Table I. Nmr Data for *t*-Butylnaphthalenes[a]

Compd	*t*-Butyls β	α	*peri*	Other resonances
5[b]	1.40	1.64		7.17–7.28 (3, m), 8.30 (1, m, *peri* H)
6	1.42	1.59		2.61 (3, s), 2.77 (3, s, *peri* CH_3), 6.99 (2, s), 7.66 (1, d, J = 2 Hz), 7.72 (1, d, J = 2 Hz)
7	1.42	1.57	1.22 1.24	7.10 (1, d, J = 8 Hz), 7.28 (1, d, J = 8 Hz), 7.43 (1, d, J = 1.8 Hz), 7.90 (1, d, J = 1.8 Hz, *peri* H)
8	1.40		1.30	7.22 (2, d, J = 1.7 Hz), 7.48 (2, d, J = 1.7 Hz)
9	1.40			2.58 (3, s), 2.62 (3, s), 7.03 (2, s), 7.46 (1, dd, J_{bc} = 9, J_{ac} = 2 Hz), 7.83 (1, d, J_{bc} = 9 Hz), 7.83 (1, d, J_{ac} = 2 Hz)
10	1.40		1.27 1.28	7.1–7.6 (5, m)

[a] In parts per million. [b] The assignments for *t*-butyl and *peri* H are consistent with data for 1,4-di-*t*-butylnaphthalene: R. W. Franck and K. Yanagi, *J. Org. Chem.*, **33**, 811 (1968).

An observation about the nmr data for the *peri* di-*t*-butyl groups can be made: the signals appear as sharp singlets, upfield from the "normal" naphthalene *t*-butyl resonances. This may be rationalized by postulating that the *peri* groups relieve crowding by bending away from each other above and below the plane of the naphthalene ring. Thus locking and/or restricted rotation of the *t*-butyl groups (and line broadening) is avoided and the protons are not in the zone of maximum deshielding. Also, this spatial arrangement of the *t*-butyl groups, as seen from models, serves to hinder the *peri* ring carbons from external acid attack.

A comparison of uv spectra (Figure 1) of the 1,3,5,8 systems **6** and **7** with 1,3,5,8-tetramethylnaphthalene is indicative of the very great strain in **7**. Similar uv spectral perturbations are observed for **8** and **10**. The spectrum of the *o*-di-*t*-butylbenzene analog **6** shows the expected slight bathochromic shifts, slight decreases in extinction, and the loss of fine structure compared to the model compound. The large deviations in the spectrum of the tetra-*t*-butyl compound **7** are good physical evidence for significant perturbation of the aromatic system.[9] When the requisite model compounds can be obtained, it is our plan to apply other physical measurements discussed by Arnett[1] to determine semiquantitatively the strain energy of our system. Also, X-ray crystallographic structural analyses and further chemical investigations are under way.[10,11]

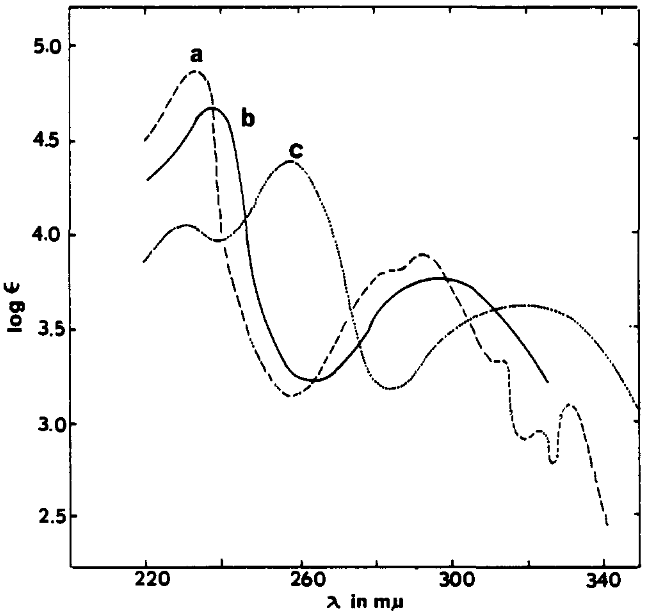

Figure 1. Uv spectra of 1,3,5,8-tetraalkylnaphthalenes: (a) 1,3,5,-8-tetramethylnaphthalene (W. L. Mosby, *J. Am. Chem. Soc.*, **75**, 3348 (1953)); (b) 1,3-di-*t*-butyl-5,8-dimethylnaphthalene (**6**); (c) 1,3,5,8-tetra-*t*-butylnaphthalene (**7**).

