Synthesis and Interconversion of Benzo $(CH)_{10}$ Hydrocarbons

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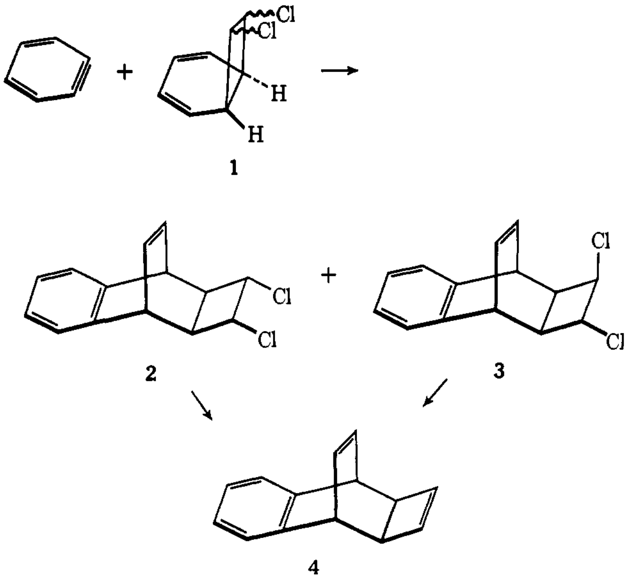
Abstract: Entry into the benzo $(CH)_{10}$ series has been gained by benzyne cycloaddition to 7,8-dichlorobicyclo-[4.2.0]octa-2,4-diene and subsequent dechlorination of the adducts. Sensitized photolysis of the *anti*-7,8-benzotricyclo[4.2.2.$0^{2,5}$]deca-3,7,9-triene (**4**) so produced gave rise chiefly to benzobasketene (**5**) and benzosemibullvalene derivative **6**. Thermal rearrangement of **4** afforded exclusively *cis*-4b,8a-dihydrophenanthrene (**8**). The Ag^+-catalyzed rearrangement of **5** to benzosnoutene (**19**) is described, as is the propensity of both **5** and **19** to thermal rearrangement. Thermolysis of **6** has been found to lead to the formation of benzotricyclo[5.3.0.$0^{4,8}$]deca-3,7,9-trienes **21** and **22**; interestingly, the latter two benzo $(CH)_{10}$ isomers undergo reversible interconversion at 425°. The photolysis of **8** proceeded rapidly to give 2,3-benzobicyclo[4.2.2]deca-2,4,7,9-tetraene (**25**); this rearrangement can be reversed thermally. When **25** was irradiated in acetone solution, the single isomer **21** was produced. Proofs of structure of several of these hydrocarbons are described and mechanisms for the various interconversions are proposed.

The recent interest in $(CH)_{10}$ hydrocarbons has evolved as a result of their fascinating propensity for thermal and photochemical interconversion, frequently under strict control of orbital symmetry,[2] and because of the remarkable capability of at least six of the isomers for degenerate isomerization,[3] a structural property of central mechanistic and theoretical significance. More recently, we have given attention to the conceptually related question of possibly altering bond relocation pathways known to be operative in the parent polyenes by occasioning preoccupation of one of the π bonds with benzenoid character.[4] The effective isolation of one of the olefinic centers in this way was expected to culminate not only in the attainability of new isomeric members of the basis set[5] (as benzo-fused derivatives), but also in added unravelling of the diverse and frequently intricate structural transformations.

Entry into the benzo $(CH)_{10}$ series was gained by cycloaddition of benzyne to the readily available 7,8-dichlorobicyclo[4.2.0]octa-2,4-diene (**1**).[6] The mixture of adducts **2** and **3** so produced (40% yield) could be readily separated by column chromatography on alumina. Whereas the nmr spectrum of cis isomer **2** shows well-defined and narrow multiplets for the four types of nonaryl protons, that of **3** exhibits multiplets that are substantially broadened, particularly in the δ 4.0–4.7 region. Treatment of these dichlorides with sodium anthracene in anhydrous tetrahydrofuran led in high yield to **4**. The anti stereochemistry of **4** follows from steric considerations,[7a] energetically favorable secondary orbital interactions expected in the transition state of the benzyne cycloaddition, and nmr data (see Experimental Section).[7b]



