

CCA-1250

YU ISSN 0011-1643

UDC 547.65

Conference Paper

Thermal Rearrangements of Aromatic Compounds. 2. Isomerization of Azulene-3a-¹³C to Naphthalene-¹³C^{1*}

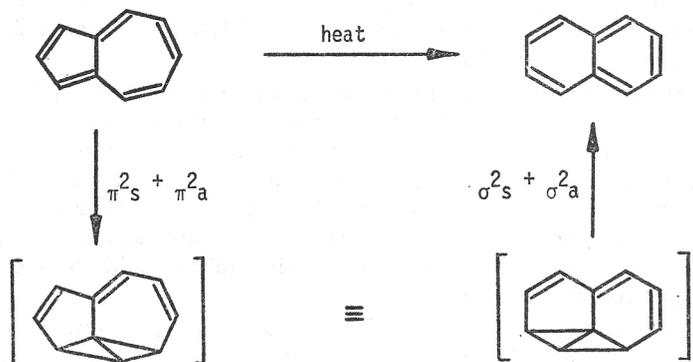
L. T. Scott, M. A. Kirms, and M. A. Minton

Department of Chemistry, University of Nevada, Reno, Nevada 89557, USA

Received September 3, 1979

A ¹³C-labelling study conclusively rules out a simple valence bond isomerization as the major pathway by which azulene rearranges thermally to naphthalene.

Thermal rearrangements, though commonplace among unsaturated aliphatic hydrocarbons,² have only rarely been observed in completely aromatic systems.³ The thermal isomerization of azulene (1) to naphthalene (2) undoubtedly qualifies as the oldest and best known example of such a skeletal reorganization and has stood as a mechanistic puzzle for many decades.^{3a-i} In particular, the question has arisen⁴ as to whether or not this rearrangement occurs via sequential, concerted, pericyclic reactions⁵ analogous to those which so often prevail in nonaromatic systems.² Scheme I depicts one plausible mechanism.⁴



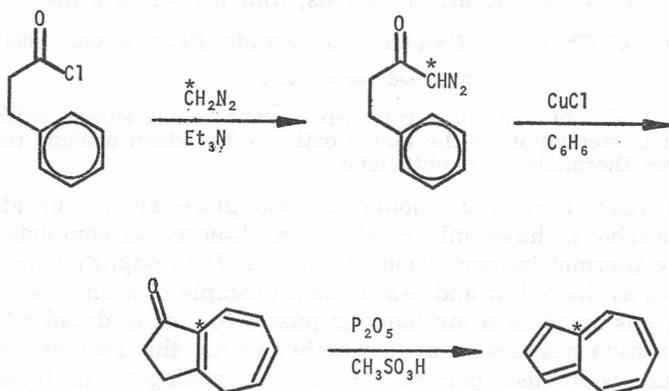
The simplicity and symmetry-allowed nature of this mechanism make it most appealing. Rudimentary thermochemical calculations⁶ place the bicyclobutane intermediate 3 above azulene ($\Delta\Delta H_f$) by 47.4 kcal/mol. This number should be compared to the activation enthalpy for the isomerization of azulene to naphthalene, which has been reported^{1c,d} (with reservation)^{1c,d} as $\Delta H^\ddagger = 48.8$ kcal/mole but may be higher.⁷ On thermochemical grounds, then, compound

* Presented in part at the International IUPAC Symposium on Aromaticity, held in Dubrovnik, Croatia, Yugoslavia, September 3—5, 1979.

3 may be considered a permissible intermediate. The stereochemical mode by which the bicyclobutane moiety in 3 would be constrained to open corresponds to the preferred mode observed in the opening of other bicyclobutanes⁸ and to the mode predicted by theory.^{5,9}

This mechanism can be tested. Since it involves only skeletal reorganizations without the breaking of C—H bonds, this mechanism requires that a ¹³C-label originating in the angular position of azulene would have to appear exclusively in the angular position of the naphthalene product; any label found in the α - or β -positions would imply the making and breaking of C—H bonds.

