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Thermal Rearrangements of $C_{10}H_8$ Species; Benzvalene Analogues and the Automerization of Naphthalene

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Abstract: The thermal rearrangements of tetracyclo$[4.4.0.0^{2,4}.0^{3,5}]$deca-5,7,9-triene (naphthvalene), tetracyclo-$[4.4.0.0^{1,3}.0^{2,4}]$deca-5,7,9-triene (isonaphthvalene), tetracyclo$[5.3.0.0^{2,4}.0^{3,5}]$deca-6,8,10-triene (azulvalene), tetracyclo-$[5.3.0.0^{1,3}.0^{2,4}]$deca-5,7,9-triene (isoazulvalene), benzofulvene, and isobenzofulvene have been studied theoretically, using the MNDO method. The results are in agreement with the available experimental evidence and also indicate that while the rearrangement of isonaphthvalene to naphthalene is "allowed", the rearrangements of naphthvalene to naphthalene and of azulvalene or isoazulvalene to azulene are "forbidden". The two latter reactions lead to unusual species derived from azulene by cis–trans isomerization about one bond in the seven-membered ring. A new mechanism for the automerization of naphthalene (AUN reaction) is suggested, based on interconversion with benzofulvene. Rearrangement to "valene" isomers appears not to play a role either in this or in the rearrangement of azulene to naphthalene (AN reaction).

In the previous paper[1] we reported a detailed MNDO[2] study of the thermal rearrangement of azulene (**1**) to naphthalene (**2**) (AN reaction) which led to a new mechanism for this rearrangement. While this did not account for *all* of the products obtained[3] by flash vacuum pyrolysis (FVP) of various labeled azulenes, it performed as well in this respect as any other mechanism yet proposed. We concluded that the unexplained products arise from another (as yet unspecified) rearrangement that is competitive with the AN reaction. It seemed possible that the azulene might have rearranged in part either to azulvalene (**3**) or to its isomer (**4**) (which may for convenience be termed isoazulvalene), resulting in scrambling of the ring carbons prior to the rearrangement of **2**. We therefore decided to study the thermolyses of **3** and **4** in order to see whether or not they may in fact play a part in the reaction. Azulvalene (**3**) has been synthesized recently,[4] and the activation parameters for its rearrangement to azulene have been reported.[4] Isoazulvalene (**4**), however, seems to be still unknown.

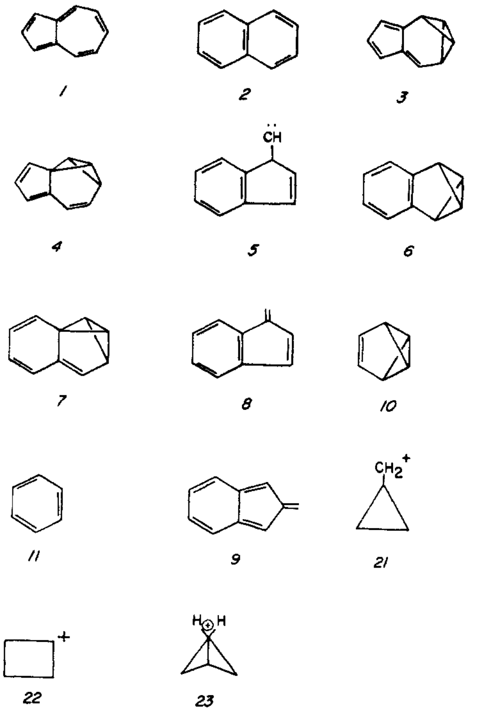
Another related and equally interesting rearrangement is that involved in the thermal scrambling of carbon atoms in naphthalene (**2**), the so-called automerization of naphthalene (AUN) reaction, which has also been extensively studied.[3] Scott et al.[5] have recently suggested that this takes place by reversible conversion of **2** to the carbene (**5**) while other possible mechanisms[3] involve analogous interconversions of **2** with naphthvalene (**6**) or isonaphthvalene (**7**). We therefore decided to extend our study of the $C_{10}H_8$ potential energy (PE) surface to include these species and also two other related molecules, benzofulvene (**8**) and isobenzofulvene (**9**), with special reference to their possible implication in the AUN reaction.

The thermolysis of **6** seemed in any case worthy of investigation because it raises points of interest in connection with the theory of pericyclic reactions. The conversion of **6** to **2** corresponds to a double electrocyclic ring opening in a bicyclobutane, a process which is "forbidden" in the case of bicyclobutane itself. The corresponding conversion of benzvalene (**10**) to benzene (**11**) is, however, "allowed[6]", a result which has been attributed[6] to participation by the C=C π electrons, thus converting an otherwise antiaromatic four-electron transition state (TS) into an aromatic six-electron one. In **6**, the C=C bond of **10** has been replaced by a benzene ring. Will this also suffice to make the rearrangement to **2** "allowed"?

Earlier unpublished MINDO/3 calculations[6b] here had indicated that the conversion of **6** to **2** is in fact "forbidden", its thermolysis being predicted to lead to benzofulvene (**8**) rather than **2**. This indeed appeared to be the case because Katz et al.,[7] who were the first to prepare **6**, had reported that its rearrangement in benzene solution led exclusively to **8**. Recently, however, Sheridan et al.[8] found that flash vacuum pyrolysis (FVP) of **6** leads to **2** as the sole product. While they were able to confirm the formation of **8** by thermolysis of **6** in benzene, they found that the conversion to **8** was retarded by potassium hydroxide and suppressed by using pyridine as the solvent. They concluded that **8** is formed from **6** by an independent acid-catalyzed reaction, not by a simple unimolecular rearrangement.

Here we report a detailed study of the thermal rearrangements of the species indicated above, i.e., **3**–**9**, with special reference to their possible involvement in the AN or AUN reaction.

Chart I



Experimental Procedure

The calculations were carried out with the standard MNDO[2] method and parameters, as implemented in the MOPAC package of computer programs.[9]

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(1) Dewar, M. J. S.; Merz, K. M., Jr. *J. Am. Chem. Soc.* **1985**, *107*, 6111.

(2) Dewar, M. J. S.; Thiel, W. *J. Am. Chem. Soc.* **1977**, *99*, 4899, 4907.

(3) Scott, L. T. *Acc. Chem. Res.* **1982**, *15*, 52.

(4) Sugihara, Y.; Sugimura, Murata, I. *J. Am. Chem. Soc.* **1984**, *106*, 7268.

(5) Scott, L. T.; Tsang, T.-H.; Levy, L. A. *Tetrahedron Lett.* **1984**, *25*, 1661.

(6) (a) Dewar, M. J. S.; Kirschner, S. *J. Am. Chem. Soc.* **1975**, *97*, 2932. (b) Kirschner, S., unpublished work.

(7) Katz, T. J.; Wang, E. J.; Acton, N. *J. Am. Chem. Soc.* **1971**, *93*, 3782.

(8) Kjell, D. P.; Sheridan, R. S. *Tetrahedron Lett* **1985**, 5731.

