

**Figure 1.** Oscillograms of the RPEB signals of  $(\text{Glu})_n$  and the applied-pulse electric field at 20 °C and at 535 nm (a) and 500 nm (b-f). The sign of the RPEB signal was positive. The concentrations of  $(\text{Glu})_n$  in mM are (a) 4.9 and (b-f) ca. 1.0. The pH, the degree of neutralization, and the molar rotation at 233 nm in  $10 \text{ deg cm}^2 \text{ mol}^{-1}$  are (b) 4.17, 0.10, and  $-1.95 \times 10^4$ ; (c) 5.09, 0.25, and  $-1.89 \times 10^4$ ; (d) 5.74, 0.40, and  $-1.75 \times 10^4$ ; (e) 6.33, 0.60, and  $-6.58 \times 10^3$ ; and (f) 7.02, 0.92, and  $-2.30 \times 10^3$ . The pH was adjusted by addition of 20 mM NaOH to the salt-free  $(\text{Glu})_n$  solution which had been dialyzed at a pH of 3.86. The electric-field strength in kV/cm and the sweep time in  $\mu\text{s}/\text{division}$  are (a) 6.4 and 100, (b) 5.6 and 50, (c) 7.5 and 50, (d) 7.0 and 50, (e) 5.9 and 50, and (f) 5.9 and 50. The Kerr law was obeyed in a low-field range up to ca. 6 kV/cm in each  $(\text{Glu})_n$  solution.

the transition (pH 6.0-6.4), the RPEB signal again shows neither minimum nor maximum (e). As  $(\text{Glu})_n$  is fully ionized (pH > 7), the RPEB signal shows a peculiar shape, i.e., a maximum with application of a normal square pulse and another much larger one for a reversed pulse (f). The electric-field strength neither affected nor altered the general pattern of the RPEB signal appreciably at each pH, but the concentration of the counterion  $\text{Na}^+$  did influence the pattern.

The  $\Delta_m$  at low pHs (<3.9) became pronounced and closer to that in DMF. This indicates that the contribution to field orientation from the counterion-induced dipole is less effective, probably because the side-chain carboxylates are mostly un-ionized and the mobility of tightly bound protons is low compared with the rotational diffusion of the whole  $(\text{Glu})_n$  molecule ( $\tau_3/\tau_1 \gg 1$ ). As the ionization proceeds, the counterion-induced dipole dominates over the permanent dipole, and the mobility of the counterions (mostly  $\text{Na}^+$ ) on the helical  $(\text{Glu})_n$  is very fast ( $\tau_3/\tau_1 \ll 1$ ); hence, almost no minimum appears in the RPEB signal. The RPEB result is direct evidence which supports the importance of the counterion-induced dipole in the electric-field orientation of an ionized polymer with intrinsically dipolar structure. The fully ionized  $(\text{Glu})_n$  can be oriented by electric field (f). This result suggests that the  $(\text{Glu})_n$  is not in the shrunken, random-coil form but rather an extended stiff coil in salt-free solutions. The RPEB pattern (f) is reproducible and dependent on field strengths to some extent and reveals a close similarity with a theoretical curve in which the transverse permanent dipole moment  $\mu_1$  contributes to the orientation ( $\beta < 0$  in Figure 2 of ref 4).

In conclusion, the orientation mechanism of  $(\text{Glu})_n$  in aqueous solutions appears to involve all of the permanent dipole moment (the longitudinal and transverse components), the fast and slow counterion-induced dipole moments, and the covalent polarizability, depending on the various conformations of  $(\text{Glu})_n$ . The

RPEB method<sup>1-4</sup> is thus shown to be powerful and applicable to the study of the behavior of counterions on the polyelectrolyte surface in aqueous solutions.