Acetone-sensitized photolysis of **4** for 80–90 min through Pyrex optics proceeded to give benzobasketene (**5**, 25%), together with **6** (27%) and its dihydro derivative (**7**, 6%).[8] The nmr spectrum of **5**, as expected, bears a striking resemblance to that of authentic bas-

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[1] The partial support of this work by National Institutes of Health Postdoctoral Fellowship No. 1-FO2-A143756 (1969–1970) and by a Grant-in-Aid from the Graduate School of The Ohio State University is gratefully acknowledged.

[2] (a) M. Jones, Jr., S. D. Reich, and L. T. Scott, *J. Amer. Chem. Soc.*, **92**, 3118 (1970), and references cited therein; (b) K. Hojo, R. T. Seidner, and S. Masamune, *ibid.*, **92**, 6641 (1970); (c) T. J. Katz, J. J. Cheung, and N. Acton, *ibid.*, **92**, 6643 (1970); (d) S. Masamune, K. Hojo, K. Hojo, G. Bigam, and D. L. Rabenstein, *ibid.*, **93**, 4966 (1971); (e) E. E. van Tamelen and B. C. T. Pappas, *ibid.*, **93**, 6111 (1971); E. E. van Tamelen, T. L. Burkoth, and R. H. Greeley, *ibid.*, **93**, 6120 (1971).

[3] The isomers which have been shown to exhibit such behavior are (a) bullvalene: W. von E. Doering and W. R. Roth, *Tetrahedron*, **19**, 715 (1963); G. Schröder, *Chem. Ber.*, **97**, 3140 (1964); W. von E. Doering, *et al.*, *Tetrahedron*, **23**, 3943 (1967); (b) bicyclo[4.2.2]deca-2,4,7,9-tetraene: W. Grimme, H. J. Riebel, and E. Vogel, *Angew. Chem.*, **80**, 803 (1968); *Angew. Chem., Int. Ed. Engl.*, **7**, 823 (1968); M. Jones, Jr., and B. Fairless, *Tetrahedron Lett.*, 4881 (1968); (c) snoutene: L. A. Paquette and J. C. Stowell, *J. Amer. Chem. Soc.*, **93**, 2459 (1971); (d) *cis*-9,10-dihydronaphthalene: L. A. Paquette, *ibid.*, **93**, 7110 (1971); (e) hypostrophene: J. S. McKennis, L. Brener, J. S. Ward, and R. Pettit, *ibid.*, **93**, 4957 (1971); (f) bicyclo[5.3.$0^{4,8}$]deca-2,5,9-triene (lumibullvalene): L. A. Paquette and M. J. Kukla, to be submitted for publication.

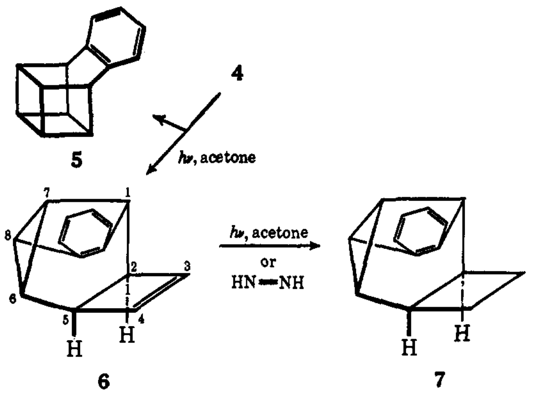
[4] For a preliminary communication which describes our early work in this area, consult L. A. Paquette and J. C. Stowell, *Tetrahedron Lett.*, 2259 (1970).