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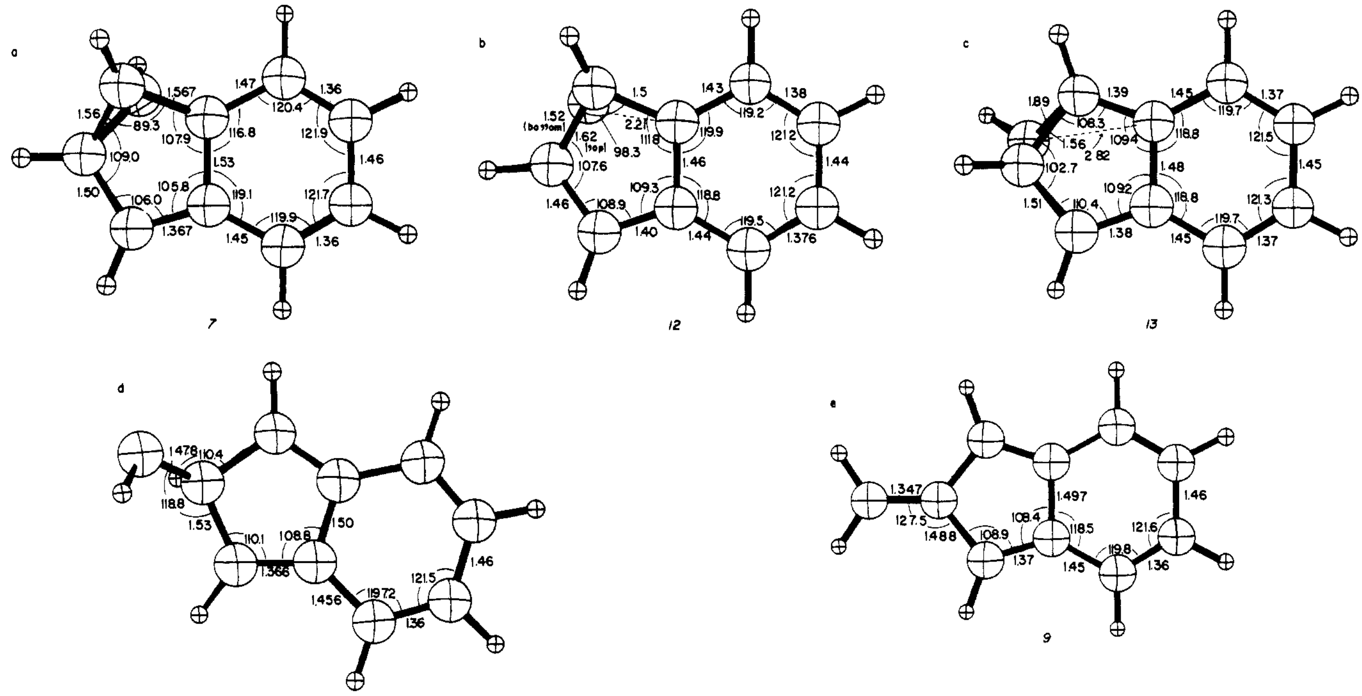

Figure 1. Geometries (bond lengths in Å) calculated for (a) **7**; (b) **12**; (c) **13**; (d) **14**; and (e) **9**.

The spin-unrestricted (UHF[10]) version (UMNDO) was used for biradical or open-shell species. In one or two cases calculations for potential biradicals were carried out with the "half-electron" version of MNDO with 3 × 3 CI[11] (MNDO-HE-CI). While this gives results that are in general somewhat superior to UMNDO, it also requires far more computing time and is therefore not well adapted to studies of reactions.

All geometries were fully optimized without making any assumptions, using the DFP procedure incorporated in MOPAC. Transition states (TS) were located by using the reaction coordinate method,[12] refined by minimizing the norm of the gradient,[13] and characterized by calculating force constants.[13]

We also used MM2 calculations[14] to obtain starting geometries for our programs, using a modified version of the MODEL[15] program. This procedure proved very effective, the MM2 geometries being good approximations to the MNDO ones. Much computer time was saved in this way.

Results and Discussion

The major part of the work reported here was concerned with the thermal rearrangements of the four "valene" $C_{10}H_8$ isomers indicated above, i.e., **3**, **4**, **6**, and **7**. This will be described first, followed by discussions of the mechanisms of the AUN and AN reactions. In connection with the former, calculations were also carried out for the rearrangements of the two fulvenes, **8** and **9**.

The study of each of the "valenes" involved formidable calculations and could well have formed the basis of an independent paper. The accounts given here are therefore necessarily very concise. However, we feel that they effectively summarize the chemically significant aspects of our work.

Scheme I

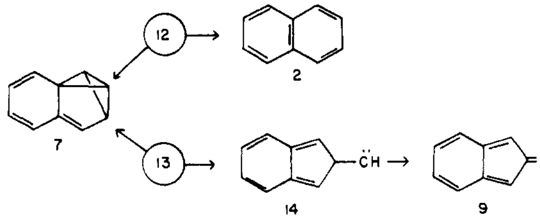

Table I shows that the heats of formation calculated for the various species studied, and Figures 1–5 show the corresponding geometries.

(A) Thermolysis of Isonaphthvalene (7). We began by studying the thermolysis of isonaphthvalene (**7**) because it seemed unlikely that it could play a role in the AUN reaction and the situation would be simplified if we could immediately exclude it. Also, for reasons indicated above, we were interested in finding whether its rearrangement to **2** is "allowed", as one would expect it to be since it contains an intact benzvalene structure, all the double bonds in it being essential double bonds.

Figure 1a shows the geometry calculated for **7** while Scheme I summarizes our mechanistic studies. Here, and subsequently, the formula numbers for transition states (TS) are shown in the arrows indicating the corresponding reactions.

As expected, **7** rearranged to **2** by an "allowed" route, the calculated activation energy (EA) being 23.5 kcal/mol. The geometry (Figure 1b) of the corresponding TS (**12**) is similar to that given[6] by MINDO/3 for the TS in the analogous rearrangment of benzvalene (**10**) to benzene (**11**). **12** is very unsymmetrical, one of the breaking bonds in it being very long and hence very weak while the other is much shorter and hence stronger. This result is not unexpected in light of the rule[16] that multibond reactions are not normally synchronous.[17]

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[9] QCPE publication 455, Department of Chemistry, Indiana University, Bloomington, IN 47405.

[10] Pople, J. A.; Nesbet, R. K. *J. Chem. Phys.* **1954**, *22*, 571.

[11] Salem, L. *Pure Appl. Chem.* **1973**, *33*, 317. For the HE method see: Dewar, M. J. S.; Hashnall, J. A.; Venier, C. G. *J. Am. Chem. Soc.* **1968**, *90*, 1953. Dewar, M. J. S.; Harshnall, J. A.; Venier, C. G. *J. Am. Chem. Soc.* **1975**, *97*, 4540. Dewar, M. J. S.; Olivella, S. J. *J. Chem. Soc., Faraday Trans. 2* **1979**, *75*, 829.

[12] Dewar, M. J. S.; Kirschner, S. *J. Am. Chem. Soc.* **1972**, *94*, 2625.

[13] McIver, J. W.; Komornicki, A. *Chem. Phys. Lett.* **1971**, *10*, 303. McIver, J. W.; Komornicki, A. *J. Am. Chem. Soc.* **1972**, *94*, 2625.

