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NET CARBON ATOM LOSS FROM 5,6-(9',10'-DIHYDRO-9',10'-ANTHRACENO)-1,2,4,6-CYCLOHEPTATETRAENE[a]

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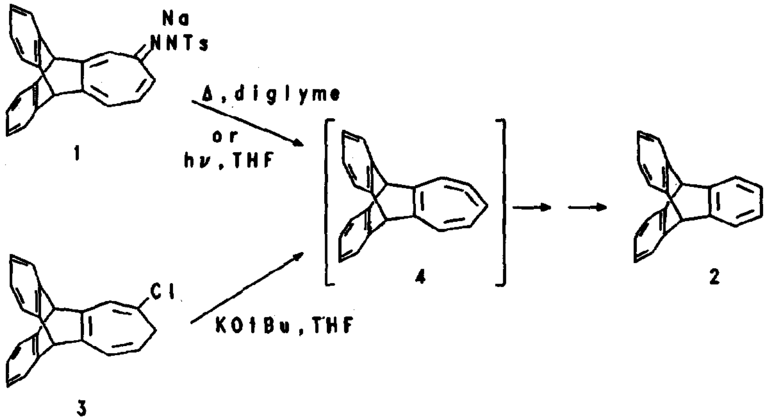
Abstract: The photolysis of the sodium salt of 4,5-(9',10'-dihydro-9',10'-anthraceno)-2,4,6-cycloheptatrien-1-one (13) in THF or the reaction of KOt-Bu with 1-chloro-4,5-(9',10'-dihydro-9',10'-anthraceno)-1,3,5-cycloheptatriene (14) in THF produced triptycene (2) in up to 30 % yield. Neither 1-triptycenyl carbene (7) nor 2-triptycenyl carbene (5) formed triptycene.

Experiments designed to constrain cycloheptatrienylidenes (and/or cycloheptatetraenes[1]) to certain conformations led to amazing results. The photolysis or thermolysis of the sodium salt of 3,4-(9',10'-dihydro-9',10'-anthraceno)-2,4,6-cycloheptatrien-1-one (1) produced triptycene (2) in up to 37% yield along with other products.[2] Likewise, the treatment of 1-chloro-3,4-(9',10'-dihydro-9',10'-anthraceno)-1,3,5-cycloheptatriene (3) with KOt-Bu also gave 2. A possible intermediate in these reactions is the anthraceno bridged cycloheptatetraene 4.[3] If this is indeed the case, there has been a *net loss of a carbon atom*. The fate of this carbon atom in THF was determined where carbon monoxide was observed along with ethylene.[2]



Since cycloheptatetraenes (or cycloheptatrienylidenes) can interconvert with aryl carbenes,[4] the possible involvement of species related to 4 has now been investigated. The aryl carbenes and cyclohepta-

