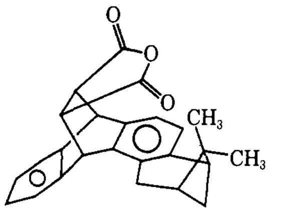
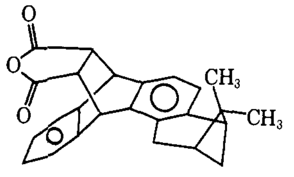
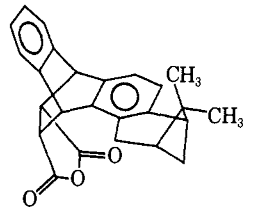


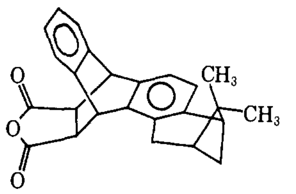
syn-**6**β, 19%



anti-**6**β, 30%



syn-**6**α, 39%



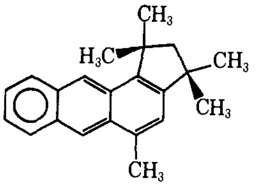
anti-**6**α, 12%

MA, hence greater susceptibility to steric factors (*cf.* the amount of *syn*-**6**β). The greater reactivity of the β face, however, is best reflected by comparing *anti*-**6**β (30%) to *anti*-**6**α (12%). Thus, with *most* dienophiles ApAn reacts preferentially from the *more hindered* side.

Why this preference? The only apparent difference is the presence of the *gem*-dimethyl group. Thus, an explanation for preferred attack on the more congested β side is that it is more nucleophilic to electrophiles such as DMAD, TCNE, $^1O_2$, TFB, and MA irrespective of steric factors.[7]

If indeed the β face of ApAn is more nucleophilic than the α face, the presence of a π-complexing agent[6] might alter the product distribution by preferentially complexing to the β face. This was shown to be erroneous, since in reactions of ApAn with MA and DMAD the only effect of 10 equiv of TNB was to decrease the reaction rate.[9] These results also rule out a solvent-related entropy effect.

While ApAn is only 1.2 times more reactive than anthracene as a benzyne scavenger, with MA (80°, CCl_4) it is 34 times[10] more reactive than anthracene, and 7.5 times more reactive than 2-*tert*-butyl-[11] and 1,2-dimethylanthracene. Only the trisubstituted anthracene **7** approaches the Diels–Alder reactivity of ApAn.[12]



7

From these preliminary results there is little doubt that ApAn, as a consequence of its structure, has chemically nonequivalent aromatic faces which we attribute to σ–π orbital overlap of the *syn*-C_3Me or *gem*-dimethyl groups with the aromatic π system. Its increased Diels–Alder reactivity may also be a result of this and/or overlap with the strained rigid cyclobutane ring.

Other manifestations of this facial nonequivalence (π-orbital distortion) are under investigation.

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(7) This may be a result of secondary orbital overlap between the σ-bonding electrons of the *gem*-dimethyl group and the π-bonding electrons within the aromatic periphery. Partial support for this idea exists: (1) ApAn, λ_{max} 265 nm; anthracene, λ_{max} 254 nm; *i.e.*, a bathochromic shift of 11 nm which also is observed with a wide variety of polycyclic apopinarenes and their corresponding parents; (2) MA and 2-substituted anthracenes give syn and anti adducts in ratios that agree with the conclusion that the transition state containing the MA fragment above the more electron-rich aromatic ring is more stable than the other possibility [F. Kaplan and H. Conroy, *J. Org. Chem.*, **28**, 1593 (1963)]. The *syn*-**6**α/*anti*-**6**α ratio (3.3:1) further supports this contention. The lower *syn*-**6**β/*anti*-**6**β ratio (2:3) can be attributed to steric interactions.[8]

(8) The thermal equilibration (syn–anti adduct isomerization) of maleic anhydride–anthracene adducts will be reported upon separately.

(9) *Cf.* B. H. Klanderman and T. R. Criswell, *J. Amer. Chem. Soc.*, **91**, 510 (1969), for related observations with benzyne and substituted anthracenes.