[14] See e.g.: Burkert, U.; Allinger, N. L. In *Molecular Mechanics*, ACS Monograph 177; American Chemical Society: Washington DC, 1982.

[15] The MODEL program is a graphcal input/MM2 optimization program developed by Clark Stille. The version used here was modified for use on our Tektronix terminals and our VAX 11/780 computer. Also, the modified version of MODEL will now dump out a data file suitable for running in our MOPAC program.

[16] Dewar, M. J. S. *J. Am. Chem. Soc.* **1984**, *106*, 209.

[17] The terminology used here, which seems to be becoming generally accepted, is as follows: A *concerted* reaction takes place in a single kinetic step. A *synchronous* reaction is a concerted one where all bond forming and breaking processes have taken place to similar extents in the TS. A *two-stage* reaction is concerted but not synchronous, some of the changes in bonding taking place mainly between the reactants and TS and the rest between the TS and products. A *two-step* process takes place in two distinct kinetic steps, via a stable intermediate.

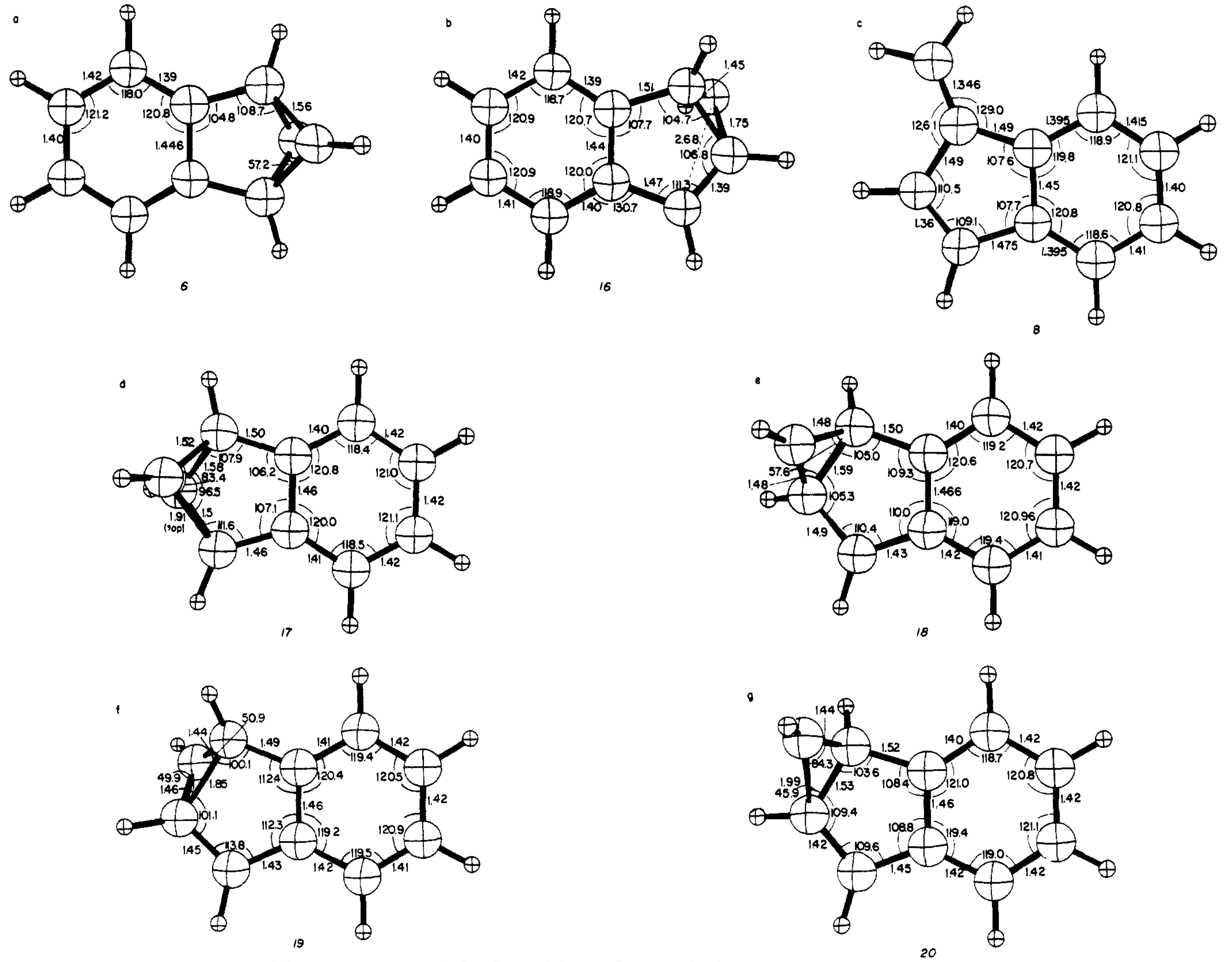


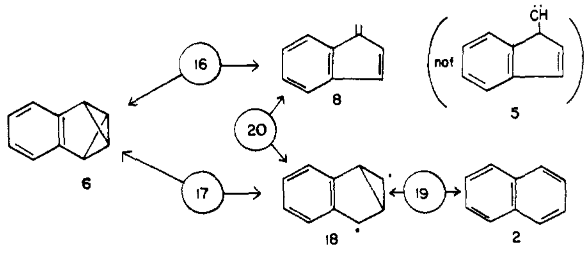
Figure 2. Geometries calculated for (a) **6**; (b) **16**; (c) **8**; (d) **17**; (e) **18**; (f) **19**; and (g) **20**.

The EA calculated for the reverse reaction, i.e., the conversion of **2** to **7**, is 111.7 kcal/mol. It is therefore very unlikely that **7** can play any role in the AUN reaction because the observed free energy of activation for the latter (86 kcal/mol[3]) is so very much less. As an additional check, we calculated the entropy of activation (see ref 18), and hence the free energy of activation, for conversion of **2** to **7**. The latter, as expected, differed little from the calcuated EA.

We also found an alternative mode of rearrangement of **7**, involving the breaking of two CC bonds to form the carbene **14**. The latter should rearrange very readily by a 1,2-hydrogen shift to form isobenzofulvene (**9**). While **9** is known,[19] it is very unstable, dimerizing at low temperatures and rearranging to **2** at higher temperatures. The calculated geometry of the TS **13** leading to **14** is shown in Figure 1c. Both the breaking bonds in **13** are very long, one of them having indeed essentially ceased to exist. The calculated EA for conversion of **7** to **14** is consequently greater, by 16 kcal/mol, than that for conversion to **2**. It therefore seems unlikely that **9** can be formed to any significant extent in the gas-phase pyrolysis of **7**. No attempt was made to locate the TS for the conversion of **14** to **9** because analogy indicates that the corresponding EA must be very small. The geometries calculated for **14** and **9** are shown in Figure 1, d and e, respectively.

Noone seems to have prepared **7**. Our calculations suggest that it should be a stable but labile species, rearranging to **2** at a measurable rate even at room temperature.

