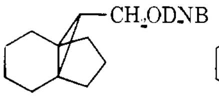
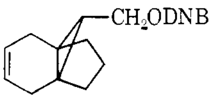
Table I. Solvolysis Data for 3,5-Dinitrobenzoates in 70:30 Acetone-Water

Compd	T, °C	k, sec^{-1} [a]	Rel rate
5	70	$(21.7 \pm 0.9) \times 10^{-6}$	8.58
6	70	$(5.18 \pm 0.44) \times 10^{-6}$	2.05
7	70	$(203 \pm 7) \times 10^{-6}$	80.2
8	70	$(10.4 \pm 0.2) \times 10^{-6}$	4.11
9	70	$(3.04 \pm 0.30) \times 10^{-6}$	1.20
10	70	$(2.53 \pm 0.13) \times 10^{-6}$	1.00

[a] Average values for duplicate runs with error limits the average deviations; good first-order kinetics were observed in every case.



5



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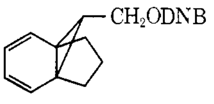

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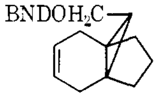

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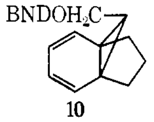

10

The prime conclusion is that a significant reactivity difference exists between the epimers **7** and **10**. Although we would forestall discussion of the origin of this difference (it clearly is not a positive through-space effect), it is seen that **7** is unusually reactive, while **10** is "normal." Comparison of **7** with **5** and **6** shows that steric crowding in the anti series is not the source of the high reactivity of **7** (a factor of *ca.* 2 appears attributable to steric factors). Thus, it seems inevitable that acceleration is due to conjugative factors, which is in disaccord with Wilcox's findings.[3] What is the "real" acceleration in **7** (*i.e.*, after factoring out inductive effects)? A factor of at least 160 seems probable; this point is being investigated further.

From a consideration of our data, some important conclusions may be drawn regarding the cycloheptatriene–norcaradiene preequilibria encountered by Sargent[2] and Paquette.[6] Let us assume their[2,6] mechanism, as shown in eq 1. A steady-state treatment of

$$\begin{array}{c}\text{cycloheptatriene}\\ \text{derivative}\end{array} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \begin{array}{c}\text{norcaradiene}\\ \text{derivative}\end{array} \xrightarrow{k_2} \text{products} \qquad (1)$$

[norcaradiene derivative] gives eq 2. Fortunately, the

$$k_1/k_{-1} = K_{\text{eq}} = k_{\text{solv}}/k_2 + k_{\text{solv}}/k_{-1} \qquad (2)$$

k_{solv}/k_{-1} term can be neglected, since k_{-1} is undoubtedly much larger than k_2.[12] The determination of k_2 may be done only in a relative fashion;[14] thus, $k_7/k_5 = 9.3$ (see Table I) gives a k_2^{rel} which can be used only since the same relative models are available from the work of Sargent[2] and Paquette.[6] Additionally, $k_7/k_6 = 39.1$ (see Table I) gives an independent k_2^{rel}.[15] Applying these numbers first to the monosubstituted cycloheptatriene studied by Sargent, we find $K_{\text{eq}}^{100°} = 2.9 \times 10^{-3}$ and 4.4×10^{-3}, respectively; this gives $\Delta F = 4.4$ and 4.1 kcal/mol.[14–16] This value is approximately 2–2.5 kcal/mol lower than that found by Huisgen[13] for the cyclooctatetraene–bicyclooctatriene valence isomerization. However, considering our uncertainties,[14,15] and the 1 kcal/mol less strain in cyclopropane (compared to cyclobutene), these appear as quite reasonable values. Clearly, the cycloheptatriene–norcaradiene energy gap is much smaller than has commonly been thought.[17]

When comparing our data with Paquette's,[6,14] only k_7/k_5 (and the corresponding $k_{10}/k_8 = 0.24$) may be used. So doing, we find $K_{\text{eq}}^{100°} = 4.4 \times 10^{-2}$ for the anti isomer (*anti*-**3**) and $K_{\text{eq}}^{100°} = 0.5$ for the syn isomer (*syn*-**3**). Interestingly, this latter value is almost identical with the one found for 7-cyano-7-trifluoromethylcycloheptatriene,[18] whereby it is suggested that both norcaradiene and cycloheptatriene forms perhaps could be observed, in the case of *syn*-**3**, by low-temperature nmr spectroscopy.[19]

Acknowledgment. We are grateful for helpful discussions with Professors Jerome Berson, Stuart Staley, Walter Trahanovsky, and Kenneth Wiberg.