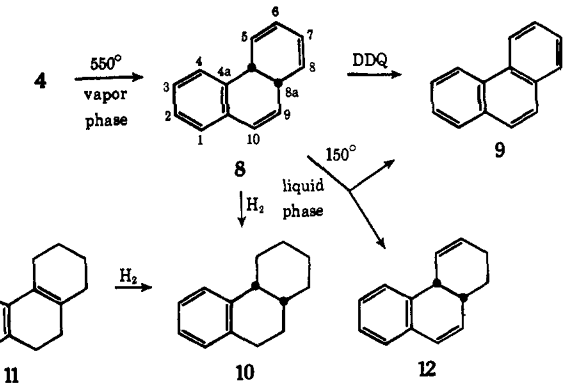
[5] The structural possibilities in the $(CH)_{10}$ series have been tabulated: A. T. Balaban, *Rev. Roum. Chim.*, **11**, 1097 (1966).

[6] R. Huisgen, G. Boche, W. Hechtl, and H. Huber, *Angew. Chem.*, **78**, 595 (1966); *Angew. Chem., Int. Ed. Engl.*, **5**, 585 (1966); J. Gasteiger, G. E. Gream, R. Huisgen, W. E. Konz, and U. Schnegg, *Chem. Ber.*, **104**, 2412 (1971).

[7] (a) L. A. Paquette and J. C. Stowell, *Tetrahedron Lett.*, 4159 (1969); *J. Amer. Chem. Soc.*, **93**, 5735 (1971); (b) hydrocarbon **4** is also available in low yield from the addition of benzyne to cyclooctatetraene: E. Vedejs and R. A. Shepherd, *Tetrahedron Lett.*, 1863 (1970).

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



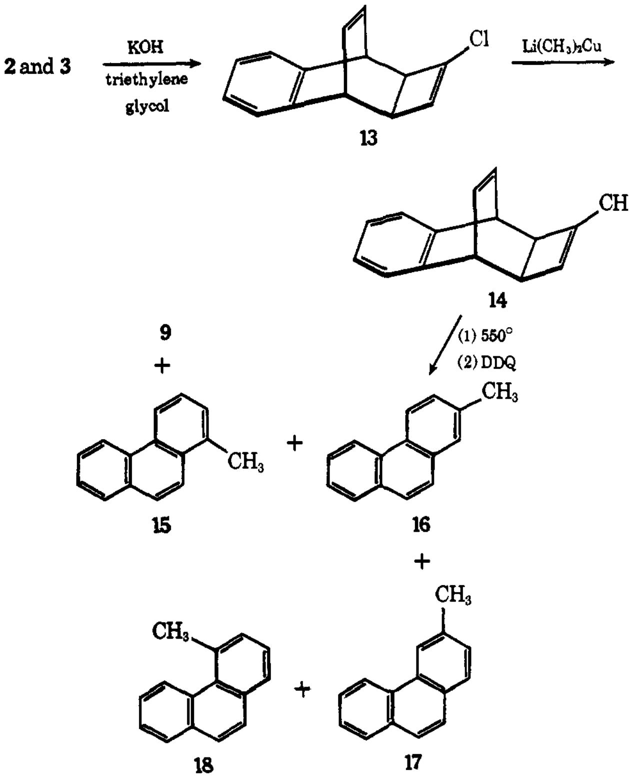


ketene.[9] Benzo $(CH)_{10}$ isomer **6** was considered to be the result of di-π-methane rearrangement analogous to that observed in the photoisomerization of mono- and dibenzobarrelenes.[10] This mechanism requires that the cyclobutene ring be positioned exo. This stereochemistry is supported by the nmr spectrum in which H_1 appears as a doublet ($J = 5.0$ Hz), coupled uniquely to H_7. Were the cyclobutene in the endo configuration, H_1 would be coupled additionally to H_2 (dihedral angle relationship $\approx 30°$) and H_3 and H_4 would experience shielding by the proximate aromatic ring (not observed).

The structure of **7** was unequivocally confirmed by diimide reduction of **6**. Furthermore, the unusual susceptibility of **6** to photoreduction under the reaction conditions was independently established.