Scheme II



(B) Thermolysis of Naphthvalene (6). Having eliminated **7** as a possible intermediate in the AUN reaction, we next turned to **6**. Figure 2a shows its calculated geometry. There are two possible ways in which **6** might isomerize, one initiated by stretching the central bond and the other by stretching a peripheral bond, in the bicyclobutane moiety; see Scheme II.

Stretching the central bond led directly to **8** rather than to the expected carbene **5**, in agreement with earlier unpublished MINDO/3 calculations[6b] here. The geometry of the corresponding TS **15** is shown in Figure 2b and that of **8** in Figure 2c. The calculated EA was 51.1 kcal/mol.

We could find no local minimum corresponding to **5** on the $C_{10}H_8$ potential energy (PE) surface, even using UMNDO. This surprised us because MNDO, and UMNDO, are known to overestimate activation energies for hydrogen migration.[20] It therefore

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(18) Dewar, M. J. S.; Ford, G. P. *J. Am. Chem. Soc.* **1977**, *99*, 7822.

(19) Gross, G.; Schulz, R.; Schweig, A.; Wentrup, C. *Angew Chem., Int. Ed. Engl.* **1981**, *20*, 1021.

(20) Dewar, M. J. S.; Zoebisch, E. G.; Healy, E. F.; Stewart, J. J. P. *J. Am. Chem. Soc.* **1985**, *107*, 3902.

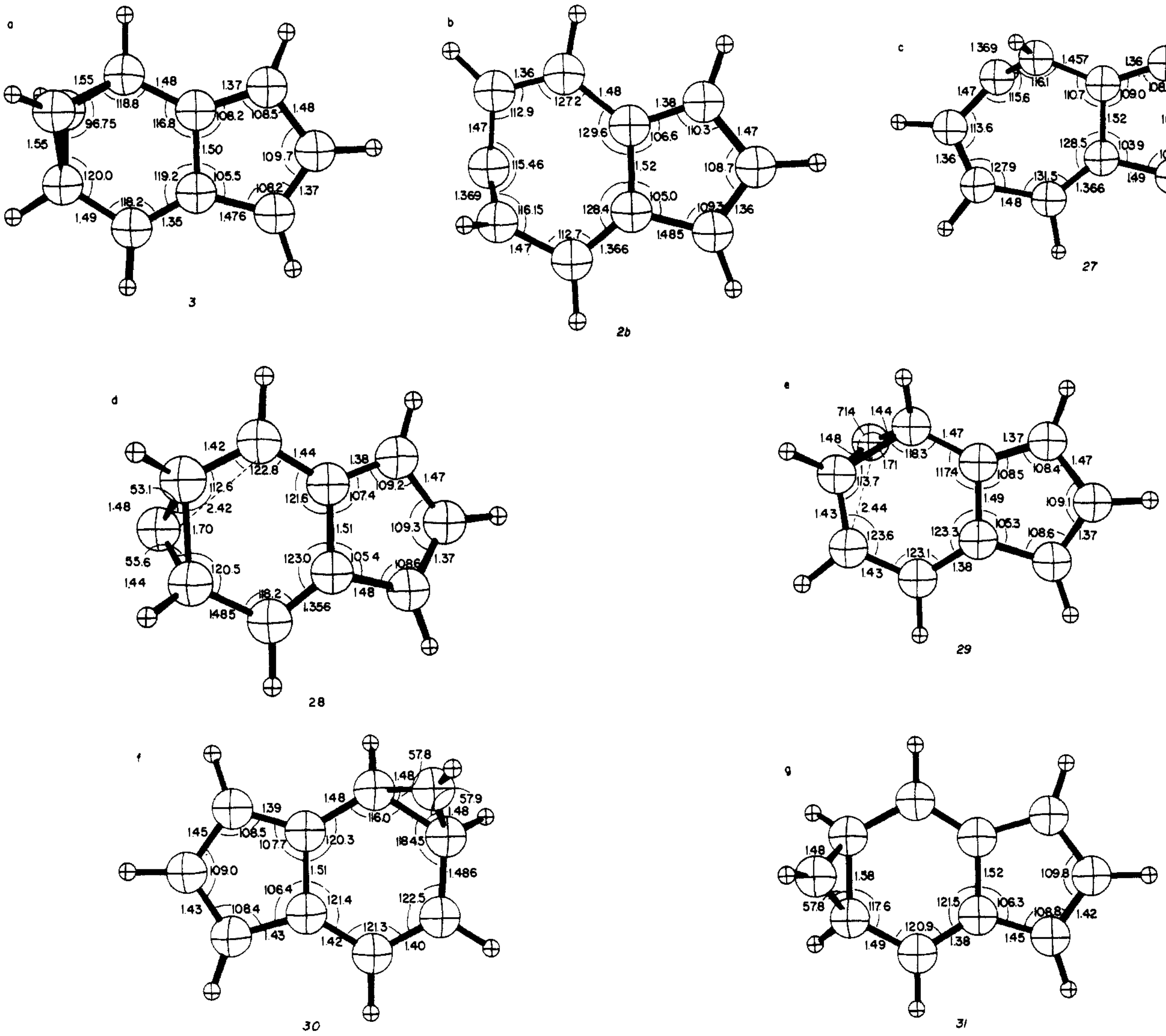

Figure 3. Geometries calculated for (a) **3**; (b) **26**; (c) **27**; (d) **28**; (e) **29**; (f) **30**; and (g) **31**.

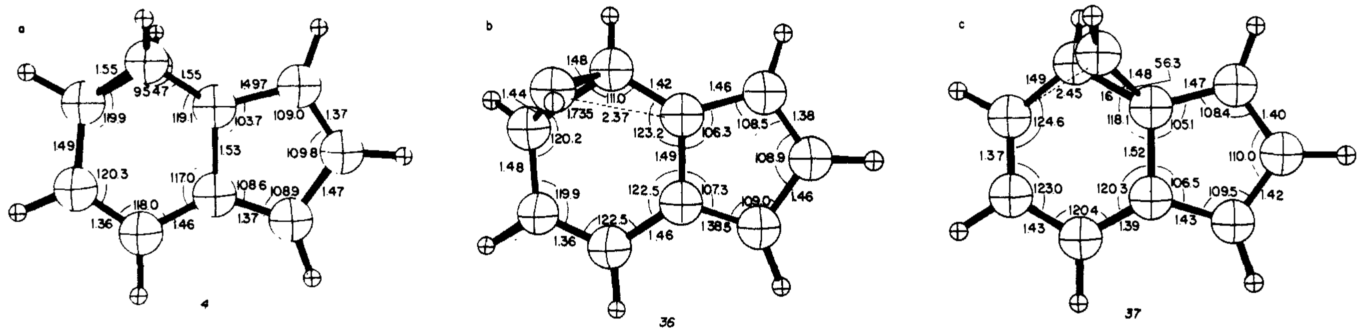

Figure 4. Geometries calculated for (a) **4**; (b) **36**; and (c) **37**.

seems very unlikely that **5** is even marginally stable. This conclusion will prove significant later in connection with the AUN reaction.

Our calculations indicate that the rearrangement of **6** to **2** is "forbidden", in agreement with the earlier MINDO/3 calculations.[6b] This is interesting, for reasons indicated in the introduction. Evidently participation by the benzene ring is not sufficient to convert the otherwise "forbidden" disrotatory/disrotatory ring opening in bicyclobutane into an "allowed" reaction.