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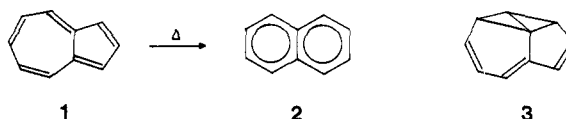
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Received January 4, 1980

### Azulene-Naphthalene Rearrangement. Involvement of 1-Phenylbuten-3-yne and 4-Phenyl-1,3-butadienyldiene<sup>1</sup>

Sir:

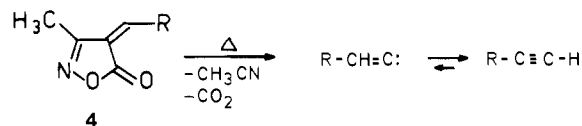
The thermal rearrangement of azulene (1) to naphthalene (2) was discovered in 1947.<sup>2</sup> Yet, the mechanism of this reaction



is still a matter for speculation. Scott and Agopian<sup>3</sup> suggested that the 1,2 carbon scrambling observed by pyrolysis of naphthalene at 1035 °C (contact time 11 s) was due to the reversible formation of azulene via the tetracyclic triene 3. Alder et al.<sup>4</sup> have demonstrated that the azulene-naphthalene rearrangement under static conditions (440 °C; 2-5.5 h) is catalyzed by radicals. Furthermore, substituted and labeled azulenes give as major products naphthalenes with retention of substituent and label position, but in addition, products of apparent substituent or label migration as well as substituent loss are obtained.<sup>5,6</sup> Two competing mechanisms based on rearrangements in azulene radical adducts have been put forward to explain the results.<sup>6</sup>

We now wish to report (i) a new mechanism which contributes to the azulene-naphthalene rearrangement, (ii) carbon scrambling in azulene itself both thermally and photochemically, and (iii) evidence that the reaction is not wholly unimolecular, even under flash vacuum pyrolysis conditions.

We have previously shown<sup>7</sup> that 4-alkylideneisoxazol-5-(4H)-ones (4) fragment thermally to vinylidenes,<sup>8</sup> the latter re-



arranging to acetylenes in high yields. Using labeled acetylenes, Brown et al.<sup>9,10</sup> demonstrated that the latter rearrangement is reversible.

(1) This work was supported in Marburg and Tübingen by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie. Presented in the Diploma Thesis of J. Becker, Marburg, January 1979, and at the EUCHEM Conference on Electron Deficient Intermediates, Geneva, Oct. 1978, and the Chemiedozententagung, Darmstadt, Germany, March 29, 1979 (Abstracts of Papers No. A 33).

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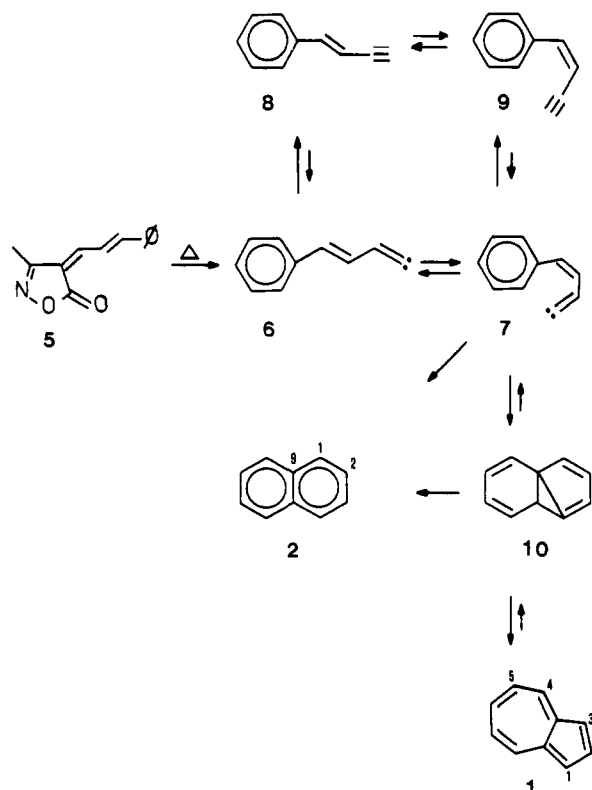
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Scheme I



