a situation that will have an appreciable effect on the entropy and free energy. The symmetry numbers and stereoisomeric pairs used in the entropy calculations are recorded in the table. The agreement with experimental values where the comparison can be made is excellent. We believe that the calculation of gas phase thermodynamic functions by a vibrational analysis using transferable potential functions with the minimum energy structure is now a very convenient and accurate way of predicting these quantities.

The calculated geometries are illustrated in Figure 2.

Acknowledgments. We are indebted to the U. S. Army Research Office (Durham) for financial support of this work. We are grateful to Dr. H. E. Simmons, Jr., Central Research Department, E. I. du Pont de Nemours Co. for furnishing the cyclopropanes, and to Professor N. L. Allinger of Wayne State University for his interest in the bicyclo[3.3.0]octanes and for providing the facilities for their synthesis. We express our appreciation to Professor P. v. R. Schleyer of Princeton University for communicating his work on goup contributions for strain energy definition to us.

Generation, Rearrangement, and Interconversion of Hydrocarbons Related to Bullvalene[1,2a–c]

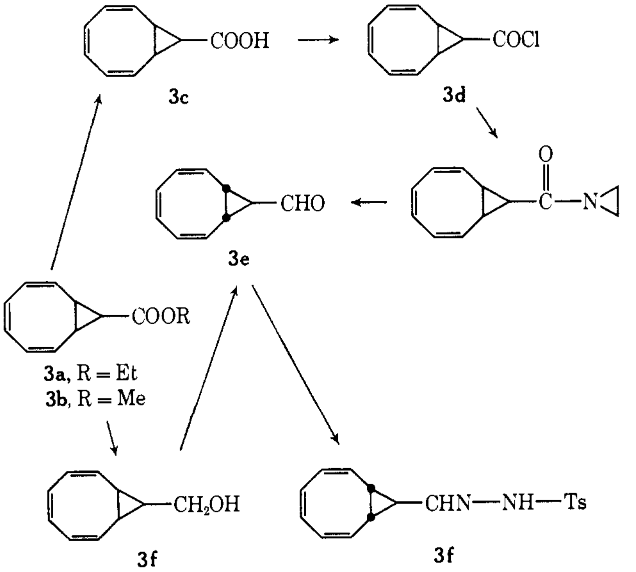
Maitland Jones, Jr.,[3] Steven D. Reich, and Lawrence T. Scott

Contribution from the Department of Chemistry, Princeton University, Princeton, New Jersey 08540. *Received September 22, 1969*

Abstract: Bicyclo[4.2.2]deca-2,4,7,9-tetraene (**8**), *cis*- and *trans*-9,10-dihydronaphthalene (**6** and **5**), and *cis*-1-phenylbutadiene (**7**) are formed on thermal decomposition of the salt of bicyclo[6.1.0]nona-2,4,6-triene-9-carboxaldehyde tosylhydrazone (**3f**). Similarly, *cis*-bicyclo[5.2.0]nona-2,4,8-triene (**20**), bicyclo[3.2.2]nonatriene (**21**), and bicyclo[4.2.1]nonatriene (**19**) are formed on thermal decomposition of the salt of bicyclo[5.1.0]octa-2,4-diene-8-carboxaldehyde tosylhydrazone (**18f**). The proofs of structure of several of these hydrocarbons are described and a mechanism involving cleavage of an initially formed carbene to a diradical proposed. The conversion of **8** to bullvalene (**1**) on photolysis is described, as is the further photolysis of **1**. The thermal conversions of several of these $(CH)_{10}$'s to **6** are described.

The discovery[4,5] that bullvalene (**1**) possessed the fully fluxional structure predicted[6,7] has been one of the most stimulating of recent years. More or less parallel to the emerging chemistry of bullvalene has been the examination of the properties of molecules closely related in either an isomeric or conceptual sense. The unravelling of the structures and interrelationships of the various $(CH)_{10}$'s has been a diverse and international effort and we describe here our part in it.

Our work began with the perhaps naive conception that the well known ring-expansion reaction of cyclopropylcarbenes[9] could be used to add a C_2H_2 unit to cyclooctatetraene[10] to produce the unknown (at that time) bicyclo[6.2.0]deca-2,4,6,9-tetraene (**2**).[11] The synthesis of the required carbene precursor proceeded through the ester **3a** or **3b**[12–14] in several ways. In practice, the route through the alcohol has been most convenient in our laboratories. In the initial addition to cyclooctatetraene, two stereoisomers are formed.



3c **3d** **3e**

3a, R = Et
3b, R = Me

3f **3f**

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(1) Support for this work through a grant from the Lilly Research Laboratories is gratefully acknowledged.

(2) This work is taken in part from the Theses of S. D. R. and L. T. S. submitted in partial fulfillment of the requirements for the A. B. degree at Princeton University. Preliminary communications have appeared. (a) M. Jones, Jr., and L. T. Scott, *J. Amer. Chem. Soc.*, **89**, 150 (1967); (b) M. Jones, Jr., and S. D. Reich, *ibid.*, **89**, 3935 (1967); (c) M. Jones, Jr., *ibid.*, **89**, 4236 (1967).

(3) Alfred P. Sloan Foundation Research Fellow, 1967–1969.

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

(5) W. von E. Doering, B. M. Ferrier, E. T. Fossel, J. H. Hartenstein, M. Jones, Jr., G. Klumpp, R. M. Rubin, and M. Saunders, *Tetrahedron*, **23**, 3943 (1967).[8]

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

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

(8) As one of those quoted (M. J., Jr.) in footnote 15 of ref 5, it is perhaps not out of order to suggest that the source of "this ignoble name" is neither lost nor contained in E. Partridge, "A Dictionary of Slang and Unconventional English," Macmillan and Co., New York, N. Y., 1961.

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

(10) We thank the Badische Anilin und Soda Fabrik for a generous gift of cyclooctatetraene.

(11) S. Masamune, C. G. Chin, K. Hojo, and R. T. Seidner, *J. Amer. Chem. Soc.*, **89**, 4804 (1967).

(12) K. F. Bangert and V. Boekelheide, *ibid.*, **86**, 905, 1159 (1964).

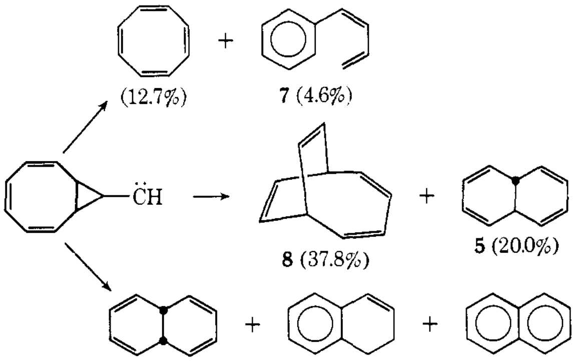
(13) S. Akiyoshi and T. Matsuda, *ibid.*, 77, 2476 (1955).

(14) D. D. Phillips, *ibid.*, 77, 5179 (1955).

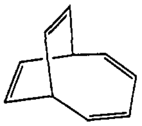
In the case of the methyl ester, **3b**, we find a *trans*:*cis* ratio of 18.

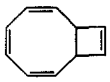
That the major isomer is the *trans* rests not only on precedent[15] but also on the magnitude of the spin–spin coupling constant between the cyclopropyl hydrogens. The observed value of 5–5.5 Hz for **3a**–**e** is consistent with a *trans* arrangement, but not a *cis*.[16] Such stereochemical arguments go back to Boekelheide[12] and were put on an unimpeachable basis by Masamune's conversion of **3c** to *trans*-cyclopropane-1,2,3-tricarboxylic acid.[11] The operations necessary to convert **3a** or **3b** into **3f** also serve to remove the last traces of the *cis* isomer as evidenced by the absence of any signal in the nmr for the *cis*-aldehyde **3e**.[17]

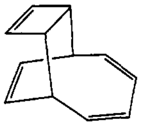
Decomposition of the dry sodium or lithium salt of **3f** led to a most complex mixture of hydrocarbons. Cyclooctatetraene, naphthalene, and compounds **5**,**6**,**7**, and **9** were identified by comparisons with authentic samples.[18] *trans*-9,10-Dihydronaphthalene (**5**), which at the time stood in some need of additional structure proof, was also hydrogenated in methanol over PtO_2 at room temperature to an 85:15 mixture of *trans*- and *cis*-decalin. Masamune, *et al.*,[19] have reported the reduction of **5** with diimide followed by hydrogen to *trans*-decalin exclusively. Identification of **8** was difficult and in particular required a rigorous distinction from the expected **2**. Spectra provided a strong indication that the correct structure was **8**. The 100-MHz nmr spectrum of **8** shows two multiplets integrating for two protons each at 604 and 565 Hz from tetramethylsilane, a symmetrical pattern centered at 546 Hz integrating for four protons, and a two-proton multiplet centered at 312 Hz. On irradiation of the 312-Hz signal, the multiplet at 546 Hz collapses to a sharp singlet. Thus this signal can be assigned to the four protons on the ethylene bridges of **8**. Norbornadiene shows a similar multiplet and identical behavior on decoupling of the bridgehead protons.[20] It is most difficult to reconcile this behavior with structure **2**.