If a reaction is "forbidden", it is likely to take place via biradical intermediates.[21,22] We therefore repeated the calculations for the rearrangement of **6**, using UMNDO to study breaking of a peripheral bond in the bicyclobutane moiety. The reaction led via the TS **17** to a biradical intermediate, benzoprefulvene (**18**), a benzo derivative of the so-called prefulvene biradical which has been postulated as an intermediate in the photolysis of benzene.[22] The geometries of **17** and **18** are shown in Figure 2, d and e, respectively.

The collapse of **18** can occur in two ways. In one, the "central" bond breaks to give **2**; in the other, an "external" bonds breaks to give either **8** or **9**. The geometry calculated for **18** (Figure 2e) shows the "central" bond in it to be very weak (bond length, 1.6

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(21) Berson, J. A. *Acc. Chem. Res.* **1972**, *5*, 406.

(22) Bryce-Smith, D. *Pure Appl. Chem.* **1968**, *16*, 47. See also: Bryce-Smith, D.; Gilbert, A. *Tetrahedron* **1976**, *32*, 1309; *ibid* **1977**, *33*, 2459.

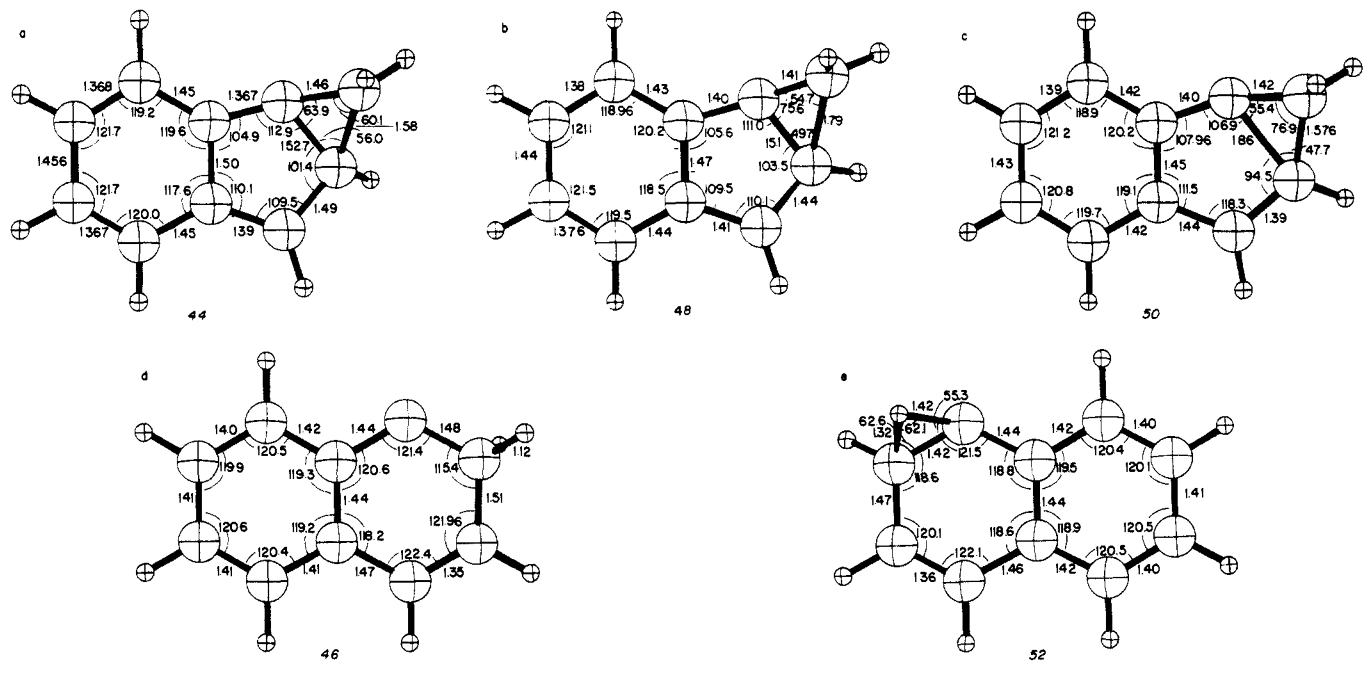
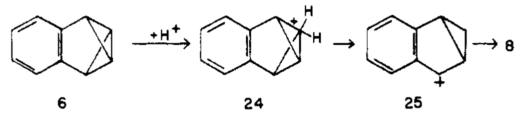


Figure 5. Geometries calculated for (a) **44**; (b) **48**; (c) **50**; (d) **46**; and (e) **52**.

Scheme III

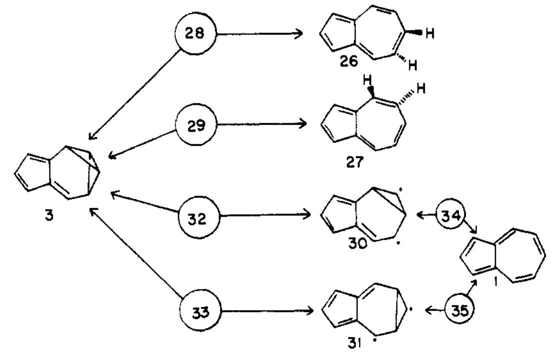


Å), implying that conversion to **2** should occur very readily. The EA for this reaction was indeed less by 26.2 kcal/mol than that for conversion of **18** to **8**. In view of this, we did not examine the conversion of **18** to **9** because the EA for this process is likely to be even higher. The geometries of the TSs for conversion of **18** to **2** (**19**) and to **8** (**20**) are shown in Figure 2, f and g, respectively.

The rate-determining step in the formation of **2** from **6** is the first, i.e., formation of **18**, the calculated heat of formation for the corresponding TS **17** being greater by 13.6 kcal/mol than that of the TS **19** for conversion of **18** to **2**; see Table I. The corresponding overall EA for conversion of **6** to **2** is 14.7 kcal/mol. While UMNDO is known[23] to overestimate the stability of biradical species by ca. 20–25 kcal/mol, the error for **17** is likely to be less than this, given that it has a structure intermediate between that of a normal closed-shell species (**6**) and a biradical (**18**). The true EA for conversion of **6** into **2** is not therefore likely to be greater than 35 kcal/mol, i.e., less by 16 kcal/mol than the EA for the formation of **8**. While MNDO often gives activation energies that are too large, independent evidence[24] suggests that the error here is unlikely to be as much as 16 kcal/mol. Our calculations therefore predict **6** to rearrange to **2** rather than to **8**, even though the latter reaction is "allowed" and the former "forbidden". As noted above, the experimental evidence indicates that this is indeed the case.[8] While the activation energy for this process is not known,[8] our estimated EA is consistent with the available evidence.

