

of CHR=CH₂ from M(CHRCH₃) are preceded. The increase in coordination number required for a β-elimination step could be accommodated since **3**, **4a**, and **6** are all 16-electron species. Such reactions offer the intriguing possibility that cis coordination sites on one face of the metalloporphyrin may be involved.

(Dichloromethyl)trimethylsilane, Cl₂CHSi(CH₃)₃, proved to be a suitable precursor to a kinetically stable carbene complex since coupling reactions should be hindered by steric bulk. Treatment of **1a** with this reagent yields the (trimethylsilyl)carbene complex Ru(TTP)(CHSi(CH₃)₃) (**7**).¹¹ The reaction of **1a** with Cl₂C=C(*p*-C₆H₄Cl)₂ yields the vinylidene species Ru(TTP)-(C=C(*p*-C₆H₄Cl)₂) (**8**). The TPP congener of this complex had previously been prepared by Balch and co-workers by an alternate route.^{12,13}

A ruthenium porphyrin hydride complex **9a** results when **1a** is treated with excess water or with 2.2 equiv of benzoic acid in THF. ¹H NMR spectroscopy indicates that the two sides of the porphyrin plane are no longer equivalent. A singlet in the ¹H NMR at -57.04 ppm is indicative of a transition-metal hydride shifted to very high field by the porphyrin ring current effect.¹⁴ We formulate **9a** as the ruthenium(II) hydride anion [Ru-(TTP)H]⁻.¹⁵ On addition of further benzoic acid the bis-THF complex **5** is formed, possibly by a second protonation and rapid elimination of dihydrogen (identified by ¹H NMR) to yield the solvato complex. The β-pyrrolic resonance of **9a** is shifted upfield in the ¹H NMR spectrum so that it lies between the two sets of phenyl resonances, in contrast to the neutral Ru(II) species where it is downfield of both. A similar upfield shift of the β-pyrrolic protons occurs in the anionic monoethyl complex [Ru(TTP)-(CH₂CH₃)]⁻ (**10**) which has been observed by ¹H NMR.¹⁶ The analogous osmium hydride K[Os(TTP)H] (**9c**) is produced by the reaction of **1c** with water.¹⁷

Treatment of **1a** with 1,3-dichloropropane in THF leads cleanly to Ru(TTP)(THF)₂ (**5**) (identified by ¹H NMR) and cyclopropane (GC and ¹H NMR).^{8,18} As reductive elimination of cyclopropane from a metallacyclobutane intermediate is a likely mechanism,¹⁹ once again the possible involvement of cis coordination sites on one face of the metalloporphyrin must be considered.

The reactions of K₂[Ru(TTP)] in THF are summarized in Scheme I.

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(11) Ru(TTP)(CHSi(CH₃)₃): NMR (THF-*d*₈, 300 MHz) H_β 8.21 (s); H_α, H_γ, H_δ, H_ε, H_ζ 7.91 (m), 7.46 (m); PhCH₃ 2.62 (s); Si(CH₃)₃ -2.05 (s, 9 H); CH 19.44 (s, 1 H) ppm. MS (NDCI) *m/z* [M]⁺ 856; [M - Si(CH₃)₂]⁺, base peak 798; [M - CHSi(CH₃)₃]⁺ 770. UV-vis (THF) λ_{max} (log ε) 408 (5.24), 527 (4.15) nm.

(12) Chan, Y. W.; Renner, M. W.; Balch, A. L. *Organometallics* **1983**, *2*, 1888-1889.

(13) Ru(TTP)(C=C(*p*-C₆H₄Cl)₂) was identified by comparison with literature data for the TPP congener.¹² NMR (THF-*d*₈, 300 MHz) H_β 8.90 (s); H_α, H_γ, H_δ, H_ε, H_ζ 8.14 (d), 7.86 (d), 7.28 (d + d); PhCH₃ 2.38 (s); *p*-C₆H₄Cl 6.42 (d), 3.92 (d) ppm.

(14) (a) K[Ru(TTP)H]: NMR (THF-*d*₈, 300 MHz) H_β 7.60 (s); H_α, H_γ, H_δ, H_ε, H_ζ 7.78 (d), 7.74 (d), 7.35 (d + d); PhCH₃ 2.55 (s); RuH -57.04 (s) ppm. (b) Rh(OEP)H constitutes the only other example of a metalloporphyrin hydride complex. NMR (C₆D₆N) RhH -32.99 (d) ppm (*J*_{RhH} = 22.5 Hz). Setsune, J.-I.; Yoshida, Z.-I.; Ogoshi, H. *J. Chem. Soc., Perkin Trans. 1* **1982**, 983-987.

(15) Although only 1 equiv of benzoic acid is required by the stoichiometry, neutralization of hydroxides arising from the potassium metal reduction step may account for the extra 1.2 equiv required for the reaction.