We have synthesized angularly-labeled azulene (azulene-3a-¹³C) by the intramolecular carbene addition route developed in our laboratory (Scheme II).¹⁰



Quantitative dilution of highly enriched precursor gave azulene with a calculated abundance of ¹³C in the angular position of 19%. This value was confirmed experimentally by comparison of the ¹³C-NMR spectra from natural abundance and enriched azulene (Figure 1.).

Thermal isomerization of the enriched azulene was conducted in a base-washed, quartz flow system. The azulene was slowly sublimed at atmospheric pressure (ca 5—10 mg/h) into a stream of nitrogen gas which carried the sample through the hot zone and into a liquid nitrogen trap. The hot zone was maintained at 820 °C with a contact time of 93 s; shorter contact times or lower temperatures resulted in incomplete disappearance of the azulene. The naphthalene was purified by sublimation (33% yield) and examined by ¹³C-NMR spectroscopy (Figure 2.).

It is immediately obvious from the ¹³C-NMR spectrum of the isolated naphthalene that the ¹³C-label does not all remain in the angular position. From a quantitative treatment of the data, we find the ¹³C-label distributed over the γ , α , and β positions of naphthalene in a ratio of 3 : 2 : 1 respectively. We, therefore, conclude that *the bicyclobutane mechanism (Scheme I) cannot be the major pathway by which azulene isomerizes to naphthalene; it may not be involved at all.*

From extensive studies on a series of methylated azulenes, Alder et al. have proposed a complicated, dual-track, free radical chain mechanism for the isomerization of azulene to naphthalene.^{1f-h} Intermediates similar to those proposed by Alder et al. have also been suggested by Prisolpski on the basis

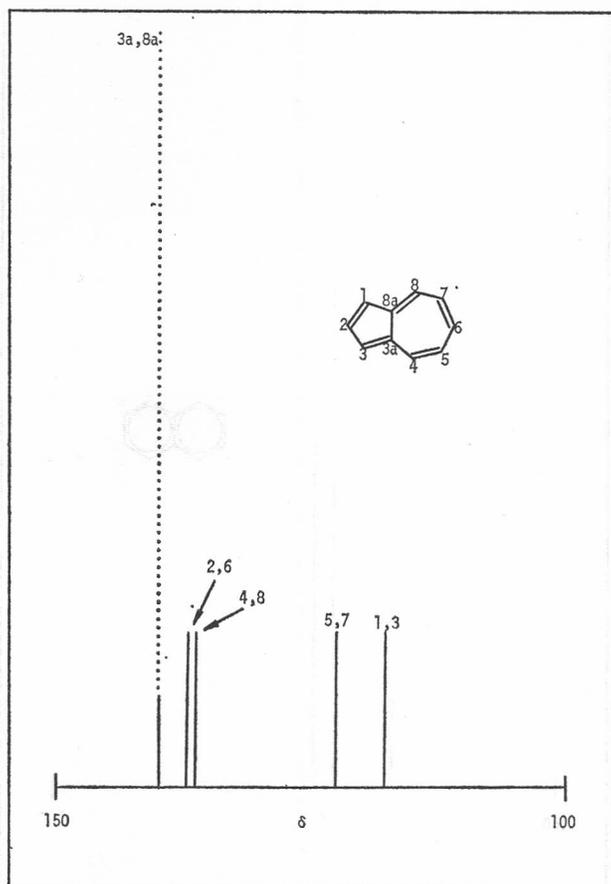


Figure 1. Proton decoupled ^{13}C -nmr spectra of natural abundance azulene (—) and of enriched azulene from the synthetic route in Scheme II (—·····).

of a more limited study.^{1e} Both investigators conclude that isomerization is probably initiated by addition of a hydrogen atom (or proton) of unknown origin, the rearrangement then taking place on the C_{10}H_9 energy surface. Scheme III illustrates an abbreviated adaptation of these proposals. This mechanism is compatible with our results only if accompanied by competing secondary processes such as those suggested by Alder et al. No single pathway has yet been proposed which can account for the results of our experiment, nor can we offer one at this time.

