

REARRANGEMENTS AND INTERCONVERSIONS OF COMPOUNDS OF THE FORMULA $(\text{CH})_n^{1a}$

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I. Introduction

That part of hydrocarbon chemistry dealing with isomers composed of only methine units has burgeoned in recent years, as even a casual examination of the indexes of *Chemical Abstracts* will reveal. The reasons for this are many but include the psychological impact of the prediction^{2,3} and rapid discovery^{4,5} of bullvalene and the chemist's surprise and joy at

the range of isomers closely related in both an energetic and conceptual sense. The behavior of the $(\text{CH})_{10}$'s has been mimicked by the other $(\text{CH})_n$'s, and the entire area has become a fertile ground for the discovery of new compounds and reactions. Indispensable to the understanding and, we are afraid, the rationalization of many reactions relating these compounds has been the advent of the idea that orbital symmetry⁶ plays an important, often determining, role in deciding what reaction paths a molecule may take.

Among the consequences of rapid expansion in an area of interest to many people is the appearance of the work in fragments. Ideally the fragments would be largely independent, nonoverlapping, and would build upon each other, in a more-or-less orderly sequence. Of course in practice the converse is true, and the journals have been flooded with an overlapping, often contradictory, and certainly not orderly succession of short articles. Full papers are conspicuously rare. So, it seems to us, the time is ripe for a review, and being among those guilty of some of the aforementioned crimes we herewith provide one. In it we shall try above all to be orderly and to sort out, or at least point out, the confusion.

We have organized the review by dealing with each class of $(\text{CH})_n$ in turn and, within each class, with reactions of each of its members. An exception to this procedure has been made in the section on $(\text{CH})_{10}$'s where the number of compounds known is so great and their reactions so varied and complex that a more general approach has been taken with organization more "by reaction" than "by compound." In all sections but the one on $(\text{CH})_{10}$'s we have used both the trivial and systematic names. The systematic names become so cumbersome in the larger compounds that we have kept entirely to the trivial names except for those most egregiously ill-conceived.

The early review by Balaban⁷ has been very useful to us and remains the excellent compendium of $(\text{CH})_n$ isomers. Other reviews include that of Kunichika⁸ on the products of the Reppe synthesis, Schröder and Oth^{8a} on bullvalene, van Tamelen and Burkoth⁹ on cyclodecapentaenes, and Leone and Schleyer¹⁰ on degenerate carbonium ions in general and $(\text{CH})_n^+$'s in particular.

(1) (a) Contribution No. 2904 from the UCLA Chemistry Department; (b) UCLA; (c) Princeton University.

(2) W. von E. Doering, *Zh. Vses. Khim. Obshchest.*, **7**, 308 (1962).

(3) (a) W. von E. Doering and W. R. Roth, *Tetrahedron*, **19**, 715 (1963);

(b) *Angew. Chem. Int. Ed. Engl.*, **2**, 115 (1963).

(4) G. Schröder, *Angew. Chem.*, **75**, 722 (1963).

(5) G. Schröder, *Chem. Ber.*, **97**, 3140 (1964).

(6) R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry," Academic Press, New York, N. Y., 1970.

(7) A. T. Balaban, *Rev. Roum. Chim.*, **11**, 1097 (1966).

(8) S. Kunichika, *Bull. Inst. Chem. Res., Kyoto Univ.*, **31**, 323 (1953).

(8a) G. Schröder and J. F. M. Oth, *Angew. Chem., Int. Ed. Engl.*, **6**, 414 (1967).

(9) T. L. Burkoth and E. E. van Tamelen in "Nonbenzenoid Aromatics," J. P. Snyder, Ed., Academic Press, New York, N. Y., 1969.

(10) R. E. Leone and P. v. R. Schleyer, *Angew. Chem. Int. Ed. Engl.*, **9**, 860 (1970).

II. (CH)₄

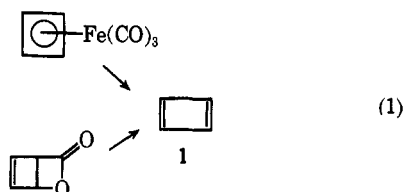
Cyclobutadiene (**1**) and tetrahedrane (tricyclo[1.1.0.0^{2,4}]butane, **2**) constitute a complete set of all possible compounds of



molecular formula (CH)₄. The intense interest generated by these two highly strained hydrocarbons is reflected in numerous theoretical calculations of energy relationships on the (CH)₄ energy surface¹¹ and in a comprehensive monograph¹² devoted entirely to the former and its derivatives.

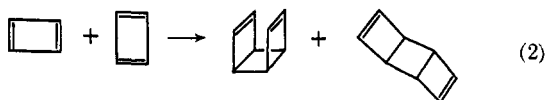
A. CYCLOBUTADIENE

Until its existence as a free, monomolecular species was recently demonstrated, cyclobutadiene stood for decades as a challenge to the synthetic chemist.¹² The free hydrocarbon has now been generated from its iron tricarbonyl complex¹³ by flash photolysis¹⁴ and from photo- α -pyrone by flash vacuum pyrolysis¹⁵ (eq 1). Passage of cyclobutadiene so generated



through the gas phase prior to mass spectrometric detection or cryo-quench in a liquid nitrogen trap argues strongly for the existence of free **1**. Other reports¹⁶ of cyclobutadiene in the gas phase have been put in doubt by these and related experiments.¹⁷

Although stable at 77°K,^{18,19} cyclobutadiene dimerizes rapidly at normal temperatures in the absence of trapping agents²⁰ (eq 2). The dimerization process may be viewed as a



Diels-Alder reaction in complete analogy with the familiar dimerization of cyclopentadiene,²¹ a simple homolog. Preferential formation of the syn dimer^{18,19,20} conforms with orbital

(11) R. J. Buenker and S. D. Peyerimhoff, *J. Amer. Chem. Soc.*, **91**, 4342 (1969), and references cited therein.

(12) M. P. Cava and M. J. Mitchell, "Cyclobutadiene and Related Compounds," Academic Press, New York, N. Y., 1967.

(13) G. F. Emerson, L. Watts, and R. Pettit, *J. Amer. Chem. Soc.*, **87**, 131 (1965).

(14) W. J. R. Tyerman, M. Kato, P. Kebarle, S. Masamune, O. P. Strausz, and H. E. Gunning, *Chem. Commun.*, 497 (1967).

(15) E. Hedaya, R. D. Miller, D. W. McNeil, P. F. D'Angelo, and P. Schissel, *J. Amer. Chem. Soc.*, **91**, 1875 (1969).

(16) (a) L. Watts, J. D. Fitzpatrick, and R. Pettit, *ibid.*, **87**, 3253 (1965); (b) R. Pettit, *Pure Appl. Chem.*, **17**, 253 (1969); (c) P. H. Li and H. A. McGee, Jr., *Chem. Commun.*, 592 (1969); (d) *Chem. Eng. News*, **47**, 51 (April 21, 1969).

(17) E. Hedaya, I. S. Krull, R. D. Miller, M. E. Kent, P. F. D'Angelo, and P. Schissel, *J. Amer. Chem. Soc.*, **91**, 6880 (1969).

(18) G. Maier and U. Mende, *Tetrahedron Lett.*, 3155 (1969).

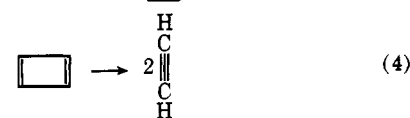
(19) R. D. Miller and E. Hedaya, *J. Amer. Chem. Soc.*, **91**, 1540 (1969).

(20) L. Watts, J. D. Fitzpatrick, and R. Pettit, *ibid.*, **88**, 623 (1966).

(21) A. Wasserman, "Diels-Alder Reactions," Elsevier, New York, N. Y., 1965.

symmetry predictions²² and the more empirical Alder endo addition rule.²³

Unimolecular reactions of cyclobutadiene are still unknown. Simple bond-switching (eq 3), a process well documented for cyclooctatetraene (see section IV.A), remains to be demonstrated for **1**.^{23a} Likewise, fragmentation to two molecules of acetylene (eq 4) finds no experimental support. The interesting possibility also remains that puckering of **1** might lead to the tricyclic isomer **2** (eq 5). Reversibility of this isomerization could interconvert 1,2- and 1,3-disubstituted cyclobutadienes. The reactions in eq 4 and 5 can be concerted only in the excited state.²⁴



B. TETRAHEDRANE

The extraordinarily tortured tetrahedrane molecule has proven even more elusive than its monocyclic isomer. Many approaches have been tested as possible synthetic routes, but most have failed to demonstrate even the fleeting existence of the compact tricyclobutane ring system.²⁵⁻²⁶ Early reports of a tricarboxylic acid derivative^{25,26} were subsequently discredited,³¹ as were those of an alleged diphenyl derivative.²⁷⁻²⁹

Nevertheless, evidence has begun to accumulate which implicates tetrahedrane as a transient intermediate in the formation of acetylene from several different precursors.³⁷⁻⁴⁰

(22) Reference 6, p 147.

(23) K. Alder and G. Stein, *Angew. Chem.*, **50**, 510 (1937).

(23a) Experimental evidence for this process may soon be forthcoming: R. Pettit (unpublished), cited by M. J. S. Dewar, M. C. Kohn, and N. Trinajstić, *J. Amer. Chem. Soc.*, **93**, 3437 (1971).

(24) R. Hoffmann and R. B. Woodward, *Accounts Chem. Res.*, **1**, 17 (1968), and references cited therein.

(25) R. M. Beesley and J. F. Thorpe, *Proc. Chem. Soc., London*, **29**, 346 (1913).

(26) R. M. Beesley and J. F. Thorpe, *J. Chem. Soc.*, **117**, 591 (1920).

(27) S. Masamune and M. Kato, *J. Amer. Chem. Soc.*, **87**, 4190 (1965).

(28) S. Masamune and M. Kato, *ibid.*, **88**, 610 (1966).

(29) E. H. White, G. E. Maier, R. Graeve, U. Zirngibl, and E. W. Friend, *ibid.*, **88**, 611 (1966).

(30) S. H. Bauer and P. Jeffers, *ibid.*, **87**, 3278 (1965).

(31) H. O. Larson and R. B. Woodward, *Chem. Ind. (London)*, 193 (1959).

(32) S. A. Kandil and R. E. Dessy, *J. Amer. Chem. Soc.*, **88**, 3027 (1966).

(33) G. L. Closs and V. N. M. Rao, *ibid.*, **88**, 4116 (1966).

(34) H. W. Chang, A. Lautzenheiser, and A. P. Wolf, *Tetrahedron Lett.*, 6295 (1966).

(35) E. H. White and A. A. F. Sieber, *ibid.*, 2713 (1967).

(36) H. A. Staab, H. Mack, and E. Wehinger, *ibid.*, 1465 (1968).

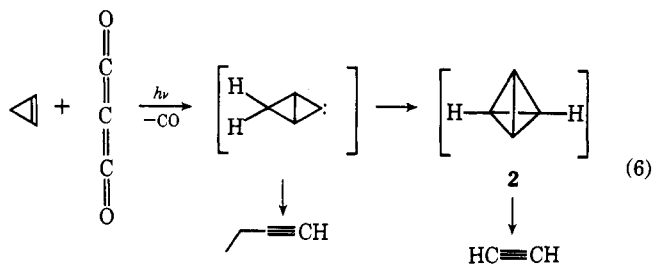
(37) H.-K. Lee, *Daehan Hwahak Hwojee*, **13** (4), 347 (1969); *Chem. Abstr.*, **73**, 87340q (1970).

(38) H. Ona, H. Yamaguchi, and S. Masamune, *J. Amer. Chem. Soc.*, **92**, 7495 (1970).

(39) R. F. Peterson, Jr., R. T. K. Baker, and R. L. Wolfgang, *Tetrahedron Lett.*, 4749 (1969).

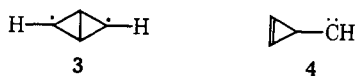
(40) P. B. Shevlin and A. P. Wolf, *J. Amer. Chem. Soc.*, **92**, 406 (1970); correction, *ibid.*, **92**, 5291 (1970).

Most compelling are the recent reports of carbon suboxide photolysis in the presence of cyclopropene^{39, 40} (eq 6). De-



tailed studies⁴⁰ employing deuterium-labeled cyclopropene and ¹⁴C-labeled carbon suboxide gave several different isotopically labeled acetylenes, the relative abundances of which are difficult to explain except by postulation of a symmetrical tetrahedrane intermediate.

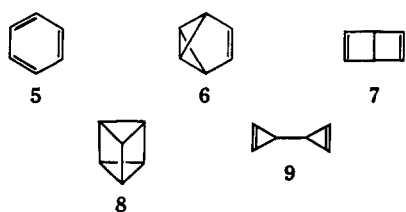
Concerted fragmentation of **2** to two molecules of acetylene is symmetry forbidden^{24, 39} although probably favorable thermodynamically.¹¹ Single bond rupture to give diradical **3** has been favored as the preliminary step.⁴⁰ The carbene **4** is



probably not an intermediate in acetylene formation since generation of similar species by other means^{28, 29, 33} leads to cyclobutadiene-derived products, and none is reported in these reactions.³⁷⁻⁴⁰ Direct rearrangement to cyclobutadiene (eq 5) likewise appears not to occur.

III. (CH)₆

The set of all possible (CH)₆ structural isomers has only five members: benzene (**5**), benzvalene (tricyclo[3.1.0.0^{2,6}]hexene, **6**), Dewar benzene (bicyclo[2.2.0]hexa-2,5-diene, **7**), prismane (tetracyclo[2.2.0.0^{2,6}.0^{3,5}]hexane, **8**), and bicyclopropenyl (**9**).



Prior to 1960, virtually nothing was known about any of these except benzene. By 1970, however, the preparation, purification, characterization, and much of the chemistry of many derivatives of all five had been reported. The complex chronology of multiple simultaneous explorations on the (CH)₆ energy surface during the decade of the 60's, although historically fascinating, is deemphasized here in order to focus more clearly on the attendant chemistry.

A. PHOTOLYSIS OF BENZENE

The irradiation of neat, liquid benzene at 2537 Å gives low yields of Dewar benzene,^{41, 42} benzvalene,^{41-44a} and fulvene

(41) H. R. Ward and J. S. Wishnok, *J. Amer. Chem. Soc.*, **90**, 1085 (1968).

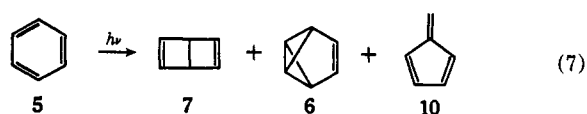
(42) H. R. Ward and J. S. Wishnok, *ibid.*, **90**, 5353 (1968).

(43) K. E. Wilzbach, J. S. Ritscher, and L. Kaplan, *ibid.*, **89**, 1031 (1967).

(44) L. Kaplan and K. E. Wilzbach, *ibid.*, **90**, 3291 (1968).

(44a) Benzvalene has recently been synthesized by a more rational route: T. J. Katz, E. J. Wang, and N. Acton, *ibid.*, **93**, 3782 (1971).

(**10**)⁴¹⁻⁴⁷ (1:5:2, respectively), all of which have been isolated and identified (eq 7).



Conservation of orbital symmetry allows concerted formation of all three products in eq 7 from the excited states of benzene,²⁴ but multistep mechanisms cannot be dismissed. In particular, the diradical **11** has been proposed⁴⁶ as a possi-

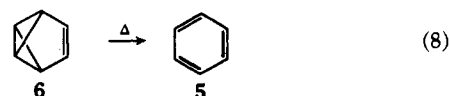


ble intermediate in the formation of **6** and **10**, although compelling evidence is lacking.

The product of benzene vapor photolysis at 1849 Å, once thought^{49, 50} to be benzvalene, was subsequently identified^{42, 51-53} as fulvene.

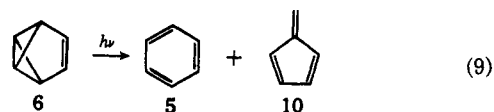
B. BENZVALENE

At room temperature, benzvalene reverts quantitatively to benzene with a half-life of about 10 days⁴³ (eq 8). This aroma-



tization is symmetry forbidden²⁴ and likely proceeds *via* diradical **11**. Pure samples of benzvalene are reported to explode.^{44a}

Vapor-phase photolysis of benzvalene⁴⁴ at 2537 Å gives both benzene and fulvene (3:1, respectively, eq 9), in agreement with the early view⁴⁷ that benzvalene might be an intermediate



in the formation of fulvene from electronically excited benzene. The observation⁴³ that fulvene is initially formed at a slower rate than benzvalene during benzene photolysis (eq 7) further supports this hypothesis.

The reversible photochemical isomerization of benzene to benzvalene can account for the well-documented light-induced

(45) J. M. Blair and D. Bryce-Smith, *Proc. Chem. Soc., London*, 287 (1957).

(46) H. J. F. Angus, J. M. Blair, and D. Bryce-Smith, *J. Chem. Soc.*, 2003 (1960).

(47) D. Bryce-Smith and H. C. Longuet-Higgins, *Chem. Commun.*, 593 (1966).

(48) D. Bryce-Smith, *Pure Appl. Chem.*, **16**, 47 (1968).

(49) K. Shindo and S. Lipsky, *J. Chem. Phys.*, **45**, 2292 (1966).

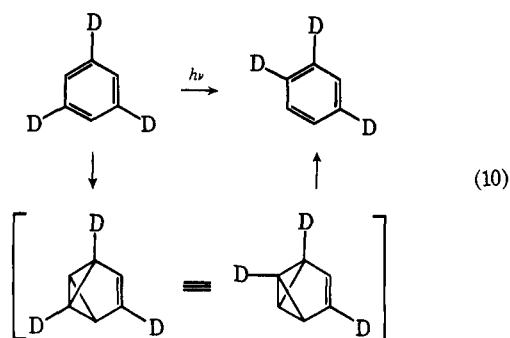
(50) J. K. Foote, M. H. Mallon, and J. N. Pitts, Jr., *J. Amer. Chem. Soc.*, **88**, 3698 (1966).

(51) H. R. Ward, J. S. Wishnok, and P. D. Sherman, Jr., *ibid.*, **89**, 162 (1967).

(52) L. Kaplan and K. E. Wilzbach, *ibid.*, **89**, 1030 (1967).

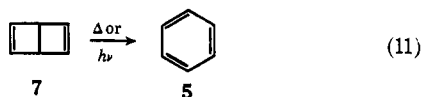
(53) L. Kaplan, S. P. Walch, and K. E. Wilzbach, *ibid.*, **90**, 5646 (1968).

scrambling of ring atoms in labeled benzene⁶⁴⁻⁶¹ as in 1,3,5-trideuteriobenzene⁵⁹ (eq 10).