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[12] In the cyclooctatetraene–bicyclooctatriene valence isomerization studied by Huisgen,[13] the analogous $k_{-1} = 5.4$ sec^{-1} was obtained. All logic suggests the two valence isomerizations are similar (*vide infra*). However, an error of 10^3 in k_{-1} would not invalidate our premise ($k_{-1} \gg k_2$).

[13] (a) R. Huisgen and F. Mietzsch, *Angew. Chem., Int. Ed. Engl.*, 3, 83 (1964); (b) R. Huisgen, F. Mietzsch, G. Boche, and H. Seidl, *Chem. Soc., Spec. Publ.*, No. **19**, 3 (1964).

[14] We must assume that the preferred conformation of the $-CH_2X$ group in **5**, **6**, and **7** is the same as in the bicyclic compounds of Sargent[2] and the tricyclic ones of Paquette.[6] There is the possibility that our systems prefer a conformation roughly 1–2 kcal/mol below the ideal solvolytic conformation. If so, our estimates for the energy gap between norcaradiene and cycloheptatriene may be *low* by that amount.

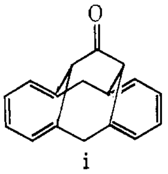
[15] In both cases, we are introducing some error by assuming that the relative rates stay constant between 70° (our temperature) and 100° (Sargent's[2] and Paquette's[6] temperature). From Paquette's[6] work, it seems that we may be, at most, 0.3–0.4 kcal/mol *low* in our estimates of ΔF, due to this factor.

[16] We assume solvolysis occurs, in this case, *via* the anti arrangement (**2**).

[17] (a) Compare the widely quoted 11–14 kcal/mol: W. von E. Doering and M. R. Wilcott, III, unpublished calculations; M. R. Wilcott, III, Ph.D. Dissertation, Yale University, New Haven, Conn., 1963. (b) T. Tsuji, S. Teratake, and H. Tanida, *Bull. Chem. Soc. Jap.*, **42**, 2033 (1969), have studied the norcaradiene–cycloheptatriene equilibrium dilatometrically. One possible conclusion, from their data (although not preferred by these authors), is that the norcaradiene–cycloheptatriene energy gap is 4.0–4.5 kcal/mol. (c) By studying various 7-substituted 2,5-diphenylcycloheptatrienes, Dr. Allan Cairncross (Dupont) has found an energy gap similar to ours for the norcaradiene–cycloheptatriene equilibrium. We thank Dr. Cairncross for this information prior to publication.

[18] E. Ciganek, *J. Amer. Chem. Soc.*, **87**, 1149 (1965).

[19] Recently [H. Günther, H. Schmickler, H. Königshofen, K. Recker, and E. Vogel, *Angew. Chem., Int. Ed. Engl.*, **12**, 243 (1973)] it has been shown that i exists in valence-tautomeric equilibrium with the norcaradiene form.



i

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Received May 14, 1973

Solution Phase Photochemistry of 2-Methylenebenznorbornene. An Apparent Diversion of the Di-π-methane Reaction[1,2]

Sir:

We have recently reported on the photochemical and photophysical properties of two nonconjugated aryl

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[1] Organic Photochemistry. XXV. Part XXIV is F. Scully and H. Morrison, *J. Chem. Soc., Chem. Commun.*, in press.