(10) (a) Lack of selectivity of benzyne relative to MA is well documented (D. M. Smith, Ph.D. Thesis, Case Western Reserve University, 1972). (b) At 80° the relative rates are: anthracene, 1.00; 1-Me, 0.84; 2-Me, 1.06.

(11) These D–A isomers are easily separated: syn, mp 216°; anti, mp 274°.

(12) Kinetic runs were conveniently made in the pmr probe in 1.0 ml of solvent containing 0.3 mmol of the anthracene and 1–10 equiv of dienophile. This technique will be reported in detail elsewhere.

The Degenerate Thermal Rearrangement of *cis*-9,10-Dihydronaphthalene[1]

Sir:

Perhaps owing to its propensity for disproportionation[2] and to its rather unflattering position as the "thermodynamic sink" on the thermal energy surface which interrelates a large number of $(CH)_{10}$ structural isomers,[2b,3] *cis*-9,10-dihydronaphthalene (**1**) has not held the degree of sustained fascination one normally anticipates for interesting molecules. Another major source of disappointment in the brief history of **1** is the early report by van Tamelen and Pappas[4] that this polyene exhibits "no overt tendency for cyclodecapentaene formation." Notwithstanding, certain theoretical considerations having their basis in orbital symmetry[5] have led us to investigate the possibility that the *cis*-9,10-dihydronaphthalene molecule (**1**) might be capable of degenerate skeletal rearrangment under conditions of thermal activation. Fundamentally at issue was the question of whether one or more of several possible carbon scrambling mechanisms (see below) were occurring at a kinetic level competitive with disproportionation schemes or with other symmetry-allowed but degeneracy-destroying reactions such as stereospecific [1,5] sigmatropic hydrogen shifts. A study of this

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(1) Support of this work by the National Science Foundation and the National Cancer Institute is gratefully acknowledged.

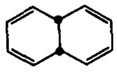
(2) (a) W. von E. Doering and J. W. Rosenthal, *J. Amer. Chem. Soc.*, **89**, 4534 (1967); (b) L. A. Paquette and J. C. Stowell, *ibid.*, **93**, 2459 (1971).

(3) (a) W. von E. Doering and J. W. Rosenthal, *ibid.*, **88**, 2078 (1966); M. Jones, Jr., and L. T. Scott, *ibid.*, **89**, 150 (1967); (c) M. Jones, Jr., *ibid.*, **89**, 4236 (1967); (d) E. E. van Tamelen and T. L. Burkoth, *ibid.*, **89**, 151 (1967); (e) W. von E. Doering and J. W. Rosenthal, *Tetrahedron Lett.*, 349 (1967); (f) M. Jones, Jr., and B. Fairless, *ibid.*, 4881 (1968); (g) S. Masamune, R. T. Seidner, H. Zenda, M. Weisel, N. Nakatsuka, and G. Bigam, *J. Amer. Chem. Soc.*, **90**, 5286 (1968); (h) S. Masamune and R. T. Seidner, *Chem. Commun.*, 542 (1969); (i) R. T. Seidner, N. Nakatsuka, and S. Masamune, *Can. J. Chem.*, **48**, 187 (1970); (j) M. Jones, Jr., S. D. Reich, and L. T. Scott, *J. Amer. Chem. Soc.*, **92**, 3118 (1970); (k) E. E. van Tamelen and R. H. Greeley, *Chem. Commun.*, 601 (1971).

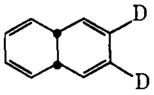
(4) E. E. van Tamelen and B. Pappas, *J. Amer. Chem. Soc.*, **85**, 3296 (1963).

(5) R. B. Woodward and R. Hoffmann, *Angew. Chem.*, **91**, 797 (1969); *Angew. Chem., Int. Ed. Engl.*, **8**, 781 (1969).

potential degeneracy phenomenon quite obviously required the availability of a dideuterated substrate of high isotopic purity. To this end, a preparation of **2** has been realized which provides material of >98% d_2 content (nmr analysis).