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(9) J. Dale, *Chem. Ber.*, **94**, 2821 (1961).

(10) Correct elemental analyses were obtained for all compounds reported.

(11) (a) Portions of this work were previously reported: R. W. Franck and E. Leser, Abstracts, 156th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept 1968, ORGN-167. (b) Financial assistance was received from the New York State Science and Technology Foundation for the purchase of a Varian A-60A spectrometer, from the National Science Foundation for a traineeship for E. L. and for partial research support through Grant GP 7754, and from Fordham University research funds.

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Migratory Aptitudes in a Thermal, Sigmatropic Rearrangement

Sir:

Sigmatropic reactions[1] of neutral molecules are of special interest because they are controlled by the conservation of orbital symmetry.[2] These reactions involve intramolecular migration of a group from one carbon to another, and an obvious experiment is to compare the migratory aptitudes of various groups in these reactions with those found in other rearrangements. The purposes of such a comparison are to provide predictive power over

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(1) G. B. Gill, *Quart. Rev.* (London), **22**, 338 (1968).

(2) R. B. Woodward and R. Hoffmann, *J. Am. Chem. Soc.*, **87**, 2511 (1965).

Table I. Substituted Indene Thermolysis Products in Diphenyl Ether Solution

Reactant	Temp, °C	Time, hr	Product
1,1,3-Triphenylindene	240	6	1,2,3-Triphenylindene
1,1-Diphenylindene	280	6	2,3-Diphenylindene
1,3-Diphenylindene	300	12	2,3-Diphenylindene, 1,2-diphenylindene[a]
1-Methyl-1-phenylindene	300	8	3-Methyl-2-phenylindene
1-Deuterio-1,3-diphenylindene	150	8	2-Deuterio-1,3-diphenylindene
1-Phenylindene	150	10	3-Phenylindene

[a] Detected in low yield by nmr. See ref 3 for the equilibration study.

the facility of sigmatropic reactions and to gain a more detailed knowledge of the transition-state structure for group migrations.

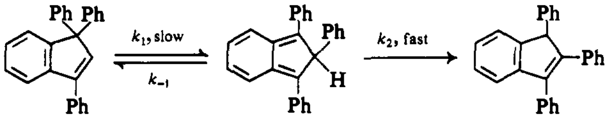
We report here on the migratory aptitudes of methyl, phenyl, and hydrogen in the thermal rearrangement of these groups from the 1 to the 2 position of indene. Phenyl rearrangements of this type have been previously observed to be promoted by heat,[3] light,[4,5] and alkali metal reduction.[6,7] Of particular interest is Koelsch and Johnson's study of thermal rearrangements over porous solids at 450–490°. More recently, Roth determined the rate of isomerization of 1-deuterioindene to 2-deuterioindene at 220° in the gas phase.[8]

The thermolysis products and the rates of rearrangement of several indenes in diphenyl ether solution are summarized in Tables I and II. The products indicated were isolated and characterized by comparison with independently synthesized samples. In each case the reaction was quite clean (>85% yield) and no exchange of groups between molecules was detected, *e.g.*, diphenylindene gave no mono- or triphenylindene. Kinetic studies were carried out using sealed tubes and nmr analysis. Good first-order rate plots and an independence of k on initial substrate concentration were obtained. Addition of quinoline as an acid scavenger or degassing did not change the rearrangement rate, and hydroquinone did not change the product for triphenylindene. These data and the specificity for 1,2 rearrangement strongly suggest a pair of intramolecular sigmatropic shifts involving an isoindene[8,9] intermediate as the mechanism of these reactions. Because of microscopic reversibility and the relative stabilities of isoindene and reactant, k_{-1} must be greater than k_1. However, since we find that phenyl migrates much slower than hydrogen in this series, k_2 must be greater than k_{-1}. This demands that isoindene formation be rate determining and essentially all the triphenylisoindene be converted to product rather than reverting to reactant.

Table II. Rate Constants for Indene Isomerizations in Diphenyl Ether Solution

Reactant	Temp, °C	10^5k, sec^{-1}	Migrating group
1,1,3-Triphenylindene	240	13.4 ± 0.6[a]	Phenyl
	235	7.0	
	235	7.5[b]	
	235	6.9[c]	
1,1-Diphenylindene	280	20.0	Phenyl
1-Methyl-1-phenylindene	300	8.0	Phenyl
1,3-Diphenylindene	300	6.2	Phenyl
1-Deuterioindene	220	7.6[d]	Deuterium
1-Phenylindene	150	5.9	Hydrogen
1,3-Diphenyl-1-deuterioindene	150	9.0	Deuterium

[a] Average of two runs at 0.20 *M*, one run at 0.30 *M*. [b] 0.15 *M* quinoline present. [c] Degassed. [d] Gas-phase data from ref 8.



