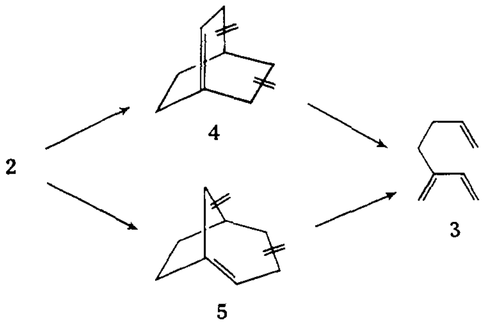
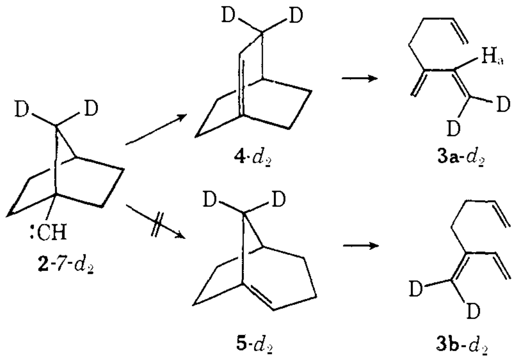
ABC spectrum[9] at τ 3.71 (myrcene shows a similar pattern at τ 3.70).[8] H_b is a multiplet at higher field and is clearly coupled to the methylene protons. Myrcene has no analogous resonance in its spectrum[8] as here H_b is no longer part of a vinyl group and appears at higher field.

In principle, carbene **2** could undergo ring expansion in two ways to give **4** and/or **5**. Either or both of these could give the observed triene **3** through a retro Diels–Alder reaction. Both **4**[10] and **5**[11] have been trapped

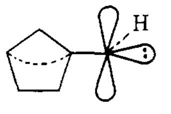


previously, but neither has been isolated. We have resolved the structural problem by noting that pyrolysis of **1**-7-d_2 (1.5 deuterium/molecule at the 7 position[12]) gave a triene whose 100-MHz nmr spectrum differed from that of **3** in two important ways. First the signal for the terminal methylene protons at τ 4.79–5.21 was reduced by 1.5 protons. Second, and most importantly, the 4-line signal for H_a was collapsed to a broad singlet. Only 3a-d_2, the product of decomposition of **4**-d_2, can



explain this spectrum and thus ring expansion must have taken place through the short bridge.[13]

Such an event is not unexpected, even though **4** contains a trans double bond in a six-membered ring and **5** a trans double bond in a seven-membered ring. One would expect ring expansion to begin by interaction of the empty p orbital with a pair of electrons in an adjacent bond, and thus carbonium ion **6** appears to be a good model for the carbene **2**. Ions such as **6** are known to undergo ring expansion to bridgehead species, and expansion through the short bridge is the normal route.[14]



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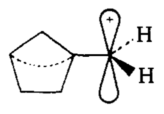

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We are hopeful of extending this method to even smaller systems[15] and think that prospects for eventual isolation of **4** and similar bridgehead olefins are bright.

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[9] For analyses of ABC spectra and diene systems see: R. T. Hobgood, Jr. and J. H. Goldstein, *J. Mol. Spectrosc.*, **12**, 76 (1964), A. A. Bothner-By and R. K. Harris, *J. Amer. Chem. Soc.*, 87, 3445 (1965), and C. N. Banwell and N. Sheppard, *Mol. Phys.*, **3**, 351 (1960).

[10] H. H. Grootveld, C. Blomberg, and F. Bickelhaupt, *J. Chem. Soc., Chem. Commun.*, 542 (1973). We thank Professor Bickelhaupt for communication of results prior to publication and for stimulating conversations.

[11] J. R. Wiseman and J. A. Chong, *J. Amer. Chem. Soc.*, **94**, 8627 (1972).

[12] Checked by examination of Eu(dpm)$_3$ shifted spectra in the related alcohol.

[13] We cannot exclude small amounts of ring expansion through the long bridge. An upper limit of *ca.* 15% could have gone undetected.

[14] R. C. Fort, Jr., "Carbonium Ions," Vol. IV, G. A. Olah and P. v. R. Schleyer, Ed., Wiley, New York, N. Y., 1973, p 1783.