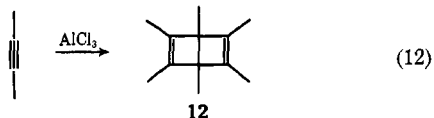
C. DEWAR BENZENE

Several years before its identification among the products of benzene photolysis, Dewar benzene was synthesized^{62,63} by a clever choice of conventional reactions and became the first valence bond isomer of benzene ever isolated. Isomerization of Dewar benzene to benzene is clean and quantitative both thermally^{62,63} and photochemically⁶³ (eq 11). At room tem-



perature, the aromatization half-life is about 2 days.^{62,63} That this strained diene exists at all is surely a consequence of the lack of symmetry-allowed concerted pathways for the ground-state opening to benzene.^{24,63,64}

The simplicity of these rearrangements (eq 11) is disappointing in some respects and encouraged many investigators to study the chemistry of closely related systems. Discovery of the remarkable trimerization of 2-butyne in the presence of aluminum chloride⁶⁵ (eq 12) has made hexamethyl(Dewar



benzene) (12) more readily available than the parent hydrocarbon and provided an excellent substrate for further detailed studies.

(54) K. Kirk, Ph.D. Thesis, University of Wisconsin, 1963.

(55) K. E. Wilzbach and L. Kaplan, *J. Amer. Chem. Soc.*, **86**, 2307 (1964).

(56) A. W. Burgstahler and P.-L. Chien, *ibid.*, **86**, 2940 (1964).

(57) A. W. Burgstahler, P.-L. Chien, and M. O. Abdel-Rahman, *ibid.*, **86**, 5281 (1964).

(58) L. Kaplan, K. E. Wilzbach, W. G. Brown, and S. S. Yang, *ibid.*, **87**, 675 (1965).

(59) K. E. Wilzbach, A. L. Harkness, and L. Kaplan, *ibid.*, **90**, 1116 (1968).

(60) I. E. Den Besten, L. Kaplan, and K. E. Wilzbach, *ibid.*, **90**, 5868 (1968).

(61) U. Mende, J. L. Laseter, and G. W. Griffin, *Tetrahedron Lett.*, 3747 (1970).

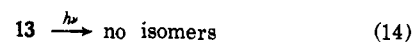
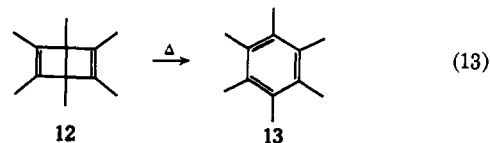
(62) E. E. van Tamelen and S. P. Pappas, *J. Amer. Chem. Soc.*, **85**, 3297 (1963).

(63) E. E. van Tamelen, S. P. Pappas, and K. L. Kirk, *ibid.*, **93**, 6092 (1971).

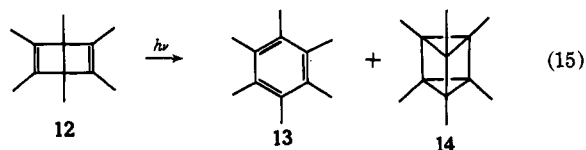
(64) Reference 6, p 174.

(65) W. Schaefer, *Angew. Chem., Int. Ed. Engl.*, **5**, 669 (1966).

On heating, 12 aromatizes slowly but cleanly⁶⁶⁻⁷⁰ (eq 13) with a half-life of 105 hr at 120°. In contrast to the unsubstituted system, however, hexamethylbenzene (13) affords no detectable isomers on irradiation at 2537 Å (eq 14).⁷¹



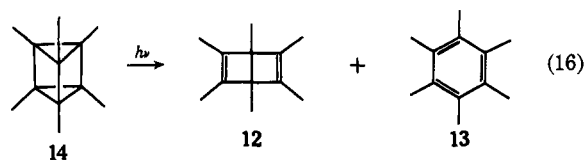
The real reward for investigations of hexamethyl(Dewar benzene) came from the photochemistry. Irradiation of 12 leads not only to aromatization but also to hexamethylprismane^{66,71} (14, eq 15), the product of symmetry-allowed,



intramolecular $\pi_2s + \pi_2s$ cycloaddition. This reaction has not been observed for the parent hydrocarbon,⁶³ nor has the (CH)₆ prismane ever been isolated.

D. PRISMANE

By a striking coincidence, all three isomers in eq 15 absorb light equally well at the wavelength of irradiation⁶⁶ (ϵ ca. 100 at 2537 Å)! One should not be surprised, therefore, to learn that the saturated hydrocarbon 14 also suffers photoisomerization⁷¹ at 2537 Å to a mixture of the same three isomers (eq 16). Whether the aromatic isomer 13 is formed in



a single, concerted step or exclusively *via* the Dewar benzene 12 remains unanswered.

The reluctance of hexamethylprismane to unfold thermally to its aromatic counterpart^{66,68-72} in a process exothermic by more than 90 kcal/mol^{68,69} must qualify among the supreme examples of the powerful restrictions imposed by the principle of conservation of orbital symmetry.⁷³ The half-life of hexamethylprismane at 100° is fully 2 hr! Detailed kinetic analysis⁶⁸⁻⁷⁰ reveals the simultaneous operation of two mechanisms for aromatization of 14. One proceeds *via* 12 which accumulates during the reaction while the other passes through hexamethylbenzvalene (15) which does not accumulate but can be detected by nmr^{68,69} (eq 17). Roughly half of the aro-

(66) W. Schaefer, R. Criegee, R. Askani, and H. Gruener, *ibid.*, **6**, 78 (1967).

(67) W. Schaefer and H. Hellmann, *ibid.*, **6**, 518 (1967).

(68) J. F. M. Oth, *Recl. Trav. Chim. Pays-Bas*, **87**, 1185 (1968).

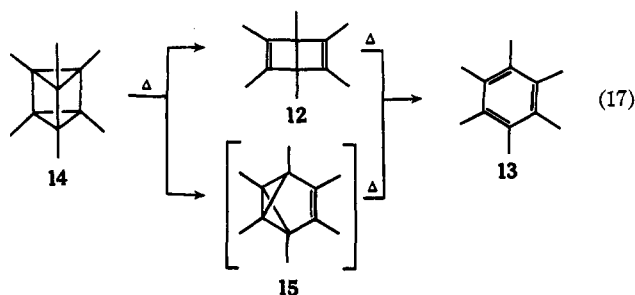
(69) J. F. M. Oth, *Angew. Chem., Int. Ed. Engl.*, **7**, 646 (1968).

(70) W. Adam and J. C. Chang, *Int. J. Chem. Kinet.*, **1**, 487 (1969).

(71) D. M. Lemal and J. P. Lokensgard, *J. Amer. Chem. Soc.*, **88**, 5934 (1966).

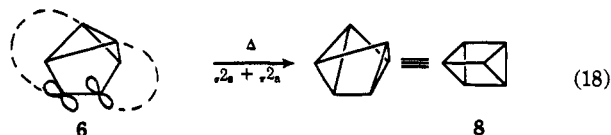
(72) H. Hogeveen and H. C. Volger, *Chem. Commun.*, 1133 (1967).

(73) Reference 6, p 107.



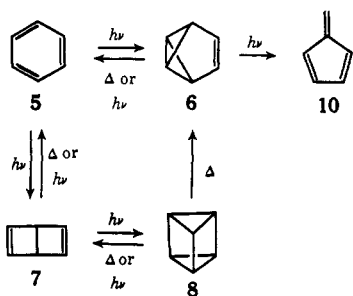
matic product is formed by each pathway,^{66, 68-70} a slight preference being shown for the benzvalene intermediate.

Although absent for the prismane to Dewar benzene isomerization, a symmetry-allowed, concerted ground-state pathway can be imagined for the conversion of prismane to benzvalene. These bonding changes are best illustrated for the reverse reaction as in eq 18.



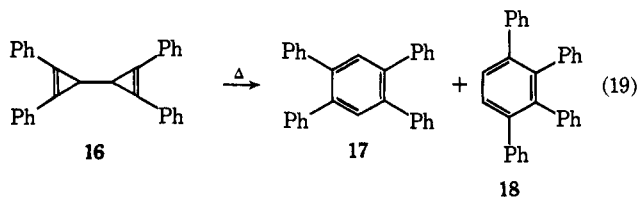
Scheme I summarizes all the foregoing observations

Scheme I
Valence-Bond Isomerism of (CH)₆ and (CCH₃)₆ Systems



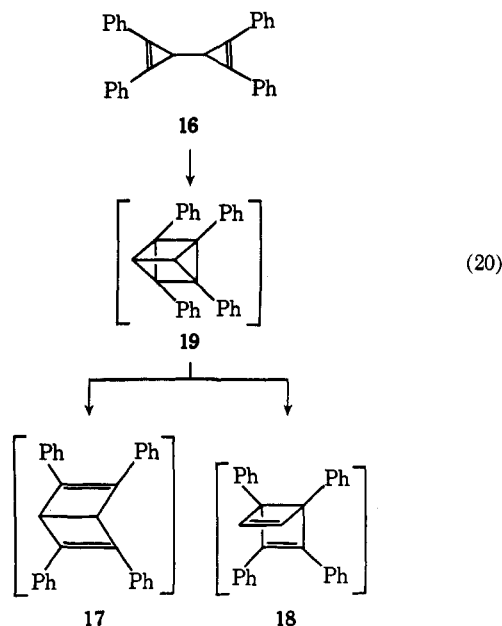
E. BICYCLOPROPENYL

Only phenyl-substituted derivatives of bicyclopropenyl have been reported,⁷⁴⁻⁷⁶ and all isomerize⁷⁶ to substituted benzenes both thermally and photochemically. The tetraphenyl derivative **16**, for example, rearranges on heating at 135° for 1 week to a 10:1 mixture of **17** and **18** (eq 19).



The major product (**17**), in which the two unsubstituted carbon atoms no longer share a σ bond, clearly indicates that aromatization of **16** is not a simple process. A three-step

mechanism which satisfactorily accounts for both products has been suggested⁷⁶ (eq 20), although no intermediates could be observed.⁷⁶



Each of the reactions in eq 20 is symmetry forbidden in the ground state. All but the first, however, have been demonstrated under milder conditions for the corresponding hexamethyl derivatives (see sections III.C and D). Perhaps more disturbing is the realization that hexamethylprismane aromatizes preferentially *via* a benzvalene intermediate (see section III.D) and that the benzvalene isomers expected from **19** cannot lead to the major product (**17**). Equation 20 could still be correct if the benzvalene pathway plays a negligible role in aromatization of **19**.

F. OTHER REARRANGEMENTS

Most of the isomerizations in the preceding sections have also been reported for numerous polysubstituted compounds such as the poly-*tert*-butyl,^{80, 77-79} polyfluoro,⁸⁰⁻⁸⁸ polyperfluoroalkyl,⁸⁷⁻⁸⁹ combinations of these,^{80, 82, 90-93} and others.⁹⁴⁻¹⁰¹

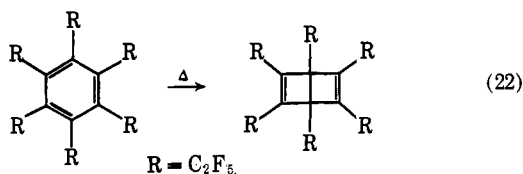
- (77) E. E. van Tamelen and S. P. Pappas, *ibid.*, **84**, 3789 (1962).
 (78) K. E. Wilzbach and L. Kaplan, *ibid.*, **87**, 4004 (1965).
 (79) E. M. Arnett and J. M. Bollinger, *Tetrahedron Lett.*, 3803 (1964).
 (80) G. Camaggi, F. Gozzo, and G. Cevidalli, *Chem. Commun.*, 313 (1966).
 (81) I. Haller, *J. Amer. Chem. Soc.*, **88**, 2070 (1966).
 (81a) G. P. Semeluk and R. D. S. Stevens, *Chem. Commun.*, 1720 (1970).
 (82) L. Cavalli, *J. Chem. Soc. B*, 384 (1967).
 (83) J. Fajer and D. R. MacKenzie, *J. Phys. Chem.*, **71**, 784 (1967).
 (84) I. Haller, *J. Chem. Phys.*, **47**, 1117 (1967).
 (85) E. Ratajczak and A. F. Trotman-Dickenson, *J. Chem. Soc. A*, 509 (1968).
 (86) E. Ratajczak, *Rocz. Chem.*, **44**, 447 (1970).
 (87) M. G. Barlow, R. N. Haszeldine, and R. Hubbard, *Chem. Commun.*, 202 (1969).
 (88) E. D. Clifton, W. T. Flowers, and R. N. Haszeldine, *ibid.*, 1216 (1969).
 (89) D. M. Lemal, J. V. Staros, and V. Austel, *J. Amer. Chem. Soc.*, **91**, 3373 (1969).
 (90) H. G. Viehe, R. Merényi, J. F. M. Oth, J. R. Senders, and P. Valange, *Angew. Chem., Int. Ed. Engl.*, **3**, 755 (1964).
 (91) H. G. Viehe, *Chem. Eng. News*, **42** (49), 38 (1964).
 (92) H. G. Viehe, *Angew. Chem., Int. Ed. Engl.*, **4**, 746 (1965).
 (93) G. Camaggi and F. Gozzo, *J. Chem. Soc. C*, 489 (1969).
 (94) R. Criegee and F. Zanker, *Angew. Chem., Int. Ed. Engl.*, **3**, 695 (1964).

(74) R. Breslow and P. Gal, *J. Amer. Chem. Soc.*, **81**, 4747 (1959).

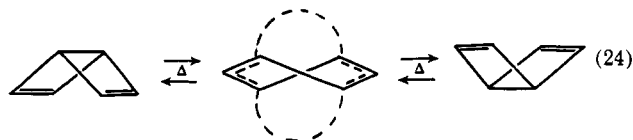
(75) R. Breslow in "Molecular Rearrangements," Part I, P. de Mayo, Ed., Interscience, New York, N. Y., 1963, pp 243-245.

(76) R. Breslow, P. Gal, H. W. Chang, and L. J. Altman, *J. Amer. Chem. Soc.*, **87**, 5139 (1965).

Many predate and are more dramatic than those chosen here, but all are more distantly related to the parent $(\text{CH})_8$ systems. Nevertheless, these derivatives offer the only examples of certain molecular rearrangements. For example, the symmetry-allowed [1,3] sigmatropic automerization from which benzvalene gets its name⁹² has been demonstrated^{60,102} only for the tri-*tert*-butyl derivative (eq 21). Also in a process unknown for any other derivative of benzene, perfluorohexaethylbenzene cyclizes to the pure Dewar benzene isomer on vacuum pyrolysis at 400° (eq 22).⁸⁸



Finally we might allude to the degenerate Cope rearrangements in eq 23⁷⁶ and 24,¹⁰³ both of which remain unexemplified.



IV. $(\text{CH})_8$

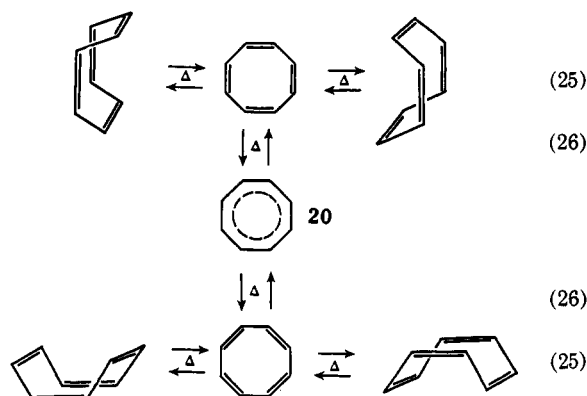
Of the 20 possible members in the $(\text{CH})_8$ family,⁷ cyclooctatetraene is the best known and most thoroughly studied.¹⁰⁴ In fact, prior to 1960 the only other members known were the dimers of cyclobutadiene. As with the benzene isomers, however, the decade following 1960 saw the birth of a substantial fraction of remaining family members and the development of their complicated consanguinity.

A. CYCLOOCTATETRAENE AND BICYCLO[4.2.0]OCTA-2,4,7-TRIENE

1. Thermal Chemistry

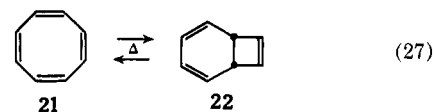
The eight trigonal carbon atoms of cyclooctatetraene force the molecule to assume a tub-shaped conformation. By increasing the internal angle at each carbon atom to 135°, however, a strained, planar conformation with alternating

single and double bonds can be achieved. This high-energy form can then collapse to either the original or the inverted tub conformation (eq 25). Alternatively, bond switching *via* the antiaromatic species **20** leads to another planar cyclooctatetraene (eq 26) which can also collapse to two tub conformations. In the absence of a label, all four tub conformations are equivalent by virtue of their S_4 symmetry.



By analyzing the temperature-dependent nmr spectrum of the cyclooctatetraene ¹³C-H satellite, Anet¹⁰⁵ determined a value of 13.7 kcal/mol for the activation energy of bond switching at -10°. This figure varies markedly among substituted cyclooctatetraenes.¹⁰⁶⁻¹¹⁰ Ring inversion, as one might expect, is slightly more facile than bond switching in those derivatives where both processes have been studied.^{106,109}

In addition to undergoing these conformational and π -bonding changes, cyclooctatetraene (**21**) also rapidly tautomerizes to bicyclo[4.2.0]octa-2,4,7-triene (**22**) at ordinary temperatures (eq 27). An activation enthalpy of 28.1 kcal/mol



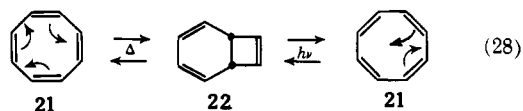
for the transannular ring closure has been determined¹¹¹⁻¹¹⁴ by a classic application of the principle of kinetic competition.¹¹⁴ An activation energy of 18.7 kcal/mol has been determined¹¹⁵ for the reverse process at 0° by using triene **22** independently synthesized^{115,116} at low temperatures. Ring opening of **22** proceeds cleanly at 0° with a half-life of 14 min.¹¹⁵

The tautomerism in eq 27 is particularly intriguing from the point of view of orbital symmetry conservation, for the unique

(95) G. D. Burt and R. Pettit, *Chem. Commun.*, 517 (1965).
 (96) L. Watts, J. D. Fitzpatrick, and R. Pettit, *J. Amer. Chem. Soc.*, **87**, 3253 (1965).
 (97) R. Criegee and F. Zanker, *Chem. Ber.*, **98**, 3838 (1965).
 (98) S. Masamune, K. Fukumoto, Y. Yasunari, and D. Darwish, *Tetrahedron Lett.*, 193 (1966).
 (99) R. Criegee and R. Askani, *Angew. Chem., Int. Ed. Engl.*, **5**, 519 (1966).
 (100) G. Schröder and Th. Martini, *ibid.*, **6**, 806 (1967).
 (101) R. Criegee, R. Askani, and H. Gruener, *Chem. Ber.*, **100**, 3916 (1967).
 (102) But see ref 98.
 (103) Reference 6, p 175.
 (104) G. Schröder, "Cyclooctatetraene," Verlag Chemie, Weinheim, 1965.