Acknowledgements. — We thank the University of Nevada Research Advisory Board and the donors of the Petroleum Research Fund, administered by the American Chemical Society for financial support of this work.

REFERENCES

1. For Part 1 see: L. T. Scott and G. K. Agopian, *J. Amer. Chem. Soc.* **99** (1977) 4506.
2. See for example: L. T. Scott and M. Jones, Jr., *Chem. Rev.* **72** (1972) 181.

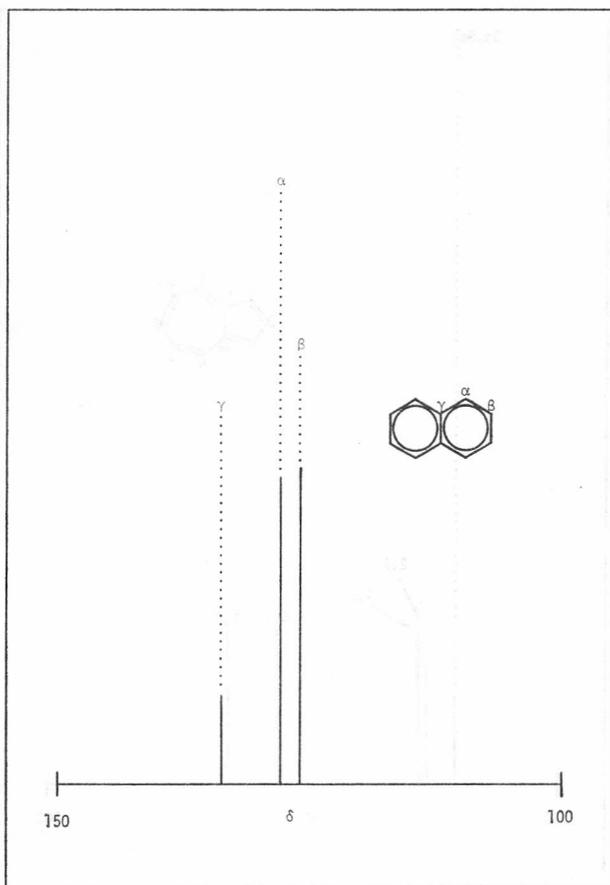
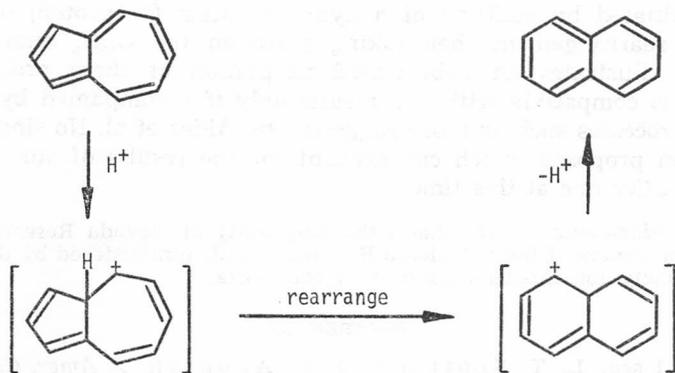


Figure 2. Proton decoupled ^{13}C -nmr spectra of natural abundance naphthalene (—) and of enriched naphthalene from thermal rearrangement of 3a- ^{13}C -azulene (—.....).



