pounds have an enhanced $n-\pi^*$ transition at 4.02 eV.[1] The lowest excited singlet state is composed primarily of $n-\pi^*$ $(n + \pi_{CC} \rightarrow \pi^*_{CO} - \pi^*_{CC})$ (54%) and alkene-carbonyl charge transfer $(\pi_{CC} - n \rightarrow \pi^*_{CO} - \pi^*_{CC})$ (32%) configurations, in agreement with the traditional explanation of the enhancement of absorption of $n-\pi^*$ transitions in β,γ-unsaturated ketones.[1]

The lowest triplet state calculated by this method is not an $n-\pi^*$ state, but consists instead mainly of a $\pi-\pi^*$ configuration $(\pi_{CC} - n \rightarrow \pi^*_{CC} + \pi^*_{CO})$ (76%). This state is predicted to lie 2.17 eV above the ground state. Although the calculated excited state energies are too low, the relative energetic ordering of states seems secure. For example, $^1n-\pi^*$ and $^3n-\pi^*$ states of simple ketones lie about 3.64 and 3.38 eV above the ground state, respectively, while $^1\pi-\pi^*$ and $^3\pi-\pi^*$ states of cyclic alkenes lie about 6 and 3.2 eV above the ground state, respectively.[10] Furthermore, phosphorescence from *trans*-5-hepten-2-one occurs from an alkene $\pi-\pi^*$ triplet indicating that a disubstituted alkene triplet is lower in energy than a carbonyl $^3n-\pi^*$ state.[11]

These calculations provide a reasonable qualitative rationalization for the differing behavior of β,γ-unsaturated ketone singlets and triplets. By noting bond order differences between the ground state and an excited state, probable bonding changes in the excited state can be predicted.[12] Thus, the first excited singlet state $(n-\pi^*)$ involves removal of an electron from a strongly α (C-2–C-3) bonding orbital and occupation of an orbital which has no α bonding and is weakly C-2–C-5 bonding, but C-2–C-4 antibonding. Clearly, α cleavage and/or C-2–C-5 bonding, leading ultimately to a 1,3-shift product, will be favored from the excited singlet state. The $n-\pi^*$ triplet state is similar in configurational composition to the $n-\pi^*$ singlet state and, due to neglect of differential overlap in this calculation, lies at 3.27 eV. Reactions from these two states should be similar.

By contrast, the lowest excited triplet state $(\pi-\pi^*)$ involves little weakening of the α bond since mainly π_{CC}–n is vacated, and an electron fills an orbital which is C-2–C-4 bonding, but C-2–C-5 antibonding. Initial bonding changes in the triplet state would lead to diradical **3** as an intermediate or as one species on the concerted reaction surface. Another bonding change which is present in the triplet state is strong weakening of the π_{CC} bond. This bond order charge is much smaller in the excited singlet state. Thus, in addition to undergoing oxa-di-π-methane rearrangement, the triplet state might be expected to undergo cis,trans isomerization and, in cyclic cases, reactions characteristic of perpendicular or highly strained *trans*-cycloalkenes.

All of the experimental evidence obtained for a wide variety of β,γ-unsaturated ketones is compatible with this model. Thus, β,γ-unsaturated ketone singlets generally undergo [1,3] sigmatropic shifts, but α cleavages have been detected in a few cases.[3a,13,14] Closely related α-phenyl ketones undergo α cleavage from a $^3n-\pi^*$ state,[15] but these molecules should have a lowest $n-\pi^*$ triplet since the triplet energy of benzene is about 3.65 eV.

β,γ-Unsaturated ketone triplets generally undergo the oxa-di-π-methane rearrangement, and, in some cases, other reactions characteristic of alkene $\pi-\pi^*$ triplets such as intra-[14,16] or intermolecular[17] [2 + 2] cycloaddition, cis,trans isomerization,[18] and photoreduction.[17] In addition, phosphorescence from a rather long-lived $(\pi-\pi^*)$ triplet has been observed with one β,γ-unsaturated ketone.[3j,11]

Further support for the validity of this rationalization may be found in our use of the Jaffé CNDO method to explain differences in 3,5-cycloheptadienone photochemistry resulting from subtle structural changes.[19] These kinds of arguments, which appear not to have been applied to nonplanar π systems previously,[20] may prove of more general applicability in considerations of photochemical reactivity.

Acknowledgment. Financial support by the Research Corporation and by the donors of the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged.