As also noted above, the thermolysis of **6** can, under certain conditions, lead to **8** rather than **2**. The evidence suggests that this alternative route is acid-catalyzed.[8] Scheme III indicates a reasonable mechanism for this reaction. Cyclopropylmethyl cation **21** is well-known to undergo a degenerate rearrangement,[25] leading to scrambling of the methylene groups, by reversible conversion to an isomeric ion which was formerly formulated as cyclobutyl cation **22**. Theoretical studies[26] have, however, indicated that the latter is in fact the bicyclobutonium ion (**23**), a nonclassical species derived by protonation of bicyclobutane at a central carbon atom. Protonation of **6** would therefore be expected to lead to a 1,2-phenylene derivative (**24**) of **23**. Rearrangement of **24** to **25** (cf. that of **23** to **21**), followed by deprotonation and ring opening, would lead to **8**.

Scheme IV



(C) Thermolysis of Azulvalene. We next examined the rearrangement of **3** because Sugihara et al.[3] have synthesized it and studied its thermolysis. Its calculated geometry is shown in Figure 3a. We were able to locate four distinct pathways for its thermal rearrangement, one leading to **26**, the second to **27**, and the third and fourth to **1** via the biradicals **30** or **31**; see Scheme IV.

Parts b and c in Figure 3 show the geometries calculated for **26** and **27**. Both are isomers of azulene (**1**), derived by cis–trans isomerization of one CC bond in the seven-membered ring. Their formation, instead of **1**, is surprizing because they must be far more energetic. Even *trans*-cycloheptene is a highly strained species, and the strain in **26** must be far greater. Indeed, it seemed to us unlikely that **26** and **27** could correspond to real minima on the $C_{10}H_8$ PE surface. There seemed a strong possibility that

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(23) Dewar, M. J. S.; Olivella, S.; Rzepa, H. S. *J. Am. Chem. Soc.* **1978**, *100*, 5650.

(24) The problem lies in the tendency of MNDO to give energies that are too positive for species in which interatomic separations are about half-way between the corresponding van der Waals and covalent bond distances. To get an estimate of the error in the present connection, we carried out three independent calculations for the rearrangement of benzvalene to benzene, using MINDO/3,[31] AM1,[17] and MNDO. The corresponding E_as were 28.2, 25.1, and 34.4 kcal/mol, respectively. We were unable to locate an experimental E_a for this reaction. However, since neither MINDO/3 nor AM1 seem to suffer from the error indicated above and since the corresponding values for E_a agree quite well with one another, it seems likely that the error in the MNDO value is <10 kcal/mol.

(25) See, for example: Saunders, M.; Vogel, P.; Hagen, E. L.; Rosenfeld, J. *Acc. Chem. Res.* **1973**, *6*, 53.

(26) Dewar, M. J. S.; Reynolds, C. H. *J. Am. Chem. Soc.* **1984**, *106*, 6388.

Table I. MNDO and UMNDO Heats of Formation (kcal/mol)

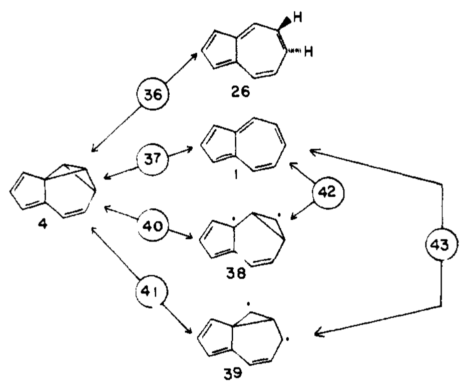
compd	MNDO	UMNDO	MINDO/3
1	77.13	56.74	
2	38.1	30.87	57.3
3	123.8	120.36	
4	124.22	117.68	
6	107.16	104.9	
7	126.55		
8	60.34	55.12	
9	75.05		
12	150.0		
13	166.51		
14	156.73		
16	158.25		
17		119.64	
18		96.8	
19		106.05	
20		132.21	
26	123.91		
27	123.69		
28	166.71		
29	164.61		
30		111.37	
31		108.4	
32		135.996	
33		134.96	
34		119.8	
35		119.26	
36	164.22		
37	164.87		
38		114.43	
39		109.82	
40		132.12	
41		132.45	
42		119.74	
43		118.75	
44	123.71		
45	131.6		116.14
46	115.06		116.55
47	118.5		116.16
48	127.56		
49	132.87		
50	139.24		
51	143.07		
52	139.01		118.27
53	140.12		
57	109.6		
58	131.02		128.65

they might in fact be less stable than the corresponding biradicals and consequently rearrange to **1** without activation. To check this possibility, we carried out 3 × 3 MNDO-HE-CI calculations for both **26** and **27**. To our surprise, both still proved to be true minima. Since MNDO-HE-CI tends, like UMNDO, to overestimate the stabilities of biradicals, it seems likely that both **26** and **27** are in fact stable species, though probably only marginally so.

The geometry of the TS **28** leading to **26** is given in Figure 3d. Note the pseudo-trans orientation of the hydrogen atom at C_5 to those at C_4 and C_6, the numbering of carbon atoms corresponding to that in **26**. One of these trans relationships is retained in the product (**26**). Similar remarks apply to **27** and the TS **29** leading to it from **3**. The EAs for the formation of **26** and **27** were respectively 42.9 and 40.8 kcal/mol. Figure 3e shows the geometry calculated for **29**. Note that the trans double bond in **26** or **27** is the one that is exo to intact three-membered ring in the corresponding TS.

The formation of these curious products is in fact easily rationalized. Each corresponds to an "allowed" conrotatory/disrotatory double electrocyclic opening of the bicyclobutane rings in **3**. The bridging group is in effect a triene so it might in principle alter the preferred stereochemistry of ring opening, as does the single bond in the corresponding reactions of **7** or **9**. The resulting TS would be isoconjugate with the Hückel C_{10} cyclic polymethine and hence aromatic. The triene moiety could, however, participate effectively in this way only by at least partial equalization of the lengths of all the CC bonds in it. A synchronous reaction involving changes in the lengths of so many bonds would be expected to be very unfavorable.[16]

Scheme V



We tried, without success, to find an "allowed" path leading directly from **3** to **1**. This failure is not of course surprising because cis and trans isomers of *any* olefin are necessarily lumomers.[27] They cannot therefore both be derived by "allowed" reactions from a common precursor.

Since the direct conversion of **3** to **1** is "forbidden" and must therefore involve biradical intermediates, we reexamined it, using UMNDO. Because of the low symmetry of **3**, there are two possible ways in which an intermediate biradical can be formed (see Scheme IV). We investigated both. The calculated EAs for the formation of the intermediate biradicals, **30** and **31**, were 15.6 and 14.6 kcal/mol, respectively. For reasons indicated above, in connection with the analogous TS **17**, these values are probably too small by ca. 15 kcal/mol. The true barrier heights are therefore probably ca. 30 kcal/mol. The geometries calculated for **30** and **31** are shown in Figure 3, f and g, respectively. The geometries of the corresponding TSs (**32** and **33**) are not given because they were similar to that of **17** (Figure 2d).

In **30** and **31**, as in **18**, the transannular bonds are very weak. Both **30** and **31** are therefore expected to collapse to **1**, just as **18** collapses to **2**. We calculated both these reactions, the corresponding EAs (see Table I) being 24.6 and 26.5 kcal/mol, respectively. The geometries of the corresponding TSs (**34** and **35**; see Scheme IV) are again not listed because they were similar to that of **19** (see Figure 2f).