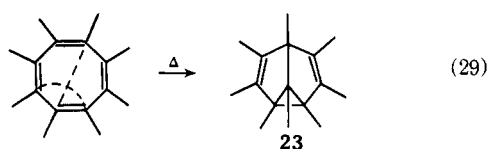
(105) F. A. L. Anet, *J. Amer. Chem. Soc.*, **84**, 671 (1962).
 (106) F. A. L. Anet, A. J. R. Bourn, and Y. S. Lin, *ibid.*, **86**, 3576 (1964).
 (107) D. E. Gwynn, G. M. Whitesides, and J. D. Roberts, *ibid.*, **87**, 2862 (1965).
 (108) J. F. M. Oth, R. Merényi, Th. Martini, and G. Schröder, *Tetrahedron Lett.*, 3087 (1966).
 (109) F. A. L. Anet and L. A. Bock, *J. Amer. Chem. Soc.*, **90**, 7130 (1968).
 (110) P. Ganis, A. Musco, and P. A. Temussi, *J. Phys. Chem.*, **73**, 3201 (1969).
 (111) R. Huisgen and F. Mietzsch, *Angew. Chem., Int. Ed. Engl.*, **3**, 83 (1964).
 (112) R. Huisgen, F. Mietzsch, G. Boche, and H. Seidl, *Chem. Soc. Spec. Publ.*, No. 19, 3 (1964).
 (113) R. Huisgen, W. E. Konz, and G. E. Gream, *J. Amer. Chem. Soc.*, **92**, 4105 (1970).
 (114) F. Mietzsch, Dissertation, University of Munich, 1965, cited in R. Huisgen, *Angew. Chem., Int. Ed. Engl.*, **9**, 754 (1970).
 (115) E. Vogel, H. Kiefer, and W. R. Roth, *ibid.*, **3**, 442 (1964).
 (116) R. Askani, *Chem. Ber.*, **102**, 3304 (1969).

arrangement of π bonds in both **21** and **22** permits the observed disrotation in both the ground state and the excited state (eq 28).¹¹⁷ For the unlabeled system, these two electro-



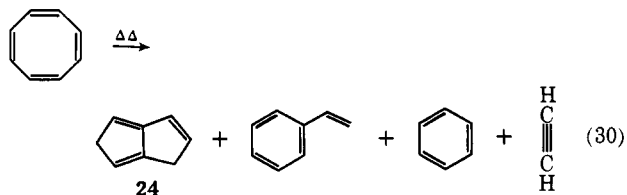
cyclic reactions are, of course, indistinguishable. Recent reports^{118,119} of substituted cyclooctatetraene tautomerizations suggest that the six-electron process is indeed preferred in the ground state, as predicted.

Yet another symmetry-allowed, thermal isomerization of cyclooctatetraene may be envisioned, this one involving the doubly antarafacial, intramolecular Diels-Alder reaction depicted in eq 29. Although never yet observed for the parent



(CH)₈ system, this atomic reorganization has been demonstrated for the octamethyl¹²⁰ and tetramethyl¹²¹ derivatives of cyclooctatetraene. The structure of octamethylsemibullvalene (tricyclo[3.3.0.0^{2,8}]octa-3,6-diene or 2a,2b,4a,4b-tetrahydrocyclopropa[*c,d*]pentalene, **23**) was assigned incorrectly in the early reports of this reaction,¹²²⁻¹²⁵ but the resulting confusion has since subsided.¹²⁰

Heating of unsubstituted cyclooctatetraene at ordinary temperatures leads primarily to dimers and higher oligomers.¹⁰⁴ Flash pyrolysis^{126,127} at 400-650°, on the other hand, gives substantial amounts of dihydropentalene (**24**), styrene, benzene, and acetylene (eq 30). The relative yields vary with temperature.



A semibullvalene intermediate analogous to **23** may be involved in the formation of **24**, although the diradical **25**, which differs from this only by the degree of 2,8 bonding, accounts equally well for the observed transformation. The aromatic products are probably derived from the bicyclic tautomer **22** via the diradical **26**; concerted fragmentation is symmetry forbidden.

(117) Reference 6, p 63.

(118) I. W. McCay and R. N. Warrener, *Tetrahedron Lett.*, 4779 (1970).

(119) I. W. McCay and R. N. Warrener, *ibid.*, 4783 (1970).

(120) R. Criegee and R. Askani, *Angew. Chem., Int. Ed. Engl.*, 7, 537 (1968).

(121) H. E. Zimmerman, and H. Iwamura, *J. Amer. Chem. Soc.*, 92, 2015 (1970).

(122) R. Criegee, *Angew. Chem., Int. Ed. Engl.*, 1, 519 (1962).

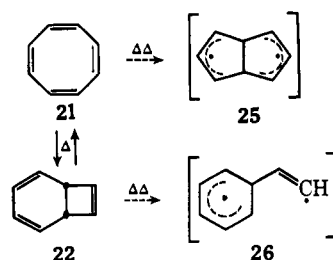
(123) R. Criegee, *Rev. Chim., Acad. Repub. Pop Roum.*, 7, 771 (1962).

(124) R. Criegee, W.-D. Wirth, W. Engel, and H. A. Brune, *Chem. Ber.*, 96, 2230 (1963).

(125) R. Criegee, *Bull. Soc. Chim. Fr.*, 1 (1965).

(126) M. Jones, Jr., and L. O. Schwab, *J. Amer. Chem. Soc.*, 90, 6549 (1968).

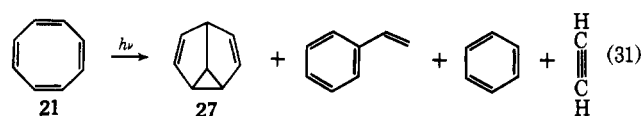
(127) I. Tanaka, *J. Chem. Soc. Jap., Pure Chem. Sect.*, 75, 212 (1954); *Chem. Abstr.*, 48, 4984c (1954).



Products related to **24** appear to have been isolated also in the (CCH₃)₈^{120,122,123,128,129} and (CCl)₈¹³⁰⁻¹³² series. 1,8-Dicarbomethoxycyclooctatetraene rearranges at 350-450° to isomeric cyclooctatetraenes.¹³³

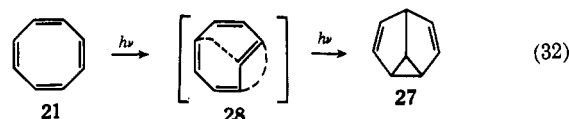
2. Photochemistry

The photolysis of cyclooctatetraene has been studied in the gas phase,¹³⁴⁻¹³⁷ in solution,^{121,138,139} and in a frozen matrix.^{140,141} Styrene, benzene, and acetylene can be found in each case, and from solution photolysis at -60° semibullvalene (**27**) can also be isolated.^{121,139} Acetone sensitization



accelerates the semibullvalene formation,^{121,139} thus implicating a triplet intermediate.

How is it that the products of photolysis correspond so closely to those of pyrolysis (*cf.* eq 30 and 31)? Initial photoisomerization of *all-cis*-cyclooctatetraene to the unknown *trans,cis,cis,cis* isomer (**28**) followed by symmetry-allowed photocyclization has been postulated¹²¹ to explain the formation of semibullvalene (eq 32). Excellent support for this hypothesis can be found in the studies of 1,2,4,7-tetraphenylcyclooctatetraene photolysis,¹⁴² from which an isomer of probable structure **29** has been isolated. At 25°, **29** reverts quantitatively to the *all-cis* isomer with a half-life of 18 hr (eq 33).



(128) R. Criegee and G. Schröder, *Justus Liebigs Ann. Chem.*, 623, 1 (1959).

(129) R. Criegee and G. Schröder, *Angew. Chem.*, 71, 70 (1959).

(130) A. Roedig, *ibid.*, *Int. Ed. Engl.*, 8, 150 (1969).

(131) A. Roedig, R. Helm, R. West, and R. M. Smith, *Tetrahedron Lett.*, 2137 (1969).

(132) R. Criegee and R. Huber, *Chem. Ber.*, 103, 1862 (1970).

(133) M. Jones, Jr., L. O. Schwab, and J. Ralph, unpublished work.

(134) I. Tanaka, S. Miyakawa, and S. Shida, *Bull. Chem. Soc. Jap.*, 24, 119 (1951).

(135) I. Tanaka and M. Okuda, *J. Chem. Phys.*, 22, 1780 (1954).

(136) H. Yamazaki and S. Shida, *ibid.*, 24, 1278 (1956).

(137) H. Yamazaki, *Bull. Chem. Soc. Jap.*, 31, 677 (1958).

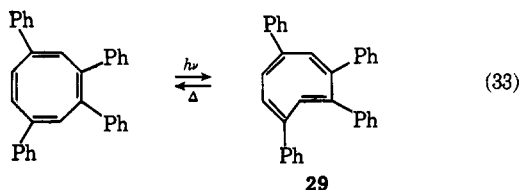
(138) G. J. Fonken, *Chem. Ind. (London)*, 1625 (1963).

(139) H. E. Zimmerman and H. Iwamura, *J. Amer. Chem. Soc.*, 90, 4763 (1968).

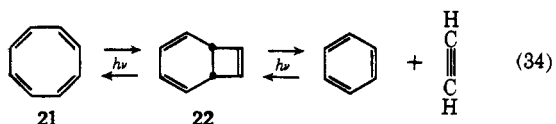
(140) S. Leach, *J. Chim. Phys. Physicochim. Biol.*, 55, 714 (1958).

(141) E. Migirdicyan and S. Leach, *Bull. Soc. Chim. Belg.*, 71, 845 (1962).

(142) E. H. White, E. W. Friend, Jr., R. L. Stern, and H. Maskill, *J. Amer. Chem. Soc.*, 91, 523 (1969).



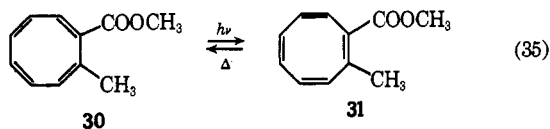
The aromatic products in eq 31 are likely derived from the bicyclic tautomer **22**. Several workers studying the photolysis of cyclooctatetraene have reported^{136-138,141} the rapid accumulation of an intermediate with λ_{max} corresponding roughly to that of authentic **22**^{115,116} (eq 34; cf. eq 28). Furthermore,



irradiation of **22**¹²¹ and several of its derivatives^{118,143} leads cleanly to benzenoid products (eq 34).

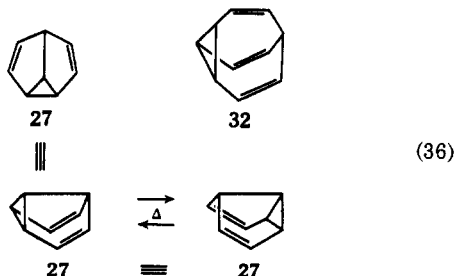
The reverse of this sequence has also been demonstrated (eq 34). Thus photolysis of benzene with acetylene¹⁴⁴⁻¹⁴⁶ or other alkynes^{106,144-150} affords **21** or its derivatives. The bicyclic intermediate has been trapped in at least one case.¹⁴⁶

Ultraviolet light also induces bond switching in the substituted cyclooctatetraene **30**.¹⁰⁹ Isomer **30** predominates in the mixture of **30** and **31** at thermal equilibrium whereas irradiation at low temperatures establishes a photostationary state in which **31** is the more abundant (eq 35). Warming reestablishes the original isomer distribution.



B. SEMIBULLVALENE

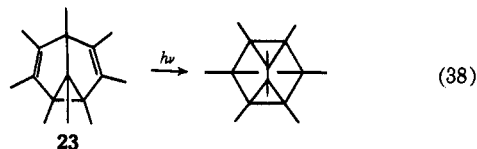
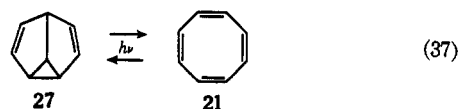
Semibullvalene (**27**), so named¹⁵¹ because of its structural similarity to bullvalene²⁻⁵ (**32**), undergoes a rapidly reversible degenerate Cope rearrangement even at temperatures below -100° ^{151,152} (eq 36). An activation energy of 6.4 kcal/mol



- (143) L. A. Paquette and J. C. Philips, *Chem. Commun.*, 680 (1969).
 (144) D. Bryce-Smith and J. E. Lodge, *Proc. Chem. Soc., London*, 333 (1961).
 (145) D. Bryce-Smith and J. E. Lodge, *J. Chem. Soc.*, 695 (1963).
 (146) D. Bryce-Smith, A. Gilbert, and J. Grzonka, *Chem. Commun.*, 498 (1970).
 (147) E. Govenstein, Jr., and D. V. Rao, *Tetrahedron Lett.*, 148 (1961).
 (148) F. A. L. Anet and B. Gregorovich, *ibid.*, 5961 (1966).
 (149) R. S. H. Liu and C. G. Krespan, *J. Org. Chem.*, **34**, 1271 (1969).
 (150) R. D. Miller and V. Y. Abrayts, *Tetrahedron Lett.*, 891 (1971).
 (151) H. E. Zimmerman and G. L. Grunewald, *J. Amer. Chem. Soc.*, **88**, 183 (1966).
 (152) H. E. Zimmerman, R. W. Binkley, R. S. Givens, G. L. Grunewald, and M. A. Sherwin, *ibid.*, **91**, 3316 (1969).

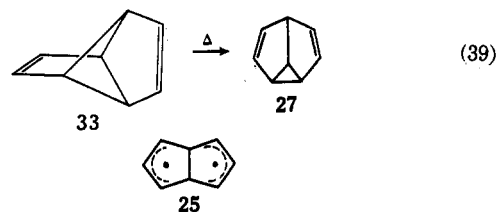
has been reported for automerization of octamethylsemibullvalene at -141° ,¹⁵³ but none has yet been determined for the parent (CH)₈.

Photolysis of **27** gives cyclooctatetraene^{121,151,152} (eq 37) in a process which is formally the reverse of eq 32. In the photostationary state at -60° with acetone sensitizer, **27** and **21** are present in a ratio of 1:7.¹³⁹ The octamethyl derivative **23**, in contrast, undergoes intramolecular $\pi_2 + \pi_2$ cycloaddition on irradiation¹²⁰ (eq 38).



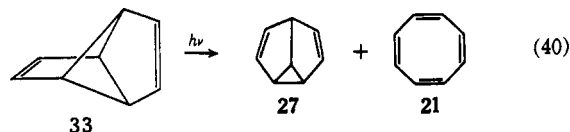
C. TRICYCLO[3.3.0.0.2,6]OCTA-3,8-DIENE

Recently the tricyclic diene **33** has been synthesized in two different laboratories.¹⁵⁴⁻¹⁵⁷ At room temperature it isomerizes rapidly¹⁵⁴⁻¹⁵⁷ to semibullvalene (**27**) in what is formally a symmetry-forbidden process (eq 39). Although no inter-



mediates have been detected during this reaction, the diradical **25**, postulated earlier in the high-temperature cyclooctatetraene-dihdropentalene rearrangement (section IV.A.1), is certainly a likely candidate.^{154,156}

At -60° , **33** is thermally stable but rearranges to **27** and **21** on direct irradiation¹⁵⁷ (eq 40). The products do not inter-

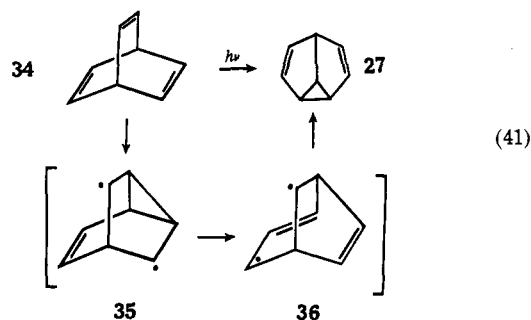


convert under these conditions in the absence of photosensitizers,^{121,139,151,152,157} and must therefore both come from **33**. Concerted rearrangement to each of the products is symmetry allowed and consistent with the lack of observable intermediates.¹⁵⁷

- (153) F. A. L. Anet and G. E. Schenck, *Tetrahedron Lett.*, 4237 (1970).
 (154) J. Meinwald and D. Schmidt, *J. Amer. Chem. Soc.*, **91**, 5877 (1969).
 (155) J. Meinwald and H. Tsuruta, *ibid.*, **91**, 5877 (1969).
 (156) H. E. Zimmerman, J. D. Robbins, and J. Schantl, *ibid.*, **91**, 5878 (1969).
 (157) J. Meinwald and H. Tsuruta, *ibid.*, **92**, 2579 (1970).

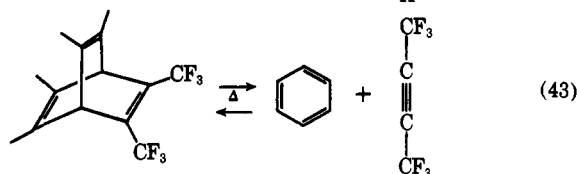
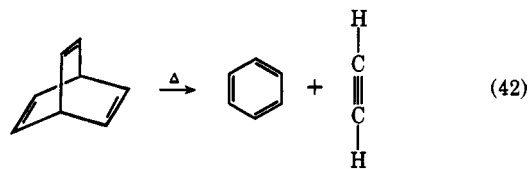
D. BARRELENE

The semibullvalene ring system is also produced by photosensitized irradiation of barrelene (bicyclo[2.2.2]octa-2,5,7-triene, **34**)^{151,152,158,169} or its derivatives^{149,160,161} (eq 41).