Vapor-phase pyrolysis of **4** in a flow system at 550° and 1 mm (N_2 entrainment, residence time <1 sec) proceeded in high (>95%) yield to afford *cis*-4b,8a-dihydrophenanthrene (**8**) contaminated with a small amount of phenanthrene (**9**) and traces of naphthalene. The electronic spectrum of **8** consists of a single maximum at 248 nm (ε 15,000). Triple resonance studies at 100 MHz revealed the following coupling constants: $J_{4b,8a} = 11$ Hz, $J_{9,10} = 10$ Hz, $J_{8a,10} = 3$ Hz. The gross structure of **8** was established by DDQ oxidation to **9**, whereas the cis stereochemistry of the ring juncture was confirmed by catalytic hydrogenation to **10** which was prepared unequivocally by similar treatment of **11**.[11] When **8** was heated for 3 hr in the liquid phase at 150°, disproportionation to **9** and tetrahydrophenanthrene **12** (ratio 1:1) was seen to be complete.

With the structure of **8** resolved, attention was turned to the mechanism of this skeletal change. In order to label an additional carbon atom in **4**, dichlorides **2** and **3** were dehydrochlorinated by means of potassium hydroxide in triethylene glycol at 180°[12] to afford **13** in 92% yield. The conversion of this vinyl chloride to **14** was effected by methylation with lithium dimethylcuprate.[13] Pyrolysis of **14** as above at 550° (1.5 mm) afforded a pale yellow oil which was oxidized directly with DDQ in benzene solution. Chromatography of the crude reaction mixture on alumina led to isolation of a hydrocarbon mixture which consisted (vpc analysis) of phenanthrene (18%),[14] methylphenanthrenes (61%), naphthalene (7%), recovered **14** (10%), and two unknown substances (2 and 1%, respectively). The methylphenanthrene fraction was collected by preparative scale vpc and analyzed quantitatively by infrared and nmr spectroscopy. Under conditions of infinite dilution, the chemical shift of a methyl group on the



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

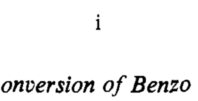
[10] (a) E. Ciganek, *J. Amer. Chem. Soc.*, **88**, 2882 (1966); (b) P. W. Rabideau, J. B. Hamilton, and L. Friedman, *ibid.*, **90**, 4465 (1968); (c) H. E. Zimmerman, R. S. Givens, and R. M. Pagni, *ibid.*, **90**, 6096 (1968).

[11] H. Christol, Y. Pietrasanta, and J.-L. Vernet, *Ann. Chim. (Paris)*, 145 (1968); H. Christol, R. Jacquier, and M. Mousseron, *Bull. Soc. Chim. Fr.*, 248 (1958). The complete absence of any *trans-as*-octahydrophenanthrene was shown by comparison with a sample of the pure trans isomer prepared by the method of J. W. Cook, C. L. Hewett, and C. A. Lawrence, *J. Chem. Soc.*, 71 (1936). Another sample of pure cis was prepared by the method of R. P. Linstead, R. R. Whetstone, and P. Levine, *J. Amer. Chem. Soc.*, **64**, 2014 (1942), thereby confirming the early literature assignments of these two isomers (trans, 900, 766 cm^{-1}; cis, 935, 759 cm^{-1}).

[12] W. Metzner and W. Hartmann, *Chem. Ber.*, **101**, 4099 (1968).

[13] E. J. Corey and G. H. Posner, *J. Amer. Chem. Soc.*, **89**, 3911 (1967); **90**, 5615 (1968).

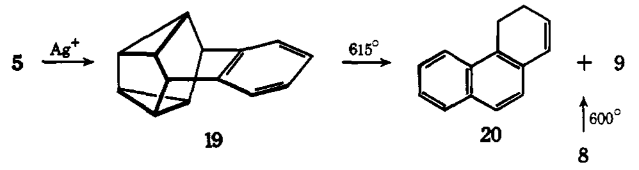
[14] The production of phenanthrene appears to be the result of the demethylation of i during the DDQ oxidation [*cf.*, for example, J. F. Bagli, P. F. Morand, K. Wiesner, and R. Gandry, *Tetrahedron Lett.*, 387 (1964)].



i

phenanthrene ring has been shown to be very characteristic of its position.[15] In the present work performed in carbon tetrachloride solution at 100 MHz, the following values were observed: 1-methyl (273.5 Hz), 2-methyl (253.8 Hz), 3-methyl (260.4 Hz), 4-methyl (313.5 Hz), and 9-methyl (270.3 Hz). The present mixture was found to consist solely of the 1-methyl- (**15**, 17%), 2-methyl- (**16**, 61%), 3-methyl- (**17**, 19%), and 4-methylphenanthrenes (**18**, 3%).