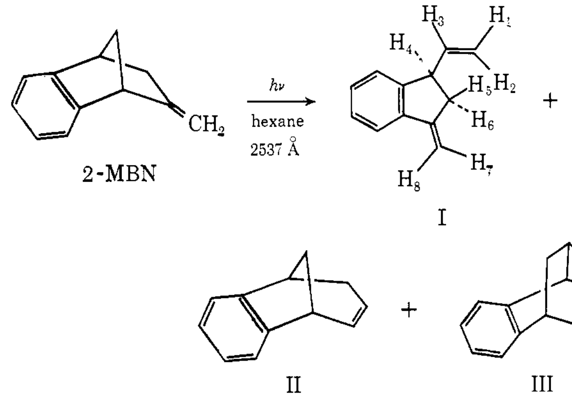
[2] Presented at the 165th National Meeting of the American Chemical Society, Dallas, Tex., April 9–13, 1973.

olefins, 1-phenyl-2-butene[3] and 6-phenyl-2-hexene.[4] The first of these molecules exemplifies facile intramolecular triplet energy transfer (irradiation with 254-nm light produces cis ⇌ trans photoisomerization), while the second molecule demonstrates rapid internal trapping of the aryl excited singlet state by the double bond (with eventual formation of 1,3-cycloaddition products). The latter phenomenon appears to require the potential for a "sandwich" arrangement of the two chromophores, an arrangement which in acyclic aliphatics seems to be optimized when there are three intervening methylene groups (the "rule of three").[4-6]

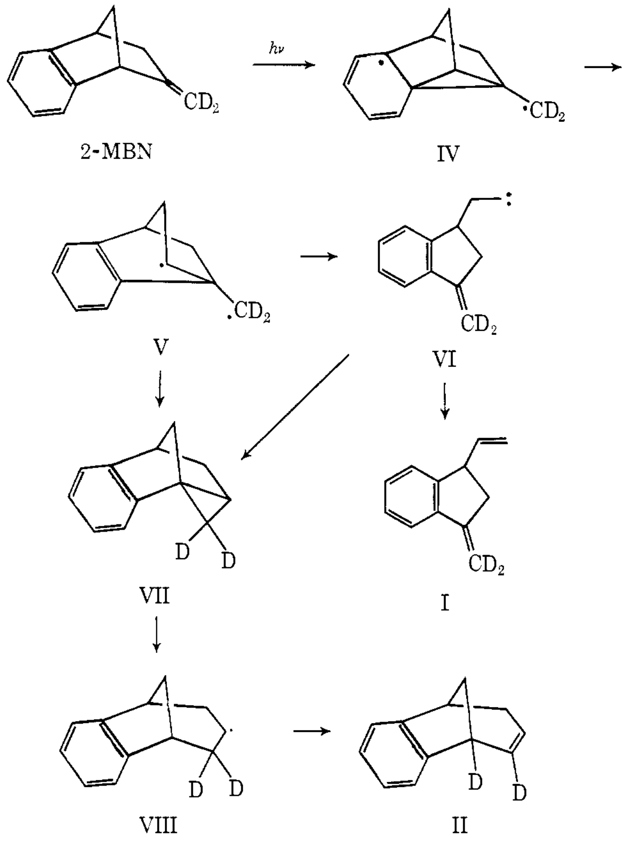
Several features of the 2-methylenebenznorbornene (2-MBN) molecule warrant an investigation of its photochemistry. First, it may be viewed as a rigid (though demethylated) analog of 1-phenyl-2-butene. Second, the p orbitals at the 2 and 6 positions are directed at each other at an angle of *ca.* 70°, by comparison with the colinear arrangement of orbitals which appears to be required for excited singlet exciplex formation. Third, 2-MBN has a di-π-methane arrangement[7] containing a "free-rotor" olefin[8] (as does, of course, 1-phenyl-2-butene).