Our calculations therefore indicate four possible alternative reaction paths for the "forbidden" conversion of **3** to **1**, two involving trans isomers of **1** as intermediates, with calculated EAs of 40.8 and 42.9 kcal/mol, while the other two involve the biradicals **30** or **31** as intermediates, with similar EAs, both ca. 30 kcal/mol. Our calculations therefore suggest that the reaction takes place by one or both of the two latter routes. Our corresponding estimated EA is moreover very close to the observed value, 28.6 kcal/mol,[4] incidentally supporting our estimate of the correction to the energy of **17**.

The corresponding activation energy for the reverse reaction, i.e., the conversion of **1** to **3**, is thus close to 75 kcal/mol. Since this is far greater than the EA (49 kcal/mol[3]) reported for the AN reaction, it seems unlikely that **3** can play any part in the latter.

(D) Thermolysis of Isoazulvalene (4). Calculations were next carried out for isoazulvalene (**4**) and for its rearrangement to **1**. The geometry calculated for **4** is shown in Figure 4a while Scheme V summarizes our mechanistic results. As in the case of **3**, four distinct modes of rearrangement were found.

Direct rearrangement of **4** to **1** is expected to be "forbidden" because it again involves either disrotatory/disrotatory opening of an effectively isolated bicyclobutane ring system or an unfavorable reorganization of the triene moiety in **4**. Indeed, the first TS located (**36**) corresponded to conversion of **4** into one of the

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[27] Dewar, M. J. S.; Kirschner, S.; Kollmar, H. W. *J. Am. Chem. Soc.* **1974**, *96*, 5240. Dewar, M. J. S.; Kirschner, S.; Kollmar, H. W.; Wade, L. E. *J. Am. Chem. Soc.* **1974**, *96*, 5242.

trans-azulenes (**26**) derived in an analogous manner from **3**. The geometry calculated for **36** (Figure 4b) also resembles those of **28** and **29**, showing the same pseudo-trans orientation of the relevant hydrogen atoms, and the calculated EA (40.0 kcal/mol) was close to the value (42.9 kcal/mol) calculated for the analogous conversion of **3** to **26**.

The next TS (**37**) led, however, directly to **1**. Its geometry is shown in Figure 4c. Comparison of b and c in Figure 4 clarifies the situation. Note the pseudo-trans orientation of the hydrogen atom at C_2 to that at C_3 and to the adjacent CC bond in the five-membered ring (C_1C_{10}). It is apparent that **4** is again trying to rearrange to an isomer of **1** derived by rotation of one CC bond through 180°. From analogy with the corresponding rearrangement of **3**, the rotation should take place about C_1C_2, i.e., the bond adjacent to the bridgehead in **1**. The resulting species would, however, be much more strained than **26** or **27**. Evidently its strain energy is in fact so great that it no longer corresponds to a minimum on the PE surface, undergoing conversion to **1** without activation. Since this complication arises only relatively late in the reaction, the TS resembles **28**, **29**, and **36**. The corresponding EA (40.65 kcal/mol) was also essentially identical with those for the other three related reactions.

The other two routes involved biradical intermediates, **38** and **39**, formed via the TSs **40** and **41**, respectively. As in the case of **3**, the (corrected) EAs are less than those for the nonradical ones, being ca. 25 kcal/mol. Likewise the heats of formation calculated for the TSs **41** and **42** for conversion of **38** and **39** to **1** were less than those for **40** and **41**, implying that the rate-determining step in the conversion of **4** to **1** is again the formation of one or other of these two possible intermediate biradicals. The geometries calculated for the various intermediates and TSs are not given because they presented no unusual features and were similar to the analogue derived from **3**; see Figures 3f,g and 2d,e,f,g.

The heats of formation calculated for **1** and **4**, together with the estimated EA for conversion of **4** to **1**, lead to an estimated EA for the reverse reaction of ca. 75 kcal/mol. Since this is far greater than the EA observed for the AN reaction, it seems clear that **4**, like **3**, can play no part in the latter.

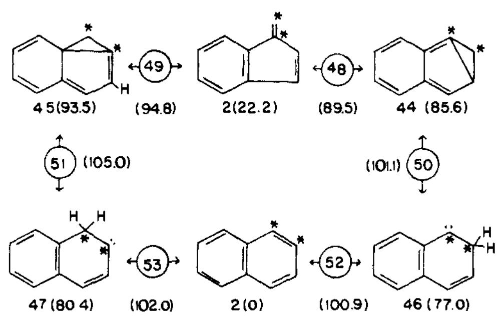
The minor products observed in labeling studies of the AN reaction (see[3]) cannot therefore be explained in terms of prior reversible conversion of **1** to **3**, leading to partial scrambling of the labels in **1** prior to rearrangement. Experimental studies have also excluded this possibility.[3]

(E) Mechanism of the AUN Reaction. Scott et al.[5] have suggested that the key intermediate in the AUN reaction is the carbene **5**, this being formed reversibly from **2**. However, as noted above, **5** is not a minimum on the MNDO $C_{10}H_8$ PE surface.

Another possibility is an analogous interconversion of **2** with naphthvalene (**6**) or isonaphthvalene (**7**). The latter reaction seems ruled out, however, by its calculated EA (112 kcal/mol) which is far greater than that observed for the AUN reaction (86 kcal/mol[3]). The uncorrected calculated EA for conversion of **2** to **6** via **17** (83 kcal/mol) seems just right. However, for reasons indicated above, the calculated EA is almost certainly too small and the error could well be as much as 15–20 kcal/mol. Furthermore, interconversion of **2** with **6** scrambles only adjacent β-carbon atoms in **2** whereas the experimental evidence indicates that a major component of the reaction leads to scrambling of adjacent α- and β-carbon atoms.[3,5] While interconversion via **7** would have this effect, it seems to be ruled out by our calculated EA.

The only other possible intermediates seem to be the two fulvenes, **8** and **9**. Thermolysis of **8** has indeed been reported[28] to lead to the formation of **2**, and Scheme VI suggests a reasonable mechanism for this reaction, a modification of that proposed by Brown et al.[28] The conversion required[8] a much higher temperature than that of **6** to **2**, as implied by our calculated EAs (79 vs. ca. 30 kcal/mol, respectively).

Scheme VI



The first step involves ring closure between the methylene group in **8** and an adjacent carbon atom, forming **44** or **45**. Analogous reactions seem to occur in the conversion of benzyl cation to tropylium[29] or of phenylcarbene to cycloheptatetraene.[30] Ring opening in **44** or **45** should lead to either of two carbenes, **46** or **47**, respectively, both of which should rearrange very readily to naphthalene (**2**). Conversion of **2** to **8** by one route, e.g., via **47** and **45**, followed by reversion via the other (**44** and **46**), would scramble C_1 and C_2 in **2**. The earlier[28] mechanism involved direct rearrangement of **8** to **46** by a 1,2-carbon migration. That in Scheme VI seems, however, more likely in view of the calculations described below and those[29,30] for the related reactions noted above.