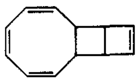


The ultraviolet spectrum showed maxima at λ_{max}^{EtOH} 280, 268, and 258 nm (ϵ 2900, 4200, and 4200, respectively). Both the nmr and uv spectra are very similar to the corresponding spectra of bicyclo[4.2.1]nona-2,4,7-triene.[21] Further analogies exist. The structures **10** and **11** were assigned by Schröder[22] to two $C_{12}H_{12}$ products. The ultraviolet spectrum of **10** showed maxima at λ_{max}^{hexane} 280, 268.5, and 258.5 nm (ϵ 2700, 5000, and 4600, respectively), while **11** exhibited only a single maximum at λ_{max}^{hexane} 258 nm (ϵ 1300).


8

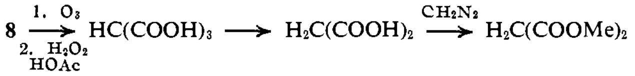

2


10


11

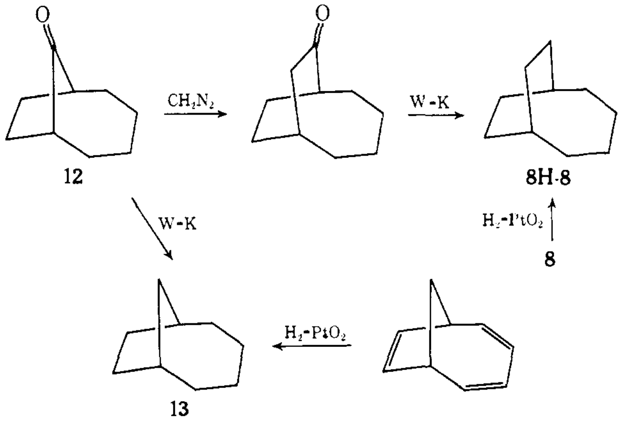
While a good case can be made for structure **8** from the spectra alone we felt that in view of the lack of an obvious structural relationship between **8** and its immediate precursor, and the orthodoxy of **2**, a chemical proof of structure was in order. Three lines of attack were used.

First, **8** was subjected to ozonolysis followed by an acid work-up and esterification with diazomethane. Only dimethylmalonate could be found. Compound **8** leads naturally to the malonate *via* the unstable methane tricarboxylic acid which decarboxylates. Compound **2**, on the other hand, should give 1,1,2,2-tetracarbomethoxyethane or, perhaps, dimethylsuccinate. Both of these compounds were sought; neither could be found.



$$\mathbf{8} \xrightarrow[\substack{2.\ H_2O_2\\ HOAc}]{1.\ O_3} HC(COOH)_3 \longrightarrow H_2C(COOH)_2 \xrightarrow{CH_2N_2} H_2C(COOMe)_2$$

Second, a synthesis of octahydro-**8** (**8H-8**) was carried out starting with the known[23] ketone **12**. Ring expansion with diazomethane followed by Wolff–Kishner reduction gave **8H-8**. The ketone **12** was a crucial material in the structure proof. As its origin involved a double ring expansion of cyclopentanone which conceivably could have given bicyclo[6.2.0]nonan-9-one, **12** itself was in need of a rigorous structure proof. Gutsche and Smith[23] had noted the infrared stretching frequency of 1737 cm^{-1} and had converted **12** to cyclooctanecarboxamide *via* a Haller–Bauer reaction. Others[24,25] had reduced **12** to bicyclo[4.2.1]nonane (**13**) which was found to be identical with material



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[15] W. Kirmse, "Carbene Chemistry," Academic Press, New York, N. Y., 1964, p 98.

[16] J. D. Graham and M. T. Rogers, *J. Amer. Chem. Soc.*, **84**, 2249 (1962).

[17] We thank S. Masamune for spectra of this compound and for private communications of results prior to publication.

[18] We thank Professor E. E. van Tamelen for nmr and uv spectra of **5** and Professor M. Pomerantz for nmr and ir spectra of **7**.

[19] S. Masamune, R. T. Seidner, H. Zenda, M. Wiesel, N. Nakatsuka, and G. Bigam, *J. Amer. Chem. Soc.*, **90**, 5286 (1968).

[20] We thank Professors M. R. Willcott, III, and B. J. Fairless for the measurement of these spectra.

[21] W. Grimme, *Chem. Ber.*, **100**, 113 (1967).

[22] G. Schröder and W. Martin, *Angew. Chem.*, **78**, 117 (1966).

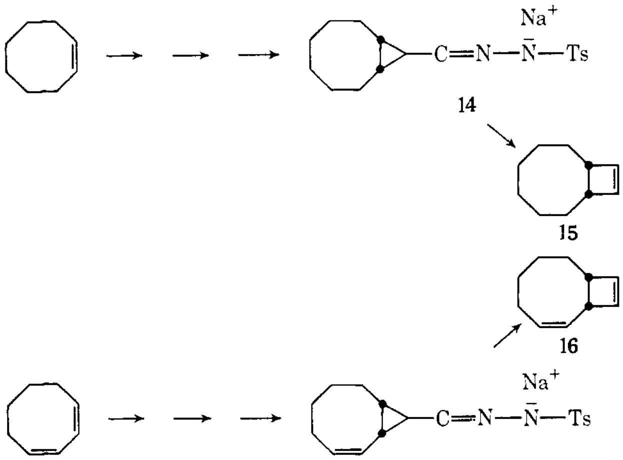
[23] C. D. Gutsche and T. D. Smith, *J. Amer. Chem. Soc.*, **82**, 4067 (1960).

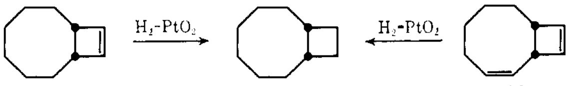
[24] P. Radlick, R. Klem, S. Spurlock, J. J. Sims, E. E. van Tamelen, and T. Whitesides, *Tetrahedron Lett.*, 5117 (1968).

[25] P. Radlick and W. Fenical, *ibid.*, 4901 (1967).

made independently. We also carried out this latter procedure, preparing **13** by hydrogenation of bicyclo[4.2.1]nonatriene (*vide infra*).

Finally, we attempted to prepare octahydro-**2** (**8H-2**). The two routes shown below were chosen. The sequence of steps paralleled that used in the fully unsaturated **3** series, and resulted in the tosyl hydrazone salts **14** and **14a**. Decomposition of **14** led to a 4.5:1 mixture of *cis*-bicyclo[6.2.0]dec-9-ene (**15**) and cyclooctene. Similarly, **14a** led to a 3.7:1 mixture of *cis*-bicyclo[6.2.0]deca-2,9-diene (**16**). Hydrogenation of either **15** or **16** gave a new hydrocarbon (**8H-2**) which was not identical with **8H-8**. It only remained to assign the stereochemistry of the ring junction with confidence. The possibility existed that the compounds designated **8H-8** and **8H-2** shared the bicyclo[6.2.0] skeleton and only differed in stereochemistry.