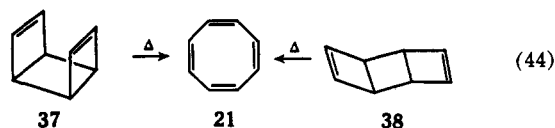


The dependence of this reaction on sensitizers has been advanced as an argument in support of triplet intermediates.¹⁵² Further insight into the mechanism has been gained from deuterium labeling studies^{152,158} which favor the intermediacy of diradicals **35** and **36**. Subsequent recognition of the generality of this photoisomerization has led to formulation of the general di- π -methane rearrangement mechanism,¹⁶² of which this is but one example.

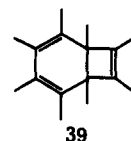
Pyrolysis of barrelene gives benzene and acetylene,¹⁶³ as one would expect (eq 42). This retrograde Diels-Alder reaction has been reported for several derivatives of barrelene, as well,^{164,165} and in some cases is reversible^{149,161,164,166-168} (eq 43).

E. TRICYCLO[4.2.0.0^{2,5}]OCTA-3,7-DIENE

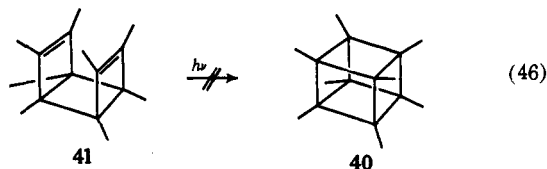
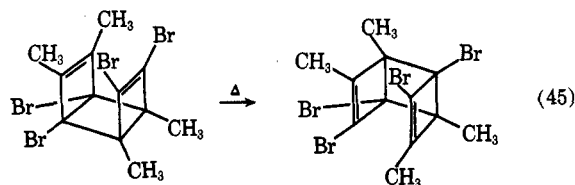
Both the syn and the anti dimer of cyclobutadiene (**37** and **38**) isomerize completely to cyclooctatetraene on heating¹⁶⁹ (eq 44), a half-life of nearly 20 min at 140° being observed in each case.



Conservation of orbital symmetry forbids concerted opening of the cyclobutene rings either simultaneously or sequentially and is likely responsible for the relative thermal stability of these strained dienes. An intermediate bicyclo[4.2.0]octa-2,4,7-triene (**39**) has been trapped¹⁷⁰ during isomerization of the *syn*-octamethyl derivative.



The proximate π bonds in **37** suggest at least two further possible reactions, neither of which has been reported for the parent (CH)₈. Cope rearrangement, which would be degenerate in the parent system, has been reported¹⁷¹ for a tetrabromo derivative (eq 45), but an attempt to prepare the cubane ring system **40** by photoinduced intramolecular cycloaddition of **41** was unsuccessful^{122,123} (eq 46).



F. CUBANE

Cubane (pentacyclo[4.2.0.0^{2,5}.0^{3,8}.0^{4,7}]octane, **42**) has been



synthesized by three different routes.¹⁷²⁻¹⁷⁴ At 200° it suffers significant decomposition,¹⁷² but neither the nature of the products nor any photochemistry has been reported.

Octaphenylcubane was at one time thought to have been isolated,¹⁷⁵ however, the structural assignment was later challenged^{176,177} and ultimately shown by X-ray diffraction

(158) H. E. Zimmerman, R. W. Binkley, R. S. Givens, and M. A. Sherwin, *J. Amer. Chem. Soc.*, **89**, 3932 (1967).

(159) H. E. Zimmerman, G. L. Grunewald, R. M. Paufler, and M. A. Sherwin, *ibid.*, **91**, 2330 (1969).

(160) R. S. H. Liu and J. R. Edman, *ibid.*, **90**, 213 (1968).

(161) R. S. H. Liu, *ibid.*, **90**, 215 (1968).

(162) H. E. Zimmerman and A. C. Pratt, *ibid.*, **92**, 6267 (1970), and references cited therein.

(163) H. E. Zimmerman and R. M. Paufler, *ibid.*, **82**, 1514 (1960).

(164) C. G. Krespan, B. C. McKusick, and T. L. Cairns, *ibid.*, **82**, 1515 (1960).

(165) C. G. Krespan, B. C. McKusick, and T. L. Cairns, *ibid.*, **83**, 3428 (1961).

(166) R. C. Cookson and J. Dance, *Tetrahedron Lett.*, 879 (1962).

(167) C. D. Weis, *J. Org. Chem.*, **28**, 74 (1963).

(168) E. Ciganek, *Tetrahedron Lett.*, 3321 (1967).

(169) M. Avram, I. G. Dinulescu, E. Marica, G. Mateescu, E. Sliam, and C. D. Nenitzescu, *Chem. Ber.*, **97**, 382 (1964).

(170) C. E. Berkoff, R. C. Cookson, J. Hudec, and R. O. Williams, *Proc. Chem. Soc., London*, 312 (1961).

(171) R. Criegee and R. Huber, *Chem. Ber.*, **103**, 1855 (1970).

(172) P. E. Eaton and T. W. Cole, Jr., *J. Amer. Chem. Soc.*, **86**, 3157 (1964).

(173) J. C. Barborak, L. Watts, and R. Pettit, *ibid.*, **88**, 1328 (1966).

(174) C. G. Chin, H. W. Cuts, and S. Masamune, *Chem. Commun.*, 880 (1966).

(175) H. H. Freedman and D. R. Petersen, *J. Amer. Chem. Soc.*, **84**, 2837 (1962).

(176) R. C. Cookson and D. W. Jones, *Proc. Chem. Soc., London*, 115 (1963).

(177) H. H. Freedman and R. S. Gohlke, *ibid.*, 249 (1963).

studies^{178,179} to be incorrect. The high-melting solid in question proved to be octaphenylcyclooctatetraene.

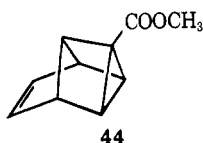
G. CUNEANE

Both cuneane (pentacyclo[3.3.0.0^{2,4}.0^{3,7}.0^{6,8}]octane, **43**)¹⁸⁰ and its octamethyl derivative¹²⁰ have been synthesized, but no unimolecular reactions of either have yet been reported.

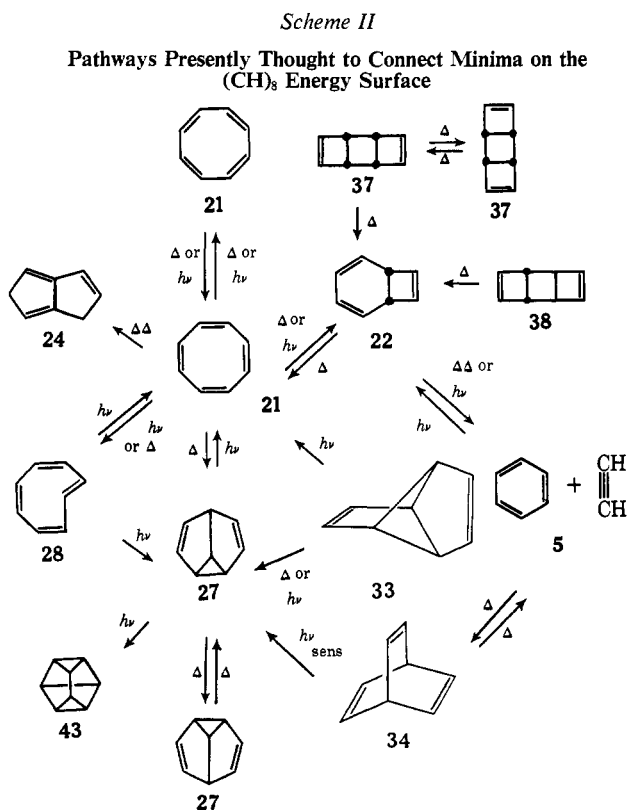


H. OTHERS

Of the many remaining possible (CH)₈ isomers,⁷ tetracyclo[3.3.0.0^{2,4}.0^{3,6}]octa-7-ene (as its 4-carbomethoxy derivative, **44**) is the only one yet prepared,¹⁸¹ and its chemistry is still unknown.



Scheme II summarizes the previous observations.



(178) H. P. Throssen, P. J. Wheatley, and H. Zeiss, *Proc. Chem. Soc., London*, 357 (1964).

(179) G. S. Pawley, W. N. Lipscomb, and H. H. Freedman, *J. Amer. Chem. Soc.*, **86**, 4725 (1964).

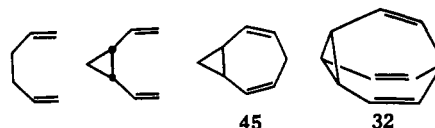
(180) L. Cassar, P. E. Eaton, and J. Halpern, *ibid.*, **92**, 6366 (1970).

(181) G. W. Klumpp, W. G. J. Rietman, and J. J. Vrieling, *ibid.*, **92**, 5266 (1970).

V. (CH)₁₀

The prediction by Doering^{2,3a} that bullvalene (**32**) would possess a fully fluxional structure and the brilliant verification by Schröder^{4,5} are the obvious foci of historical attention in this area. Nevertheless, the roots of the recent renaissance in hydrocarbon chemistry are deeper, and Doering's prediction a natural, if inspired, outgrowth of previous work.

The beginnings are really marked by the determination of the four-center structure of the transition state of the Cope rearrangement by Doering and Roth in 1962.¹⁸² The elaboration of this work to the homotropilidene rearrangement has been described,^{3,183} and it seems fair to say that comparable in importance to Schröder's synthesis of bullvalene was Roth's recognition^{3a} of the temperature-dependent nmr spectrum of homotropilidene. The conceptual transition from 1,5-hexadiene through *cis*-divinylcyclopropane and homotropilidene (**45**) to bullvalene seems straightforward today, but represents chemical creativity and experimental expertise of the highest order.



An early source of C₁₀H₁₀'s was the Reppe¹⁸⁴ synthesis of cyclooctatetraene. This polymerization of acetylene yields not only cyclooctatetraene but also several other compounds. Indeed, Reppe reported (erroneously) as early as 1946¹⁸⁵ the isolation of the "deep blue" cyclodecapentaene and 12-annulene as well. Later, two other compounds, the "orange-yellow" hydrocarbon and the "yellow" hydrocarbon, were described.¹⁸⁶ The blue compound is almost certainly azulene,¹⁸⁷ and workers in Japan, Great Britain, and the United States have found the other two to be vinylcyclooctatetraene and *cis*-1-phenylbutadiene.¹⁸⁷⁻¹⁹⁰ A review of this early work and of the question of the structures of the C₁₀ compounds, in particular, is available.⁸ We feel it possible that many fascinating compounds lurk in the residues of the Reppe synthesis, but apparently the hazards of the process have proved a sufficient deterrent to further investigation.^{190a}

A. SYNTHESSES OF (CH)₁₀'s

The reaction of cyclooctatetraene with maleic anhydride provided an entry to the first genuine (CH)₁₀ reported,¹⁹¹

(182) W. von E. Doering and W. R. Roth, *Tetrahedron*, **18**, 67 (1962).

(183) W. von E. Doering, B. M. Ferrier, E. T. Fossell, T. H. Hartenstein, M. Jones, Jr., G. Klumpp, R. M. Rubin, and M. Saunders, *ibid.*, **23**, 3943 (1967).

(184) W. Reppe, O. Schlichting, K. Klager, and T. Toepel, *Justus Liebigs Ann. Chem.*, **560**, 1 (1948).

(185) W. Reppe, *Mod. Plast.*, **23**, 169 (1946).

(186) W. Reppe, O. Schlichting, and H. Meister, *Justus Liebigs Ann. Chem.*, **560**, 93 (1948).

(187) A. C. Cope and S. W. Fenton, *J. Amer. Chem. Soc.*, **73**, 1195 (1951).

(188) N. Hagihara, *J. Chem. Soc. Jap.*, **73**, 323 (1953).

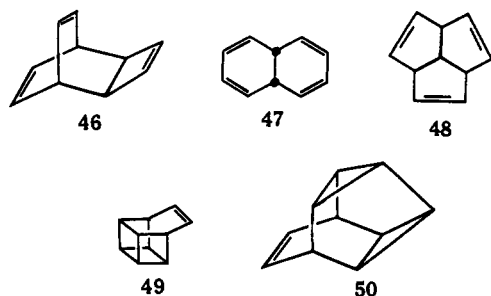
(189) L. E. Craig and C. E. Larrabee, *J. Amer. Chem. Soc.*, **73**, 1191 (1951).

(190) D. W. Withey, *J. Chem. Soc.*, 1930 (1952).

(190a) NOTE ADDED IN PROOF. The above hope is unfounded. In addition to compounds previously identified, only 1,2-dihydronaphthalene and an unidentified, but aromatic, hydrocarbon can be found in the residues of the Reppe synthesis: M. Jones, Jr., unpublished observation. We thank Professor P. v. R. Schleyer for a sample of the residues.

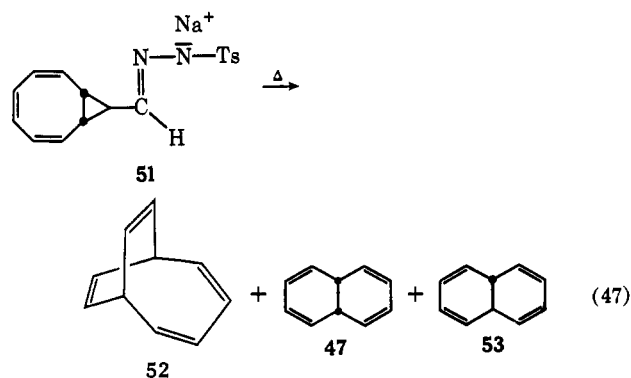
(191) M. Avram, E. Sliam, and C. D. Nenitzescu, *Justus Liebigs Ann. Chem.*, **636**, 184 (1960).

"Nenitzescu's hydrocarbon" (46). Three years later, two new isomers, bullvalene (32) and *cis*-9,10-dihydronaphthalene (47),¹⁹² appeared. In contrast to 32 and 47 which have been pivotal compounds in the mapping of the energy surface, triquinacene (48) synthesized the next year has only rarely appeared.^{193,194} "Basketene" (49) was made by two groups¹⁹⁵⁻¹⁹⁸ although one other claim is in error,¹⁹⁹ inadvertently

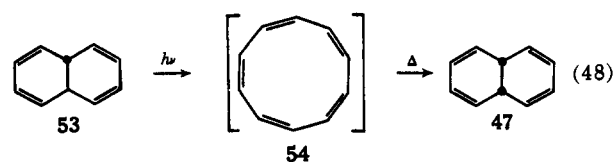


silver-ion catalyzed conversion to 50 having occurred.²⁰⁰⁻²⁰²

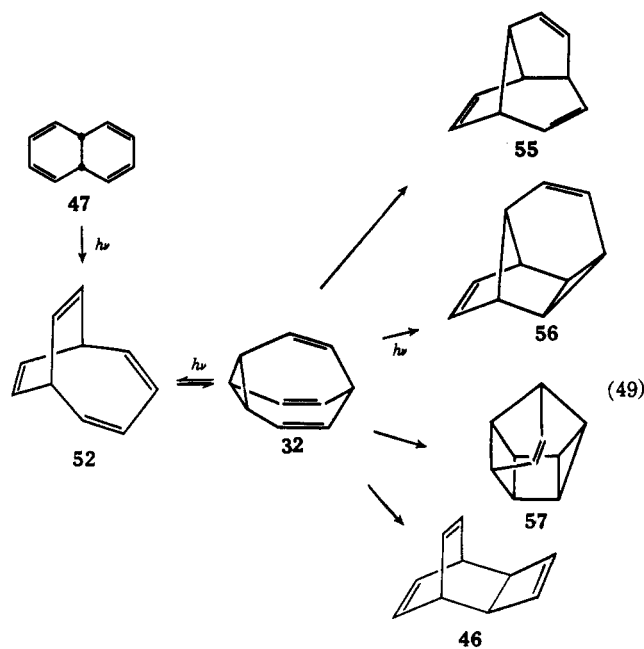
The next year syntheses of several new compounds were announced. Decomposition of the tosylhydrazone salt 51



gave bicyclo[4.2.2]deca-2,4,7,9-tetraene (52) and *trans*-9,10-dihydronaphthalene (53) as well as the known 47 and other minor products^{203,204} (eq 47). A more conventional synthesis of 53 was simultaneously advanced^{205,206} along with the photolytic conversion of 53 to the (presumably) *all-cis*-cyclodecapentaene 54 (eq 48), which was trapped by hydrogenation to cyclodecane. Some controversy followed these latter



claims, but has since diminished (*vide infra*). Photolysis of 47 gave 52 which regenerated 47 on heating.²⁰⁷ An unknown compound, "lumibullvalene" (55), was also reported on photolysis of 47. Identification followed the isolation of 55 from the direct photolysis of bullvalene (eq 49), along with 56, 57 and the previously known 46 and 52.²⁰⁸ Compound 52 had previously^{203,204} been shown to give 32 on photolysis (eq 49).



Photochemical decomposition of 51 (eq 50) gave a product mixture similar to that reported^{203,204} for the thermal reaction, except that 47 could not be found and 55 appeared.²⁰⁹ Structure 58 was tentatively preferred for 55 (and 58 appears in a recent review⁹) but was revised in a later paper wherein a firm structure proof of 55 appears.²¹⁰ When the photolysis was run at low temperature, 53 could not be found, and in its stead 59 appeared. On warming 59 was quantitatively converted to 53. Additionally, 9,10-dihydrofulvalene (60), another molecule not to reappear often, was isolated from the vacuum pyrolysis of nickelocene,²¹¹ and, later,²¹² from 61 (eq 51).

1968 found the synthesis of 62, formed along with 47, 52, 53, and 32 from photolysis of 59 at -100° ²¹³ (eq 52). Warming

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

(193) R. B. Woodward, T. Fukunaga, and R. C. Kelly, *ibid.*, **86**, 3162 (1964).

(194) I. T. Jacobson, *Acta Chem. Scand.*, **21**, 2235 (1967).

(195) S. Masamune, H. Cuts, and M. G. Hogben, *Tetrahedron Lett.*, 1017 (1966).

(196) See also E. N. Cain, R. Vukov, and S. Masamune, *Chem. Commun.*, 98 (1969).

(197) W. G. Dauben and D. L. Whalen, *Tetrahedron Lett.*, 3743 (1966).

(198) W. G. Dauben, C. H. Schallhorn, and D. L. Whalen, *J. Amer. Chem. Soc.*, **93**, 1446 (1971).

(199) R. Furstoss and J.-M. Lehn, *Bull. Soc. Chim. Fr.*, 2497 (1966).

(200) W. G. Dauben, M. G. Buzzolini, C. H. Schallhorn, D. L. Whalen, and K. J. Palmer, *Tetrahedron Lett.*, 787 (1970).