[15] This method has been applied to a synthesis of 3-homoadamantene, M. Fărcaşiu, D. Fărcaşiu, R. T. Conlin, M. Jones, Jr., and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **95**, 8207 (1973).

[16] Petroleum Research Fund Postdoctoral Fellow, 1972–1973.

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A Photochemical 1,3-Sigmatropic Vinyl Rearrangement. Mechanistic and Exploratory Organic Photochemistry[1]

Sir:

In our earlier studies[2] we have reported the occurrence of the di-π-methane rearrangement of acyclic 1,4-dienes *via* the singlet excited state and have noted that it is one of the more ubiquitous photochemical processes. For a majority of these molecules the triplet is too rapidly deactivated to give observable photochemistry.

One di-π-methane reactant whose singlet photochemistry we have previously described is 1,1,4-triphenyl-3,3-dimethyl-1,4-pentadiene (**1**).[2b] We now (1) report a relatively efficient rearrangement of the triplet of triphenylpentadiene **1**,[2d] (2) note that this rearrangement formally involves a 1,3-vinyl migration, (3) provide evidence favoring one of the two potential routes, (4) comment on the failure of a potential free rotor to inhibit triplet reactivity, and (5) describe an unusual selectivity controlling the steady state between reactant and product.

Preparative irradiation of 500 mg of triphenylpentadiene **1** in *tert*-butyl alcohol, using a 450-W medium pressure lamp with Pyrex filter and acetophenone sensitizer,[3] afforded 242 mg of 1,1,4-triphenyl-5-methyl-1,4-hexadiene (**2**) along with 139 mg of recovered reactant **1**.

The structure of triphenylhexadiene **2** was suggested by its spectrum which contained a vinyl triplet at τ 4.03 (J = 7.0 Hz, 1 H), a methylene doublet at 6.82 (J = 7.0 Hz, 2 H), and two methyl singlets at 8.31 and 8.48. This assignment was confirmed by synthesis from methyl 4-phenyl-5-methyl-4-hexenoate (**3**) using phenylmagnesium bromide followed by thionyl chloride–pyridine elimination of the resulting carbinol.

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[1] (a) This is paper LXXXII of the series. (b) For the previous publication note H. E. Zimmerman, D. P. Werthemann, and K. S. Kamm, *J. Amer. Chem. Soc.*, **95**, 4606 (1973).

[2] (a) See H. E. Zimmerman and P. S. Mariano, *J. Amer. Chem. Soc.*, **91**, 1718 (1969) as a leading reference; (b) H. E. Zimmerman and A. A. Baum, *ibid.*, **93**, 3646 (1971); (c) note S. S. Hixson, P. S. Mariano, and H. E. Zimmerman, *Chem. Rev.*, 73, 531 (1973); (d) the previous report[2b] of the lack of triplet reactivity of pentadiene 1 was in error.

[3] Complete experimental detail will be given in our full paper; all compounds analyzed satisfactorily.

Methyl ester **3** was obtained by reaction of 1-bromo-2-phenyl-3-methyl-2-butene with diethyl sodiomalonate followed by saponification, decarboxylation, and re-esterification with diazomethane.[3]

The quantum yield of the sensitized rearrangement of triphenylpentadiene **1** to triphenylhexadiene **2** was determined using the Black Box apparatus.[3,4] A value of $\phi = 0.0179$ was obtained.

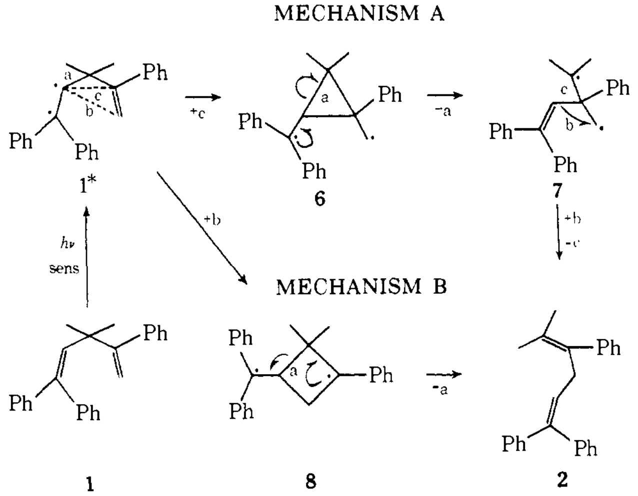
Contrasting with the sensitized result, the direct irradiation of triphenylpentadiene **1** gives a di-π-methane rearrangement as reported.[2b] Thus, the present rearrangement to give triphenylhexadiene **2** is a triplet process as opposed to the singlet di-π-methane rearrangement.