(16) K[Ru(TTP)(CH₂CH₃)]: NMR (THF-*d*₈, 300 MHz) H_β 7.50 (s); H_α, H_γ, H_δ, H_ε, H_ζ 7.79 (d + d), 7.33 (d); PhCH₃ 2.54 (s); CH₂CH₃ -2.77 (t); CH₂CH₃ -7.22 (q) [*J*(CH₂CH₃) = 7.5 Hz] ppm.

(17) K[Os(TTP)H]: NMR (THF-*d*₈, 300 MHz) H_β 7.28 (s); H_α, H_γ, H_δ, H_ε, H_ζ 7.66 (m), 7.35 (m); PhCH₃ 2.54 (s), OsH -66.06 ppm.

(18) GC analysis indicates traces of propene, comprising less than 2% of the volatile products, are also formed.

(19) Yang, G. K.; Bergman, R. G. *J. Am. Chem. Soc.* **1983**, *105*, 6500-6501.

Mechanism of the Azulene to Naphthalene Rearrangement

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According to a recent review,¹ "no single mechanism yet proposed can adequately account" for the rearrangement of azulene (**1**) to naphthalene (**2**) (AN reaction). Here we report a theoretical study which has provided further insight into the solution of this long-standing mechanistic problem.

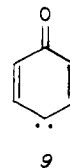
The calculations were carried out using MNDO² for closed-shell species and the spin-unrestricted³ version of MNDO (UMNDO) for biradical or open-shell ones, as implemented in the MOPAC package of computer programs.⁴ All geometries were fully optimized, transition states (TS) located, and stationary points characterized, by procedures included in MOPAC.

The intramolecular mechanisms that have been suggested are outlined in Schemes I⁵ and II.⁶ We first calculated the activation energy (*E*_a) for the mechanism outlined in Scheme II. The UMNDO *E*_a for the homolytic cleavage of **1** to **4** was 75.2 kcal/mol and the UMNDO *E*_a for the hydrogen shift from **4** to **5** was 49.8 kcal/mol. Since MNDO tends to give activation energies for hydrogen migrations that are too positive by about 20 kcal/mol,⁷ the (corrected) *E*_a for **1** to **5** is 104 kcal/mol (see Table I). This *E*_a is much larger than the activation energies we have calculated for other possible mechanisms (see below); hence this mechanism can be eliminated as a major contributor to the AN reaction. The heats of formation calculated for the various stable species and TSs are given in Table I.

In Scheme I, **3** undergoes ring cleavage to a vinylidene (**6**) which then rearranges either to **2** or to 1-phenylbuten-3-yne (**7**). Becker et al.⁵ have shown that independent generation of **6** does indeed lead to **1**, **2**, and **7** and that the pyrolysis of **7** does give **1** and **2**. We were, however, unable to locate a TS corresponding to the direct formation of **6** from **3** and the heat of formation (Δ*H*_f) calculated for **6** is very high. If **6** is an intermediate, it seems clear that it cannot be formed in this way.

Further study of the potential energy surface led to an alternative mechanism; see Scheme III.

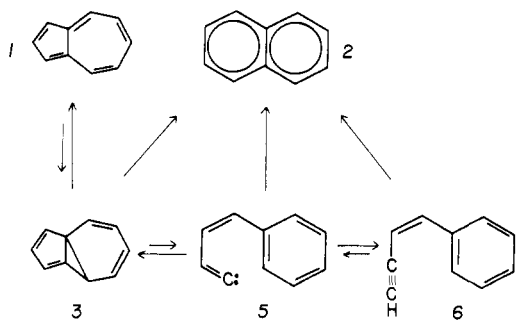
The first step is the same as in the mechanism proposed by Becker et al., but the second step involves cleavage of just one bond in **3**, the product being a carbene (**8**) or a biradical (**9**). These are distinct orbital isomers, their wave functions differing in symmetry, because **9**, unlike **8**, contains an unpaired π-electron. This kind of isomerism seems to have been first pointed out by Dewar and Narayanaswami⁸ in the case of an analogous species (**10**) derived from benzene 1,4-diazooxide, the carbene being the more stable form. Here the biradical **9** seems to be the lower in



energy, even allowing for the known tendency of UMNDO to

- (1) Scott, L. T. *Acc. Chem. Res.* **1982**, *15*, 52.
- (2) Dewar, M. J. S.; Thiel, W. *J. Am. Chem. Soc.* **1977**, *99*, 4899, 4907.
- (3) Pople, J. A.; Nesbet, R. K. *J. Chem. Phys.* **1954**, *22*, 571.
- (4) QCPE publication 455, Department of Chemistry, Indiana University, Bloomington, IN 47405.
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- (6) Scott, L. T.; Kirms, M. A. *J. Am. Chem. Soc.* **1981**, *103*, 5875.
- (7) Dewar, M. J. S.; Zobeisch, E. G.; Healy, E. F.; Stewart, J. J. P. *J. Am. Chem. Soc.* **1985**, *107*, 3902. Brown, S. B.; Dewar, M. J. S.; Ford, G. P.; Nelson, D. J.; Rzepa, H. S. *J. Am. Chem. Soc.* **1978**, *100*, 7832.
- (8) Dewar, M. J. S.; Narayanaswami, K. *J. Am. Chem. Soc.* **1964**, *86*, 2422.