1

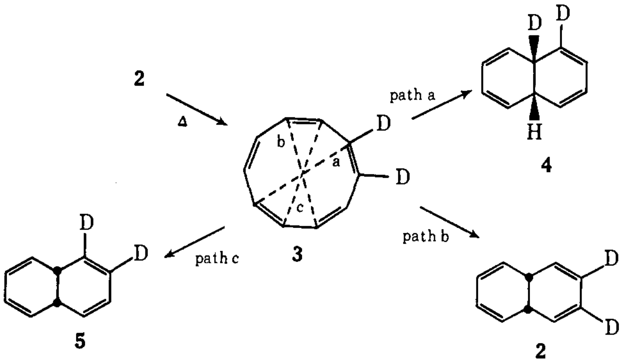


2

Under conditions where **2** was slowly introduced in the gas phase (510° (30 mm N_2 atmosphere)) through a quartz tube packed with quartz chips (contact time ≤ 1 sec) and subsequently repurified by vpc (10% SE-30 on Chromosorb W at 115°),[6] the tetraene had undergone extensive scrambling of its deuterium labels. Whereas isomerically pure **2** displays three multiplets at approximately δ 5.81 (2.0 H), 5.42 (4.0 H), and 3.25 (2.0 H),[7] the nmr spectrum of recovered *cis*-9,10-dihydronaphthalene showed a proton composition of 3.4 H, 3.3 H, and 1.4 H, respectively.[8]

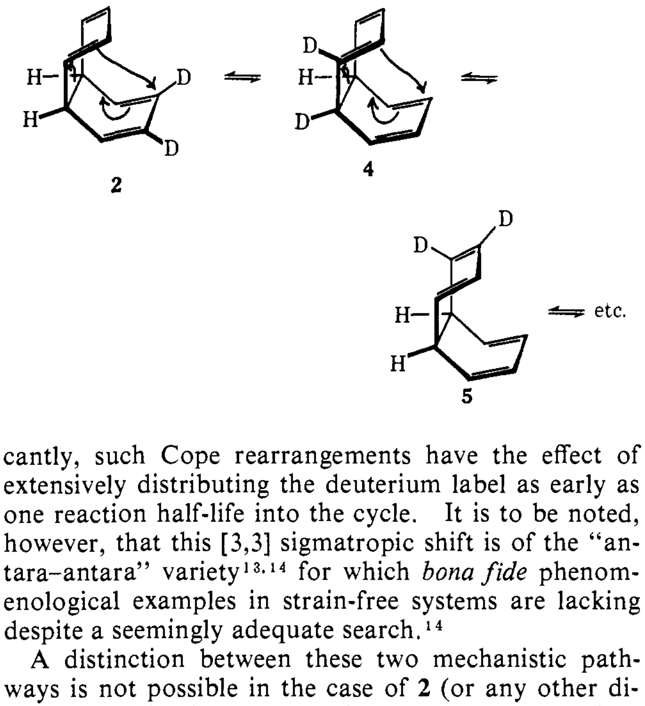
Two reasonable mechanisms[9,11] are capable of explaining the rather indiscriminate scrambling of deuterium between all possible positions. The first of these (Scheme I) is an electrocyclic disrotatory ring opening process leading to *cis*^{5}-cyclodecapentaene-d_2 (**3**) which subsequently undergoes thermal disrotatory closure in all possible directions.[12] Cyclization according to paths a and c leads to isomers **4** and **5**, respectively; path b, in contrast, regenerates **2**. Partitioning of intermediate **3** between the three possible options would give rise to *cis*-9,10-dihydronaphthalene with the observed nmr spectrum.

Scheme I



Alternatively, **2** could be experiencing symmetry-allowed [3,3] sigmatropic shifts (Scheme II). Significantly, such Cope rearrangements have the effect of extensively distributing the deuterium label as early as one reaction half-life into the cycle. It is to be noted, however, that this [3,3] sigmatropic shift is of the "antara-antara" variety[13,14] for which *bona fide* phenomenological examples in strain-free systems are lacking despite a seemingly adequate search.[14]

Scheme II



A distinction between these two mechanistic pathways is not possible in the case of **2** (or any other dideuterio derivative of **1**). The use of two deuterium atoms as tracers is, however, the minimum modification of **1** consistent with studying the parent hydrocarbon itself. In any event, *cis*-9,10-dihydronaphthalene (**1**) now joins bullvalene,[15] bicyclo[4.2.2]decatetraene,[3f,16] pentacyclo[3.3.2.0^{2,4}.0^{3,7}.0^{6,8}]dec-9-ene,[2b] and tetracyclo[5.3.0.0^{2,6}.0^{3,10}]deca-4,8-diene[17] in the expanding list of (CH)$_{10}$ hydrocarbons which enjoy the fascinating capability for degenerate rearrangement.