Interestingly, the sensitized irradiation of triphenylhexadiene **2** revealed that it did not revert to triphenylpentadiene **1**. The steady state was found to favor the formation of **2** minimally by 100:1.

The rearrangement of triphenylpentadiene **1** to triphenylhexadiene **2** is formally a 1,3-sigmatropic vinyl migration. One precedent is found in the formation of exceedingly minor quantities of 1,1,5,5-tetraphenyl-3,3-dimethyl-1,4-pentadiene (**4**) from sensitized irradiation of 1,1,3,3-tetraphenyl-5-methyl-1,4-hexadiene (**5**).[5]

Two reaction mechanisms are depicted in Chart I for conversion of **1** to **2**.

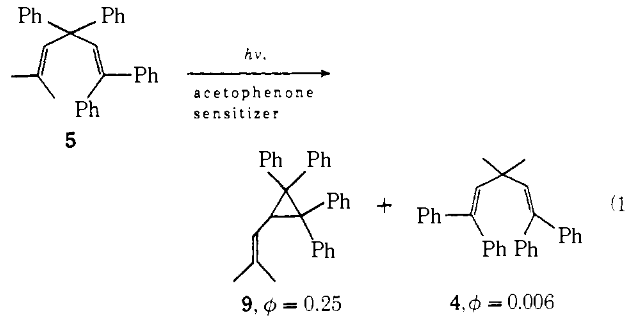
Chart I. Possible Pathways for Rearrangement of Pentadiene **1**



Mechanism A begins with the ordinary vinyl–vinyl bridging of the di-π-methane rearrangement (*i.e.*, formation of bond c). However, the second step involves fission of bond a (note structure **6**) which is the reverse of the regioselectivity normally observed in the di-π-methane mechanism and which normally seems to be energetically unfavorable.[2,5] Were this process to occur, a 1,2-vinyl migration in biradical **7** would afford product **2**; it is recognized that any such 1,2-vinyl migration occurs by first bridging of the π system to the odd electron center (*i.e.*, bond b formation) followed by scission of bond c, the σ bond holding the vinyl group to the biradical moiety. Thus, bond c is formed only to be lost subsequently in this mechanism.

Mechanism B proceeds by 2,5 bridging of the excited state (*i.e.* with formation of bond b) followed by loss of bond a in diradical **8**.

Inspection of Chart I reveals that the two mechanisms are skeletally equivalent. Both involve net formation of bond b and loss of bond a. Mechanism A seems less likely because of the energetically unfavorable mode of three-ring opening in species **6** and also because species such as **7** are known[2,5] to afford vinylcyclopropanes and none was presently found. Our previous research[5] showed that when the triplet acyclic di-π-methane rearrangement does occur, it proceeds with the normal regiospecificity in ring opening. Thus vinylcyclopropane **9** is the sole di-π-methane product formed from tetraphenylhexadiene **5** on sensitized photolysis (note eq 1). Also, that 1,3-vinyl migration is the major reaction course in the case of triphenylpentadiene **1** but was only a very minor product (eq 1) in the case of tetraphenylhexadiene **5** seems explicable in terms of the extra delocalization afforded by the phenyl at C-4 in biradical **8** (note Chart I). Another factor may be the easier steric access of the terminal $=CH_2$ of triphenylpentadiene **1** compared with the terminal isopropylidene of tetraphenylhexadiene **5** in approaching the second π bond.