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[12] R. Daudel, *Advan. Quantum Chem.*, **3**, 161 (1967); **5**, 1 (1970); J. P. Malrieu, *Photochem. Photobiol.*, **5**, 291, 301 (1966); G. Feler, *Theor. Chim. Acta*, **10**, 33 (1968); H. E. Zimmerman, *Photochem. Photobiol.*, 7, 519 (1968); H. E. Zimmerman and A. A. Baum, *J. Amer. Chem. Soc.*, **93**, 3646 (1971), and references therein.

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[20] F. B. Tinland and C. Decoret, *Tetrahedron Lett.*, 3019 (1971).

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Received May 5, 1972

Intramolecular Thermal Cycloadditions of 1,8-Divinylnaphthalene and 1,8-Distyrylnaphthalene

Sir:

As an extension of our studies of the intramolecular photochemical cycloaddition reactions of 1,8-divinylnaphthalene (Ia) and *trans*,*trans*-1,8-distyrylnaphthalene (II),[1,2] we have examined the corresponding thermal ring closures of these compounds. Thermal [2 + 2] cycloadditions of simple olefins are not common,[3] and

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[1] J. Meinwald and J. W. Young, *J. Amer. Chem. Soc.*, **93**, 725 (1971).

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[3] J. D. Roberts and C. M. Sharts, *Org. React.*, **12**, 1 (1962); see also ref 4.

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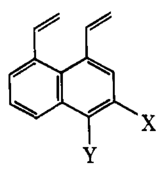
the constraints imposed upon such reactions by orbital symmetry factors[5] make them of more than usual mechanistic interest.

Heating Ia in solution above 150° gave a nearly quantitative yield of two isomeric products, *peri*-naphthobicyclo[3.1.1]heptene (IIIa) and *peri*-naphthobicyclo[3.2.0]heptene (IVa) in a ratio of about 3:1. The same two products are obtained from the irradiation of Ia in cyclohexane, but in a ratio of about 10:1.[1] As in the photochemical process, the product ratio from the thermal reaction was unaffected by changes in solvent (α-chloronaphthalene, triethylene glycol, bromobenzene, and dimethyl maleate).

The effects of substituents on the rate and course of the cycloreaction were probed using 3- and 4-bromo-1,8-divinylnaphthalene (Ib and Ic) prepared by the method of Mitchell and Sondheimer[6] from the correspondingly substituted 1,8-naphthalic anhydrides.[7,8]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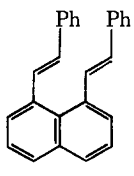
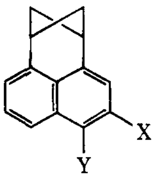

II

a, X = Y = H
b, X = Br; Y = H
c, X = H; Y = Br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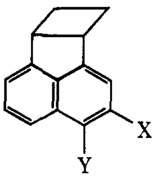
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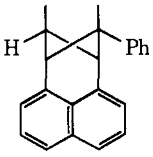
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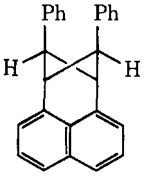
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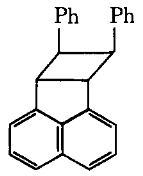
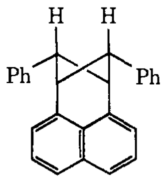

VII


VIII

The anticipated cycloadducts (IIIb,IVb and IIIc,IVc) were obtained on heating, and product ratios and kinetic data, measured by nmr (in pentadeuteriobromobenzene at 136.0 ± 0.5°), are presented in Table I. The modest shifts in the product ratios for the 4-bromo case could arise from resonance interactions, conformational distortions due to a second pair of peri interactions,[9] or, in the photochemical reaction, an internal heavy atom effect.[10] The minuscule rate effects are in the direction expected for reactions leading to an electron-deficient center.

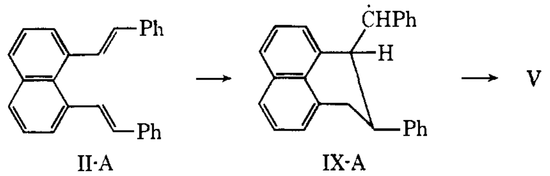
Since the photochemistry of *trans,trans*-1,8-distyrylnaphthalene (II) is closely related to that of the unsubstituted 1,8-divinylnaphthalene (I),[1,2] and since the phenyl substituents in II provide an opportunity to follow the steric course of these reactions, we turned next to the thermal reactions of II. Heating II in triethylene glycol at 160° was found to give but a single monomeric product, V. This is in marked contrast to the photochemical reaction of II, which yields V (40%), along with VI (38%) and VII (5%).[1] At temperatures above 180°, small amounts of still another isomer are also obtained. Spectral evidence (nmr, ir, mass spectrometry) and chemical degradation (ozonolysis and esterification to give *cis,cis,cis*-1,2,3,4-tetracarbomethoxycyclobutane[1]) are consistent with structure VIII for this additional isomer.