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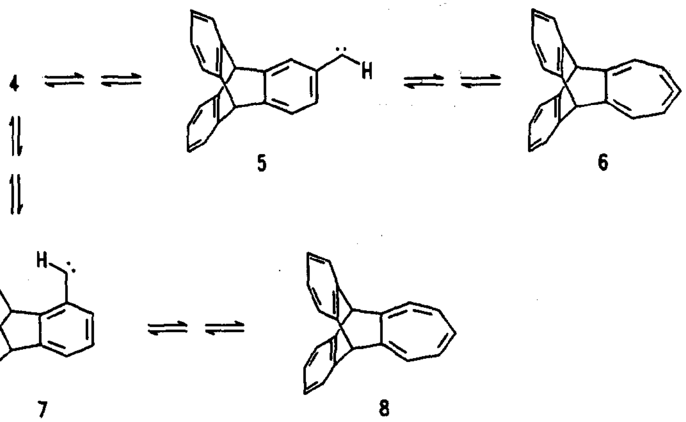
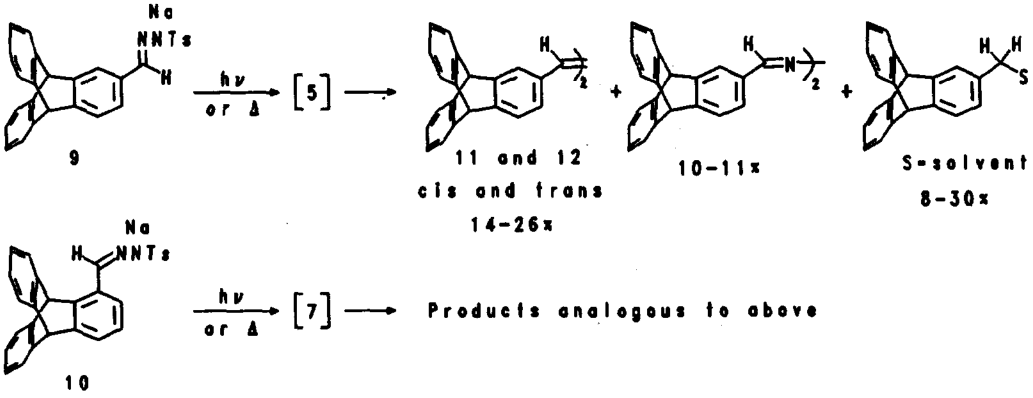
[a] Dedicated to Professor Wolfgang Kirmse on the occasion of his sixtieth birthday.

tetraenes of interest are shown below without elaborating on the precise interconversion routes. The formation of small amounts of triptycene-1-carboxaldehyde and triptycene-2-carboxaldehyde from **1**[2] indicated a rearrangement of **4** to **5** and **7** followed by trace air oxidation.



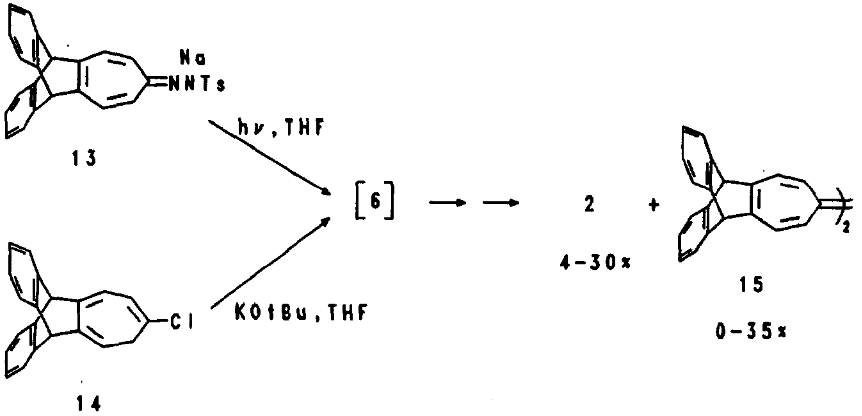
The classical precursors to **5**-**7** have been synthesized and the appropriate reactions have been carried out with the following results.[5] The salts **9** and **10** give normal aryl carbene products[6] upon photolysis in THF or thermolysis in diglyme. The yields of the alkene dimers, azines and solvent insertion products varied with the starting concentration of **9** and **10**.[7] The most important observation was that triptycene was not observed.[8]

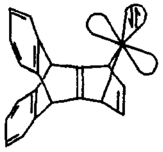


The intermediate **6** was approached via the salt **13** and chloride **14**. The results here paralleled those for **1** and **3**. The yield of triptycene depended on precursor concentration, being greatest at low concentrations where dimerization was minimized. The dimer **15** was exceedingly unstable, suffering polymerization and/or oxidation very easily.

The present results show that even though **4** and **6** both give carbon atom loss, *this does not occur via* **5** *or* **7**. Speculation on why the carbon atom loss occurs in the anthraceno bridged systems at as low as room temperature might center on the stabilization of a more loosely held carbon atom by a benzo ring.

Transformation of **4** and **6** to **16** via norcaradienylidenes **17** and **18** might be possible. Such norbornadienylidenes and norcaradienylidenes have been considered in aryl carbene rearrangements.[4e] Additional work concerning the possible stabilization by the benzo ring is in progress.





