

A FACILE PHOTOCHEMICALLY INDUCED ARYLCARBENE -
AROMATIC CARBENE REARRANGEMENT IN SOLUTION

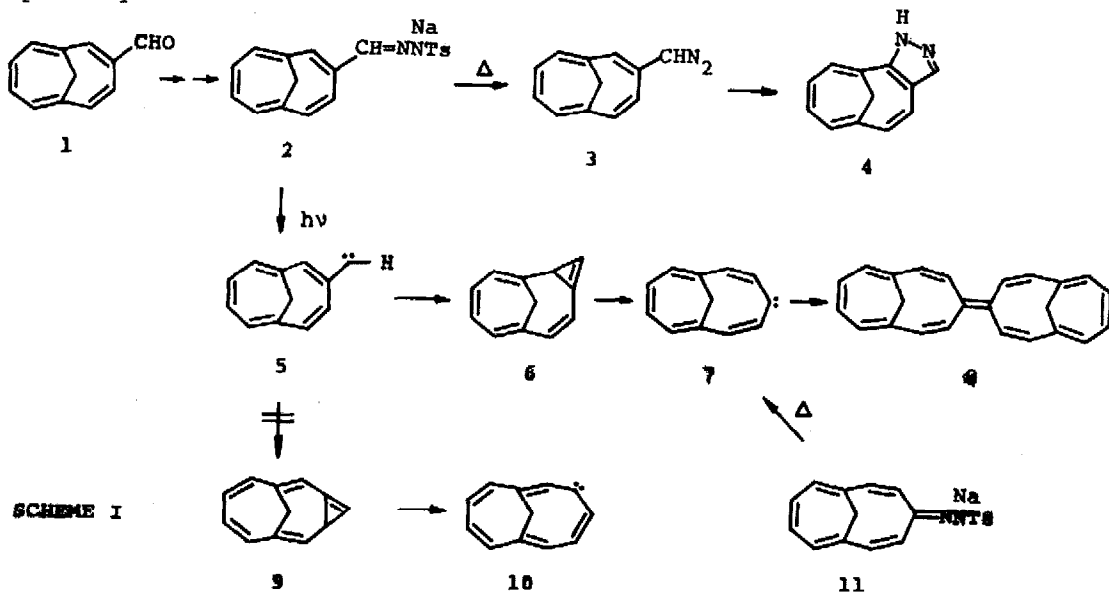
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(Received in USA 3 November 1975; received in UK for publication 15 January 1976)

The interconversion of aryl and aromatic carbenes has been explored in both the gas phase¹ and solution^{1,2}. In the latter medium, a number of aromatic carbenes have been found to convert to their aryl counterparts at modest temperatures³ but, to date, only one example of a solution phase rearrangement of an arylcarbene to its aromatic counterpart has been recorded⁴ and in this case, the rearrangement only occurred upon thermal decomposition of the corresponding tosylhydrazone salt.

At this time we report the low temperature (as low as -70°) carbene-carbene rearrangement of the methanoannulenylcarbene 5 to one of its two possible isomeric methanoannulenylidenes 7. This constitutes the first example of a low temperature rearrangement of an arylcarbene to an aromatic carbene, a reaction which is remarkable not only for its facility but for its high degree of regio-specificity.

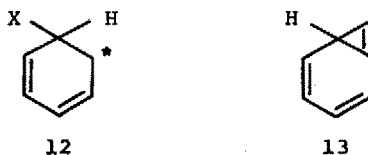


The tosylhydrazone salt 2 was synthesized from 3-formyl-1,6-methano[10]-annulene 1 which was, in turn, prepared by the ten step synthesis developed by Vogel and Sombroek⁵. In interesting contrast to the tosylhydrazone salt of 2-formyl-1,6-methano[10]annulene, which upon pyrolysis at 135° gave up to 60% of products from carbene 10⁴, pyrolysis of 2 at temperatures ranging from 150° (diglyme) to 250° (tetraglyme) gave only the novel pyrazole 4 (mp 122.5-124.5°; 83% at 150°)⁶.

On the other hand, photolysis (Pyrex, 550 W, Hanovia) of 2 at lower temperatures (-45 to -50°) gave 41% of fulvalene 8 (and 35% of 4) (17% of 8 at -70°, furan present) which is also formed from pyrolysis of 11⁷. No trace of products from 10 were detected. By analogy with other rearrangements, 8 is suggested to arise from the carbene-carbene rearrangement pictured in Scheme I.