One further point is of general importance. The excited triplet has a potential free rotor (*i.e.*, the $=CH_2$ moiety) and we have pointed out that such moieties provide a route for rapid triplet energy dissipation.[2] Although this was discussed in connection with the di-π-methane rearrangement, the effect should be more general. That the reaction presently encountered does occur, despite the presence of a free rotor, is therefore of interest. Accordingly, it is important to recognize that the presence of a free rotor does not guarantee lack of molecular reactivity. Rather, inhibition of photochemistry is expected only if the triplet reactions available to the molecule are not sufficiently rapid so as to compete successfully with this mechanism of radiationless decay.[6] In fact, the greater success in free rotor inhibition of triplet processes relative to singlet pathways merely reflects the greater rate constants often encountered in unimolecular singlet rearrangement processes.

A last intriguing feature is the lack of reversibility of the 1,3-vinyl migration. Thus, photolysis of triphenylhexadiene **2** with acetophenone sensitizer gave no de-

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(4) H. E. Zimmerman, *Mol. Photochem.*, **3**, 281 (1971).

(5) H. E. Zimmerman, R. J. Boettcher, and W. Braig, *J. Amer. Chem. Soc.*, **95**, 2155 (1973).

(6) Thus a number of di-π-methane rearrangements have been observed from the triplet despite the presence of potential free rotors.[7] These examples can be seen to merely indicate that the di-π-methane rearrangements must be unusually rapid in these triplets and no inconsistency is present.

(7) (a) K. G. Hancock and D. A. Dickinson, *J. Amer. Chem. Soc.*, **94**, 4396 (1972); (b) P. S. Mariano and J. K. Ko, *J. Amer. Chem. Soc.*, **94**, 1766 (1972); (c) M. J. Bullivant and G. Pattenden, *J. Chem. Soc., Chem. Commun.*, 864 (1972); (d) Z. Goldschmidt and A. S. Kende, *Tetrahedron Lett.*, 4625 (1971).

tectable (*i.e.*, quantum yield $< 10^{-4}$) reaction to form triphenylpentadiene **1**. This can be understood as a preference for fission of bond a rather than bond b in biradical **8** to give triphenylhexadiene **2**. Also, the lack of central methyl substitution in triphenylhexadiene **2** and the presence of terminal methyl substitution makes the 2,5 bonding more unlikely from entropy and steric vantage points.

Acknowledgment. Support of this research by National Institutes of Health Grant No. GM 07487 and the U. S. Army Research Office (Durham) is gratefully acknowledged. Similarly, National Science Foundation and Wisconsin Alumni Research Foundation predoctoral fellowships to L. M. T. are appreciated. Thanks are due undergraduate research students Sue D. Boettger and Mark R. Johnson.

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*Book Reviews**

Soviet-Urethane Technology. Volume I. Soviet Progress in Polyurethanes Series. Edited by ARTHUR M. SCHILLER (American Cyanamid Co.). Technomic Publishing Co., Inc., Westport, Conn. 1973. vii + 258 pp. $35.00.

"Soviet-Urethane Technology" should be a welcome addition to the library of polymer chemists and plastics engineers. The book provides a rare insight into some of the Soviet research projects carried on at the Institute of the Chemistry of High-Molecular Compounds of the Ukrainian Soviet Socialist Republic and the All-Union Scientific-Research Institute of Synthetic Rubber.

Although the papers presented in this book are generally of high quality, several sections deserve special attention.

Section II is an excellent summary of some synthetic work which could benefit those doing research in the area of flame-retardant fibers for woven garments.

Section IV could prove valuable to those engaged in producing more thermally stable materials. Thermal stability and dissociation temperatures are discussed under several headings. These would also benefit those scientists and engineers doing work in the area of flammability. The papers which deserve special attention are those which describe methods of increasing thermal stability (Chapter 30), effect of structure on dissociation temperatures (Chapters 31 and 33), thermo-oxidative stability (Chapter 32), and kinetics of dissociation (Chapters 34 and 35).

In Chapters 24 and 25, uv stability of the high molecular weight compounds is an important fact to be considered in coating research.

There is one shortcoming of the book—some of the most interesting articles are too short.