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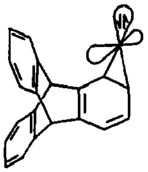

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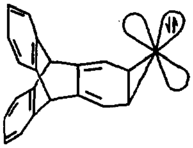

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REFERENCES AND NOTES

1. The cyclohetatrienylidene/cycloheptatetraene problem has been the subject of considerable experimental and theoretical work.

Experimental: (a) Kirmse, W.; Sluma, H.-D. J. Org. Chem. **1988**, 53, 763. (b) Kirmse, W.; Loosen, K.; Sluma, H.-D. J. Am. Chem. Soc. **1981**, 103, 5935. (c) McMahon, R. J.; Abelt, C. J., Chapman, O. L.; Johnson, J. W.; Kreil, C. L.; LeRoux, J.-P.; Mooring, A. M.; West, P. R. J. Am. Chem. Soc. **1987**, 109, 2456. (d) Jones, W. M.; Ennis, C. L. J. Am. Chem. Soc. **1969**, 91, 6391.

Theoretical: (e) Janssen, C. L.; Schaefer III, H. F. J. Am. Chem. Soc. **1987**, 109, 5030. (f) Kassaee, M. Z.; Nimlos, M. R.; Downie, K. E.; Waali, E. E. Tetrahedron, **1985**, 41, 1579. (g) Tyner, R. L.; Jones, W. M.; Ohrn, Y.; Sabin, J. R. J. Am. Chem. Soc. **1974**, 96, 3765.

2. Tivakornpannarai, S; Waali, E. E., J. Am. Chem. Soc., **1986**, 108, 6058.

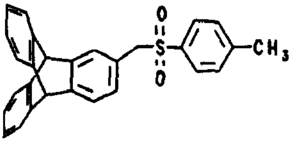
3. For the sake of simplicity, the cycloheptatetraene structure will be used for various intermediates in this paper.

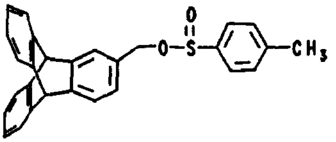
4. (a) Jones, W. M., Acc. Chem. Res. **1977**, 10, 353. (b) Hackenburger, A.; Dürr, H., Chem. Ber. **1984**, 117, 2644. (c) Chapman, O. L.; McMahon, R. J.; West, P. R.; J. Am. Chem. Soc. **1984**, 106, 7973. (d) Trahanovsky, W. S.; Scribner, M. E.; J. Am. Chem. Soc. **1984**, 106, 7976. (e) Gaspar, P. P.; Hsu, J.-P.; Chari, S; Jones, M., Jr., Tetrahedron **1985**, 41, 1479. (f) Wentrup, C.; Mayor, C.; Becker, J.; Lindner, H. J.; Tetrahedron **1985**, 41, 1601.

5. New compounds were characterized by their NMR spectra and high resolution mass spectra, except for dimer **13** whose instability precluded mass spectral analysis.

6. Nozaki, H.; Noyori, R.; Sisido, K.; Tetrahedron **1964**, 20, 1125.

7. A few other products were observed from **9** and **10** in addition to the ones indicated. Small amounts of the analogous aldehydes were found, presumably from the reaction of **5** and **7** with trace amounts of oxygen. A 17% yield of 1-methyltriptycene was isolated from the photolysis of **10** (5% yield from its thermolysis). Finally, the following sulfone (see reference 6) and sulfinate were observed from the thermolysis of **9**. These are the subjects of an ongoing study.





8. Flash vacuum pyrolysis (350°) of **9** gave small yields (<5%) of **11**, **12**, triptycene-2-carboxaldehyde, and anthracene in addition to a considerable amount of intractible tar. It is not known if the anthracene was a retro-Diels-Alder product of triptycene itself or one of the substituted triptycenes that were obviously present. No further studies were done.

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