The data in Tables I and II show that the rearrangement of hydrogen is much faster than that of phenyl which in turn migrates in preference to methyl. This order appears to be primarily due to transition-state stabilization by the migrating group rather than by the group that remains behind. Hydrogen rearrangement in 1-phenylindene and phenyl migration in 1,1-diphenylindene involve different migrating groups but the same nonmigrating moiety, and the hydrogen again migrates much faster than phenyl. This very large difference must be attributed to the effective bridging capabilities of hydrogen in the transition state since it would otherwise seem to require an unexpected steric acceleration for 1-phenylindene compared to 1,1-diphenylindene. Similar comparisons can be made with other pairs in order to estimate the substituent effects at C-1 and C-3 and measure migratory aptitudes. These will be treated in detail in a future publication.

Although migratory aptitudes can be controlled by orbital symmetry,[4] the highest filled molecular orbital[10] of the indenyl radical has a node at C-2,[11] indicating that in this reaction none of the group migrations violates the conservation of reaction orbital symmetry.[12] This is

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(3) C. F. Koelsch and P. R. Johnson, *J. Am. Chem. Soc.*, **65**, 567 (1943).

(4) J. J. McCullough, *Can. J. Chem.*, **46**, 43 (1968).

(5) G. W. Griffin, *et al.*, *Tetrahedron Letters*, 2951 (1965).

(6) C. F. Koelsch, *J. Am. Chem. Soc.*, **56**, 480 (1934); K. Ziegler and F. Crossman, *Ber.*, **62**, 1768 (1929).

(7) Rearrangements of substituted indenes upon electron-transfer oxidation and reduction are currently under investigation. These reactions presumably involve ion radicals and will provide a comparison of migratory aptitudes in sigmatropic rearrangements from four electronic states of the same atomic array.

(8) W. R. Roth, *Tetrahedron Letters*, 1009 (1964).

(9) J. A. Berson and G. B. Aspelin, *Tetrahedron*, **20**, 2697 (1964); K. Alder, F. Pascher, and H. Vagt, *Ber.*, **75**, 1501 (1942).

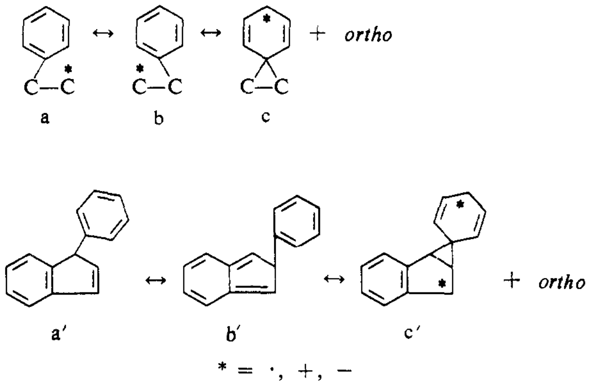
(10) C. A. Coulson and A. Streitwieser, "Dictionary of π-Electron Calculations," W. H. Freeman and Co., San Francisco, Calif., 1965, p 210.

(11) The frontier orbital electron density also indicates that coupling of a pair of radicals as in a cleavage recombination mechanism at C-2 is unlikely.

(12) The effect of a node in the frontier orbital at one of the migration terminals has also been discussed for photochemical rearrangements in the cycloheptatriene series: A. G. Anastassiou, *Chem. Commun.*, 15 (1968).

supported by the observation that phenyl, which has low-lying π orbitals of inverted symmetry,[4] migrates with efficiency intermediate between hydrogen and methyl. These aptitudes are in direct contrast to those found in 1,2-anionic,[13] free-radical,[14] and cationic[15] rearrangements where phenyl always migrates as well as or to the exclusion of hydrogen and methyl. This incongruity can be rationalized by considering the transition-state structures shown in Scheme I. Structure c can account for the preference for phenyl migration in anion, cation, and radical rearrangements. In thermal, neutral molecule rearrangements, however, structure c′ should be considerably less important since it is diradical or dipolar and a′ and b′ are not. This indicates that in the absence of a necessity to delocalize charge or an odd electron, hydrogen may ordinarily be a better migrating group, *i.e.*, a bridged hydrogen is more stable relative to its unbridged precursor than is a bridged carbon relative to its precursor. Although energy matching is washed out by the comparison of reactants and transition states, the overlap capabilities of the undirectionalized hydrogen orbital compared with carbon orbitals is a credible explanation for this difference. We hope to test these speculations by making a more extensive study of migratory aptitudes in the indene series and in other thermal, neutral molecule sigmatropic rearrangements.