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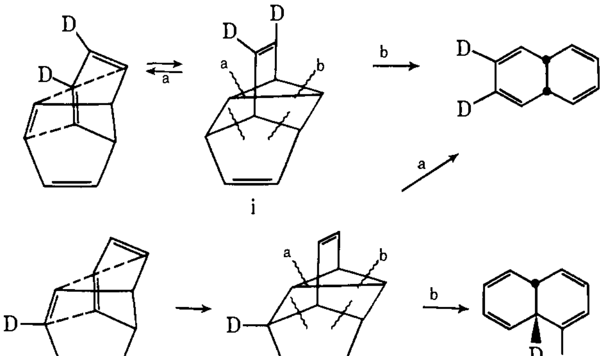
(6) (a) Small quantities of naphthalene, 1,2-dihydronaphthalene, and 1,4-dihydronaphthalene were also produced during the pyrolysis.[2b] (b) Appropriate control experiments with **2** indicated clearly that no deuterium scrambling was operative under the vpc conditions employed.

(7) Compare the published nmr spectrum of **1**.[4]

(8) These values were derived from repeated manual integration of several CAT-amplified nmr spectra at 100 MHz. The average experimental error of ±0.3 H can be construed to mean that the theoretical random ratio of 3.2/3.2/1.6 had probably been realized (see ref 12).

(9) The incursion of the intramolecular (4 + 2) cycloaddition pathway[10] and subsequent thermal rearrangement[3j] of the resulting polycyclic hydrocarbons i and ii do not appear to operate because the distribution of isotopic label by this mechanism is too discriminating in favor of the 2,3-d_2 isomer.



(10) T. L. Burkoth and E. E. van Tamelen, "Nonbenzenoid Aromatics," Vol. I, Academic Press, New York, N. Y., 1969, pp 97–99.

(11) A fourth possibility involving stereospecific [1,5] sigmatropic shifts of carbon atoms has not been considered because of the higher energies of activation customarily associated with carbom migrations compared to related hydrogen shifts.[5]

(12) The deuterium isotope effects which are surely operative are sufficiently small to be negligible in the present context.

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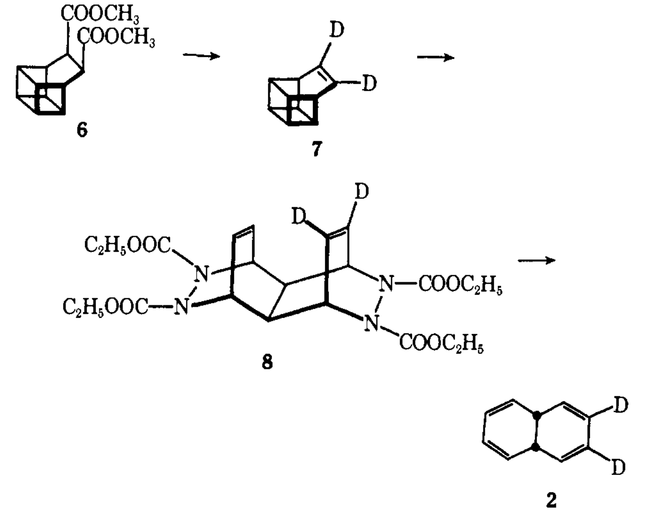
The synthesis of **2** began with the preparation of 9,10-dideuteriobasketene (**7**). This was achieved by heating *cis*-dimethyl ester **6** in CH_3OD containing sodium methoxide, hydrolysis of the resulting labeled *trans*-diester in $NaOD-D_2O$, and subsequent electrolytic bisdecarboxylation of the diacid as previously described.[18] The deuterium content of **7** was >98% d_2 by nmr analysis. Cycloaddition of diethyl azodicarboxylate to **7** gave **8** by analogy to the recent work of Shen.[19] The deuterium labeling pattern in **8** was clearly evident from its nmr spectrum: δ 5.8–6.5 (m, 2, olefinic), 4.5–5.1 (m, 4, C*H*N), 4.23 (q, 8, OCH_2), 2.93 (br s, 2, methine), and 1.25 (t, 12, CH_3). Hydrolysis–decarboxylation of **8** under a carefully deoxygenated nitrogen atmosphere and subsequent oxidation of the corresponding hydrazine afforded **2** with the high isotopic purity discussed above.