Scheme I



Scheme II

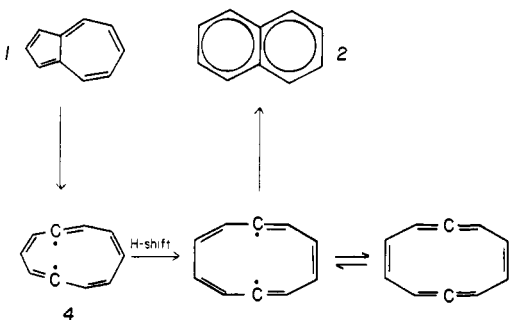


Table I. Heats of Formation (kcal/mol) Calculated by MNDO for Molecules and Transition States (TS)

compd	RHF	UHF	TS	RHF	UHF
1	77.1	56.7	1-3	135.3	
2	38.1	30.9	1-4		131.9
3	134.0	124.7	3-11		145.6
4	^a	131.5	3-8	153.0	
5	116.6	108.0	4-5		181.3
6	158.1	155.0	3-9		131.5
7			6-8	169.8	
8	140.5		6-9		163.0
9		104.3	8-2	155.6	
11		128.5	9-2		144.7

^a Does not exist on the MNDO surface.

calculate ΔH_f^\ddagger 's that are too low by 20–25 kcal/mol for biradicals.⁹ Applying this correction to the calculated ΔH_f^\ddagger of **9** gives a ΔH_f^\ddagger of ca 130 kcal/mol.

The last step involves conversion of **9** (or **8**) to **2** by 1,2 migration of hydrogen. Since MNDO is known⁷ to overestimate E_a for hydrogen migrations (see above), the calculated E_a is probably too large. Indeed, since the reaction here is very exothermic, it may well take place without activation. Our calculations also indicate that **6** should cyclize to **8** almost without activation (11.7 kcal/mol see Table I). This accounts for the results reported by Becker et al.⁵

Opening of the three-membered ring in **3** can take place in a third way, leading to a spiro diradical (**11**) whose calculated heat of formation is less positive than that of **3**. However, since the corresponding E_a was very large, it seems unlikely that **11** can play a significant role in the AN reaction.

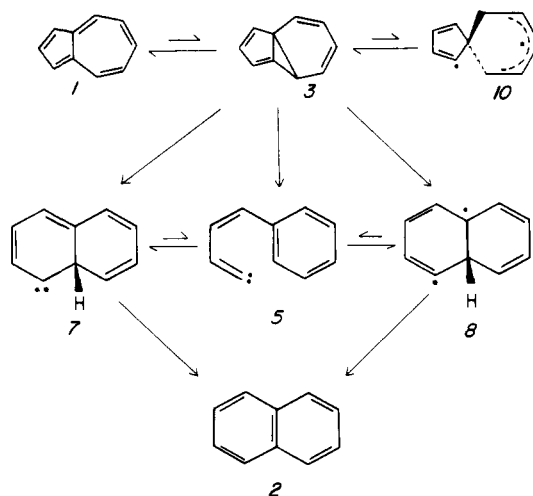
Heilbronner¹⁰ has reported, with some reservations, an E_a for the AN reaction of 48.8 ± 0.8 kcal/mol, approximately 26.5 kcal/mol less than the MNDO values (**1-8** $E_a = 75.9$ kcal/mol; **1-9**, $E_a = 74.8$ kcal/mol). MNDO, however, gives an E_a for the electrocyclic conversion of cyclobutene to butadiene that is also too large by a comparable amount (16.88 kcal/mol¹¹) so our results are consistent with Scheme I, assuming the second step is rate-determining.

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(11) Thiel, W. *J. Am. Chem. Soc.* **1981**, *103*, 1420.

Scheme III



The mechanism presented here generally agrees with the available labeling data,^{5,6,12} accounting for 80–90% of the labeled products. Indeed, other intramolecular mechanisms have also been able to account for 80–90% of the observed labeled products, but our calculations have now eliminated these as possibilities. A detailed search of the potential surface, which will be reported elsewhere, indicated that the remaining species are probably not formed from **1** by intramolecular rearrangement because the E_a for all reasonable routes were too large.

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Intramolecular Photochemical Electron Transfer. 3. Solvent Dependence of Fluorescence Quenching and Electron Transfer Rates in a Porphyrin-Amide-Quinone Molecule[†]

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Synthetic porphyrins covalently linked to quinones have received much attention as models of the primary electron transfer in photosynthesis.¹ As an extension of our own work² in this area

[†] Publication 342, Photochemistry Unit, Department of Chemistry, University of Western Ontario.

(1) For a comprehensive list of recent references, See: Joran, A. D.; Leland, B. A.; Geller, G. G.; Hopfield, J. J.; Dervan, P. B. *J. Am. Chem. Soc.* **1984**, *106*, 6090–6092.

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