(201) L. A. Paquette and J. C. Stowell, *J. Amer. Chem. Soc.*, **92**, 2584 (1970).

(202) L. A. Paquette and J. C. Stowell, *ibid.*, **93**, 2459 (1971).

(203) M. Jones, Jr., and L. T. Scott, *ibid.*, **89**, 150 (1967).

(204) M. Jones, Jr., S. D. Reich, and L. T. Scott, *ibid.*, **92**, 3118 (1970).

(205) E. E. van Tamelen and T. L. Burkoth, *ibid.*, **89**, 151 (1967). Note that the uv spectrum reported in this paper is in error.

(206) E. E. van Tamelen, T. L. Burkoth, and R. H. Greeley, *ibid.*, **93**, 6120 (1971); see also E. E. van Tamelen and R. H. Greeley, *Chem. Commun.*, 601 (1971).

(207) W. von E. Doering and J. W. Rosenthal, *Tetrahedron Lett.*, 349 (1967).

(208) M. Jones, Jr., *J. Amer. Chem. Soc.*, **89**, 4236 (1967).

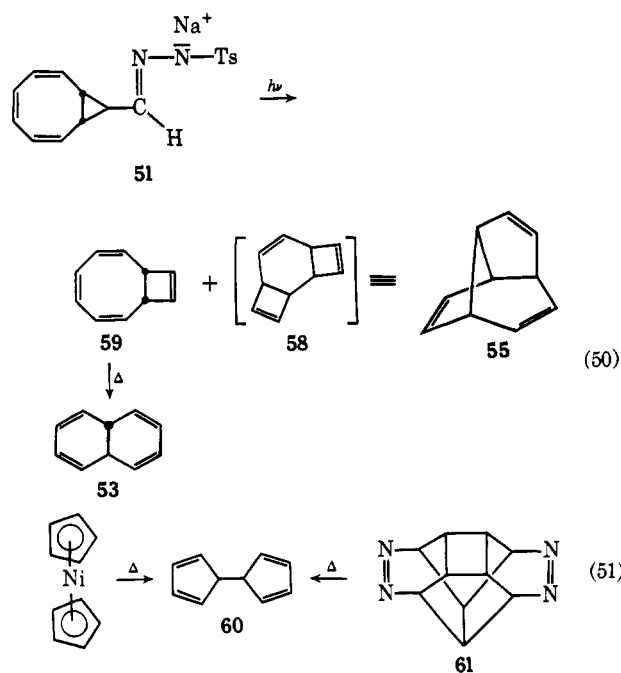
(209) S. Masamune, C. G. Chin, K. Hojo, and R. T. Seidner, *ibid.*, **89**, 4804 (1967).

(210) S. Masamune, H. Zenda, M. Wiesel, N. Nakatsuka, and G. Bigam, *ibid.*, **90**, 2727 (1968).

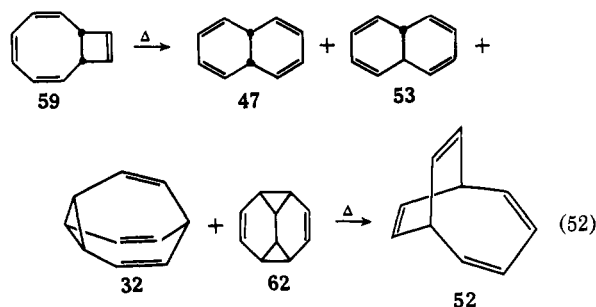
(211) E. H. Hedaya, D. W. McNeil, P. Schissel, and D. J. McAdoo, *ibid.*, **90**, 5285 (1968).

(212) K. Shen, *ibid.*, **93**, 3064 (1971).

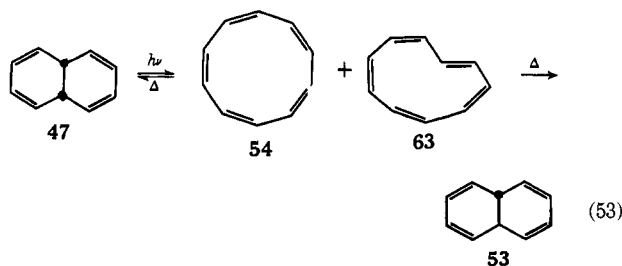
(213) S. Masamune, R. T. Seidner, H. Zenda, M. Wiesel, N. Nakatsuka, and G. Bigam, *ibid.*, **90**, 5286 (1968); correction, *ibid.*, **92**, 1810 (1970).



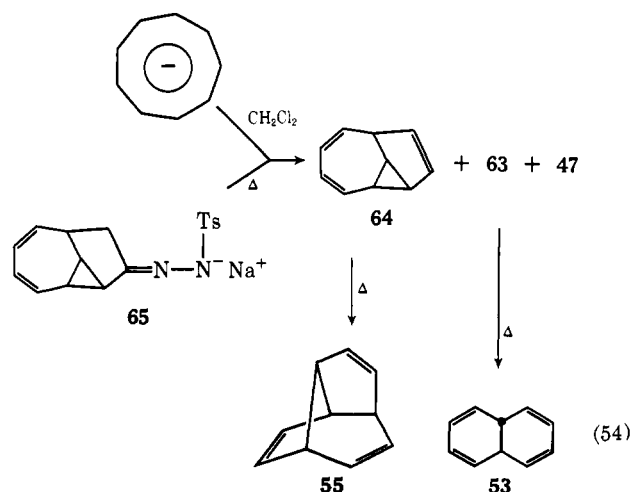
of **62** led to **52**, in a rapid and quantitative conversion. Another pair of very important compounds, **54** and **63**, appeared the following year²¹⁴ from low-temperature photolysis of **47** (eq 53). Important differences between this work and that



mentioned previously²⁰⁵ were noted. These and their partial reconciliation will be discussed later.

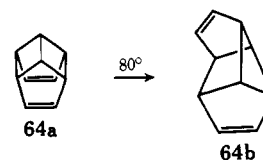


The next $(CH)_{10}$ to be isolated was **64**, first proposed as an intermediate in 1969,²¹⁵ in the reaction of sodium cyclononatetraene with methylene chloride to give, ultimately, **55**. Decomposition of the tosylhydrazone **65** also gave only **55** and not the expected **64**²¹⁶ (eq 54).



Compound **64** was isolated by two groups the following year^{217, 218} and its rapid conversion to **55** verified. One of these groups also isolated the cyclodecapentaene **63** and confirmed it as the source of the small amount of **53** found in the above reaction^{215, 217} (eq 54).

Compound **64a**, tetracyclo[5.3.0.0^{2,6}.0^{3,10}]deca-4,8-diene, has recently been made. The degenerate *cis*-divinylcyclobutane rearrangement is slow on the nmr time scale, but can be detected by labeling studies. At 80° **64a** is converted to **64b**.^{218a}



Thus the known $(CH)_{10}$'s include **32**, **46**, **47**, **48**, **49**, **50**, **52**, **53**, **54**, **55**, **56**, **57**, **59**, **60**, **62**, **63**, **64**, **64a**, and **64b**. The others, so far escaping synthesis, may be found in the compilation of Balaban.^{7, 218b}

B. MECHANISMS OF $(CH)_{10}$ FORMATIONS AND INTERCONVERSIONS

1. Formation of $(CH)_{10}$'s from Cyclopropylcarbenes

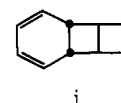
It is clear²⁰⁴ that the thermal decomposition of **51** was expected to give **59**, not the complex mixture of products observed.^{203, 204} Analogy abounds for such a ring expansion,²¹⁹ and the authors were led to propose **59** and **63** as intermediates in the formation of the observed **53** (eq 55). Orbital symmetry considerations⁶ support the hypothesis that **59** could lead to **63** which in turn would close to **53**. That this was indeed the path was verified when photolysis of **51** was shown²⁰⁹ to give **59**, which smoothly rearranged to **53** at 42–70°. The presumed

(217) K. Hojo, R. T. Seidner, and S. Masamune, *ibid.*, **92**, 6641 (1970).

(218) T. J. Katz, J. J. Cheung, and N. Acton, *ibid.*, **92**, 6643 (1970).

(218a) J. S. McKennis, L. Brener, J. S. Ward, and R. Pettit, *ibid.*, **93**, 4957 (1971).

(218b) Tricyclo[4.4.0.0^{2,5}]deca-3,7,9-triene (i) has now been made: E. Vedejs, *Chem. Commun.*, 536 (1971).

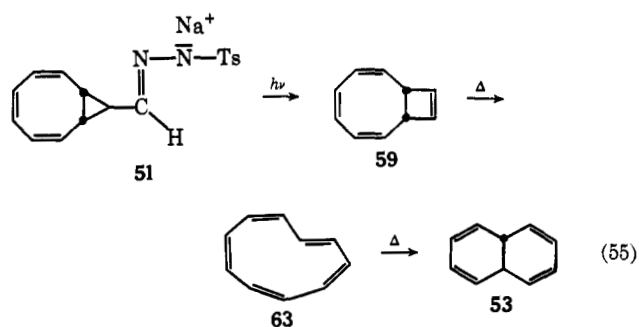


(219) W. Kirmse and K.-H. Pook, *Chem. Ber.*, **98**, 4022 (1965).

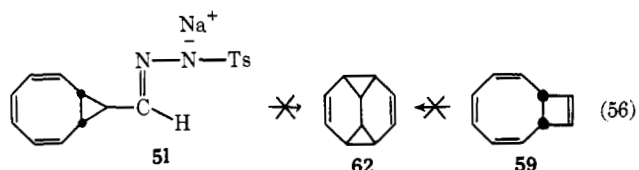
(214) S. Masamune and R. T. Seidner, *Chem. Commun.*, 542 (1969).

(215) T. J. Katz and J. J. Cheung, *J. Amer. Chem. Soc.*, **91**, 7772 (1969).

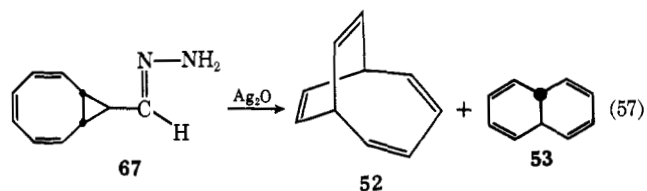
(216) E. Vedejs, R. A. Shepherd, and R. P. Steiner, *ibid.*, **92**, 2158 (1970).



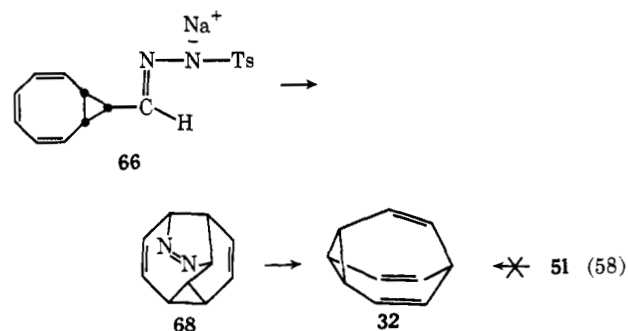
intermediate in this transformation, **63**, was later isolated and shown to behave as expected.²¹⁴ Another major product (**52**) of the decomposition of the tosylhydrazone salt, **51**, poses a more difficult problem. It does not arise from **59**²⁰⁹ nor does it seem likely that **62** can be involved, as the stereochemistry of



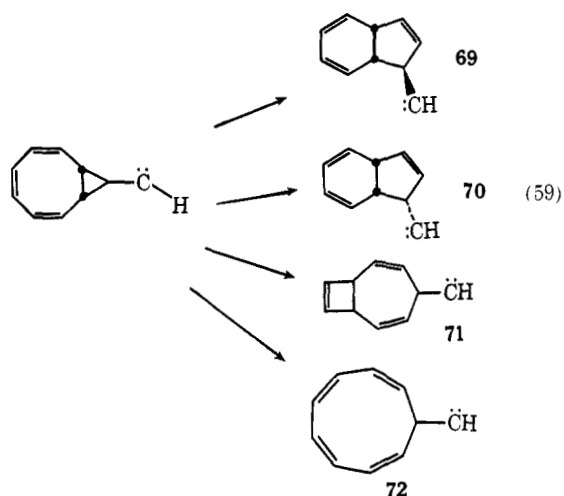
51 does not permit access to the remote double bond (eq 56). Epimerization of **51** to **66** also seems unlikely under the reaction conditions,^{203,204} and formation of **52** on oxidation of the hydrazone **67** at room temperature lends credence to the hypothesis that stereochemical changes are not involved in the reaction (eq 57). Moreover, heating the tosylhydrazone salt **66** is known to form a pyrazoline **68**, which leads to some



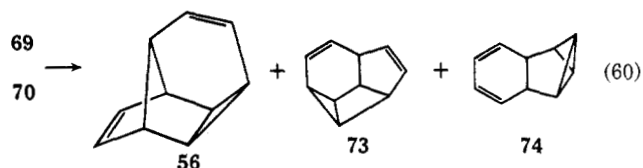
bullvalene (**32**) on decomposition (eq 58). No **32** can be found on decomposition of **51**, and thus **66** is not an intermediate. Other possibilities for the formation of **52** include isomeriza-



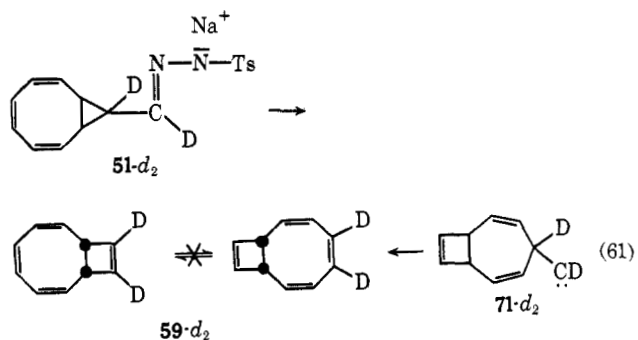
tion of the bicyclo[6.1.0] system to **69**, **70**, **71**, or **72** (eq 59), all of which processes have precedent in the complicated isomerizations of C₉H₁₀'s and their relatives.²²⁰ Hypothetical intermediates **69** and **70** seem appropriate, if untested, sources of **47**, as cyclopentenylcarbene does yield some cyclohexadiene.²²¹ No obvious route to **52** is apparent, however, as



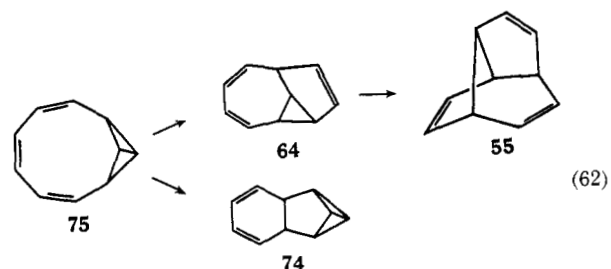
intramolecular cycloaddition of **69** and **70** would give only the known **56** and/or the unknown **73** and **74** (eq 60). Carbene **72** is already implicated in the formation of **53** and does not give **52** (*vide infra*). Carbene **71** has a poor stereochemical arrange-



ment for intramolecular addition, but might ring expand to **59**. However, the **59** formed from dideuterated **51** is specifically labeled as shown²²² and cannot arise from **71** (eq 61). Compound **59** had been shown previously not to undergo a degenerate rearrangement.²¹³



Unprecedented formation of the bicyclobutane **75** is another possibility, but **75**'s only obvious further pathways lead to the unknown **74**, or *via* a vinylcyclopropane rearrangement, or [1,5] shift, to **64** and thence to the unobserved **55** (eq 62).

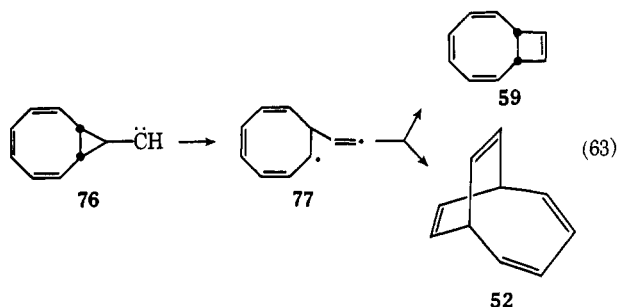


(220) S. W. Staley, *Intra-Sci. Chem. Rep.*, **5**, . . . (1971).

(221) D. M. Lemal and K. S. Shim, *Tetrahedron Lett.*, 3231 (1964).

(222) R. T. Seidner, N. Nakatsuka, and S. Masamune, *Can. J. Chem.*, **48**, 187 (1970).

