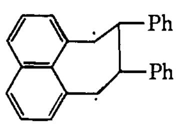
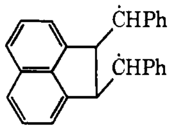
resulting from larger nonbonding interactions in II compared to I. Alternatively, either preferential cyclization to IX rather than X (which has much less favorable interaction of the radical sites with the aromatic system) or the steric inhibition to ring closure and hence slower rate of reaction of the highly stabilized biradical XI could accommodate our observations. In the case of I, thermal closure to form the unsubstituted analogs of IX and X appears to be almost comparably good. While a detailed picture of these reactions is not yet available, our results may be most simply interpreted on the basis of an unusually easy, sterically facilitated bond formation between unsaturated 1,8 substituents on a naphthalene nucleus, producing 1,4 biradicals which collapse to the observed cycloadducts.



X



XI

Acknowledgment. We are grateful to the National Science Foundation for partial support of this research. The award of a postdoctoral fellowship to J. A. K. by the National Institutes of Health (Fellowship No. GM42620) is also acknowledged with pleasure.

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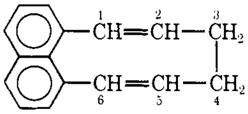
Thermal Rearrangements of 1,6-(1′,8′-Naphthalene)-1,5-hexadienes

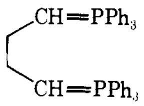
Sir:

The title compound **1** is of particular interest because of the large amount of π strain[1] expected since the peri bridge holds the olefinic frameworks roughly perpendicular to the plane of the naphthalene ring, and hence forces the olefinic π clouds against each other. Attempted preparation of **1** by reaction of the Wittig reagent derived from 1,4-dibromobutane (**2**)[2] with 1,8-napthaldehyde (**3**)[3] in refluxing ether–benzene gave a 20% yield of *cis*-divinylacenaphthene (**4**), mp 79.5–80.5°, as the major isolated hydrocarbon. For **4**, the following characteristics were observed: nmr ($CDCl_3$) δ 4.07 (m, 2 benzylic H), 5.0–6.2 (m, 6 vinyl H), 7.1–7.9 (m, 6 H); uv (hexane) λ_{max} 218 nm (log ϵ 4.77), 229 (4.88), 266 (3.65), 277 (3.85), 288 (3.93), 299 (3.76), 305 (3.56), 315 (3.16), 319 (3.16); mass spectrum *m/e* 206 (M^+, 45), 152 (100). The cis stereochemistry of **4** was proven by its formation in 94% yield by the *tert*-butyllithium cleavage of the cyclobutane derivative **5**, which was prepared from the photoadduct of maleic anhydride and acenaphthalene.[4]

When the reaction of **2** and **3** was carried out at room temperature, in addition to **4**, two thermally labile isomers of **1** were formed; they were separated on silver nitrate impregnated silica gel tlc plates. The isomer with the higher R_f factor [nmr (CCl_4) δ 1.8–2.6 (m, 4 allylic H), 5.15–5.7 (m, 2 vinyl H), 6.82 (d, J = 11, 2 Hz, vinyl H), 6.9–7.8 (m, 6 H); ir (CCl_4) 3030, 1449, 694, 675 cm^{-1}; uv (hexane) λ_{max} 234 nm (log ϵ 4.44), 305 (3.89)] was assigned as the cis,cis isomer (**1a**) on the basis of the nmr and ir spectra, and this was verified by epoxidation with *m*-chloroperbenzoic acid. The bisepoxide had a 4.0-Hz coupling of the protons attached to the epoxide ring, within the range expected for a cis epoxide.[5] The more thermally labile, lower R_f isomer was never completely separated from **4**, but is clearly the cis,trans isomer **1b** from the nmr spectrum of the vinyl hydrogens next to the ring, which appear as two doublets at δ 6.58 (J = 16 Hz, trans) and 6.67 (J = 11.5 Hz, cis). The ratio of **1a** to **1b** was about 2:1.



1a, cis,cis
b, cis,trans



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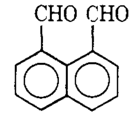

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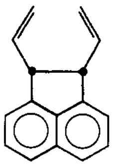

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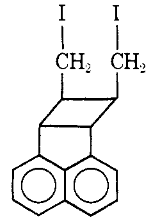
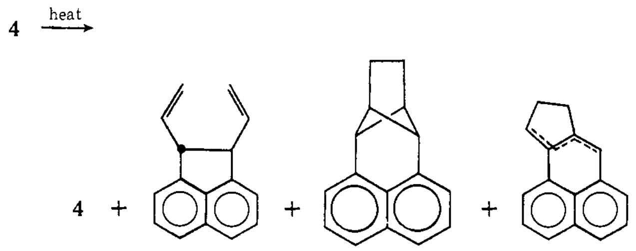


5

Acceleration of Cope rearrangements by forcing the olefinic π systems into each other is well documented by the work of Wharton and coworkers[6] on *trans,trans*-cyclodeca-1,5-dienes. The parent compound rearranges to *trans*-divinylcyclohexane, which has a 6.7 kcal/mol lower heat of formation, with a half-life of 144 min at 40°.[6b]

Evidence for the reverse Cope rearrangement, *i.e.*, for the process **4** → **1**, was obtained from the high-temperature pyrolysis of **4**. Upon heating, **4** is converted to a mixture of starting material, the trans isomer **6**, a 2 + 2 cycloadduct **7**, and a hydrogen migration product; the relative amounts of these products are shown in Table I.