2-MBN was synthesized by addition of benzyne to cyclopentadiene, hydroboration (to benznorbornen-2-ol), oxidation (to the ketone), and a Wittig condensation (to give the olefin).[9] The product so obtained had physical and spectral properties identical with those previously observed.[9] It was typically photolyzed as a 0.01 *M* solution in argon-degassed hexane, using a low-pressure mercury arc filtered through Vycor. Three photoproducts were isolated by glpc (Scheme I) and have been identified on the basis of spectral analysis (I)[10] or by comparison with spectra of authentic samples (II, III).[11,12] The assignment of structure I to the major photoproduct is derived from analysis of its spectra. The mass spectrum shows a molecular ion at *m/e* 156 and the infrared spectrum (neat) indicates the presence of a monosubstituted olefin (10.10 and 10.93 μ) as well as a methylene group (11.35 μ). The latter absorption is comparable to that (11.51 μ) reported for 1-methyleneindan.[13] The nmr spectrum is essentially first order and shows: a four-proton multiplet at δ 7.05–7.65 (aromatic hydrogens), typical monosubstituted olefin absorption with three eight-line patterns at δ_1 5.06 (J_{12} = 2.0, J_{13} = 9.8, J_{14} = 0.6 Hz), δ_2 5.14 (J_{23} = 17.1, J_{24} = 0.9 Hz), and δ_3 5.90 (J_{34} = 8.2 Hz), δ_4 3.82 overlapping doublet of triplets broadened by long-range coupling to H_1 and H_2 (J_{45} = 8.2, J_{46} = 6.0 Hz), a characteristic geminal group with two quartets of triplets at δ_5 3.06 (J_{56} = 16.5, J_{57} = 2.05, J_{58} = 2.05 Hz), and δ_6 2.59 (J_{67} = 2.50, J_{68} = 2.50 Hz), and the exocyclic methylene hydrogens as two triplets, broadened due to long-range coupling, at δ_7 5.04, δ_8 5.45 (J_{78} = 0.3 Hz).

Scheme I



Scheme II



Quantum efficiencies have been determined[12] as: ϕ_{dis} = 13.5 × 10^{-3}, ϕ_{I} = 8.78 × 10^{-3}, and ϕ_{II} = 2.46 × 10^{-3}. Compound III is a known[14] photoproduct of II and control experiments as well as labeling studies (see below) give results consistent with its formation as a secondary photoproduct. 2-MBN deuterated at the vinyl carbon could be readily prepared using triphenylmethyl-d_3 phosphonium bromide.[15] It

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(3) H. Morrison and R. Peiffer, *J. Amer. Chem. Soc.*, **90**, 3428 (1968); H. Morrison, J. Pajak, and R. Peiffer, *ibid.*, **93**, 3978 (1971). See also, C. S. Nakayama and P. Sigal, *J. Chem. Phys.*, **52**, 3277 (1970).

(4) W. Ferree, Jr., J. B. Grutzner, and H. Morrison, *J. Amer. Chem. Soc.*, **93**, 5502 (1971).

(5) G. Hirayama, *J. Chem. Phys.*, **42**, 3163 (1965).

(6) For a recent discussion of the validity of the "rule of three," see J. Put and F. C. DeSchryver, *J. Amer. Chem. Soc.*, **95**, 137 (1973).

(7) H. E. Zimmerman and P. S. Mariano, *J. Amer. Chem. Soc.*, **91**, 1718 (1969).

(8) H. E. Zimmerman and A. C. Pratt, *ibid.*, **92**, 1409 (1970); H. E. Zimmerman and G. A. Epling, *ibid.*, **94**, 8749 (1972).

(9) G. L. Trittle, Ph.D. Thesis, Purdue University, 1966. We thank Professor H. C. Brown for making spectra of 2-MBN available to us.

(10) *Anal.* Calcd for $C_{12}H_{12}$: C, 92.26; H, 7.74. Found: C, 92.42; H, 7.55.

(11) We thank Professor Roger Hahn for a sample of II and spectra of III.

(12) A fourth product is formed in trace amounts (ϕ = 1.73 × 10^{-3}) and has not yet been isolated in sufficient quantity to permit its unambiguous identification.

(13) J. W. Wilt, L. L. Maravetz and J. F. Zawadzki, *J. Org. Chem.*, **31**, 3018 (1966).

