Tetrahedron Letters* 931 (1971); T.A. Antkowiak, D.C. Saunders, G.B. Trimitsis, J.B. Press and H. Schechter, *J.Amer.Chem.Soc.* **94**, 5366 (1972).
8. This reaction has been briefly reported to give a mixture of three dihydropentalenes. [P.J. Van Vuuren, *Dissertation Abstracts* **31B**, 7201 (1971)].
9. When (XIV) is complexed to iron tricarbonyl, the reaction follows a completely different course [P.J. Van Vuuren, R.J. Fletterick, J. Meinwald, and R.E. Hughes, *J.Amer.Chem.Soc.* **93**, 4394 (1971)].
10. Irradiation of the signal at τ 6.21 caused the signals at 3.19 and 3.32 to collapse to an AB double-doublet (*J* = 5 Hz) andthe signal at 6.39 to collapse to a sharp double-doublet.
11. The spectrum showed complex olefinic signals at τ 3.4 - 4.2 (5H) and a multiplet at 6.07 (1H) but the remaining protons were obscured by other signals. On warming the sample to 40° the signal at τ6.07 disappeared completely in *ca.* 15 min.
12. Irradiation at τ7.27 caused all the olefinic signals to be decoupled (τ3.82 to br. doublet, *J* = 3 Hz, 3.95 to d, *J* = 6 Hz and 4.2 to d, *J* = 6 Hz). Irradiation at τ6.0 removed the 1.5 Hz coupling from the signals at 7.66 and 8.1, while irradiation at 3.82 caused the signal at 6.0 to be sharpened considerably.
13. The hydrocarbon was not thermally stable, but the n.m.r. spectrum of a crude sample showed signals at τ3.4 - 3.8 (4H, m), 7.1 (4H, br. s).