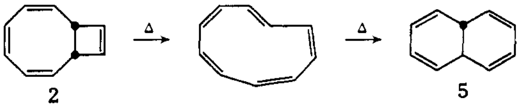




15 8H-2 16

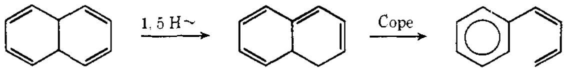
Compound **15** and the corresponding *trans* isomer have now been made by Radlick, *et al.*[24] **8H-8** is neither of these. The assignment of the ring junction in **15** and **16** still rests, however, on the authors' faith in the stereochemical integrity of the ring expansion of cyclopropylcarbenes, bolstered somewhat by the application of the Woodward–Hoffmann rules to the ring-opening reactions of these compounds.[25] Whatever faint doubts may remain about the stereochemistry of **15** and **16**, it is clear from all three chemical structure proofs that **8** is the correct structure. Subsequent to this work Masamune, *et al.*,[11] succeeded in synthesizing **2**, which is indeed quite different from **8**.

With the structures of the products settled, attention naturally turns to the mechanism of the reaction which produces such great skeletal changes. Cyclooctatetraene finds its origin in the two-bond cleavage reaction typical of cyclopropylcarbenes.[26,27] One might note at this point that the mechanism of this reaction can be described today only in operational terms and very little is really known about it. *trans*-9,10-Dihydronaphthalene (**5**) seemed to us[2b] to be a likely product of rearrangement of the "expected" compound, **2**. Application of the Woodward–Hoffmann rules for the opening and closing of such systems[28,29] permits the expectation that **2** would open thermally to give *cis,cis,cis,cis,trans*-cyclodecapentaene which could remove the *trans* double bond only by closing to **5**.



2 5

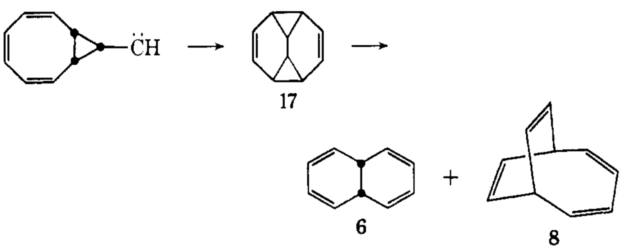
Masamune, *et al.*,[11] have verified that this is indeed the path followed by **2** and have shown the conversion to be both rapid and quantitative. *cis*-9,10-Dihydronaphthalene (**6**) and *cis*-1-phenylbutadiene, although minor products, provide mechanistic mysteries. The source of neither is known, although **7** may owe its existence to a 1,5-hydrogen shift in either **5** or **6** followed by a Cope rearrangement. This scheme at least has the virtue of automatically generating the proper stereochemistry.



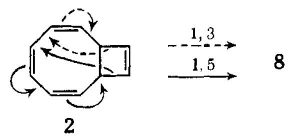
5 or 6 7

The structural difficulties posed by **8** were paralleled by mechanistic problems. One possibility was that during the decomposition the salt of tosylhydrazone **3f** or the related carbene underwent epimerization to the all-*cis* isomer. This could then add to the remote double bond to give an intermediate **17** with the potential of opening in two ways to give both **6** and **8** (path A). A second possibility was that **2**, already shown to be intermediate in the formation of **5**, was similarly responsible for **8** (path B). An attractive mechanism involved the sigmatropic[30] shift of order; order 1,3 or 1,5. Precedent for such a process existed in the work of Katz, *et al.*,[31] and Schönleber.[32] The third possibility was that a rearrangement of the carbene itself led directly to **8** (path C).

Path A



Path B



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(26) P. B. Shevlin and A. P. Wolf, *J. Amer. Chem. Soc.*, **88**, 4735 (1966).

(27) A. Guarimo and A. P. Wolf, *Tetrahedron Lett.*, 655 (1969).

(28) R. B. Woodward and R. Hoffmann, *J. Amer. Chem. Soc.*, **87**, 395 (1965).

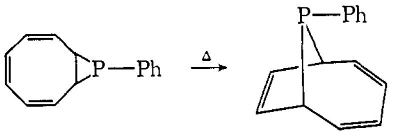
(29) J. J. Vollmer and K. L. Servis, *J. Chem. Educ.*, **45**, 214 (1968).

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

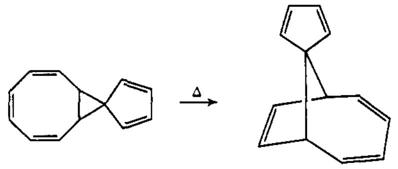
(31) T. J. Katz, C. R. Nicholson, and C. A. Reilly, *ibid.*, **88**, 3832 (1966).

(32) D. Schönleber, *Chem. Ber.*, **102**, 1789 (1969).

Katz

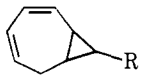


Schönleber

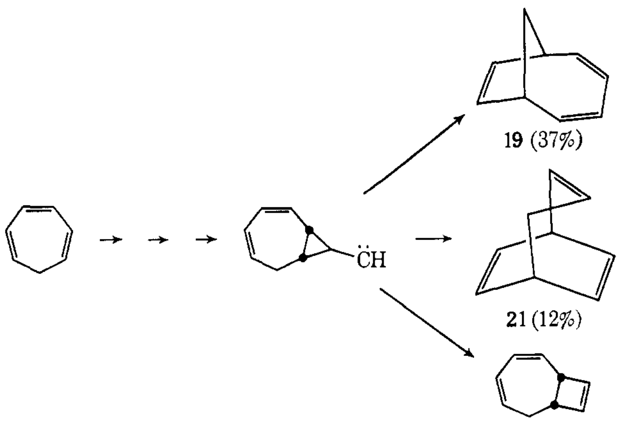


Path A seemed a remote possibility as many of the bicyclo[6.1.0] compounds were treated at temperatures approximating that of the decomposition and did not epimerize. Further, oxidation of the hydrazone of **3e** at room temperature gave a mixture of **5**, **6**, **7**, and **8** almost identical with that found from the pyrolysis of the dry salt of **3f**. Epimerization at room temperature seems unlikely indeed. Finally the *cis*-tosylhydrazone is known[33] to give a pyrazoline by intramolecular cyclization which, when decomposed, gives **1** as well as other hydrocarbons. No **1** can be detected in our reactions.

Path B seemed attractive to us and, as **2** was then unknown,[11] and labeling experiments difficult, we decided to test for the shift in a related system. We chose to reduce the symmetry by replacing one of the carbon-carbon double bonds with a methylene group. This plan had the virtue of differentiating the hypothetical 1,3 and 1,5 shifts and of giving us a better chance of isolating the cyclobutene itself. Happily for us, Korte, Büchel, and Wiese had provided an entry into the series years earlier,[34] and Mislow, Kondo, and Egan[35] have recently determined the stereochemistry by converting optically active **18b** into *optically active* 1,2-dicarboxycyclopropane-3-acetic acid which must have the *trans* arrangement of carboxy groups. The synthesis of tosylhydrazone **18f** proceeded, as before, through the acid and acid chloride **18b** and **18c**, or the alcohol **18d**, to the aldehyde **18e**. The salt of **18f** was decomposed to give another complex mixture of hydrocarbons. Bicyclo[4.2.1]nonatriene (**19**) was known[21,36] but both bicyclo[5.2.0]nonatriene (**20**) and bicyclo[3.2.2]nonatriene (**21**) were not. *cis*-Bicyclo[5.2.0]non-8-ene (**22**) was[37,38] prepared from cycloheptene by the method of Kirmse,[9] and hydrogenated to the known[39] *cis*-bicyclo[5.2.0]nonane identical with material prepared by the hydrogenation of **20**. Thus, both the skeleton and ring fusion of **20** became securely known. Bicyclo[3.2.2]nonatriene (**21**) was hydrogenated to bicyclo[3.2.2]nonane which, in turn, was made from the known[40] bicyclo[3.2.2]non-6-en-2-one (**23**) by hydrogenation followed by Wolff–Kischner reduction.