We are left with the mechanism originally proposed^{203,204} in which the cyclopropylcarbene (76) cleaves one bond to give a diradical (77), which closes to 52 and 59 (eq 63). This mechanism at least has the practical virtue of correctly predicting the products of a variety of similar reactions.^{204,223}

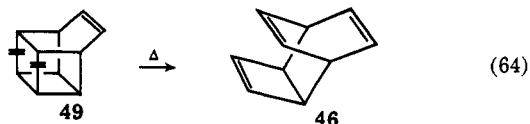


nism at least has the practical virtue of correctly predicting the products of a variety of similar reactions.^{204,223}

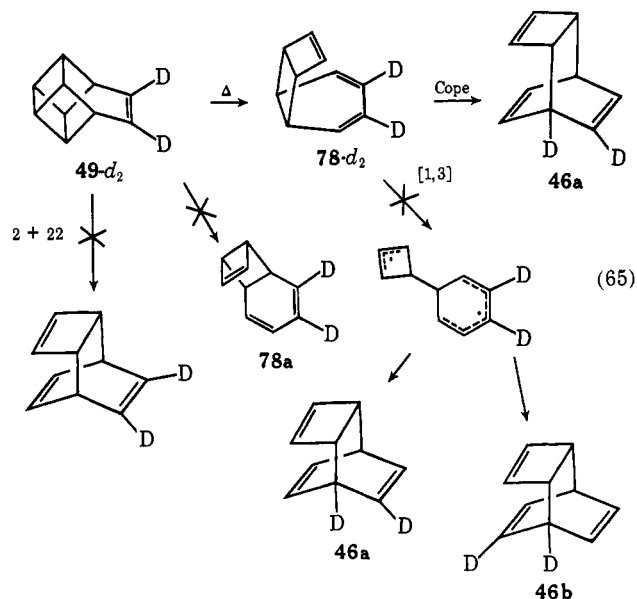
2. Thermal Interconversions of $(CH)_{10}$'s

a. Conversion of "Basketene" (49) to "Nenitzescu's Hydrocarbon" (46)

This reaction (eq 64) was noticed almost as soon as 49 was made¹⁹⁵⁻¹⁹⁷ and has an obvious mechanism, which is, of course, wrong. Formation of 46 does not involve a simple retro 2 + 2 cycloaddition, but proceeds instead through an



intermediate $(CH)_{10}$ (78), the product of a retro 2 + 4 reaction.^{224,224a} That this is the mechanism is revealed by the distribution of deuterium as shown below in eq 65. The deuterium

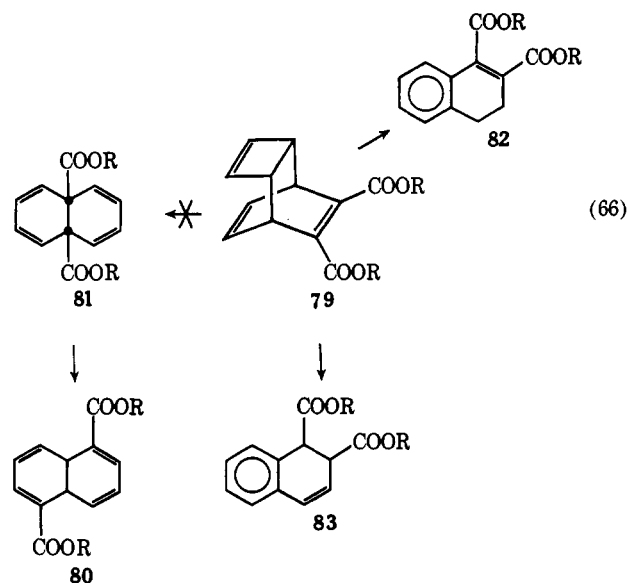


distribution further serves to delineate the mechanism of rearrangement of 78 to 46. Two paths, an allowed Cope re-

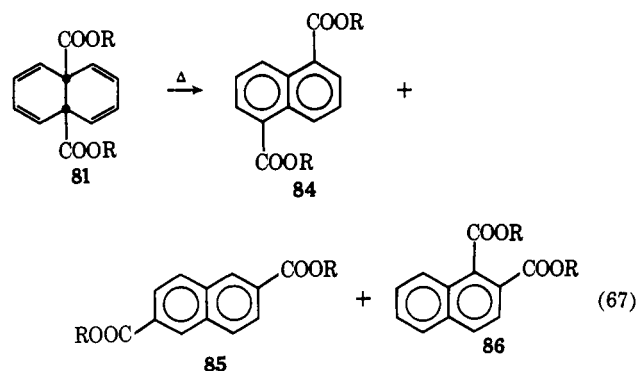
arrangement and a forbidden (and therefore probably non-concerted)⁶ [1,3] sigmatropic shift exist. The latter process would lead to deuterium in the 1 and 10 positions (46b), as well as the observed 1 and 8 (46a, eq 65). A mechanism not considered involves a retro 2 + 2 reaction to give 78a followed by a sigmatropic shift. The exclusive formation of 46a argues against this process, however.

b. Thermal Rearrangements of "Nenitzescu's Hydrocarbon" (46) and 9,10-Dihydronaphthalenes

Initial reports^{225,226} of the rearrangement of 79 to 80, supposedly *via* 81, have been corrected.^{227,228} The product is actually a mixture of 82 and 83 (eq 66). Compound 81 was later syn-



thesized²²⁹ and shown to rearrange to 84 and 85 and a small amount of 86 (eq 67). This last compound was rationalized *via* a Diels-Alder addition of 81 to give 87 which underwent a



reverse Diels-Alder in the opposite direction to give 86 (eq 68). The parent of 87, 56, does rearrange easily to 47 (eq 69),²⁰⁸ and it had earlier been shown that 88 gave 89 (eq 70).²³⁰

(223) M. Jones, Jr., S. D. Reich, L. T. Scott, and L. E. Sullivan, *Angew. Chem., Int. Ed. Engl.*, **7**, 644 (1968).

(224) H. H. Westberg, E. N. Cain, and S. Masamune, *J. Amer. Chem. Soc.*, **91**, 7512 (1969); correction, *ibid.*, **92**, 5291 (1970).

(224a) Compound 78 has been isolated and its rapid conversion to 46 at 70° noted.^{218b}

(225) M. Avram, C. D. Nenitzescu, and E. Marica, *Chem. Ber.*, **90**, 1857 (1957).

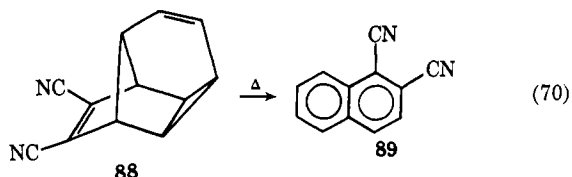
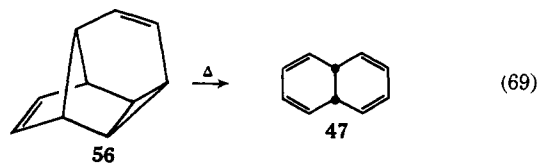
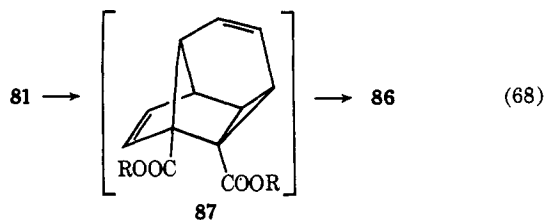
(226) M. Avram, G. Mateescu, and C. D. Nenitzescu, *Justus Liebigs Ann. Chem.*, **636**, 174 (1960).

(227) R. C. Cookson, J. Hudec, and J. Marsden, *Chem. Ind. (London)*, **21** (1961).

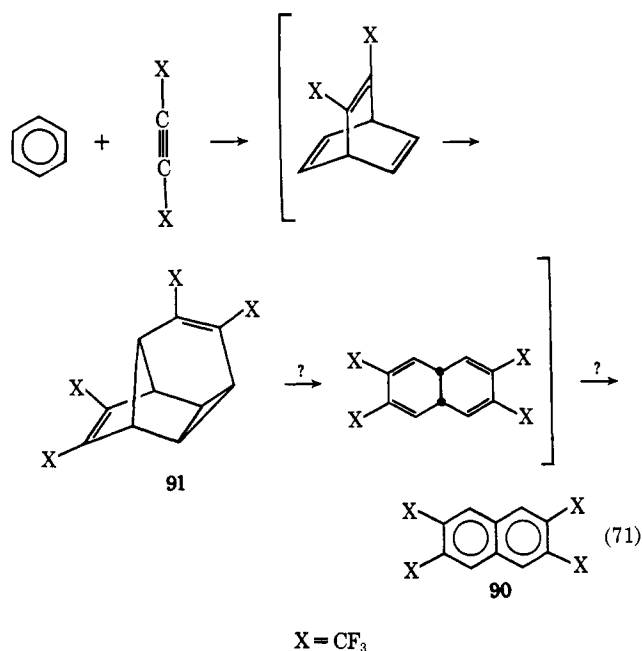
(228) B. C. T. Pappas, *Diss. Abstr.*, **24**, 5004 (1964).

(229) E. Vogel, W. Meckel, and W. Grimme, *Angew. Chem., Int. Ed. Engl.*, **3**, 643 (1964).

(230) H. E. Zimmerman and G. L. Grunewald, *J. Amer. Chem. Soc.*, **86**, 1434 (1964).



Isolation of the 1,2-substituted **89** renders obscure the formation of **90** from the following reaction sequence (eq 71).¹⁶⁴ Originally **91** was proposed as an intermediate in the formation of **90** but is no longer a reasonable choice, as it should not lead to the substitution pattern observed. The source of **90** remains unknown.



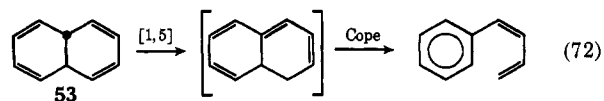
The formation of naphthalenes from 9,10-dihydronaphthalenes finds analogy in the reactions of the parent compound **47**, which gives 1,2-dihydronaphthalene, 1,4-dihydronaphthalene, and naphthalene at 390° in a flow system.^{183,281} The fate of the hydrogen lost by **47** in its conversion to naphthalene is revealed by the presence of hydrogenated products noticed by several groups.^{207,208,215,232} The stereochemistry of the transfer was investigated and found to be specifically *cis*.²³²

High-temperature gas chromatography of **53** results in some conversion to *cis*-1-phenylbutadiene (eq 72).²⁰⁶ This was

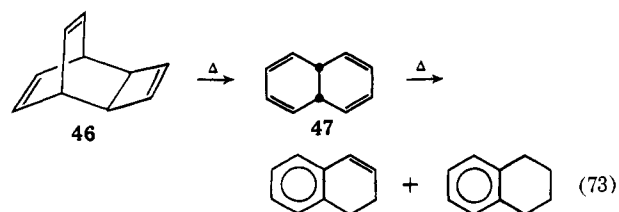
(231) W. von E. Doering and J. W. Rosenthal, *J. Amer. Chem. Soc.*, **88**, 2078 (1966).

(232) W. von E. Doering and J. W. Rosenthal, *ibid.*, **89**, 4534 (1967).

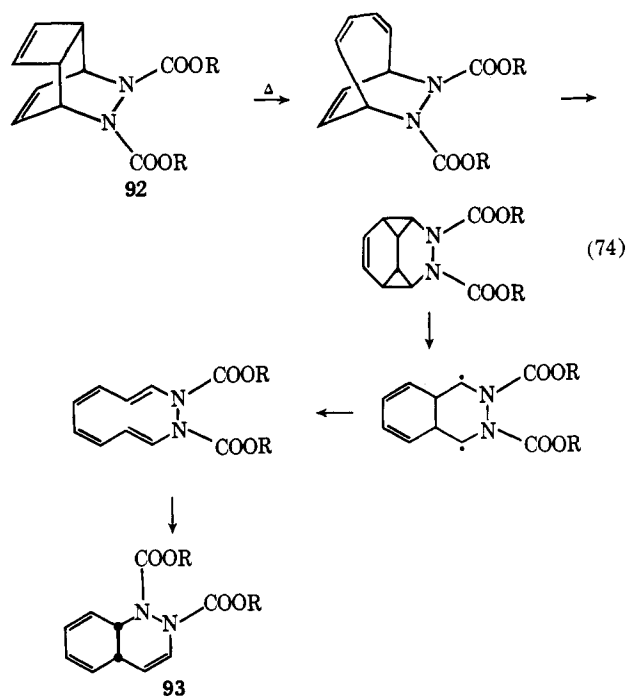
rationalized by a mechanism involving a [1,5] hydrogen shift followed by a Cope rearrangement, a process previously suggested for the formation of the phenylbutadiene.^{203,204}



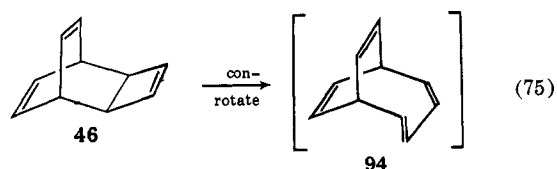
Nenitzescu's hydrocarbon itself (**46**) was reported to give naphthalene, 1,2-dihydronaphthalene, and tetrahydronaph-



thalene at 300° (eq 73).²³³ As might be guessed from these products, 9,10-dihydronaphthalene is an intermediate and was isolated from pyrolysis of **46** in a flow apparatus.²³¹ Conversion of **92** to **93** led Maier to suggest²³⁴ the mechanism shown below (eq 74) and to implicate **52** in the conversion of **46** to **47**. This seems inherently unlikely in view of the for-



biddens of such a reaction, which "should" yield **94**, not **52** (eq 75).⁶ A further suggestion for the mechanism came from Vedejs²³⁵ who envisioned **95** as the key intermediate (eq 76).

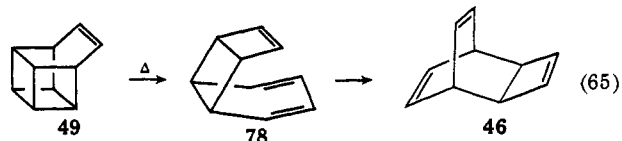
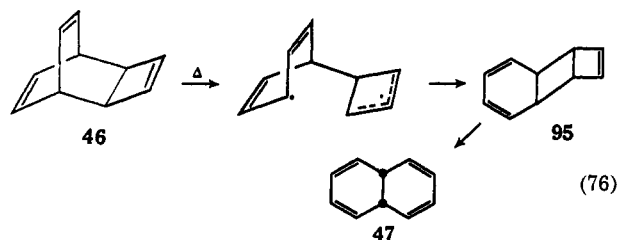


(233) C. D. Nenitzescu, M. Avram, I. I. Pogany, Gh. D. Mateescu, and M. Farcasiu, *Acad. Rep. Pop. Rom. Stud. Cercet. Chim. (Filiala Bucaresti)*, **11**, 7 (1963).

(234) G. Maier, *Chem. Ber.*, **102**, 3310 (1969).

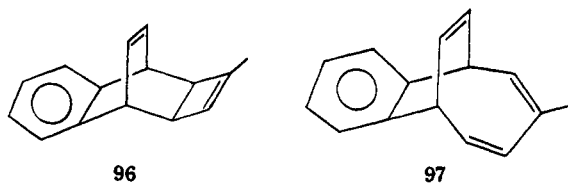
(235) E. Vedejs, *Tetrahedron Lett.*, 4963 (1970).

Compound **95** may or may not be identical with the species **78** postulated²²⁴ in the basketene to **46** conversion (eq 65),

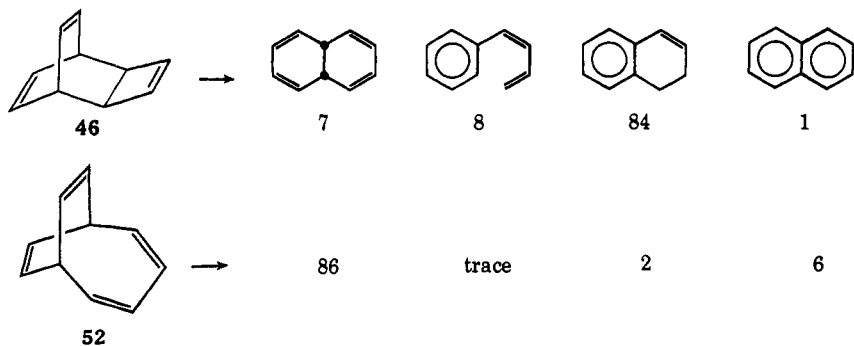


as the two can differ in stereochemistry. The Cope rearrangement which leads **78** so easily to **46** cannot occur in **95**, which could thus be a source of **47** (eq 76). However, **46** is converted to **47** at 280°, substantially higher than the 110° of the **49** to **46** rearrangement. The higher temperature may suffice to drive **78** on to **47** and thus a compound of the stereochemistry of **95** is not required.

Data on compounds in the benzo-(CH)₁₀ series support Vedejs' rejection of **52**, as **96** does not rearrange to the pyrolysis products of **97**. Vedejs further notes that pyrolysis of

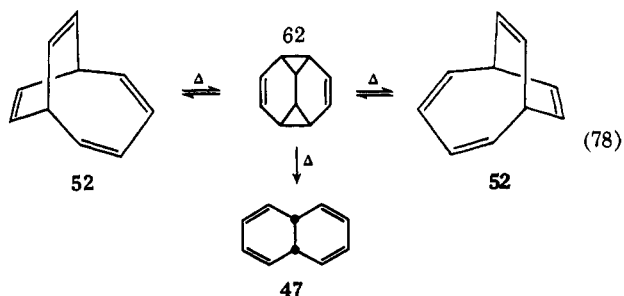


52 gives a mixture of products quite different from that produced from **46** (eq 77).

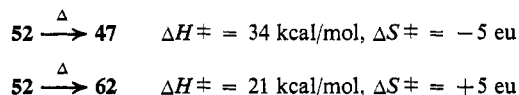


c. Degenerate Rearrangement of Bicyclo[4.2.2]deca-2,4,7,9-tetraene (**52**)

Strongly implicated in the conversion of **52** to **47** is the tetracycle **62**. However, the forbiddenness⁶ of the reverse 4 + 4 cycloaddition led several groups to suspect that equilibration of **52** and **62** would precede formation of **47** (eq 78).^{222, 236, 237} Labeling experiments confirmed this expectation, and it was

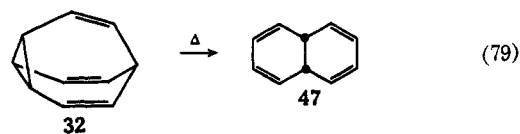


possible to estimate the activation parameters as shown.²²² Isolation of **62** confirmed its easy opening to **52**.²¹³



d. Pyrolysis of Bullvalene (**32**) and Lumibullvalene (**55**)

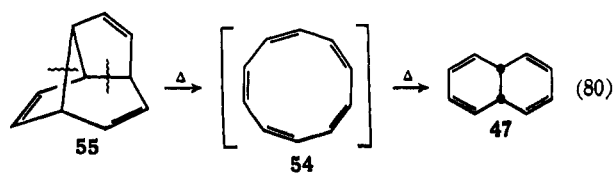
Perhaps the most obscure of all these reactions is the conversion of **32** to **47** (eq 79). Several compounds were originally noticed on pyrolysis of **32**,^{5, 231} but it is now clear that the initial species produced is **47**.¹⁸³ The estimated activation



enthalpy for this reaction is 45 kcal/mol, with an entropy of activation of +2 eu,²²² and is above that required for the transformation of other compounds into **47**. This fact coupled with the difficulties inherent in labeling **32** makes mechanistic comment especially difficult.

Compound **55** was cited as a potential source of **47** before its identification.²³¹ Little information is available about the

mechanism of its conversion to **47**, reported^{204, 208} to occur at 280° in a flow system. Speculation centers upon a two-bond



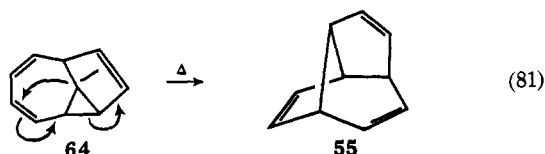
cleavage to cyclodecapentaene (**54**)²³¹ (eq 80), but nothing more than speculation is available.

(236) W. Grimme, H. J. Riebel, and E. Vogel, *Angew. Chem., Int. Ed. Engl.*, 7, 823 (1968).