Flash vacuum pyrolysis of the cinnamylideneisoxazolone **5** at 680–750 °C ( $10^{-1}$ – $10^{-3}$  Torr) afforded a mixture of (*E*)- and (*Z*)-1-phenylbuten-3-ynes (**8** and **9**) (Scheme I), naphthalene, and azulene (ca. 27:15:36:1), determined by  $^1\text{H}$  NMR and gas chromatography. Due to the very low volatility of **5**, the overall yield was poor when **5** was sublimed into a horizontal pyrolysis tube at  $10^{-4}$  Torr. Total yields of ca. 50% were obtained by allowing powdered **5** to drop into a vertical pyrolysis tube. Compounds **8** and **9** are the products expected from hydrogen shifts in the vinylidenes **6** and **7**. *Z/E* isomerism in the acetylenes (**8**  $\rightleftharpoons$  **9**) occurred already on injection into a gas chromatograph at 250 °C.

The formation of azulene (**1**) and naphthalene (**2**) is readily explained in terms of the vinylidene **7**. Carbene addition to a benzene double bond yields **10** which is the norcaradiene valence isomer of azulene (**1**). The reaction **10**  $\rightarrow$  **2** is a cyclopropane-propene rearrangement. Alternatively, **2** may be formed directly from **7** in a carbene C–H insertion, or by cyclization of **9**. The thermal interconversion of acetylenes and vinylidenes as demonstrated by Brown<sup>9</sup> requires that the same products be formed by pyrolysis of **8** and **9**. This was confirmed by isolating a mixture of **8** and **9** by gas chromatography and subjecting it to flash pyrolysis at 950–1000 °C ( $10^{-2}$  torr). Compounds **1** and **2** were identified by  $^1\text{H}$  NMR and thin-layer chromatography of the pyrolyzate. The formation of **1** and **2** parallels the pyrolytic formation of benz[*a*]azulene and phenanthrene from 2-ethynylbiphenyl.<sup>10,11</sup>

In principle, all unimolecular reactions are reversible, given a sufficiently high energy. If this is realized in the present case, the pyrolysis of azulene should yield not only naphthalene but also the acetylenes **8** and **9**. Indeed, we found that flash pyrolysis of azulene<sup>12</sup> at 1100 °C ( $10^{-2}$  Torr) resulted in **2** as the major product, together with small amounts (up to 3%) of **8** and **9** (ratio ca. 70:30), identified by gas chromatography (Apiezon M and

(11) (a) Low yields of **8**, **9**, **2**, and **1** were also obtained by pyrolysis of  $\alpha$ -phenylfurfuryl acetate.<sup>11b</sup> It seems likely that the mechanism shown in Scheme I applies to the formation of **1** and **2** in this case also. (b) W. S. Trahanovsky and D. L. Alexander, *J. Am. Chem. Soc.*, **101**, 142 (1979).

(12) We thank Professor K. Hafner (Darmstadt) for generous gifts of azulene.

Scheme II

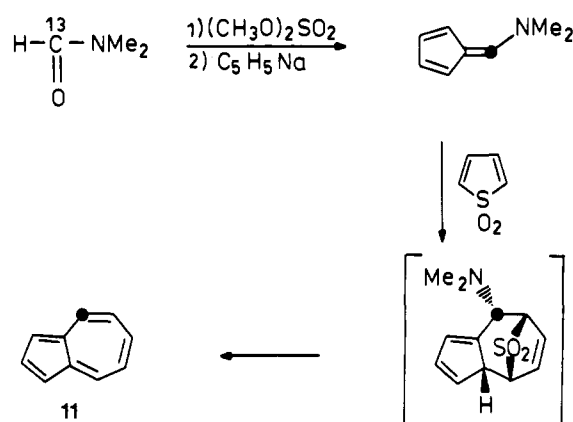


Table I. Label Distribution in Naphthalene and Azulene Formed by Pyrolysis and Photolysis of Azulene-4-<sup>13</sup>C<sup>a</sup>

conditions	naphthalene			azulene		
	C-9	C-1	C-2	C-4	C-5	C-1
pyrolysis, 1000 °C	32	57	10	92	5.4	2.7
pyrolysis, 1150 °C	32	54	14			
pyrolysis, 1180 °C	32	53	14.5			
photolysis	39	52	9	94	5	0.5–1