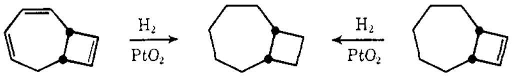
18a, $R = COOCH_3$
b, $R = COOH$
c, $R = COCl$
d, $R = CH_2OH$
e, $R = CHO$
f, $R = C{=}N{-}NH{-}Ts$



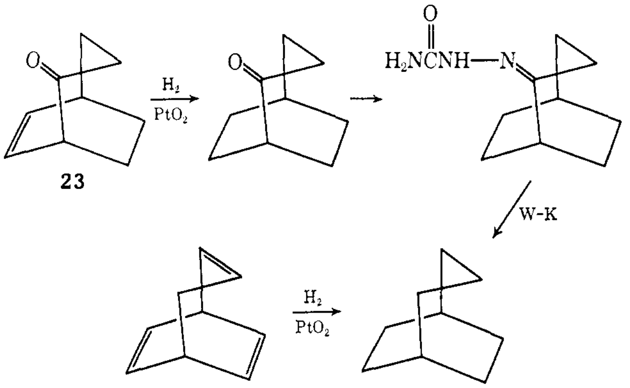
19 (37%)

21 (12%)

20 (27%)



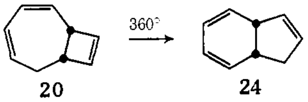
20 **22**



23

21

The decomposition of **18f** gives not only both the product of the expected 1,5 shift (**19**) and the unexpected 1,3 shift (**21**) but also the hoped for cyclobutene **20**. Pyrolysis of **20** confirmed that the shift mechanism (path B) was not operating. The cyclobutene **20** was converted not to **19** or **21** but instead to *cis*-8,9-dihydroindene (**24**).[41] That **19** was not an intermediate in the transformation of **20** to **24** was confirmed by the isolation of unchanged **19** pyrolyzed under the same conditions.[42] One can now reject both path A and



20 **24**

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[33] S. Masamune, H. Zenda, M. Wiesel, N. Nakatsuka, and G. Bigam, *J. Amer. Chem. Soc.*, **90**, 2727 (1968).

[34] F. Korte, K.-H. Büchel, and F. F. Wiese, *Ann.*, **664**, 114 (1963).

[35] K. Mislow, K. Kondo, and W. M. Egan, unpublished work. We thank these authors for a private communication with permission to cite.

[36] L. Cannell, *Tetrahedron Lett.*, 5967 (1966).

[37] K. M. Shumate and G. J. Fonken, *J. Amer. Chem. Soc.*, **88**, 1073 (1966).

[38] K. M. Shumate, P. N. Neuman, and G. J. Fonken, *ibid.*, **87**, 3996 (1965).

[39] N. L. Allinger, M. Nakazaki, and V. Zalkow, *ibid.*, **81**, 4074 (1959).

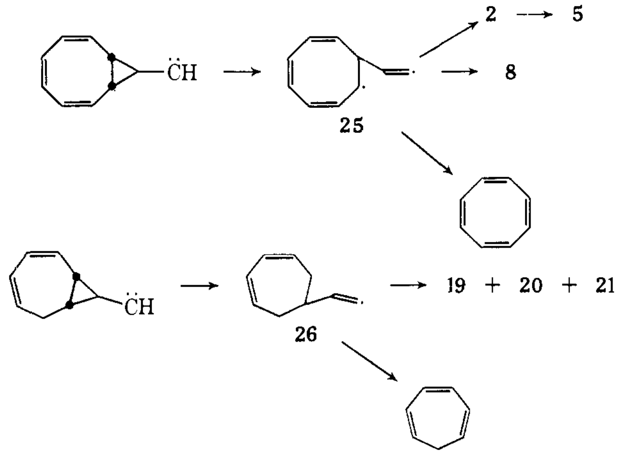
[40] J. A. Berson and M. Jones, Jr., *ibid.*, **86**, 5017, 5019 (1964). We thank Professor Berson for a sample of **23**.

[41] E. Vogel, W. Wiedemann, H. Kiefer, and W. F. Harrison, *Tetrahedron Lett.*, 673 (1963).

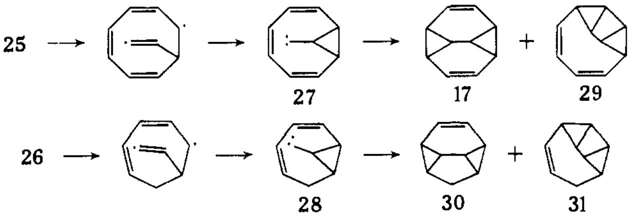
[42] Under more severe conditions **19** is converted to **24**. J. A. Berson and R. R. Boettcher, private communication with permission to cite.

path B, and only path C remains. The carbene must be rearranging directly to products.

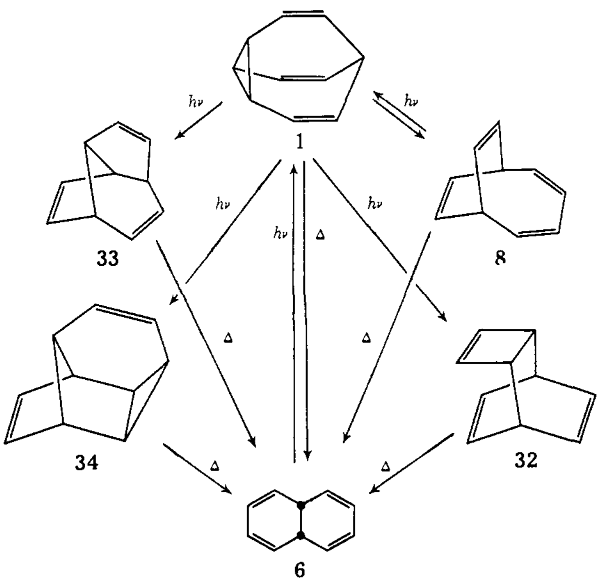
The general mechanistic scheme we favor is shown below. The carbene fragments to give a diradical which recloses at all possible positions to give the observed products. Further cleavage of the diradical could lead to cyclooctatetraene or cycloheptatriene. In the case of the (CH)$_{10}$'s the intermediate diradical **25** can only fragment to cyclooctatetraene and acetylene or reclose to give **8** or **2**. Compound **2** then rearranges to give the observed **5**. The intermediate **26** formed in the C$_9$H$_{10}$ series has an additional point of closure and here three cyclized products are obtained, **19**, **20**, and **21**.



A mechanistic variant on this scheme exists, but seems very unlikely to us. The diradicals **25** and **26** could undergo rotation as shown, followed by reclosure to the *cis*-carbenes, **27** and **28**. These, in turn, might add to the available double bonds to give, in the C$_{10}$ case, **17** and/or **29**, and in the C$_9$ case, **30** and **31**. These hypothetical compounds have paths available which could give all the observed products except the cyclobutene **20**, which might arise by some more simple ring-expansion reaction. The rotation called for in this mechanism is necessary in any event and we see no reason for the rotated diradicals to choose reconversion to the high-energy carbenes over the simple recyclization to give the stable bicyclic products.

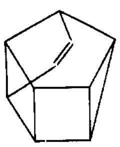


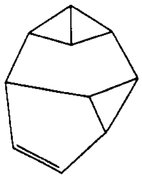
One of the sources of fascination with these molecules is their tendency toward rearrangement and, especially, interconversion. The photochemical interconversions are especially complex and, in our hands at least, began with the efficient conversion of **8** to **1**. This change which occurs slowly in Pyrex but rapidly in quartz, is of the di-π-methane type and has been discussed in general by Zimmerman.[43] While this transformation is clean and efficient the further photolysis of **1** which ensues in quartz, but not in Pyrex, is quite the opposite in character. A large variety of compounds, some old, some new, is formed. In addition to the establishment of a photoequilibrium with a small amount of **8**, four other (CH)$_{10}$'s are formed. One of them, Nenitzescu's[44] hydrocarbon (**32**), is known and easily identified. Of the others, **33** was originally[2c] identified by examination of spectra but now rests even more firmly on Masamune's synthesis of the hexahydro derivative.[33]

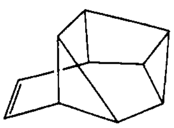


Compound **34** is the parent of two substituted molecules synthesized by Zimmerman from barrelene.[45] The nmr spectrum consists of a triplet (J = 2 Hz) of area 2 at τ 3.41, multiplets of area 1 at τ 3.67, 4.16, 7.52, and 7.78, a broad singlet of area 2 at τ 8.21, and a doublet (J = 6.3 Hz) of area 2 at τ 8.62. This spectrum, which is most strikingly similar to those reported by Zimmerman,[45] implies that one of the two double bonds is of the symmetrical norbornyl type and the other unsymmetrical. The only (CH)$_{10}$ fitting this description is **34**.[46]

The pentacyclic hydrocarbon **35** has only been tentatively identified. The compound has two different vinyl hydrogens as shown by the nmr spectrum. This limits the choice to **35a**, **35b**, or **35c**. The magnitude of the spin–spin coupling constant between the two vinyl hydrogens serves to render **35c** most unlikely. The value of 5.8 Hz is appropriate for the five-membered ring of **35a** or **35b** but unacceptable for the six-membered ring of **35c**.[47,48] Compound **35b** suffers a fair amount of mechanistic improbability as well as a lack


35a


35b


35c

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

(44) M. Avram, E. Sliam, and C. D. Nenitzescu, *Ann.*, **636**, 184 (1960).