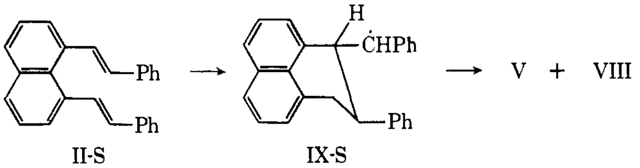
Table I

Starting material	Product ratio II/III Photochemical[a]	Thermal[b]	Rate[c]
Ia	10	2.5	$1.19 \pm 0.03 \times 10^{-3}$
Ib	11	2.5	$0.98 \pm 0.07 \times 10^{-3}$
Ic	7	6.0	$1.07 \pm 0.06 \times 10^{-3}$

[a] In cyclohexane (0.002 *M*) using a 450-W Hanovia lamp with Pyrex filter. [b] In triethylene glycol at 200°. [c] Thermal reaction in pentadeuteriobromobenzene, min^{-1}, at 136.0 ± 0.5°.

The clean transformation of II to V at 160° might result either from a stereospecific, concerted s,a cycloaddition,[5] or from the generation of a long-lived 1,4 biradical[11] (IX-A) from the sterically favored anti conformation of II (II-A), since rotation of the terminal benzylic site into the sterically most expeditious conformation for ring closure would lead to V. At higher temperatures, a 1,4 biradical might also arise from the energetically less favored syn conformer II-S.[12] Ring closure to give the 1,4 biradical IX-S, followed by ring inversion, could yield both isomer V and the minor product VIII.





The thermal ring closure of II is some four times faster than that of I, consistent with the increased stability that the phenyl substituent should confer upon intermediates of type IX. The absence of the "head-to-head" isomer VII among the thermal products produced from II (while IVa comprises over a quarter of the thermal cycloadducts from Ia) could reflect the reduced importance of the requisite conformer II-S

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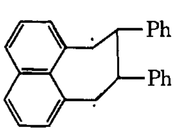
(10) N. J. Turro, "Molecular Photochemistry," W. A. Benjamin, New York, N. Y., 1965.

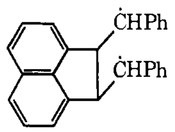
(11) No radical intermediate could be intercepted by carrying out the reaction in dimethyl maleate or dimethyl fumarate. However, isomerization of dimethyl maleate to the cis diester at 180° was accelerated in the presence of II. In the nmr at 200° in α-chloronaphthalene or a biphenyl melt, the transformation of II was accompanied by a persistent, strong, complex absorption at about δ 4 ppm.

(12) For evidence that this pathway may indeed dominate the thermal ring closure of Ia, see ref 4.

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

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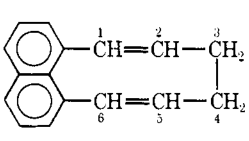
Thermal Rearrangements of 1,6-(1′,8′-Naphthalene)-1,5-hexadienes

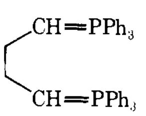
Sir:

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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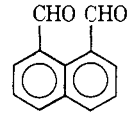

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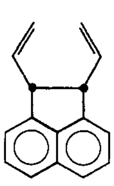

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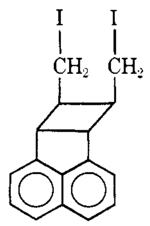
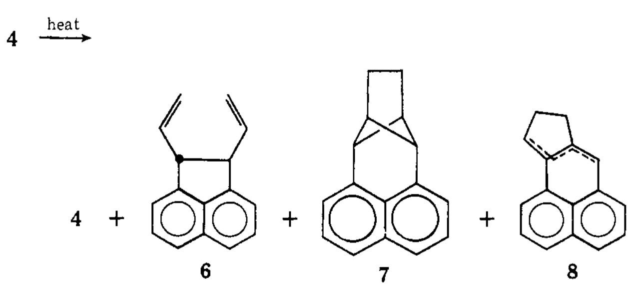


5

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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(1) S. F. Nelsen and J. P. Gillespie, *J. Amer. Chem. Soc.*, **94**, 6238 (1972).

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

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