One of the more interesting features of carbene-carbene rearrangements of methanoannulenylcarbenes is their facility. This is especially striking when compared with other aryl carbenes which tend to undergo preferential intermolecular reaction with surroundings faster than they rearrange⁸. In principle, this could result from either (or both) abnormally facile rearrangement of the annulenylcarbene or abnormally slow reaction with surroundings. Although the latter cannot be excluded as contributing to the behavior of annulenylcarbenes, at least one theoretical argument suggests that the former may be important.

All evidence to date points to fused cyclopropenes as intermediates in carbene-carbene rearrangements in solution². Regardless of the detailed mechanism of the cyclopropene formation, during the ring closure, aromaticity must be destroyed in much the same way as in electrophilic, nucleophilic or radical attack on an aromatic ring. The primary difference, of course, is that, in the intermediate 13 a double bond has replaced the active site of the classical



sigma complex 12. As a result, a comparison of localisation energies for substitutions on appropriate aromatic rings could shed light on the relative ease of cyclopropene formation. Fortunately, Dewar and his co-workers^{9,10}, have calculated relative localization energies for electrophilic, nucleophilic and radical substitution on benzene, naphthalene, phenanthrene and 1,6-methano[10]-annulene, four systems in which carbene-carbene rearrangements have been studied^{8,11,12}. These are summarized in Table I.

Table I

Relative Localization Energies

	Point of Attack	Electrophilic Attack		Nucleophilic Attack		Radical Attack	
		PPP	SPO	PPP	SPO	PPP	SPO
		Benzene ⁹	0.000	0.000	0.000	0.000	0.000
Naphthalene ⁹	C-1	-0.907	-0.905	-0.915	-0.912	-0.424	-0.452
Naphthalene ⁹	C-2	-0.498	-0.539	-0.500	-0.544	-0.161	-0.248
Phenanthrene ⁹	C-9	-1.060	-1.066	-1.067	-1.081	-0.460	-0.492
1,6-methano[10]annulene ¹⁰	C-2	-1.361	-1.530	-1.358	-1.525	-0.885	-1.186
1,6-methano[10]annulene ¹⁰	C-3	-1.289	-1.444	-1.289	-1.444	-0.869	-1.166

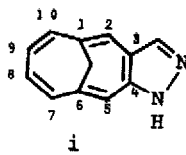
From this data, it is clear that regardless of how the ring closure of the carbene is pictured, it would be expected to occur much more rapidly in the methanoannulene system than any of the other aromatics (including the 9-position of phenanthrene). From the Table it is also interesting to note that the localization energy for breaking the aromaticity of the methanoannulene ring at C-2 is more negative (closure more favorable) than at C-3 (which is equivalent to C-4). From this it is reasonable that carbene 5 should close onto C-2 (which gives the observed carbene product) more rapidly than C-4, which should lead to 10. Neither of the dimers of 10 (one of which was checked and found to be photostable under the reaction conditions) were observed in the photolysis reactions.

Finally, it should be pointed out that formation of the fulvalene from this rearrangement takes on a special significance in that, insofar as this is analogous to other carbene-carbene rearrangements⁸, it is the first example of fulvalene formation in solution resulting from dimerisation of precursors that must be free of nitrogen.

Acknowledgment: The authors gratefully acknowledge the support of this work that was received from the National Science Foundation and the University of Florida and the Fulbright-Hays programs for fellowships to U. H. B. The authors are also indebted to Prof. W. S. Brey, Jr., for his assistance in obtaining and interpreting the ¹³C nmr spectrum of 4.

References and Notes

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- 6 Structure proof includes elemental analysis, high resolution ms (calc. 182.0843; found 182.0839), pmr: δ (CDCl_3) 7.89 (1H, s), 7.29-6.65 (6H, m), 1.5 and -0.08 (2H, AB system, $J=9.8$ Hz) N-H varies and ^{13}C mr (decoupled spectrum (CDCl_3); ppm from tms) 34.7, 104.8, 117.4, 119.0, 119.6, 122.8, 123.4, 125.4, 127.9, 128.1, 135.6, and 143.8. The undecoupled resonance at 119.6 (assigned to C-4) is particularly important in distinguishing 4 from its possible isomer i in that (with the exception of C-8 and C-9) among the annulene ring carbons, it uniquely showed no "meta" coupling.



In i, both C-2 and C-5 should show similar coupling; i.e. either both or neither should show broadening from "meta" coupling.

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