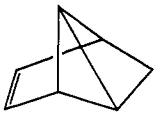
(45) H. E. Zimmerman and G. L. Grunewald, *J. Amer. Chem. Soc.*, **86**, 1434 (1964).

(46) A. T. Balaban, *Rev. Rom. Chim.*, **11**, 1097 (1966).

(47) P. Laszlo and P. von R. Schleyer, *J. Amer. Chem. Soc.*, **85**, 2017 (1963).

(48) R. G. Miller and M. Stiles, *ibid.*, **85**, 1798 (1963).

of spectral resemblance to the parent **36**.[49] In the nmr spectrum of **36** the two vinyl protons appear close together centered at τ 4.4 and are very highly split.



36

By contrast, **35** shows two four-line patterns, the lower field one appearing at τ 3.7 (J = 2.0,5.8 Hz) and the higher at τ 4.6 (J = 2.5, 5.8 Hz). We prefer **35a** for these reasons and because it can be formed by an intramolecular cyclization of **33**. Small amounts of **35** appear to be formed on direct irradiation of **33**, but the amount does not seem sufficient to account for the rather large amounts of **35** formed on extended irradiation of **1**. The possibility of a photosensitized ring closure of **33** is quite real, however.

Mechanisms of these conversions are quite difficult to determine as after a short time many species are present, and several direct and possibly some photosensitized decompositions are taking place. Initially **33** is the major product of low retention time of either the photolysis of bullvalene or the prolonged irradiation of Schröder's dimer.[50] At longer times the amount of **33** relative to **32**, **34**, and **35** decreases. Careful monitoring of the reaction by gas chromatography allows isolation of substantial amounts of most products (Table I).

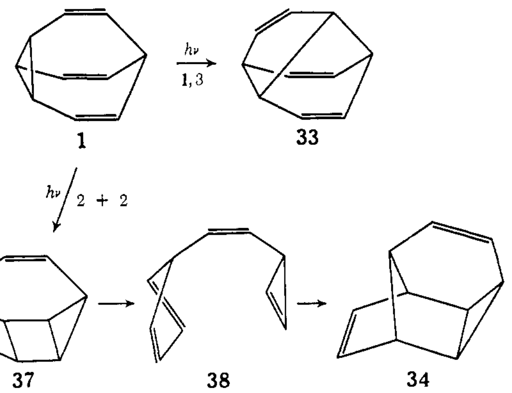
Table I. Photolysis of Bullvalene (**1**) through Vycor[a]

Time (min)	1	32	33	34	35	8
0	605	0	0	0	0	0
25	450	4	11	3	0	12
59	432	16	24	14	4	9
128	357	30	28	31	15	8
270	201	53	23	51	36	6
473	100	73	16	75	50	3
530	42	91	9	91	41	0

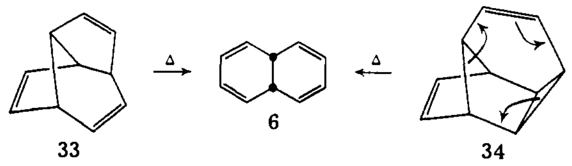
[a] Figures shown are relative areas not corrected for varying thermal conductivities.

The most attractive pathway leading to **33** is the vinylcyclopropane rearrangement of bullvalene. Photochemical rearrangements of this type are known,[51] and the rules of Woodward and Hoffmann permit a concerted suprafacial shift of order [1,3].[30]

Compound **34** may be formed by the 2 + 2 cyclization of **1**, another allowed[52] photochemical event, followed by cleavage to the intermediate **38**, which being held *cis*, zips together in Diels–Alder fashion to give **34**. A 1,3 shift in **37**, analogous to that postulated as the source of **33**, would lead to the pentacyclic hydrocarbon **35a**. The source of **32** remains obscure, and as alternatives to the mechanisms postulated above exist, further speculation is profitless.



Although the photochemical conversions noted above are bewildering in their complexity the thermal transformations share a common product and are often very simple. Doering, *et al.*,[5,53,54] have recorded that **1**, **32**, and **8** are converted to **6** on pyrolysis. We have also investigated this last case[55] and have discovered through deuterium labeling that intermediate between **8** and **6** is **17**. Both **34** and **33** are also converted to **6** on heating, the former easily at 100°, the latter more slowly. The former case has an obvious mechanism, the reverse Diels–Alder reaction shown; the latter does not.



Experimental Section

General. Infrared spectra were measured on a Perkin-Elmer Model 237B Grating Infrared spectrometer. Nmr spectra were measured on a Varian Associates A-60-A or HA-100 instrument.[57] Ultraviolet spectra were measured on a Cary Model 14 Ultraviolet spectrometer. High-resolution mass spectra were obtained on an AEI MS-9 instrument.[58] Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn. Gas-chromatographic analyses and collections were performed on a Varian-Aerograph A-90-P instrument: column "A," 6 ft, 20% Dow-Corning DC-710 on 45–60 mesh Chromosorb P; column "B," 5 ft, 15% SE-30 on 60–80 mesh Chromosorb W; column "C," 3.5 ft, 20% Carbowax 20M on 45–60 Chromosorb P.

Ethyl or Methyl Bicyclo[6.1.0]nona-2,4,6-triene-9-carboxylate (3a and 3b). A mixture of 150 ml of cyclooctatetraene and 15 g of cuprous sulfate in a four-necked flask fitted with a mechanical stirrer, thermometer, addition funnel, nitrogen inlet device, and efficient reflux condenser was maintained at 105–110° under nitrogen as 113 g of freshly prepared ethyl or methyl diazoacetate[59] was slowly added. The addition took 2 hr and the temperature was not allowed to rise above 120°. The brown solution was cooled, filtered, and the unreacted cyclooctatetraene (77 ml) recovered by distillation at the water pump. The black residue was

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(49) P. R. Story, *J. Amer. Chem. Soc.*, **83**, 3347 (1961). We thank Professor Story for copies of the nmr spectrum of **36**.

(50) G. Schröder, J. F. M. Oth, and R. Merényi, *Angew. Chem.*, 77, 774 (1965).

(51) R. N. Warrener and J. B. Bremner, *Rev. Pure Appl. Chem.*, **16**, 117 (1966).

(52) R. Hoffmann and R. B. Woodward, *J. Amer. Chem. Soc.*, **87**, 2046 (1965).

(53) W. von E. Doering and J. W. Rosenthal, *ibid.*, **88**, 2078 (1966).

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

(55) M. Jones, Jr., and B. Fairless, *ibid.*, 4881 (1968). Extensive details of similar work will shortly appear in *Can. J. Chem.*[56]

(56) Note Added in Proof. R. T. Seidner, N. Nakatsuka, and S. Masamune, *Can. J. Chem.*, **48**, 187 (1970).

(57) We thank the National Science Foundation and the National Aeronautics and Space Administration for providing the funds for the purchase of this instrument.

(58) We thank the National Science Foundation for providing funds for the purchase of this instrument under Grant No. GP-5200. The Instrument Laboratory at Princeton is supported in part by Biomedical Sciences Support Grant No. FR-07057.

(59) N. E. Searle, "Organic Syntheses," Coll. Vol. IV, John Wiley & Sons, Inc., New York, N. Y., p 424.

distilled to give 66 g (34%) of a pale yellow liquid [bp (**3b**) 82° at 0.25 mm (lit.[13] 89–90° at 0.8 mm)].

Bicyclo[6.1.0]nona-2,4,6-triene-9-carboxylic Acid (3c). A mixture of 66 g of **3b** and 44 g of NaOH in 800 ml of H_2O was refluxed for 15 hr. The homogeneous solution was cooled, extracted with 3 × 100 ml of ether, and acidified to pH 3 with 10% H_2SO_4. After 1.5 hr the solution was filtered to give 49 g (88%) of a tan solid. Sublimation at 120° and 0.8 mm gave white, crystalline **3c**, mp 164–165° (lit.[13] 162–163°).