<sup>a</sup> Fourier transform  $^{13}\text{C}$  NMR spectra were recorded on a Varian XL-100 instrument ( $\text{CDCl}_3$  solutions). The products were purified by gas chromatography (Varian Aerograph Model A-90-P3 on Apiezon M columns at 130 °C). The products obtained at the different temperatures were measured in one continuous series, together with a spectrum of natural naphthalene. The 1000 and 1180 °C pyrolyses were repeated and measured once more in an independent series. The deviation was less than 6%.

SE 52 columns) and  $^1\text{H}$  NMR. Some unchanged azulene was recovered. Since naphthalene is by far the thermodynamically most stable end product of all these reactions, it is obvious that it would be difficult to obtain a high yield of **8** and **9**. The fact that azulene does give the phenylbutenyne (**8** and **9**), and these in turn were found to pyrolyze to naphthalene, together with the well-established acetylene–vinylidene interconversion<sup>9</sup> requires that the process shown in Scheme I is one of the mechanisms by which azulene rearranges to naphthalene.<sup>13</sup>

We do not claim that the mechanism shown in Scheme I is the only contributing pathway. In order to assess the possible extent to which this process is involved, we prepared azulene-4-<sup>13</sup>C (**11**) (92 atom % <sup>13</sup>C) from *N,N*-dimethylformamide-1-<sup>13</sup>C via 6-dimethylaminofulvene-6-<sup>13</sup>C as shown in Scheme II.<sup>14</sup> Flash

(13) (a) With group increments,<sup>13b</sup> the heat of formation of **9** is calculated as ca. 91 kcal/mol. The theoretical enthalpy difference between acetylene and vinylidene is 34–40 kcal/mol.<sup>13c</sup> This gives a  $\Delta H_f^\circ$  for the carbene **7** of 125–131 kcal/mol. Heats of formation of azulene between 69 and 74.5 kcal/mol have been reported.<sup>13d</sup> Adding to this the very preliminary<sup>6,13e</sup> activation energy for the azulene–naphthalene rearrangement (roughly 50 kcal/mol) gives a transition-state energy of roughly 119–125 kcal/mol. Thus, the formation of the vinylidene **7** is qualitatively consistent with the thermochemistry. (b) S. W. Benson, F. R. Cruickshank, D. M. Golden, G. R. Haugen, H. E. O'Neal, A. S. Rodgers, R. Shaw, and R. Walsh, *Chem. Rev.*, **69**, 279 (1969). (c) L. Radom, *Aust. J. Chem.*, **31**, 1 (1978); C. E. Dykstra and H. F. Schaefer, III, *J. Am. Chem. Soc.*, **100**, 1378 (1978). (d) E. Kovats, H. H. Günthard, and P. A. Plattner, *Helv. Chim. Acta*, **40**, 2008 (1957); J. D. Cox and G. Pilcher, "Thermochemistry of Organic and Organometallic Compounds", Academic Press, London and New York, 1970; E. Morawetz, *J. Chem. Thermodyn.*, **4**, 455 (1972); J. Kao and N. L. Allinger, *J. Am. Chem. Soc.*, **99**, 975 (1977). (e) H. J. Kallen, Dissertation, Eidgenössische Technische Hochschule Zürich, 1958; E. Heilbronner in "Non-Benzenoid Aromatic Compounds", D. Ginsburg, Ed., Wiley-Interscience, New York, 1959.