(14) R. C. Hahn and L. J. Rothman, *J. Amer. Chem. Soc.*, **91**, 2409 (1969).

(15) Aldrich Chemical Co.

was photolyzed under identical conditions, the products were isolated by glpc, and the location of the deuterium atoms was ascertained by nmr (see Scheme II).[16]

It has already been noted that 2-MBN can be viewed as a di-π-methane system and the formation of I and II is explicable when approached in this manner. A plausible mechanistic scheme is presented below. Aryl olefin bonding (to give IV) and rearomatization (to give V), is unextraordinary and a typical di-π-methane sequence. However, because the normal di-π-methane product VII is so highly strained, formation of the carbene VI and its rearrangement to 1-methylene-3-vinylindan (I) is preferred. We propose that VII is formed in small amounts, either from V and/or VI, but reopens to VIII which gives, *via* a 1,2-hydrogen shift, the observed minor product II. Support for Scheme II comes from studies[17] of dibenznorbornadienes, where a photoproduct analogous to I has been isolated and a postulated carbene analogous to VI has been trapped.

With regard to the excited state responsible for the photochemistry of 2-MBN, we can only say at this time that both the excited *singlet* (67% reduction in fluorescence intensity ($\phi_f = 0.08$) and lifetime ($\tau = 4.5$ nsec) relative to a dihydro derivative) and *triplet* (no observable phosphorescence) give evidence for bichromophoric interaction.[18] However, it is worth noting that the excited singlet interaction, though marked, is considerably less than the 96% reduction in emission and lifetime observed with 6-phenyl-2-hexene (where the requisite "sandwich" arrangement of chromophores is feasible) and the complete lack of fluorescence in benznorbornadiene[19] (where both p lobes of the olefin are in a position to interact with the benzene ring).[20]

Acknowledgments. We are grateful to the National Science Foundation for support of this research and to Professor Fred Lytle for assistance in the lifetime measurements.

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[16] (a) The dideuterated analog of I showed the triplets due to H_7 (δ 5.04) and H_8 (δ 5.45) to be absent. (b) An analysis of the nmr spectrum of II follows from the discussion of H. Tanida, K. Tori, and K. Kitahonoki (*J. Amer. Chem. Soc.*, **89**, 3212 (1967)) on the nmr spectra of the benzo[6,7]bicyclo[3.2.1]octa-2,6-dien-4-yl system (symbols are from the reference but note the numbering change). The assignments are as follows: aromatic hydrogens δ 7.0–7.4 (m), δ_5 3.31 (m, $J_{54_{eq}} = 1.9$, $J_{54_{ax}} = 5.0$, $J_{58_n} = 4.5$, $J_{58_x} = 0.9$, $J_{53} = 1.2$ Hz), $\delta_{4_{ax}}$ 2.59 (a doublet of a pair of overlapping triplets, $J_{4_{ax}4_{eq}} = 18.0$, $J_{4_{ax}3} = 3.0$, $J_{4_{ax}2} = 3.0$ Hz), $\delta_{4_{eq}}$ (also a doublet of a pair of overlapping triplets, but with each peak split by W-plan coupling to H_{8_n}; $J_{4_{eq}3} = 3.4$, $J_{4_{eq}2} = 1.9$, $J_{4_{eq}8_n} = 0.8$ Hz), δ_3 5.24 (m, $J_{32} = 9.5$ Hz), δ_2 6.15 (m, $J_{12} = 6.4$, $J_{28_n} < 1$ Hz), δ_1 3.27 (multiplet superimposed on H_5, $J_{18_n} = 4.5$ Hz), δ_{8_n} 2.34 (overlapping doublet of triplets, $J_{8_x8_n} = 10.0$ Hz), δ_{8_x} 2.05 (doublet). The dideuterated analog of II showed the absence of H_2 and the absence of one bridgehead proton at $\delta \sim 3.3$. The missing proton was assigned as H_1 because the 5-Hz coupling between H_5 and $H_{4_{ax}}$ is retained. The 3.0-Hz coupling of $H_{4_{ax}}$ to H_2 has been lost, as would be expected.