Calvin J. Benning, *International Paper Company*

Molecular Evolution: Prebiological and Biological. Edited by D. L. ROHLFING (University of South Carolina) and A. I. OPARIN (A. N. Bakh Institute of Biochemistry, Academy of Sciences of the USSR). Plenum Press, New York, N. Y. 1972. xix + 481 pp. $24.00.

"Molecular Evolution: Prebiological and Biological" is a collection of 35 contributed essays and is dedicated to Sidney W. Fox. The 58 contributors cover 10 nations and many disciplines. Category breakdown of contributions in the Table of Contents assigns five (70 pages) to History and Scope, four (50 pages) to Thermodynamic and Philosophical Considerations, four (42 pages) to Micromolecules, twelve (172 pages) to Macromolecules, seven (100 pages) to Protocells and Cells, two (18 pages) to Academic Aspects, and one (3 pages) to Man and Evolution. This accolade to Fox reveals the impact his contributions have made. It is recommended to those who have followed developments in the area and want to be informed on philosophical speculations as well as reviews of experimental data.

J. H. Boyer, *University of Illinois Chicago Circle Campus*

The Porous Structure of Catalysts and Transport Process in Heterogeneous Catalysis. The Fourth International Congress on Catalysis. Symposium III. Novosibirsk. Edited by G. K. BORESKOV (Academy of Sciences USSR). Akademiai Kiadó, Budapest. 1972. 498 pp. $14.00.

This volume presents the twenty-seven papers (with discussion) and the text of the plenary lecture given by Professor Boreskov at this symposium, held subsequent to the Fourth International Congress on Catalysis at Novosibirsk in 1968. In spite of the four years lag between presentation and publication, those with research or teaching interests in this field will find this volume most valuable. The papers encompass a wide range of topics including experimental and theoretical studies of catalyst intraparticle transport properties, surface diffusion in adsorbate layers, and the theory of diffusion and reaction in terms of both activity and selectivity effects. Most valuable are the papers presenting experimental data on transport effects in various catalytic systems such as V_2O_5–SO_2 oxidation, SiO_2–Al_2O_3–butene isomerization, supported Ni–aromatics hydrogenation, and others. It is notable that in most of these experimental studies the authors report poor agreement between their theoretical estimates of transport limitation and the actual results.

John B. Butt, *Northwestern University*

Advances in Chemical Physics. Volume XXIII. Edited by I. PRIGOGINE (University of Brussels) and STUART A. RICE (University of Chicago). John Wiley and Sons, New York, N. Y. 1973. x + 358 pp. $22.50.

Continuing the distinguished tradition of this series of review volumes, this latest book contains six timely articles on selected aspects of chemical physics. The articles and their authors are: "Recombination of Gaseous Ions," by Bruce H. Mahan, a topic of importance to those interested in electrical discharges, flames, etc.; "Vibration → Vibration Energy Transfer," by C. Bradley Moore, again an important process in discharges and many other nonequilibrium systems; "ESCA," by David A. Shirley, a thorough review of chemical shifts in core-electron binding energies, their interpretation and calculation by *ab initio* and semiempirical procedures, and a discussion of multiplet splittings in paramagnetic molecules and magnetially ordered solids; "Ab Initio Calculations on Small Molecules," by J. C. Browne and F. A. Matsen, a review concentrating on computational progress on He_2^+, excited states of He_2, and LiH; "Picosecond Spectroscopy and Molecular Relaxation," by P. M. Rentzepis, a description of experimental procedures together with results for several organic molecules; and "Some Modern Aspects of Exciton Theory," by Michael R. Philpott, a detailed and lengthy (114 pp) account of the various theories of single exciton states with zero spin (singlets). The volume is highly recommended to those researchers who wish to become more familiar with the rapid advances in these areas of chemical physics.

Lawrence L. Lohr, Jr., *University of Michigan*

NMR: Basic Principles and Progress/Grundlagen und Forschritte. Volume 7. By C. W. HILBERS, C. MACLEAN (Vrij Universiteit), and H. PFEIFER (Karl Marx Universität). Springer-Verlag, New York, N. Y. 1972. 153 pp. $24.80.

This volume continues the philosophy, developed in earlier volumes of this series (except for Volume 4), of presenting material

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* Unsigned book reviews are by the Book Review Editor.