We were able to locate minima on the $C_{10}H_8$ PE surface, corresponding to the postulated intermediates, **44**–**47**, and also the TSs **48**–**53** for the various steps indicated in Scheme VI. Their energies, in kcal/mol relative to that of **2**, are shown in parentheses next to the formula numbers in Scheme VI. Figure 5a shows the geometry calculated for **44** and Figure 5b that of the TS **48** for its formation from **8**. Figure 5d shows the geometry calculated for **46** and c and e in Figure 5 show the TSs for formation of **46** from **44** and **2**, respectively. The geometries for the species involved in the alternative route from **8** to **2** are not shown because they resemble those in the first.

While the energies calculated for several of the intermediates are a good deal greater than the observed EA for the AUN reaction, there are reasons for believing that they are all too large.

(a) As noted above, MNDO is known[20] to overestimate the EAs for 1,2-hydrogen migrations, commonly by ca. 20 kcal/mol. The EA calculated for the first step in each of the routes from **2** to **8** is therefore likely to be correspondingly too large. Indeed, it is difficult to believe that the EAs can possibly be as great as Scheme VI implies in view of the ease with which carbenes rearrange to olefins by hydrogen migration, especially since the rearrangement of **46** or **47** leads to the formation of a new aromatic ring. As an additional check, we carried out MINDO/3[31] calculations for the rearrangement of **46** to **2**. The heats of formation (kcal/mol) calculated for the relevant species were as follows: **46**, 116.6; **52**, 118.3; **2**, 57.3.

The EA calculated for **46** → **2** is thus 1.7 kcal/mol. Since MINDO/3 has given good results for a number of other reactions involving hydrogen migrations, it seems clear that the real EA for this reaction must indeed be small.

(b) The energy of **45** is also probably overestimated, because MNDO is known[2] to give heats of formation that are too positive for molecules containing quaternary carbon atoms.

(c) Since the conversion of **44** to **46**, or of **45** to **47**, involves a disrotatory electrocyclic ring opening, each of the corresponding TSs (**50** and **51**) is of Hückel type.[32] The products, **46** and **47**, are moreover isoconjugate with cations of odd alternant hydrocarbons (AH), i.e., **46** with 1-phenylallyl cation (**54**) and **47** with

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[28] Brown, R. F. C.; Gream, G. E.; Peters, D. E.; Solly, R. K. *Aust. J. Chem.* **1968**, *21*, 2223.

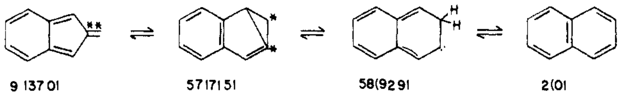
[29] Cone, C.; Dewar, M. J. S.; Landman, D. *J. Am. Chem. Soc.* **1977**, *99*, 372.

[30] Dewar, M. J. S.; Landman, D. *J. Am. Chem. Soc.* **1977**, *99*, 6179.

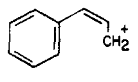
[31] Bingham, R. C.; Dewar, M. J. S.; Lo, D. H. *J. Am. Chem. Soc.* **1975**, *97*, 1285, 1292, 1302, 1307.

[32] See: (a) Dewar, M. J. S. *Angew. Chem., Int. Engl.* **1971**, *10*, 761. (b) Dewar, M. J. S.; Dougherty, R. C. *The PMO Theory of Organic Chemistry*; Plenum Publishing Corp.: New York, 1975; p 106 and Sections 5.26 and 5.27.

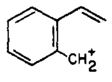
Scheme VII



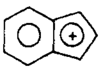
o-vinylbenzyl cation (**55**). Each of the reverse reactions, e.g., conversion of **46** to **44**, involves a bonding interaction analogous to that involved in converting **54** or **55** to indenyl cation (**56**). The latter, however, is antiaromatic. It follows that the TSs **50** and **51** are also antiaromatic. The conversion of **46** to **44**, or of **47** to **45**, is therefore "forbidden". It is of course well-established that closed shell (RHF) MO treatments give activation energies for "forbidden" reactions that are too large. There is therefore every reason to believe that the heats of formation calculated by MNDO for **50** and **51** are both too positive.



54



55



56

The mechanism indicated in Scheme VI therefore seems the most promising yet suggested for the AUN reaction. It can of course lead to scrambling only of adjacent α- and β-carbon atoms in **2**, e.g., C_1 and C_2. However, an analogous interconversion of **2** with isobenzofulvene (**9**) could lead to scrambling of adjacent β-carbon atoms; see Scheme VII.

Because of the uncertainties indicated above, we have not yet studied these reactions in detail. However, we have calculated the intermediates (**57** and **58**) and their heats of formation are listed in Table I. Scheme VII shows in parentheses the energies of the various species involved, relative to that of naphthalene. Clearly this mode of scrambling of carbon atoms in **2** is much less favorable than that indicated in Scheme VI, as would of course be expected in view of the quinonoid nature of **9** and **57**.

The nature of the subsidiary scrambling in **2** thus remains uncertain. It is still possible that the scrambling of adjacent α- and β-carbon atoms takes place by reversible conversion either to **6** or to **9**. Our calculations are not inconsistent with either. The possible errors cannot be estimated because of the lack of thermochemical data for comparison, in particular for **6** and **9**.

As noted above, the explanation of the minor products formed in the AN reaction[3] remains even more elusive. Our calculations, and experiment, have apparently eliminated the only two unexplored possibilities that seem feasible on energetic grounds. It is beginning to seem more and more likely that these species are not in fact formed by simple unimolecular thermal rearrangement of **1**.

Theoretical Implications

The AN and AUN reactions are clearly of very little practical importance. They are nevertheless of theoretical interest because one would not have expected them to take place so cleanly and because there are no immediately obvious mechanisms for them in terms of current qualitative theories. Their study by quantitative theoretical procedures therefore involves very extensive exploration of a relatively complex PE surface, made harder by the fact that many of the species involved are biradical-like and consequently require use of appropriate open-shell treatments. Indeed, the investigation reported here represents by far the most complex of its kind yet attempted by any quantum chemical procedure. It therefore serves as a useful demonstration of the present scope of the methods developed here and of their value as an adjunct to experiment in studies of reaction mechanisms. As we have repeatedly emphasized, such a combined experimental–theoretical approach provides by far the best way to study reactions, and our procedures are intended for use by those engaged in such experimental work. They represent in effect a new practical "experimental" technique for the chemist's armoury.

The system studied here represents the limit of practicality with use of computers of the VAX 11-780 class. Much of our work here was in fact carried out with the IBM 3081 computer at the University of Texas Graduate School of Business. Extensive tests indicate that our programs run ca. 12 times faster on this than on our VAX 11-780.[33] The time required to locate each of the more intransigent TSs was reduced in this way to 5–10 h. Computers of comparable performance are, however, now becoming available at a cost comparable with that of the VAX 11-780. Comparative timings of MOPAC on a wide variety of computers will be published shortly.[33]

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Registry No. 1, 275-51-4; **2**, 91-20-3; **3**, 92622-71-4; **4**, 103191-80-6; **6**, 34305-47-0; **7**, 103191-81-7; **8**, 2471-84-3; **9**, 6596-86-7.

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[33] Dewar, M. J. S.; Healy, E. F., to be published.