Scheme I



(13) H. E. Zimmerman in "Molecular Rearrangements," P. de Mayo, Ed., Interscience Publishers, New York, N. Y., 1963, p 391.

(14) C. Walling in ref 13, p 409.

(15) See S. Winstein, B. K. Morse, E. Grunwald, K. C. Schreiber, and J. Corse, *J. Am. Chem. Soc.*, **74**, 1113 (1952), and references cited there.

(16) Participant in National Science Foundation Research Participation for High School Teachers Program, Colorado State University.

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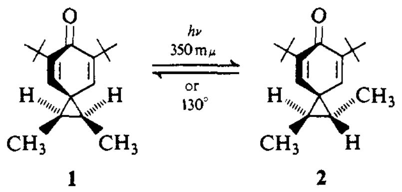
Stereospecificity and Wavelength Dependence in the Photochemical Rearrangement of Spiro[2.5]octa-4,7-dien-6-ones to Quinone Methides

Sir:

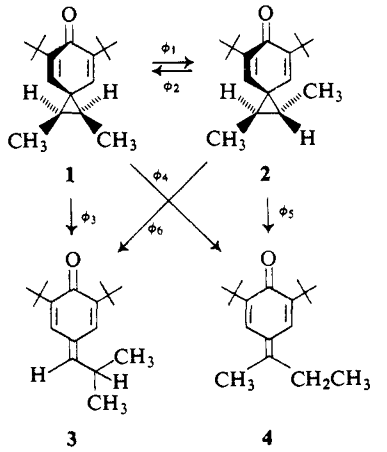
The photochemistry of spirodienones **1** and **2** is of unusual interest. Not only do these compounds undergo stereospecific photochemical rearrangements, but the type of reaction observed is dependent upon the wavelength of the incident light.

Spirodienones **1** and **2** are thermally and photochemically interconvertible. *n*-Decane solutions of the *cis* isomer **1** isomerize to the *trans* isomer **2** with a half-life of *ca.* 1 hr at 150° and afford a 1.8 ± 0.2:1.0 equilibrium mixture with the *trans* isomer predominating. Prolonged heating at 240° affords no other detectable[1] products and does not appreciably alter the equilibrium position. Irradiation[2] of *only* the long-wavelength absorption bands of **1** or **2** (λ_{max} 352 mμ (ϵ 38 or 39, respectively)) affords, in cyclohexane, a 4:1 photostationary mixture favoring *trans*-**2** and leads to no other products, or to material loss.[1] The absorption spectra of **1** and **2** are sufficiently similar so that no appreciable optical pumping can occur in the ultraviolet region. Photosensitized *cis–trans* isomerization also occurs with results comparable[3] to those of the 350-mμ direct irradiation.



In contrast, 254-mμ irradiation[4] of **1** or **2** (degassed 0.4 *M* cyclohexane solutions in quartz nmr tubes) leads not only to *cis–trans* isomerization but also affords quinone methides **3** and **4** *via* methyl or hydrogen migration.[5] Figures 1 and 2 illustrate the relative concentrations of **1**, **2**, **3**, and **4** as a function of time. Since no other products are detectable,[1] total concentrations are assumed to remain constant. From Figures 1 and 2, it is qualitatively apparent that, in competition with the faster *cis–trans* isomerization, *cis*-**1** affords preferential methyl migration while *trans*-**2** affords preferential hydrogen migration. Using the experimentally deter-

Scheme I



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(1) Analyses were performed *via* 100-MHz nmr spectroscopy.

(2) Irradiations were conducted using Pyrex vessels in a Rayonet photochemical reactor equipped with 3500-Å lamps. Solutions were degassed and maintained at *ca.* 5° during irradiation. Dienone concentrations were such that >99% of the incident light was absorbed.

(3) During the 350-mμ irradiation of 1, the presence of sufficient acetophenone-d_5 (deuteriated to simplify nmr analysis) to absorb *ca.* 40% of the incident light fails to affect either the rate of attainment or the position of the photoequilibrium relative to that of an unsensitized but otherwise identical control.

(4) Irradiations were conducted at *ca.* 5° in a Rayonet photochemical reactor equipped with 2537-Å lamps. At least 99% of the incident light was absorbed.

(5) W. H. Pirkle and G. F. Koser, *Tetrahedron Lett.*, 129 (1968).