Bicyclo[6.1.0]nona-2,4,6-trienecarbonyl Chloride (3d). The acid **3b** (12.0 g) was refluxed for 2 hr in 50 g of thionyl chloride. The excess thionyl chloride was removed at the water pump and the crude black product distilled to give 10.6 g (88%) of **3c**, mp 38–43°.

Bicyclo[6.2.1.]nona-2,4,6-triene-9-carboxaldehyde (3e). Method 1. The acid chloride **3d** (10.6 g) was dissolved in 75 ml of dry diglyme and cooled with stirring to −70°. A slurry of 60 ml of a 1 *M* solution of $LiAlH(OC_4H_9)_3$[60,61] in diglyme was slowly added. The temperature was maintained below −60° during the addition. After the addition, the solution was allowed to stir at −65° for 0.5 hr, allowed to warm to room temperature, and poured onto ice. The mixture was filtered and extracted with 7 × 50 ml of H_2O, dried over Na_2SO_4, and concentrated. The residual yellow liquid was distilled to give 3.4 g (39%, bp 79–83°, mp *ca.* 20°) of **3e**.

Method 2. To 9.5 g of aziridine in 20 ml of triethylamine and 100 ml of dry ether maintained at 0° was added a solution of 39 g of **3d** in 50 ml of ether. During the addition which took 0.75 hr a white precipitate formed. The precipitate was filtered and the salmon-pink solution cooled to 0°. A 1.7 *M* ethereal solution of $LiAlH_4$ (30 ml) was added over 0.5 hr. The solution was stirred for an additional 1 hr and 5% H_2SO_4 added. The solution was filtered, the aqueous layer washed with 2 × 30 ml of ether, and the combined ether layers washed with 2 × 50 ml of H_2O, 2 × 50 ml of $NaHCO_3$, and 2 × 50 ml of H_2O. The ethereal solution was dried over Na_2SO_4 and distilled to give 7.5 g of **3e** (24%).

Method 3. A solution of 60 g of **3a** in 80 ml of ether was added dropwise to a mixture of 15 g of $LiAlH_4$ in 600 ml of dry ether. The addition was regulated so as to maintain a gentle reflux. After completion of the addition the solution was refluxed for an additional 1.5 hr, allowed to cool, quenched with 20 ml of a 10% NH_4Cl solution, and filtered. The precipitate was washed with 3 × 50 ml of ether, the ethereal solution dried over Na_2SO_4, and concentrated. The crude alcohol was used directly in the next step.

The alcohol was dissolved in 600 ml of pyridine and added slowly to a mixture of 140 g of CrO_3 in 1300 ml of pyridine.[62] The dark brown mixture was stirred for 24 hr then extracted with 16 × 150 ml of ether. The combined ether layers were washed with 6 × 100 ml of 3% HCl, 5 × 100 ml of $NaHCO_3$, 3 × 150 ml of H_2O, dried over $MgSO_4$, and concentrated. Distillation of the residue gave 14 g of **3e** (30%). The washing procedure can be replaced with a continuous extraction of the solution formed by pouring the dark brown oxidation mixture into 10 l. of H_2O.

Bicyclo[6.1.0]nona-2,4,6-triene-9-carboxaldehyde Tosylhydrazone (3f). To a slurry of 5.25 g of *p*-toluene sulfonyl hydrazine in 60 ml of EtOH was added 3.5 g of **3e**. The solution was heated for 2 hr at 60° and 30 ml of H_2O added. Crystallization yielded two crops of an off-white solid **3f** (4.6 g, 61%, mp 142–143 dec).

Bicyclo[6.1.0]nona-2,4,6-triene-9-carboxaldehyde Hydrazone. Using the method of Newkome and Fishel,[63] the dimethylhydrazone was first prepared by heating a solution of 1 g of **3e** and 1.68 g of unsym-dimethylhydrazine in 3 ml of EtOH at 50° for 5 hr. The solvents were removed under vacuum to leave a dark oil which was distilled in a kugelrohr device (bp 85° at 1 mm) to give 1 g of a fish-smelling yellow oil. The above oil was dissolved in 5 cc of EtOH and 2.4 ml of anhydrous 95% hydrazine added. This solution was refluxed for 5 hr during which time it lightened in color slightly. The solvents were removed under vacuum to leave a dark oil which was oxidized directly.

Formation of the Lithium Salt of 3f. In a typical procedure 0.5 g of **3f** was dissolved in 5 ml of dry tetrahydrofuran (THF) and cooled to 0°, and 1.25 ml of a 1.6 *M* solution of butyllithium in hexane added through a serum cap. The addition of excess butyllithium was signaled by the development of a purple color. The solution was stirred for 0.5 hr at 0° and the solvent removed at the water pump to leave a dark solid coated on the walls of the flask.

Formation of the Sodium Salt of 3f. A mixture of 0.5 g of **3f** and 0.15 g of $NaOCH_3$ was dissolved in 7 ml of dry THF and allowed to stir under nitrogen overnight. The solvent was removed at the water pump to leave a light tan solid coating the walls of the flask.

Decomposition of the Salt of 3f. The flask containing the dry salt was connected *via* a short-path distilling head to a trap. A high vacuum was applied in the often vain hope that all traces of THF could be removed. The trap was cooled to −78° and the flask raised quickly to 70°, then more slowly to 90–100°, at which time decomposition set in. The products were removed from the trap, analyzed, and collected by gas chromatography on column A at 100°. Among the hydrocarbons produced, only **8** was new. Table II lists spectra of many of these $(CH)_{10}$'s.

Anal. Calcd for $C_{10}H_{10}$: C, 92.26; H, 7.74. Found: C, 92.41; H, 7.67.

Hydrogenation of *trans*-9,10-Dihydronaphthalene (5). A solution of 3 mg of **5** in 0.5 ml of MeOH was hydrogenated at atmospheric pressure and room temperature over platinum oxide. Absorption of hydrogen ceased after the uptake of 104% of the theoretical amount. Analysis on gas chromatography column A operated at 105° revealed two peaks in the ratio 8:1 with retention times equal to those of authentic *trans*- and *cis*-decalin, respectively. Collection of the major peak and analysis by infrared spectroscopy showed it to be *trans*-decalin.

Ozonolysis of Bicyclo[4.2.2]deca-2,4,7,9-tetraene (8). Ozone was passed into a solution of 12 mg of **8** in 1 ml of methyl acetate maintained at 0°. After 0.25 hr the solution was pale yellow but became colorless again after 1 hr. A mixture (1.5 ml) of 1:1 30% hydrogen peroxide and acetic acid was added and the solution refluxed for 1 hr. The solvents were removed under vacuum, ether added, and the solution esterified with diazomethane. Analysis on gas chromatography column A revealed dimethyl malonate but no methyl ethane-1,1,2,2-tetracarboxylic acid or dimethyl succinate.

Ring Expansion of Bicyclo[4.2.1]nonan-9-one (12). To 350 mg of **12** (prepared by the method of Gutsche[23] and purified by gas chromatography) in 4 ml of ether was added a solution of diazomethane prepared from 1.2 g of *N*-nitroso-*N*-methylurea in 10 ml of ether and 28 mg of LiCl. The solution was allowed to stand overnight at 0°. Analysis by gas chromatography on column A operated at 160° revealed starting material (relative retention time 1, relative area 12) and a new material (relative retention time 2.3, relative area 1). Collection yielded 25 mg of bicyclo[4.2.2]decan-7-one, ir 1700 cm^{-1}, semicarbazone mp 205–207°; precise mass measurement calcd for $C_{10}H_{16}O$: 152.120109. Found: 152.121283.

Reduction of Bicyclo[4.2.2]decan-6-one. A mixture of 34 mg of the semicarbazone of bicyclo[4.2.2]decan-7-one and 50 mg of $NaOCH_3$ in 0.5 ml of EtOH was sealed under nitrogen in a Pyrex bomb and heated at 195–200° for 14 hr. The tube was cooled, opened, and 0.5 ml of H_2O added. The solution was then extracted with 3 × 0.3 ml of pentane. Analysis by gas chromatography on column A operated at 130° revealed a peak of the same retention time as **8H-8**. Collection and comparison of infrared spectra revealed the identity of the two; precise mass measurement calcd for $C_{10}H_{18}$: 138.140844. Found: 138.140768.