(14) The overall yield of **11** was better than 20%. The procedures were adopted from K. Hafner, K. H. Vöpel, G. Ploss, and C. König, "Organic Syntheses", Collect. Vol. V, Wiley, New York, 1973, p 431. S. E. Reiter, L. C. Dunn, and K. N. Houk, *J. Am. Chem. Soc.*, **99**, 4199 (1977); D. Copland, D. Leaver, and W. B. Menzies, *Tetrahedron Lett.*, **1977**, 639. The position of the label was confirmed by  $^{13}\text{C}$  NMR.

vacuum pyrolysis of **11** at 1000 °C ( $10^{-3}$  torr) caused very little conversion to naphthalene (ca. 6.5%). At 1180 °C ( $10^{-3}$  torr), the azulene/naphthalene product ratio was 1:5. The labeled naphthalene was separated from azulene by gas chromatography and examined by  $^{13}\text{C}$  NMR spectroscopy. The results are collected in Table I. The labeled **11** was also subjected to gas-phase photolysis<sup>15</sup> at 50 °C (ca. 0.07 torr) by using a 450-W medium-pressure Hanovia lamp. After 6 days, 2–3% of naphthalene had formed. The naphthalene and azulene were again separated and examined by  $^{13}\text{C}$  NMR (see Table I). A control experiment showed that no detectable amount of naphthalene was formed at 50 °C in the absence of light.

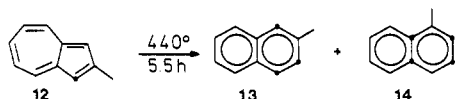
The pyrolysis and photolysis results are remarkably similar (Table I). Notably, both conditions cause partial carbon scrambling in azulene itself, and the extent of scrambling is of the same order of magnitude as the yield of naphthalene. The real problem is now the elucidation of the mechanism of carbon scrambling in azulene, and to this end we plan double-labeling experiments. From the data in Table I, it is clear, however, that the Scott-Agopian mechanism<sup>3</sup> could account at most for 52–57% of the conversion into naphthalene, since this mechanism predicts labeling of C-1 only. By repyrolysis of the labeled naphthalene isolated from the 1180 °C pyrolysis, we established that no further scrambling in naphthalene takes place under our conditions. The mechanism given in Scheme I predicts labeling of C-9 and C-1 only, and in equal amounts. Since C-1- and C-5-labeled azulenes are formed during the reactions, these, too, would rearrange to naphthalenes and thereby increase the amount of label found in positions 1 and 2 in naphthalene. Thus, the experimental data (Table I) are in qualitative agreement with Scheme I.

A further complication arose as we discovered that the azulene-naphthalene rearrangement cannot be wholly unimolecular, even under flash vacuum pyrolysis conditions. Azulene-4-*d* was prepared by adaptation of the method given in Scheme II and pyrolyzed at 1180 °C as described above. The naphthalene formed was examined by  $^1\text{H}$  NMR and low-voltage mass spectrometry. Yields of 12%  $d_0$ , 12%  $d_2$ , and 76%  $d_1$  naphthalene-*d* were obtained, with an integrated ratio  $H_\alpha/H_\beta \approx 0.9$ . The recovered azulene was  $\approx 100\%$   $d_1$ . In another experiment, 50 mg of azulene-4-*d* was pyrolyzed statically in a 50-mL Pyrex tube [previously silylated with  $(\text{CH}_3)_2\text{SiCl}_2$ ] at  $400 \pm 5$  °C for 20 h. Yields of 13%  $d_0$ , 14%  $d_2$ , and  $73 \pm 1\%$   $d_1$  naphthalene-*d* with  $H_\alpha/H_\beta \approx 0.87$  were obtained. These results show that at least 25% of the reaction is *intermolecular* under both sets of conditions. This is surprising for low-pressure gas-phase reactions and indicates that an appreciable part of the reaction takes place on the quartz surface in the flash pyrolysis experiments. The mechanisms put forward by Alder<sup>6</sup> involve rearrangements in radical adducts of azulene under static conditions. The similarity of our static and flash pyrolytic results demonstrates that Alder's mechanisms can also contribute in our reactions.<sup>16</sup>

In conclusion, several mechanistic pathways appear to contribute to the azulene-naphthalene rearrangement. One of these is the norcaradiene-vinylidene pathway shown in Scheme I. The possible weights of the various pathways cannot be assessed without a

(15) (a) The photochemical conversion of azulene to naphthalene (quantum yield  $\leq 10^{-5}$ ) has been reported.<sup>15b</sup> The first excited singlet state of azulene ( $\sim 116$  kcal/mol) is near the heat of formation of the transition state for the thermal reaction.<sup>4,13a</sup> (b) J. Olmsted, III, *Mol. Photochem.*, **1**, 331 (1969); M. Comtet and H. D. Mettee, *ibid.*, **2**, 63 (1970).