Exposure of dilute chloroform solutions of benzobasketene (**5**) to catalytic amounts of silver fluoroborate for 1 hr at room temperature, or elution of **5** through a column of silica gel–silver nitrate (5%), resulted in quantitative conversion to benzosnoutene (**19**).[3c,8] The nmr spectrum of **19** is very similar to that of snoutene;[8] furthermore, **19** shares with its $(CH)_{10}$ counterpart a surprising thermal stability. Rearrangement was observed to occur at 615° in the gas phase; at lower temperatures, **19** was recovered unchanged. Under these conditions, there was isolated a 3:1 mixture of 3,4-dihydrophenanthrene (**20**) and phenanthrene (**9**).

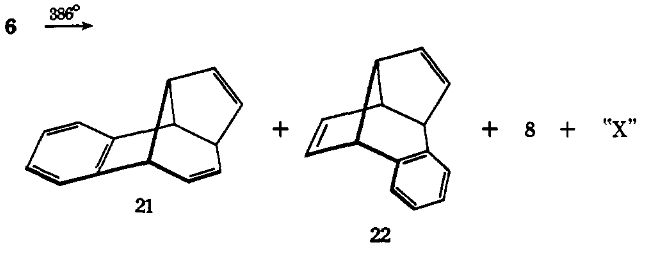


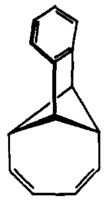
Because our mechanistic rationalization of this transformation suggested that dihydrophenanthrene **8** likely intervened in this bond reorganization, we were led to pyrolyze **8** at the requisite elevated temperature. At 600°, **8** likewise gave rise to **9** and **20**.

Benzobasketene (**5**), in contrast, was found to undergo thermal rearrangement at 350°. The particular bonding arrangement inherent in a cubic structure as found in **5** appears to be well suited to thermally induced retrograde (2 + 2) cycloadditions[16] and benzobasketene is no exception. Thus, decomposition of **5** resulted in the formation of **4** and its subsequent thermal product **8**.

$$5 \xrightarrow{350°} 4 + 8$$

Pyrolysis of benzosemibullvalene derivative **6** at 386° yielded an interesting array of products, chief among which were **21** (36%) and **22** (7%). The assignment of structure to **21** was based upon the identity of its physical and spectral properties with those previously reported by Vedejs[17] for this substance. In the case of **22**, the ultraviolet datum showed no evidence for extended conjugation [$\lambda_{max}^{C_2H_5OH}$ 251 (ϵ 650) and 259 nm (660)]. Its nmr spectrum revealed that this hydrocarbon encompasses symmetrical features capable of being found in only a very few triply unsaturated $(CH)_{10}$ isomers. In fact, of the three qualified[5] structural possibilities, **23** was easily rejected on the basis of the electronic spectrum and **24** was not adopted because of the gross dissimilarity of its spectral properties with those described for triquinacene[18] and dihydrotriquinacene.[19] That the correct structure was indeed **22** (C_2 symmetry) was established by double resonance studies at 100 MHz (see Experimental Section).[20]