Hydrogenation of Bicyclo[4.2.2]deca-2,4,7,9-tetraene (8). A solution of 8.2 mg of **8** in 2.4 ml of MeOH was hydrogenated at atmospheric pressure and room temperature over platinum oxide. In 11 min 100% of the theoretical amount of hydrogen was absorbed and uptake ceased. The solution was filtered and analyzed directly by gas chromatography on column A at 130°. The sole product, **8H-8**, was collected and shown to be identical with that made by reduction of bicyclo[4.2.2]decan-7-one.

***cis*-Bicyclo[6.2.0]deca-9-ene (15).** In a procedure paralleling that used to make compounds in the **3** series, cyclooctene was converted *via* ethyl bicyclo[6.1.0]nonan-9-carboxylate (bp 88–92° at 0.29 mm, lit.[13] 100–105° at 3 mm), bicyclo[6.1.0]nonan-9-carboxylic acid (mp 107–109°, lit.[13] 113.5–114.8°), bicyclo[6.1.0]nonan-9-carbonyl chloride (bp 86.5–89° at 1 mm), and bicyclo[6.1.0]nonan-9-carboxaldehyde (method 1, bp 85–86° at 3 mm) to the tosylhydrazone **13** (mp 126–128° dec). Compound **13** was converted to the lithium salt and decomposed to give cyclooctene and **15**. Gas-chromatographic analysis and collection were on column **B** operated at 130°.

***cis*-Bicyclo[6.2.0]deca-2,9-diene (16).** In a procedure paralleling that used to prepare **15**, 1,3-cyclooctadiene was converted *via* *cis*-ethyl bicyclo[6.1.0]non-2-ene-9-carboxylate (bp 89–95° at 0.8–1

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[60] H. C. Brown and R. F. McFarlin, *J. Amer. Chem. Soc.*, 80, 5372 (1958).

[61] H. C. Brown and B. C. Subba Rao, *ibid.*, **80**, 5377 (1958).

[62] G. I. Poos, G. E. Arth, R. E. Beyler, and L. H. Sarett, *ibid.*, 75, 422 (1953).

[63] G. R. Newkome and D. L. Fishel, *J. Org. Chem.*, 31, 677 (1966).

Table II. Spectral Properties of $(CH)_{10}$'s

Compd	Infrared[a]	Nmr[b]	Uv[c]	Rel retention time[d]
5	3022 (s), 2920, 2730 (s), 1694, 1632, 1609, 1546, 1419, 1399, 1374, 1344, 1244, 1203, 1154, 1061, 1043, 959, 940, 884, 868, 688 (s)	4.13 (6 H, s) 7.18 (2 H, s)	*e*, *f*	1.81
6	3025, 2910, 2838, 1716, 1636, 1570, 1445, 1434, 1410, 1359, 1307, 1175, 1100, 1036, 996, 960, 909, 920, 692 (s)	*g*	*g*	2.00
8	3035 (s), 3010 (s), 2958, 2915 (s), 1670, 1655, 1623, 1585, 1570, 1546, 1415, 1396 (s), 1365, 1314, 1300, 1273, 1246, 1238, 1171, 1149, 1025, 1010, 975 (s), 945 (s), 915, 904, 662 (s), 637 (s)	*h*	280 (2900) 268 (4200) 258 (4200)	2.92
33	3145, 3050 (s), 3028, 2935 (s), 1575, 1360 (s), 1322 (s), 1300, 1279, 1230, 1203, 1102, 1025, 990, 955, 933, 911, 855, 712 (s), 677 (s)	3.43 (2 H, d of d's) 4.19 (2 H, tr) 4.49 (2 H, d of d's) 6.90 (2 H, br s) 7.62 (2 H, br s)	238 (sh) (1400)	1.11
34	3100, 3035 (s), 2960 (s), 2850, 1656, 1626, 1551, 1406, 1345, 1306 (s), 1276, 1211, 1203, 1136, 1066, 1049, 1015, 985, 912 (s), 896, 877, 840, 716 (s), 676 (s)	3.41 (2 H, tr) 3.67 (1 H, m) 4.16 (1 H, m) 7.52 (1 H, m) 7.78 (1 H, m) 8.21 (2 H, br s) 8.62 (2 H, d)	*i*	1.21
35	3040 (s), 2992, 2950 (s), 1653, 1595, 1585, 1396, 1362, 1330, 1296 (s), 1283, 1262 (s), 1233 (s), 1193, 1158, 1124, 1101, 1076, 1035, 1018, 996, 980, 960, 931 (s), 924 (s), 900, 880, 855, 825, 674 (s)	(100 MHz) 3.76 (1 H, d of d's) 4.65 (1 H, d of d's) 6.62 (2 H, m) 7.32 (2 H, m) 7.61 (1 H, m) 7.80 (1 H, m) 8.42 (2 H, br d)		1.30
32	3100, 3039 (s), 2948 (s), 2909 (s), 2848, 1580, 1550, 1352, 1319, 1301, 1282, 1239, 1205, 1179, 1141, 1119, 1097, 1068, 976, 925, 896, 700 (s), 670 (s)	(100 MHz) 3.72 (2 H, d of d's) 4.09 (2 H, d of d's) 3.98 (2 H, s) 6.66 (2 H, m) 7.54 (2 H, m)		1.00
1	*j*	*j*	*j*	5.45

[a] cm^{-1}, s = strong, as CCl_4 solutions. [b] 60 MHz unless specified, τ scale, d = doublet, s = singlet, tr = triplet, m = multiplet, br = broad. [c] Nm (ϵ), solutions in EtOH. [d] Dow-Corning DC-710 silicone oil column operated at 100° with a He flow of 100 ml/min. [e] E. E. van Tamelen and T. L. Burkoth, *J. Amer. Chem. Soc.*, **89**, 151 (1967). [f] Reference 19. [g] E. E. van Tamelen and B. Pappas, *J. Amer. Chem. Soc.*, **85**, 3296 (1963). [h] Reference 55. [i] This compound is extremely difficult to free from traces of **6** because of the ease of the **34**–**6** rearrangement. The ultraviolet spectrum shows a peak at 247 nm, apparent ϵ 500, which may well be due to residual **6**. [j] Reference 4.

mm), *cis*-bicyclo[6.1.0]non-2-ene-9-carboxylic acid (mp 58–73°), *cis*-bicyclo[6.1.0]non-2-ene-9-carbonyl chloride (bp 84.5–85° at 1.1 mm), and *cis*-bicyclo[6.1.0]non-2-ene-9-carboxaldehyde (method 1) to the tosylhydrazone **14** (mp 137–139° dec). Compound **14** was converted to the lithium salt and decomposed to give 1,3-cyclooctadiene and **16**. Analyses and collections were on gas chromatography column B, operated at 130°.

Bicyclo[6.2.0]decane (8H-2). Hydrogenation of 15. A solution of 7.2 mg of **15** in 4 ml of MeOH was hydrogenated at atmospheric pressure and room temperature over platinum oxide. Uptake of hydrogen ceased after 130% of the theoretical amount had been absorbed and the single product was isolated by gas chromatography on column B operated at 120°.

Bicyclo[6.2.0]decane (8H-2). Hydrogenation of 16. A solution of 5.7 mg of **16** in 3 ml of MeOH was hydrogenated at atmospheric pressure and room temperature over platinum oxide. Hydrogen uptake ceased after absorption of 96% of the theoretical amount. Analysis and collection on gas chromatography column B operated at 120° yielded the single product **8H-2**, identical with that made above by hydrogenation of **15** but not identical with **8H-8**.

Oxidation of Bicyclo[6.1.0]nona-2,4,6-triene-9-carboxaldehyde Hydrazone. To the crude hydrazone prepared previously in 10 ml of ether was added HgO. A vigorous reaction ensued and addition was continued until it subsided. The solution was filtered, an additional 2 g of HgO added, and the mixture allowed to stir overnight. Analysis by gas chromatography of the filtered solution on column C operated at 105° revealed **5**, **6**, **7**, and **8** as well as 1,2-dihydronaphthalene and naphthalene. Compounds were isolated and spectra compared with those of the compounds produced from the tosylhydrazone salt.