(16) (a) The vinylidene-acetylene interconversion  $7 \rightleftharpoons 9$  would lead to scrambling of the acetylenic carbon atoms and is thus in excellent agreement with the label distribution in the major product (**13**) of the static pyrolysis<sup>6</sup>



of **12**. However, this mechanism completely fails to explain the minor product (**14**). In general, the norcaradiene-vinylidene mechanism is consistent only with the *major* products obtained in the studies of Alder et al.<sup>4-6</sup> The mechanism is in agreement with the pyrolytic formation of 1,2- and 2,3-dimethylnaphthalenes from 1,2-dimethylazulene.<sup>16b</sup> (b) M. Magon and G. Schröder, *Justus Liebigs Ann. Chem.*, 1379 (1978).

detailed knowledge of the mechanism of carbon scrambling in azulene itself.

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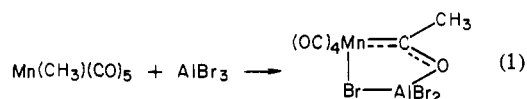
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## Surface-Induced Alkyl Migration Reactions in Metal Carbonyls

Sir:

The surface chemistry of the reaction between organometallic complexes and such oxides as alumina and silica has provided interesting parallels with homogeneous organometallic chemistry. Initial chemisorptive reaction of the complexes may involve nucleophilic displacement of carbon monoxide by the basic oxide or hydroxide ions of the surface of alumina [for example, in reaction with  $\text{Mo}(\text{CO})_6$ ], formation of Lewis acid adducts between the carbonyl oxygen atom and exposed ions of  $\text{Al}^{3+}$ ,<sup>2,3</sup> and protonolysis of alkyl or allyl groups in complexes by surface hydroxide ions.<sup>4</sup> In the case of complexes of more electropositive metals in low oxidation states, subsequent activation may liberate hydrogen from surface hydroxide ions with consequent oxidation of the metal atom. In the present research, we investigated the possibility that surface Lewis acid and Lewis base sites could promote the methyl migration reaction in a manner similar to that observed with molecular Lewis acids (eq 1).<sup>5</sup> It will be noted



that  $\text{AlBr}_3$  displays diphilic properties in this reaction, with the Al serving as a Lewis acid toward the acetyl oxygen and bromide serving as a base toward the Mn atom.

Reactions between metal carbonyls and alumina were monitored by infrared spectroscopy at 25 °C with a Nicolet 7199 FT-IR spectrometer and by analysis of the gases issuing from a micro-reactor.<sup>1</sup> The infrared spectroscopy was performed on transparent  $\gamma$ -alumina films,<sup>6</sup> onto which a pentane solution of the organometallic complex had been injected. Prior to this injection, the degree of dehydroxylation of the alumina was adjusted by heating the film for 1 h at 500 °C to yield partially dehydroxylated  $\gamma$ -alumina (PDA), the surface of which contained roughly equal proportions of  $\text{O}^{2-}$ ,  $\text{OH}^-$ , and oxygen vacancies which exposed  $\text{Al}^{3+}$ ,<sup>7</sup> or by heating at 1000 °C for 1 h to produce a nearly fully dehydroxylated mixture of  $\gamma$ - and  $\delta$ -alumina (DA).<sup>6</sup> During the dehydroxylation and the subsequent infrared spectroscopic measurements, a flow of ultrapure helium was maintained through the cell which was sandwiched between two columns of  $\text{MnO}/\text{SiO}_2$ . These served both to protect the sample from oxygen and to detect any leakage of air into the system.<sup>8</sup>

When a pentane solution of  $\text{Mn}(\text{CH}_3)(\text{CO})_5$  or  $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CH}_3)(\text{CO})_2$  is injected onto PDA or DA, an immediate color

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