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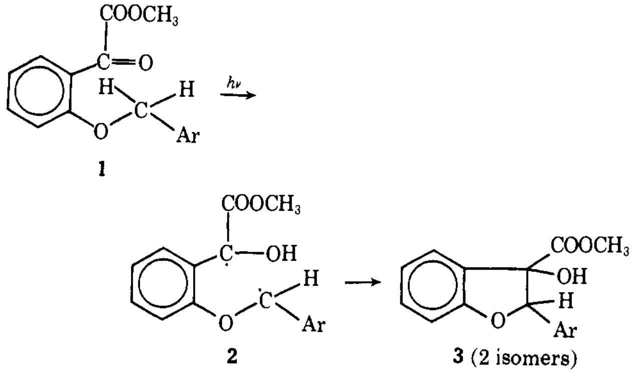
Heavy-Atom Effects on the Stereochemistry of Photoabstraction–Cyclization in a Carbonyl System[1]

Sir:

The effects of halogen substituents and halogen-containing solvents (heavy-atom effect) on the spectroscopic behavior of aromatic compounds are well documented and have been attributed to enhanced rates of S–T transitions.[2] The effect has also been observed on the photoreactivity of acenaphthalene.[3] On the other hand, theoretical arguments have been advanced against the importance of the heavy-atom effect on carbonyl systems,[4] and experimental evidence tends to support this prediction.[5] Herein, we report a heavy-atom effect on the stereochemistry of the photocyclization of methyl *o*-benzyloxyphenylglyoxylate (**1a**).



a, Ar = C_6H_5
b, Ar = C_6H_4-*p*-CH_3
c, Ar = C_6H_4-*p*-Cl

A mechanistic study on the phototransformation **1a** → **3a** has demonstrated the intermediacy of a reactive n,π* triplet which undergoes intramolecular H abstraction from the benzyloxy carbon.[6] Both the quantum yields of product formation and the stereoselectivity were found to be significantly lower in the polar solvents acetonitrile and *tert*-butyl alcohol relative to benzene and *n*-hexane.[6,7] However, as indicated in Table I, the stereochemical results in chloroform, bromoform, and, to a lesser extent, bromobenzene provide a striking con-

Table I. Solvent and Substituent Effects on the Phototransformation **1** → **3**

Compd	Solvent	Cis/trans[a] (temp, °C)	ϕ_{+3}[b]	$1/\tau$,[c] 10^7 sec^{-1}
1a	$(Me)_3COH$	1.0 (35)[d]	0.47	1.3
	MeCN	2.2 (35)[d]	0.56	3.7
	C_6H_6	6.7 (35)	0.89	4.3
	C_6H_6[e,f]	14.6 (0)		
	C_6H_5Br[e]	17.7 (0)		
	$CHCl_3$	28.2 (0)	0.65	
	$CHBr_3$[e]	90.0 (0)	0.65	
1b	C_6H_6[e,f]	16.0 (0)	0.69	3.5
1c	C_6H_6[e,f]	21.2 (0)	0.78	2.1
1a-d_1	MeCN	2.1 (35)	0.52	
	C_6H_6	7.2 (35)	0.86	
1a-d_2	MeCN	1.9 (35)	0.41	
	C_6H_6	7.4 (35)	0.81	

[a] Ratio of isomers **3** with respect to the geometric relationship of the 2-phenyl and 3-hydroxyl groups; estimated error ±5%. [b] Quantum yields for formation of **3** at 35° and 366 nm by ferrioxalate actinometry; 0.06 *M* **1**; conversions, <15%; estimated error, ±8%. [c] Reciprocal lifetimes obtained from slopes ($k_q\tau$) of Stern–Volmer quenching plots utilizing literature values for k_q (see ref 6). These values correspond to maximum rates for hydrogen abstraction. Minimum rates may be obtained by multiplying these values by ϕ_{+3}. [d] Little or no temperature effect on the isomer ratios in these solvents. [e] Contained 20% by volume of cyclohexane for melting point depression. [f] The same ratios were obtained in *n*-hexane.

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(1) Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research.

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