***cis*-Bicyclo[5.1.0]octa-2,4-diene-8-carboxaldehyde (18e).** To a stirred solution of 10.0 g of **18d** (prepared by the method of Korte[34]) in 75 ml of dry diglyme maintained at −70° was added 72 ml of a 1 *M* solution of $LiAlH(OC_4H_9)_3$ in diglyme. The temperature was maintained below −65° during the addition. The mixture was allowed to stir for an additional 0.25 hr, warmed to room temperature, and poured onto ice. The resultant mixture was filtered and extracted with 4 × 50 ml of ether. The residual salts were leached with several portions of ether and the combined ether washings were washed with 5 × 100 ml of H_2O and dried over $MgSO_4$. Concentration gave 4 g (50%) of **18e** which was used as obtained.

***cis*-Bicyclo[5.1.0]octa-2,4-diene-8-carboxaldehyde Tosylhydrazone (18f).** In our hands the following is the only way to consistently obtain crystalline **18f**. All other means tried gave, at least on occasion, sensitive oils which could not be crystallized. To a suspension of 14 g of *p*-toluenesulfonyl hydrazine in 7 ml of MeOH maintained at 0° was slowly added 9.2 g of **18e**. After the addition the slightly yellow homogeneous solution was warmed to 50° for 1 hr. On cooling, two crops of white crystals were collected, totaling 9.5 g (mp 134–135° dec, 45%).

Anal. Calcd for $C_{16}H_{18}N_2O_2S$: C, 63.61; H, 5.91. Found: C, 63.39; H, 6.14.

Formation of the Sodium and Lithium Salts of 18f. The procedures used were identical with those employed to make the salts of 3f.

Decomposition of the Salt of 18f. The flask containing the salt was connected through a short-path distillation head to a trap. A high vacuum was applied to the often vain hope of removing all the THF. The trap was then cooled to −78° and the flask warmed quickly to 70° and then more slowly to 90–100° at which point decomposition began. The products were removed from the trap and analyzed and collected by gas chromatography on column A operated at 100°. Two new hydrocarbons, *cis*-bicyclo[5.2.0]nona-2,4,8-triene (**20**) and bicyclo[3.2.2]nonatriene (**21**) were isolated, in addition to the known bicyclo[4.2.1]nonatriene; precise mass measurement (**20**) calcd for C_9H_{10}: 118.07862; found: 118.078247; precise mass measurement (**21**) found: 118.078456.

Hydrogenation of *cis*-Bicyclo[5.2.0]nona-2,4,8-triene (20). A solution of 5.3 mg of **20** in 3 ml of MeOH was hydrogenated at atmospheric pressure and room temperature over platinum oxide. After 70% of the theoretical uptake absorption of hydrogen ceased. The single product was isolated by gas chromatography on column C operated at 90°.

Hydrogenation of *cis*-Bicyclo[5.2.0]non-8-ene (22). The sodium salt of bicyclo[5.1.0]nonan-8-carboxaldehyde tosylhydrazone (prepared by the method of Kirmse and Pook[9]) was decomposed to give **22** identical with that prepared by these authors.[9] A solution of 14.1 mg of **22** in 1.5 ml of MeOH was hydrogenated at atmospheric pressure and room temperature to give, after collection from gas chromatography column C operated at 95°, *cis*-bicyclo[5.2.0]nonane identical with that from the hydrogenation of **20** and with that produced by Allinger, *et al.*[39]

Hydrogenation of Bicyclo[3.2.2]nonatriene (21). A solution of 4.2 mg of **21** in 2.5 ml of MeOH was hydrogenated at atmospheric pressure and room temperature over platinum oxide. After absorption of 92% of the theoretical amount of hydrogen, uptake ceased. Isolation by gas chromatography on column C operated at 90° gave bicyclo[3.2.2]nonane (mp 157–158° lit.[64] 159°).

Hydrogenation of Bicyclo[3.2.2]non-6-en-2-one (23). Bicyclo[3.2.2]nonan-2-one Semicarbazone. A solution of 46.1 mg of **23** in 6 ml of MeOH was hydrogenated at atmospheric pressure and room temperature over platinum oxide. After 114% of the theoretical amount of hydrogen had been absorbed uptake ceased. The filtered solution was used directly for the formation of the semicarbazone (mp 187–190° dec).

Bicyclo[3.2.2]nonane. A mixture of 25 mg of bicyclo[3.2.2]nonan-2-one semicarbazone and 45 mg of $NaOCH_3$ in 0.5 ml of EtOH was sealed under nitrogen in a Pyrex bomb and heated at 195° for 12 hr. The bomb was cooled, opened, and 2 ml of H_2O added. The solution was extracted with 10×0.2 ml of pentane. Gas chromatography of the dried pentane solution gave bicyclo[3.2.2]nonane identical with that produced above.

Pyrolysis of Bicyclo[5.2.0]nona-2,4,8-triene (20). A flowing system, consisting of an 18-cm Pyrex tube heated over 5 in. of its length to 360° and fitted with a nitrogen inlet and a trap at the exit, was used to pyrolyze 7.2 mg of **20**. Nitrogen flowing at the rate of 60 ml/min was allowed to pass over the liquid **20** thus slowly passing it through the hot tube and into the trap. Analysis by gas chromatography on column A operated at 100° showed only *cis*-8,9-dihydroindene.

Pyrolysis of Bicyclo[4.2.1]nonatriene (19). In the above flowing system 10 mg of **19** was pyrolyzed in exactly the same fashion. Infrared analysis of the single product showed it to be recovered **19**.

Photolysis of Bicyclo[4.2.2]deca-2,4,7,9-tetraene (8). A solution of 6.5 mg of **8** in 0.3 ml of pentane was irradiated through Pyrex at room temperature with a Hanovia 450-W medium-pressure mercury arc. After 23 min, analysis and collection of the products gave 4 mg of recovered **8** and 1.2 mg of **1**.

Photolysis of Bullvalene (1). A solution of 330 mg of **1** in 75 ml of ether was irradiated through a Vycor shield with a 450-W Hanovia medium-pressure mercury arc. Analysis on gas-chromatography column A at 100° revealed five products: Nenitzescu's hydrocarbon (**32**), tricyclo[5.3.0.0^{4,8}]deca-3,7,9-triene (**33**), tetracyclo[4.4.0.0^{2,8}0^{5,7}]deca-3,9-diene (**34**), the pentacyclic hydrocarbon **35**, and bicyclo[4.2.2]deca-2,4,7,9-tetraene (**8**). Of these **34** and **35** are new; precise mass measurement (**34**) calcd for $C_{10}H_{10}$: 130.078247. Found: 130.078296.

Anal. (**35**) Calcd for $C_{10}H_{10}$: C, 92.26; H, 7.74. Found: C, 92.02; H, 7.81

Pyrolysis of Tricyclo[5.3.0.0^{4,8}]deca-3,7,9-triene (33). In the flowing system described previously 10 mg of **33** were pyrolyzed at 280°. Analysis and collection on gas-chromatographic column C operated at 110° gave *cis*-9,10-dihydronaphthalene (**6**, 50%) and starting material (50%).

Pyrolysis of Tetracyclo[4.4.0.0^{2,8}0^{5,7}]deca-3,9-diene (34). A solution of 20 mg of **34** in CCl_4 was heated at 130° for 20 min. Analysis by nmr revealed conversion to a mixture of 50% *cis*-9,10-dihydronaphthalene, 35% starting material, and 15% naphthalene.

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The Claisen Rearrangement of 3,4-Dihydro-2H-pyranylethylenes. A New Method for the Synthesis of Cyclohexenes[1]

G. Büchi and J. E. Powell, Jr.[2]

Contribution from the Department of Chemistry,
Massachusetts Institute of Technology, Cambridge, Massachusetts 02139.
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Abstract: The Claisen rearrangement of 3,4-dihydro-2H-pyranylethylenes provides a useful method for the preparation of substituted cyclohexenes. It complements the method of Diels and Alder by allowing the structurally specific synthesis of cyclohexenes often not available by the latter method. The ease of rearrangement is critically dependent upon the geometry of bulky substituents attached to the terminal carbon atom of the aliphatic double bond. The thermolysis of *trans*-olefins proceeds rapidly and efficiently but the rearrangement of *cis*-olefins is only of limited preparative value.

Of the various methods available for the synthesis of cyclohexenes, that associated with the names of Diels and Alder is perhaps the most versatile.[3] Condensation of dienes with dienophiles is characterized by high stereospecificity,[4] but the structural specificity is less pronounced and the combination of unsym-

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