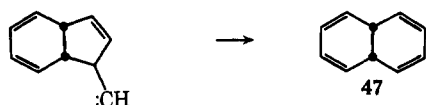
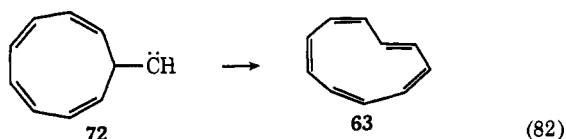
(237) M. Jones, Jr., and B. J. Fairless, *Tetrahedron Lett.*, 4881 (1968).

e. Conversion of Isobullvalene (64) to Lumibullvalene (55)

The reaction appears to be a simple *cis*-divinylcyclopropane rearrangement and occurs quite readily (eq 81).²¹⁵⁻²¹⁸ The

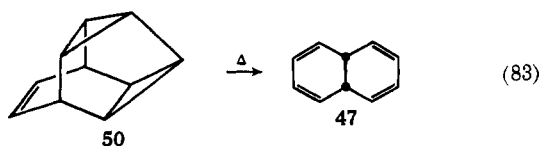


reaction of sodium cyclononatetraene and methylene chloride gave not only 64 but also small amounts of 63 and 47 (eq 82).^{217, 218} Compound 63 possibly arises from ring expansion of cyclononatetraenylcarbene (72), and 47 from isomerization of the cyclononatetraene to the bicyclo[4.3.0] system which then ring expands.²²¹

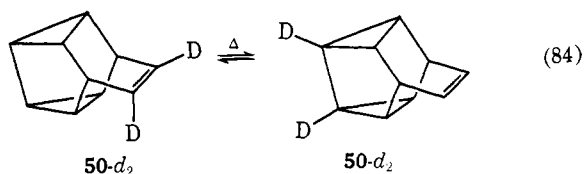


f. Rearrangement of Pentacyclo[4.4.0.0^{2,4}.0^{3,8}.0^{5,7}]decene (50) to *cis*-9,10-Dihydronaphthalene (47)

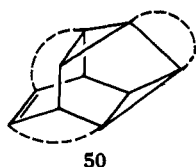
At 530°, 50 rearranged to 47 and products of the further decomposition of 47 (eq 83).²⁰²



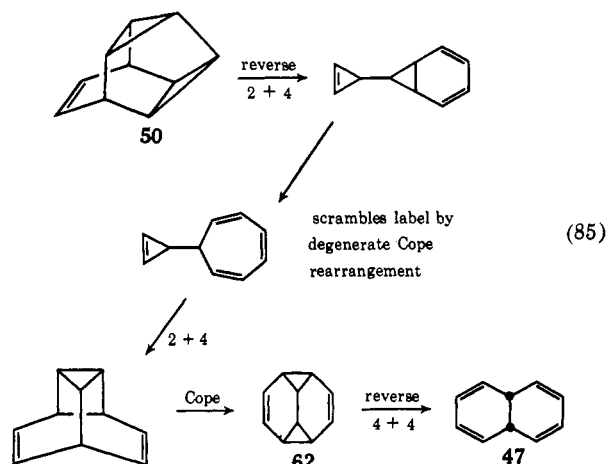
Rearrangement of labeled 50 established the degenerate equilibration shown in eq 84. An allowed $\sigma_2s + \sigma_2s + \pi_2a$



process has been suggested.²⁰² Further scrambling is evident



in the deuterium content of 47 which has the two deuterons randomly disposed. This requires either the process shown in eq 85 or scrambling in 47 itself at 530°. ²⁰² This latter process could occur *via* a combination of [1,5] hydrogen shifts

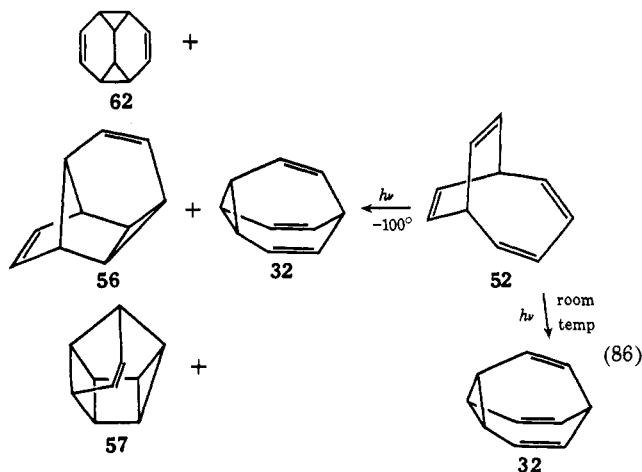


and/or a $\pi_2a + \pi_2a + \sigma_2s$ Cope rearrangement. Compound 47 does not scramble hydrogens at 410°, however.^{202, 237a}

3. Photochemical Transformations of (CH)₁₀'s

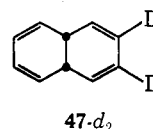
a. Conversion of Bicyclo[4.2.2]deca-2,4,7,9-tetraene (52) to Bullvalene (32)

In contrast to many of the photochemical transformations of (CH)₁₀'s, the room temperature photolysis of 52 gives 32 in a very clean, high yield reaction, quite uncomplicated by side products.^{203, 204, 207} Photolysis at -100° is more complex, giving 62 and 32 as major products along with other compounds in minor amounts (eq 86).²¹⁷ Compounds 56 and 57 as well, perhaps, as 62 are probably further photolysis prod-



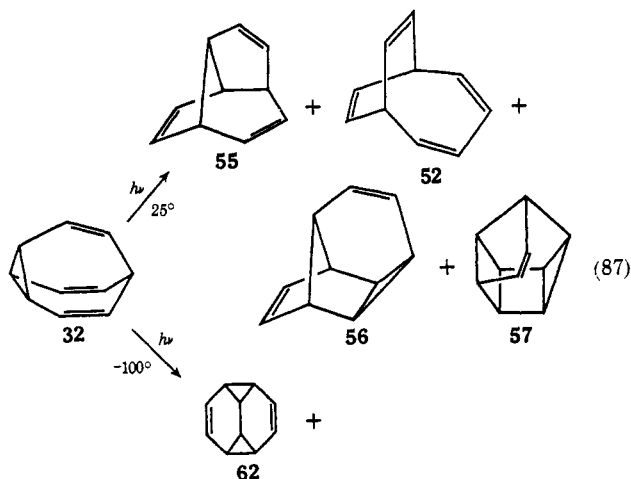
ucts of 32. Little can be said about mechanism; conversion of 52 to 32 is an allowed⁶ reaction of the $\sigma_2s + \pi_2s + \pi_2a + \pi_2a$ type, but many of the di- π -methane reactions are triplet in nature,¹⁸² and a concerted reaction is by no means certain.

(237a) NOTE ADDED IN PROOF. Dideuterio-9,10-dihydronaphthalene (47-d₂) undergoes extensive scrambling of its deuterium labels at 510°: L. A. Paquette, *J. Amer. Chem. Soc.*, **93**, 7110 (1971).

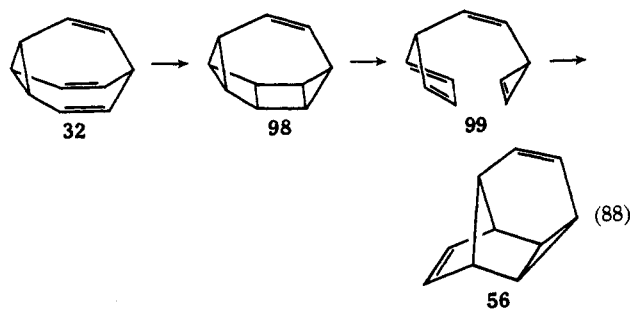


b. Photochemical Reactions of Bullvalene (32) and Isobullvalene (64)

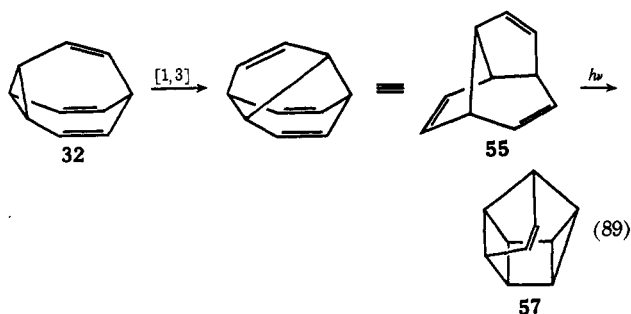
As noted above, these reactions are far more complicated, the products of photolysis of 32 at room temperature and at -100° being those shown in eq 87.^{208, 217}



Mechanisms have been suggested, but not proved, for some of these changes.^{204, 208} Compound 56 was thought to arise *via* an intramolecular 2 + 2 cycloaddition of 32 to 98 followed by reversal to 99 and an intramolecular Diels-Alder reaction (eq 88). Compound 55, it was suggested,^{204, 208} arose through a simple [1,3] shift and was then transformed through intra-

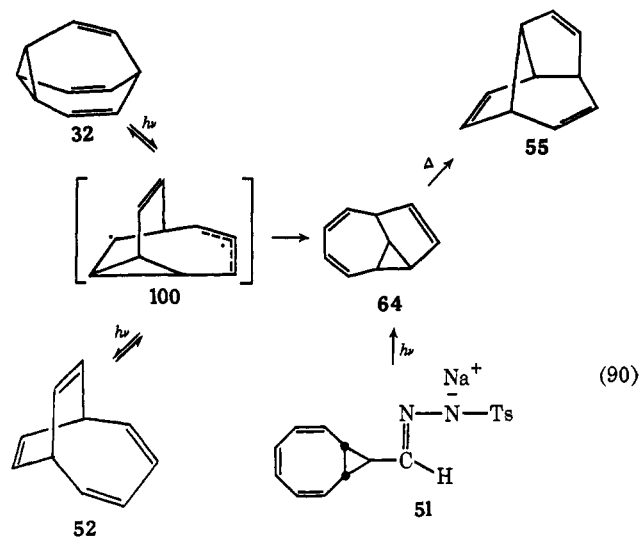


molecular cycloaddition to 57 (eq 89). That this last postulate is reasonable was shown when 55 was rapidly converted to 57 at -100° .²¹⁷ Another view of the photochemical reactions

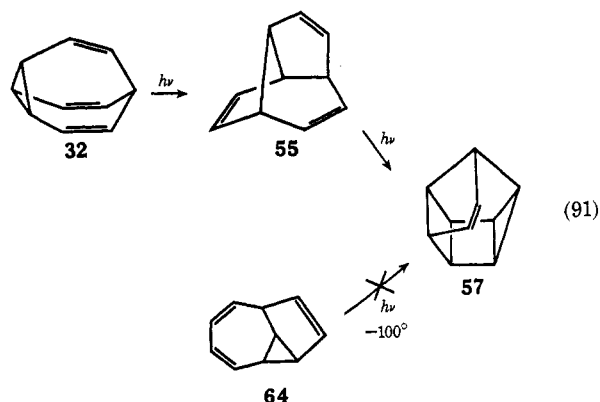


in general, and of the rearrangement of 32 to 55 in particular, has come from Katz and Cheung.²¹⁵ They assumed that in all photochemical reactions producing 55 isobullvalene (64) was the crucial intermediate. It is certainly true that were 64 to be formed it would rapidly rearrange to 55.^{217, 219} Compound 64 could be formed directly from 76, the carbene related to 51, by ring expansion of the bicyclo[6.1.0] system to a cyclo-nonatetraene followed by intramolecular addition or in the

other cases through diradical 100 (eq 90). Intermediate 100 can decompose in three ways to give 64, 52, or 32 (eq 90). It was thought significant that 64 was always accompanied by 52 and/or 32.



We are reluctant to abandon the simple [1,3] shift in the rearrangement of 32 to 55, and there is some evidence that a direct path exists.²¹⁷ It was found that under conditions where 64 does not yield 55 (-100°), but where 55 does rapidly close to 57, bullvalene (32) gave 57 on photolysis, while 64 did not. Thus 32 probably has a direct route to 55 and need not proceed to 55 through 64 (eq 91).



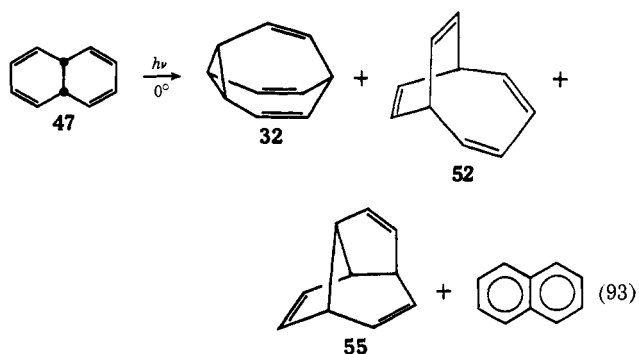
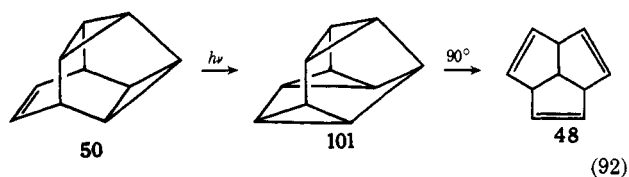
c. Photochemical Conversion of Pentacyclo[4.4.0.0^{2,4}.0^{3,8}.0^{5,7}]decene (50) to Triquinacene (48)

Compound 50 closes on irradiation (eq 92) to an intermediate, 101, which opens at 90° ($t_{1/2} \cong 60$ min) to triquinacene (48).^{238, 238a}

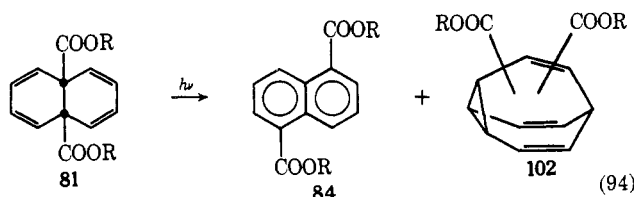
d. Photochemistry of *cis*- and *trans*-9,10-Dihydronaphthalenes (47 and 53)

Early work reported naphthalene, 32, 52, and 55 as the products of the irradiation of 47 at 0° (eq 93).^{208, 232}

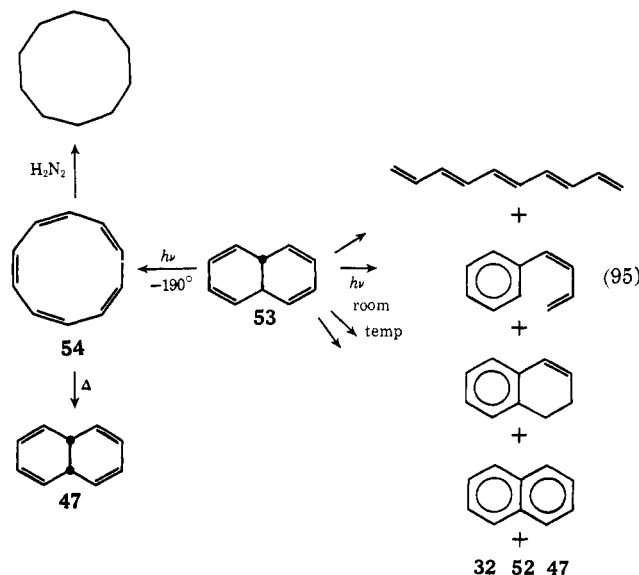
(238) H. Prinzbach, Pacific Coast Lecture, UCLA, April 1, 1971; see also H. Prinzbach and D. Stusche, *Helv. Chim. Acta*, **54**, 755 (1971).
(238a) A. deMeijere, D. Kaufmann, and O. Schallner, *Angew. Chem., Int. Ed. Engl.*, **10**, 417 (1971).



Diester **81** had been reported to give **84** and dicarboethoxybullvalene, **102** (eq 94).²³⁹ The trans compound **53** gave



decapentaene, *cis*-1-phenylbutadiene, naphthalene, 1,2-dihydronaphthalene, **47**, **52**, and **32** at room temperature, and at -190° , a compound which hydrogenated to cyclodecane and gave **47** on warming (eq 95). On these grounds it was

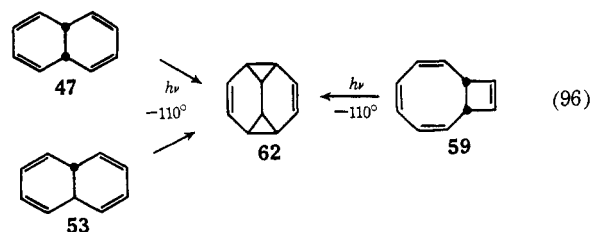


identified as *all-cis*-cyclodecapentaene **54**.^{205, 206} Somewhat later, apparently contradictory data were published^{213, 214} which lead us directly to the next section on the roles of the cyclodecapentaenes.

(239) E. Vogel, W. Grimme, W. Meckel, and H. J. Riebel, *Angew. Chem., Int. Ed. Engl.*, **5**, 590 (1966).

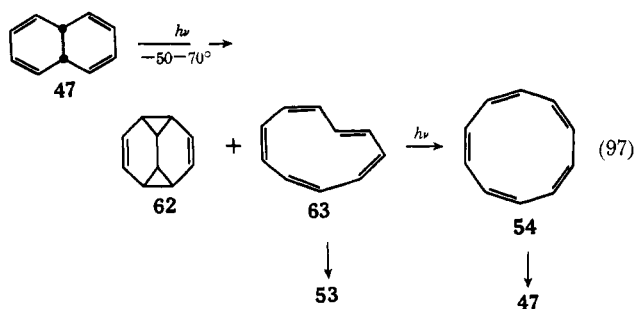
e. Cyclodecapentaenes

Both **47** and **53**, as well as **59**, were shown to give mainly **62** on irradiation at -110° (eq 96).²¹³ It was hinted in this work



that cyclodecapentaenes were involved and later reported²¹⁴ that, in conflict with previous work,²⁰⁵ (1) only **47**, but not **53**, led to **54**, (2) that the photoreaction was fast at 0° but not at -190° , and (3) that reduction by diimide did not compete effectively with thermal rearrangement of [10]annulene at -78° .

Two cyclodecapentaenes could be detected on irradiation of **47** at -50 to -70° . Nmr signals for **54** (temperature independent) and **63** (temperature dependent) could be observed and their disappearance correlated with the appearance of signals for **47** and **53**, respectively (eq 97).



The apparent conflicts between this work²¹⁴ and that previous²⁰⁵ have been at least partially resolved by further work²⁰⁶ which claims that the photolytic conversion of **53** to **54** at -190° is observed only in dilute solution. In the newer work, the reported yields of cyclodecane were somewhat lower than before. However, it is still not clear to us why reduction proceeds in Stanford, California, but not in Edmonton, Alberta. Schemes III and IV summarize the thermal and photochemical interconversions of the (CH)₁₀'s.