SCHEME III

3. Rearrangements of azulene:
- a E. Heilbronner, P. A. Plattner, and K. Wieland, *Experientia*, **3** (1947) 70;
 - b E. Heilbronner and K. Wieland, *Helv. Chim. Acta* **30** (1947) 947;
 - c H. J. Kallen, *PhD. Thesis*, Eidgenössischen Technischen Hochschule, Zürich, 1958;
 - d E. Heilbronner in *Nonbenzenoid Aromatic Compounds*, D. Ginsburg, Ed., Interscience, New York, N. Y., 1959, pp 263—8;
 - e M. C. Prislowski, *M. S. Thesis*, Wesleyan University, Middletown, Conn., 1973;
 - f R. W. Alder and G. Whittaker, *J. Chem. Soc. Perkin II*, (1975) 714;
 - g R. W. Alder and C. Wilshire, *J. Chem. Soc. Perkin II*, (1975) 1464;
 - h R. W. Alder, R. W. Whiteside, G. Whittaker, and C. Wilshire, *J. Amer. Chem. Soc.* **101** (1979) 629;
 - i M. A. Kirms, *M. S. Thesis*, University of Nevada, Reno, Nevada, 1979;
- Rearrangements of benzenes:
- j E. D. Clifton, W. T. Flowers, and R. N. Haszeldine, *Chem. Commun.*, (1969) 1216;
 - k J. K. van Straten, W. H. de Wolf, and F. Bickelhaupt, *Tetrahedron Lett.* (1977) 4667;
- Rearrangements of pyridazines:
- l R. D. Chambers, M. Clark, J. R. Maslakiewicz, W. K. R. Musgrave, and P. G. Urben, *J. Chem. Soc. Perkin I*, (1974) 1513;
 - m R. D. Chambers, C. R. Sargent, and M. Clark, *J. Chem. Soc. Chem. Commun.* (1979) 445;
 - n R. D. Chambers and C. R. Sargent, *J. Chem. Soc. Chem. Commun.* (1979) 446;
- Rearrangements of naphthalene: see ref. 1.
- 4. R. B. Woodward, research group meeting, Harvard University, 1970, and ref. 3.
 - 5. R. B. Woodward and R. Hoffmann, *The Conservation of Orbital Symmetry*, Verlag Chemie, Weinheim, Germany, 1970.
 - 6. S. W. Benson, *Thermochemical Kinetics*, 2nd ed., Wiley, New York, N. Y., 1976, chapt. 2.
 - 7. Unpublished observations by R. W. Alder and by W. C. Herndon (personal communication from each) and in our own laboratory¹ strongly indicate that azulene isomerizes more slowly than predicted by Kallen's activation parameters.
 - 8. G. L. Closs and P. E. Pfeffer, *J. Amer. Chem. Soc.* **90** (1968) 2452; W. G. Dauben and F. G. Willey, *Tetrahedron Lett.* (1962) 893; W. G. Dauben and W. T. Wipke, *Pure Appl. Chem.* **9** (1964) 539.
 - 9. M. J. S. Dewar and S. Kirschner, *J. Amer. Chem. Soc.* **97** (1975) 2931.
 - 10. L. T. Scott, *J. Chem. Soc. Chem. Commun.* (1973) 882; L. T. Scott and M. A. Minton, *J. Org. Chem.* **42** (1977) 3757; L. T. Scott, M. A. Minton, and M. A. Kirms, *J. Amer. Chem. Soc.* **102** (1980) 6311; M. A. Minton, *PhD. Thesis*, UCLA, 1977; see also ref. li.

SAŽETAK

Termička pregrađivanja aromatskih spojeva. 2. Izomerizacija azulena-3a-¹³C u naftalen-¹³C

L. T. Scott, M. A. Kirms i M. A. Minton

Termička izomerizacija azulena u naftalen stoji već više desetljeća kao mehanistička zagonetka. Najprivlačnijim se činio biciklobutanski mehanizam jer je jednostavan i simetrijski dozvoljen. Međutim, ¹³C-NMR spektar naftalena je pokazao da se oznaka ¹³C, uvedena u angularni položaj u azulenu, nakon izomerizacije nalazi na γ-, α- i β-položajima naftalena u omjeru 3 : 2 : 1. Stoga, ni jedan do sada predloženi jedinstveni put, uključujući i biciklobutanski mehanizam, ne može objasniti rezultate toga mehanizma.

ODJEL ZA KEMIJU
SVEUČILIŠTA NEVADE
RENO, NEVADA, SAD

Prispjelo 3. rujna. 1979.