[17] J. Ipaktschi, *Chem. Ber.*, **105**, 1989 (1972). The trapping experiment was done with a 7-spiro derivative of dibenznorbornadiene.

[18] For a discussion of a coupling of the chromophores, and the ORD spectrum of 2-MBN, see D. J. Sandman and K. Mislow, *J. Amer. Chem. Soc.*, **91**, 645 (1969). See also W. H. Inskeep, D. W. Miles, and H. Eyring, *ibid.*, **92**, 3866 (1970).

[19] J. R. Edman, *J. Amer. Chem. Soc.*, **91**, 7103 (1969).

[20] Attempts to sensitize the reaction with acetone have so far been without success.

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Book Reviews

Progress in Solid State Chemistry. Volume 7. Edited by H. Reiss and J. O. Caldin. Pergamon Press, Inc., New York, N. Y. 1972. xi + 273 pp. $30.00.

This volume is a continuation of the series presenting advances in fundamental and technological areas of solid-state chemistry. The volume covers a broad spectrum of topics, written by various experts at different degrees of depth and breadth. Despite these inevitable variations, a common thread of critical presentation, present interest, and significance runs throughout the six articles of the volume. The theory of the thermoelectric power of solid-state cells with electrolytes displaying mixed ionic and electronic conduction is presented in the first article by C. Wagner. As far as this reviewer is concerned, this is the first time that the calculation of the Soret effect for these dual conduction systems is carried out. The derivations are developed to the point of permitting the comparison with experimental results for cases of prevailing cationic or anionic transport. In the second article, M. B. Panish and M. Ilegems examine the phase equilibria of III–V ternary systems. They present calculations of the phase boundaries and the detailed description of several temperature–composition diagrams. The computational approach followed is that of treating a ternary system as a mixture of two binaries. This is a somewhat pragmatic approach that gives generally quite satisfactory results.

In the third article, A. V. Novoselova, V. P. Zlomanov, S. G. Karbanov, O. V. Matveyev, and A. M. Gas'kov review binary phase and composition diagrams of Ge, Sn, and Pb chalcogenides. They include X-ray reflection data, unit cell parameters, partial pressures, enthalpies and entropies of formation, and equilibrium constants for various defect reactions. The topic of liquid phase epitaxy is treated in the fourth article by L. R. Dawson. Interest in this area stems primarily from determining the conditions for optimum growth of semiconductor materials. The article discusses factors influencing epitaxial deposition from solution, reviews the advantages of the method, and considers the application to specific growth systems with emphasis on III–V semiconductors.

In the fifth article, J. T. Kummer reviews several physicochemical properties of β-Al_2O_3 with emphasis on electrochemical characteristics, chiefly ion-exchange behavior in molten salts, aqueous and nonaqueous solutions, ionic diffusion, ionic conductivity, and dielectric loss. Throughout the discussion, the role of the crystal structure and of the atomic arrangements in β-Al_2O_3 on the electrochemical properties is emphasized. The article is noteworthy for its clarity, critical outlook, and emphasis on practical applications. The last article by L. A. Bursill and B. G. Hyde is an account of the structure, texture, mechanism, and thermodynamics of crystallographic shear in titanium oxides. Experimental and theoretical structural studies on oxides with various stoichiometries ($1.66 \leq O/Ti \leq 2$) together with pictorial models and various reactions for the production of crystallographic shear are shown and analyzed. The article is critically written and it extends to cover the presence of hysteresis loops, the effect of texture on phase thermodynamics. Researchers currently active in the above areas, as well as those interested in the broader fields of solid state chemistry, would find the book very useful indeed.

G. Parravano, *University of Michigan*

Molecules and Life. By Joseph S. Fruton. John Wiley and Sons, Inc., New York, N. Y. 1972. x + 579 pp. $19.95.

Fruton traces the development of the chemical basis for biological processes in this historical treatise. The period covered by the