VI. (CH)₁₂

The (CH)₁₂ isomers have been much less thoroughly investigated than the lower (CH)_n families, although a number of interesting and complex interrelationships have already been uncovered.

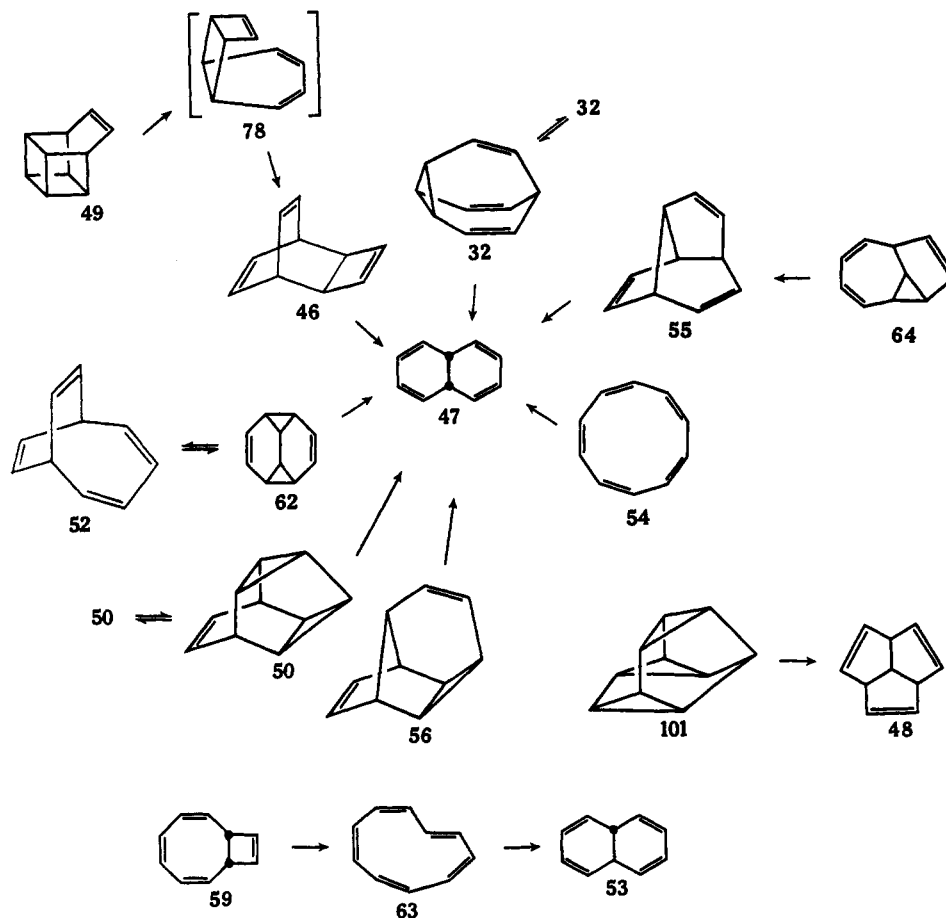
A. CYCLODODECAHEXAENE AND FUSED RING SYSTEMS

Cyclododecahexaene (**103**) is formed in greater than 70% yield^{240, 241} by photolysis of *syn*-tricyclo[8.2.0.0^{2,9}] dodeca

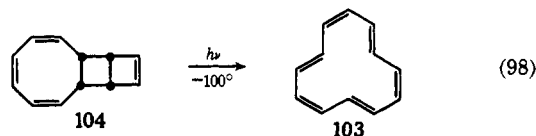
(240) J. F. M. Oth, H. Röttele, and G. Schröder, *Tetrahedron Lett.*, 61 (1970).

(241) H. Röttele, W. Martin, J. F. M. Oth, and G. Schröder, *Chem. Ber.*, **102**, 3985 (1969).

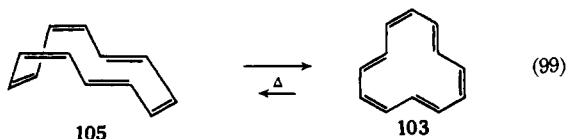
Scheme III
Thermal Interconversions of (CH)₁₀'s



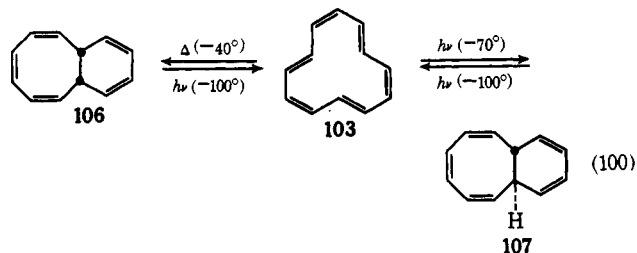
3,5,7,11-tetraene²⁴² (**104**) at -100° (eq 98). Nmr studies²⁴³ have established the pattern of alternating cis and trans double bonds in **103** as well as the occurrence of rapid conformational changes, even at low temperatures, and the absence of bond switching (*cf.* cyclooctatetraene, section IV.A.1).



Orbital symmetry conservation does not allow the direct formation of **103** from **104**. To account for this and many subsequent reactions, a dynamic equilibrium between **105**, a symmetry-allowed photoproduct, and **103** has been proposed²⁴⁰ (eq 99). Facile cis-trans isomerizations of this sort are well documented²⁴⁴ for the higher homolog [16]annulene. The equilibrium in eq 99 must lie far in the direction of **103**, however, since no nmr signals for **105** can be seen.^{240, 243}



At -40° **103** isomerizes cleanly to *cis*-bicyclo[6.4.0]dodeca-2,4,6,9,11-pentaene (**106**)^{240, 241} with an activation energy of 17.4 kcal/mol whereas photolytically it closes to the trans isomer **107**²⁴⁰ (eq 100). Photolysis of both **107** and **106** at



-100° regenerates **103**²⁴⁰ (eq 100). Again the intermediacy of the less stable [12]annulene **105** has been forwarded²⁴⁰ to explain these observations with respect to the restrictions of orbital symmetry conservation.

At -30° under the influence of uv light, **107** and **106** interconvert²⁴¹ presumably *via* cyclododecahexaene. Prolonged irradiation at this temperature leads to 1-phenylhexatriene (**108**) at the expense of both **107** and **106**²⁴¹ (eq 101).

Formation of **108** is best explained by a symmetry-allowed [1,7] hydrogen shift to give intermediate **109** which subsequently undergoes electrocyclic opening to the observed product²⁴¹ (eq 102).

At $+30^\circ$ the trans bicyclic pentaene **107** can be isolated,²⁴⁵

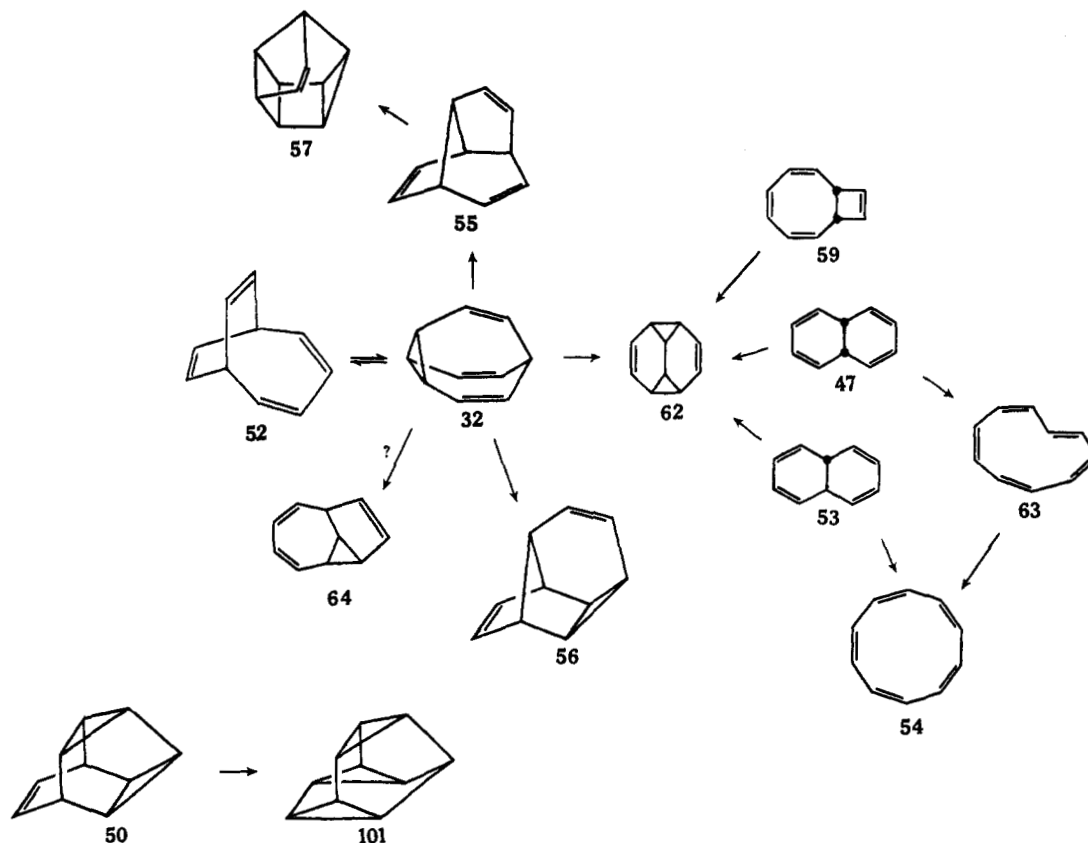
(242) G. Schröder and W. Martin, *Angew. Chem., Int. Ed. Engl.*, **5**, 130 (1966).

(243) J. F. M. Oth, J.-M. Gilles, and G. Schröder, *Tetrahedron Lett.*, **67** (1970).

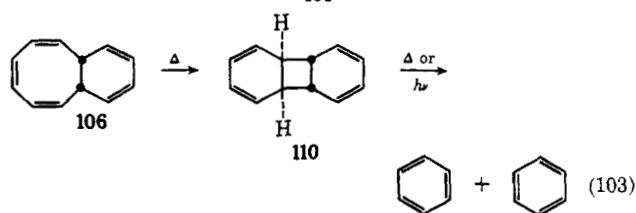
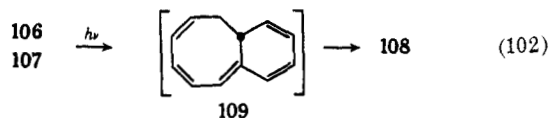
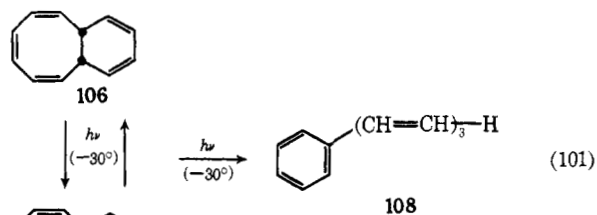
(244) J. F. M. Oth and J.-M. Gilles, *ibid.*, 6259 (1968).

(245) G. Schröder, W. Martin, and H. Röttele, *Angew. Chem., Int. Ed. Engl.*, **8**, 69 (1969).

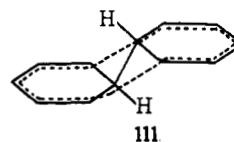
Scheme IV
Photochemical Interconversions of (CH)₁₀'s



but the *cis* isomer rearranges further to the tricyclic compound **110**^{240, 241} with an activation energy of 23.3 kcal/mol (eq 103). Further heat^{240, 241, 245, 246} or light^{240, 241} splits **110** in half to provide two molecules of benzene (eq 103). The free energy of activation for thermal cleavage is 24.7 kcal/mol at +30°.²⁴⁰

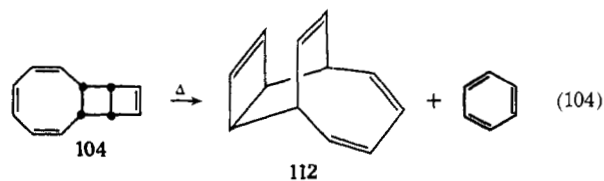


The realization that concerted cleavage of **110** is symmetry allowed only in the excited state prompts hypothesis of the interesting bis homoaromatic diradical **111** as a likely inter-



mediate in the ground-state reaction.²⁴⁷ No stereoisomers of **110** have been reported.

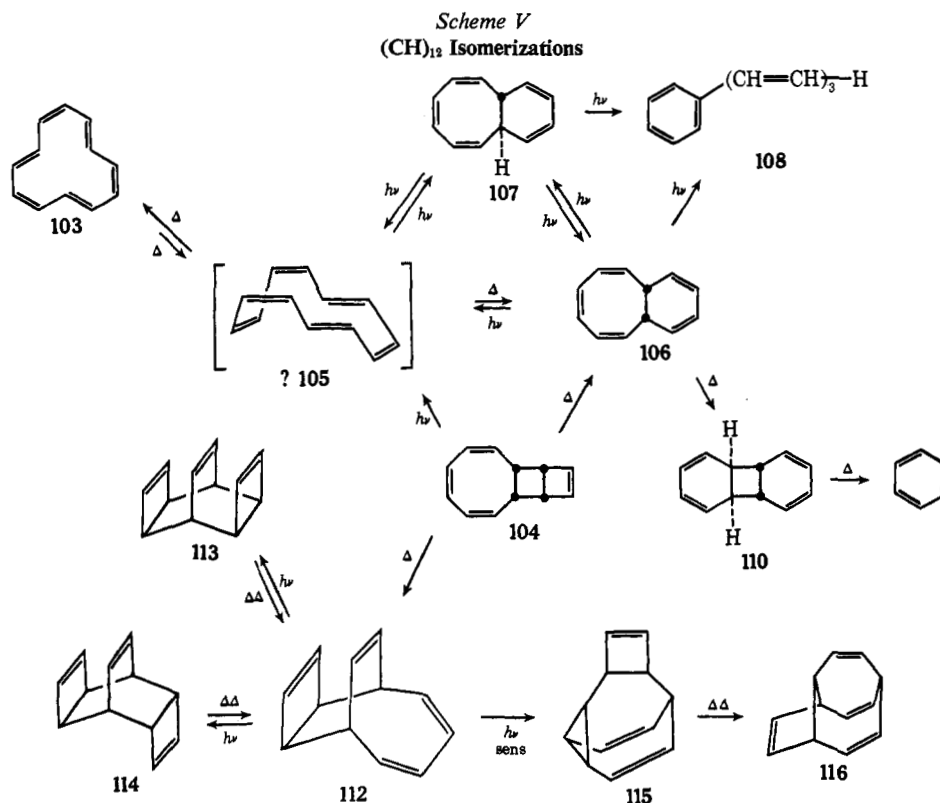
The ancestry of all known fused-ring (CH)₁₂ isomers can be traced ultimately to the photolysis of **104**, itself derived from a dimer of cyclooctatetraene.²⁴² The following section reveals that **104** has served also as progenitor of all known bridged-ring (CH)₁₂ isomers. Thus, prolonged heating of **104** at 120° converts it to the bridged tetraene **112** and benzene in roughly equal amounts^{242, 248} (eq 104). Formation of **112** may be viewed either as a Cope rearrangement or as a [1,5] sigmatropic shift, whereas the benzene is probably formed in a nonconcerted process *via* **106** (*cf.* eq 103).



(246) E. H. Gold and D. Ginsburg, *J. Chem. Soc. C*, 15 (1967).

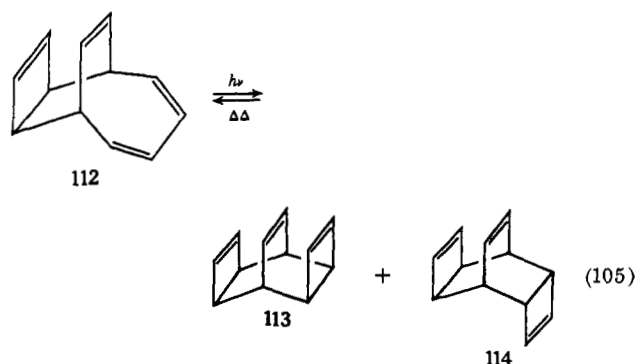
(247) R. B. Woodward, Research Group Seminar 5.II.70.

(248) L. A. Paquette and J. C. Stowell, *Tetrahedron Lett.*, 4159 (1969).



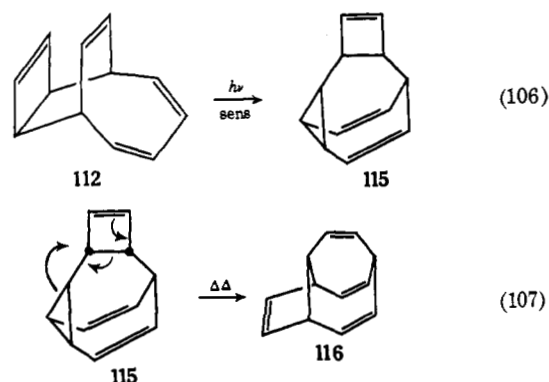
B. BRIDGED RING SYSTEMS

Tricyclo[4.4.2.0^{2,5}]dodeca-3,7,9,11-tetraene (**112**) is thermally stable, at least under the conditions of its formation (eq 104), but undergoes electrocyclic ring closure to two new hydrocarbons (**113** and **114**) on irradiation at room temperature^{248, 249} (eq 105). The products revert to **112** on vacuum pyrolysis at 500°²⁴⁸ (eq 105). No explanation has been offered for exclusive cleavage of the endo cyclobutene ring in **114** nor for the seemingly incongruous observation that it opens more slowly than the exo cyclobutene of **113**.²⁴⁸ Detailed studies of this latter rate difference have been carried out and rationalized in simpler systems.²⁵⁰



In contrast to the direct irradiation in eq 105, acetone-sensitized photolysis²⁴⁸ of **112** gives a completely different triene **115** (eq 106). Here again is another example of the ubiquitous di- π -methane rearrangement.¹⁶²

Pyrolysis at 480° of this product, which has also been synthesized²⁵¹⁻²⁵³ from a dimer of cyclooctatetraene, brings about an interesting rearrangement to **116**²⁵⁴ (eq 107). Although multistep mechanisms have been hypothesized²⁵⁴ for this transformation, the symmetry-allowed, concerted $\pi_2s + \sigma_2s + \sigma_2s$ process indicated in eq 107 merits consideration.



Scheme V summarizes these few (CH)₁₂ isomerizations.

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(249) G. Schröder and W. Martin, unpublished results cited in G. Schröder and J. F. M. Oth, *Angew. Chem., Int. Ed. Engl.*, **6**, 414 (1967).
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