6 **7** **8**

The major product **7**, mp 136–137°, clearly has the crisscross structure given from its spectral data [nmr (CCl_4) δ 1.97 (s, 4 H), 2.67 (s, 2 H), 2.86 (s, 2 H), 6.8–7.6 (m, 6 H); uv (hexane) λ_{max} 231 nm (log ϵ 4.53),

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[3] J. K. Stille and R. T. Foster, *J. Org. Chem.*, **28**, 2703 (1963).

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[5] F. A. Bovey, "Nuclear Magnetic Resonance Spectroscopy," Academic Press, New York, N. Y., 1969, p 361.

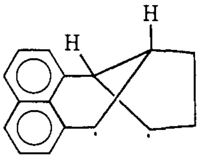
[6] (a) P. S. Wharton and R. S. Kretchmer, *J. Org. Chem.*, **33**, 4258 (1968); (b) D. J. Johnson, Ph.D. Thesis, University of Wisconsin, 1968.

Table I. Pyrolysis of *cis*-Divinylacenaphthene

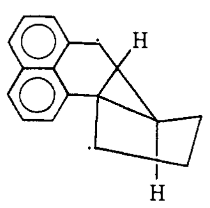
Starting material	Temp, °C	Residence time[a]	Relative amounts, %[b] 4	6	7	8	Material balance, %[c]
4	472	2.5	32	11	51	6	81
	439	2.5	44	2	54	0	
	418	2.5	71	1	28	0	88
	408	24	53	2	45	0	97
6	475	2.1	1	88	7	4	
7	472	2.5	30	5	55	10	96
	416	2.4	7	<0.5	93	0	95
	407	22	9	<0.5	90	1	102

[a] In arbitrary units, based on flow rate of nitrogen through the column. [b] Calculated from vpc peak areas (0.25 in., 10% FFAP column); the numbers appear to be reproducible to about 1%. [c] Using weight of starting material and vpc peak areas relative to that of acenaphthylene weighed into the collection trap.

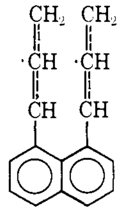
237 (4.55), 272 (3.69), 281 (3.88), 292 (3.97), 302 (3.82), 307 (3.54), 317 (3.07), 321 (3.01); mass spectrum *m/e* 206 (M^+, 85%), 165 (100)], which should be compared to those of the compound lacking the ethylene bridge, the major thermal[1] or photoproduct[7] from 1,8-divinylnaphthalene. We suggest that **7** most reasonably arises from 1,5 bonding in the mixture of **1** isomers formed from **4** by Cope rearrangement. Only relatively facile rotations are required to give diradical *cis*- and *trans*-**9** from **1** isomers, and 1,4-diradical cleavages would be expected to isomerize the **1** isomers readily. Only *cis*-**9** is geometrically capable of closure to **7**. Table I shows that **7**, which is a bicyclo[2.1.1]hexane derivative, is thermally stabler than **4**, which indicates that there must be a large π strain in **1**. Condensation of the pyrolysate from **4** directly on a liquid nitrogen cold finger did not give nmr detectable quantities of **1** isomers, indicating that they are considerably less thermodynamically stable than **4**.



cis-**9**



trans-**9**



10

Product **8** was assigned as a hydrogen shift product derived from **9** because it clearly has a *peri*-naphthalene-type structure from its mass spectrum (*m/e* 206 (M^+, 100%), 205 ($M^+ - H$, 55), 165 (69)), and is formed in highest yield from the pyrolysis of **7**. Since it is not formed in detectable amounts from **4** at lower temperatures, this product has not been extensively investigated. *trans*-Divinylacenaphthene (**6**) was always a minor product, and it is not clear whether it is formed from "leakage" to diradical **10**, or whether it arises from Cope rearrangements of unstable **1** conformers. No **6** was detected by vpc in the Wittig products. The thermal stability of **6** is clearly greater than that of **4** or **7** on the basis of data given in Table I.

Some of the products reported by Mitchell and Sondheimer[8] from the reaction of **3** and the Wittig reagent from 1,8-bis(bromomethyl)naphthalene appear to be derivable by reactions similar to those reported here.

Further studies of the reported and similar reactions are in progress, to gain a clearer understanding of the thermodynamics and reaction pathways involved.

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Thermal Rearrangement of 1,8-Divinylnaphthalene

Sir:

Although it is a common photochemical reaction, the thermal cycloaddition of olefins to give cyclobutanes is quite rare in hydrocarbon systems. Low yields of cyclobutane derivatives have been observed from thermal reactions of styrene, butadiene, and a few other conjugated olefins,[1] and *cis,trans*-1,5- and 1,3-cyclooctadienes dimerize at the trans olefin groups in good yield.[2]

The only intramolecular cases of such a reaction we have been able to find were reported by Wittig and coworkers,[3a] who found that heating one isomer of 1,2,-3,4,7,8,9,10-tetrabenzocyclododecahexaene to 180° gave a bis(biphenylene)cyclobutane, which cleaved to phenanthrene at 240°, and by Mitchell and Sondheimer,[3b] who report a similar example in an 11-membered ring case. Stiles and Burckhardt[4] studied the thermal isomerization of 3,4-diphenyl-1,2,5,6-dibenzocyclooctatetraene to the 3,7-diphenyl isomer, where a cyclobutane intermediate is definitely implicated, but the cyclobutane was not detected, even in low-temperature photolyses.

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[4] M. Stiles and U. Burckhardt, *J. Amer. Chem. Soc.*, **86**, 3396 (1964).