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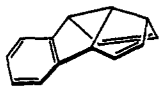
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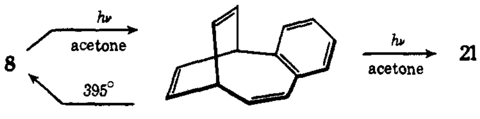
The thermal rearrangement of **6** also gave rise in low yield to dihydrophenanthrene **8** (7%) and to a fourth isomeric product termed "X" which was not characterized due to very limited amounts of material (4% yield). Studies at higher temperatures indicated that the proportions of **8** and **22** were substantially increased relative to those of **21** and "X." Accordingly, the thermal instability of **21** was established independently. At 425° in the gas phase (contact time ≤ 1 sec), **21** was converted to **22** and **8** in the ratio of 1.27:2.15; quantities of **21** (relative ratio 1.00) were also recovered. Significantly, when **22** was thermolyzed (425°) in the same manner, it was found to undergo partial reconversion to **21**.

$$21 \xrightarrow{425°} 8 + 22$$

$$22 \xrightarrow{425°} 8 + 21$$

Finally, the photochemical behavior of **8** was examined. Under conditions of acetone sensitization, a single photoisomer (**25**) was produced. The ultraviolet spectrum of **25** in isooctane solution was characterized by a series of maxima at 252 sh (ϵ 5300), 260 (7900), 270 (9800), and 280 nm (6600). The nmr spectrum displayed, in addition to aryl peaks, two multiplets of area 1 at δ 3.3 and 3.9 for the methine protons, a three-line olefinic pattern (4 H) at δ 5.9, and a two-proton olefinic doublet at δ 6.2. Upon double irradiation of the olefinic protons at 100 MHz, the individual methine multiplets collapsed to broadened singlets. However, because this information was not considered sufficient to remove the possibility that **26** was the photoproduct in question, the polyene was subjected to ozonolysis.



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(15) (a) P. Durand, J. Parello, and N. P. Buu-Höi, *Bull. Soc. Chim. Fr.*, 2438 (1963); (b) R. J. Ouellette and B. G. van Leuwen, *J. Org. Chem.*, 34, 62 (1969).

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

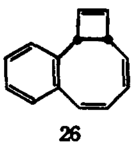
(17) E. Vedejs, R. A. Shepherd, and R. P. Steiner, *J. Amer. Chem. Soc.*, **92**, 2158 (1970).

(18) R. P. Woodward, T. Fukanaga, and R. C. Kelly, *ibid.*, **86**, 3162 (1964).

(19) R. Srinivasan, *ibid.*, **92**, 7542 (1970).

(20) Compare also the nmr spectrum of the parent $(CH)_{10}$ system: M. Jones, Jr., *ibid.*, **89**, 4236 (1967).

Esterification of the crude diacid so obtained afforded dimethyl homophthalate (**27**), thereby providing con-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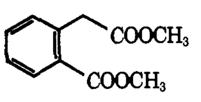

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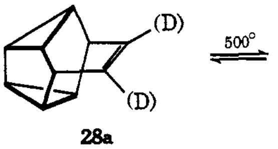
vincing experimental confirmation of assignment **25**. Interestingly, **25** was found to undergo thermal retrogression to **8** at 395° and slow photoisomerization to **21** under triplet conditions.

Discussion

Having established the structures of the various products, we now turn our attention to the pathways which seem likely for these skeletal changes. Earlier,[4] the suggestion was made that the thermal rearrangement of *anti*-7,8-benzotricyclo[4.3.3.0^{2,5}]deca-3,7,9-trienes such as **4** and **14** to *cis*-4b,8a-dihydrophenanthrenes could involve initial cyclobutene ring cleavage, 1,5-sigmatropic shift of the ethylene bridge, penultimate benzo[10]-annulene formation, and ring closure. A number of previous observations with related structures[21,22] were equally in agreement with this tentative proposal. However, the more recent work of Vedejs[23] and Masamune[24] clearly point to the operation in **4** and **14** of a Cope rearrangement or, more likely, its diradical equivalent.[25] The compatibility of the methyl labeling inherent in **14** to this mechanistic pathway is outlined in Scheme I.[26] As noted by Vedejs, this sequence of steps accounts nicely for the appearance of cis-fused dihydrophenanthrene to the exclusion of the trans-fused isomer. We note additionally that the benzo-annelation found in **4** and **14** efficiently blocks the operation of certain competitive symmetry-allowed processes which appear to be available to the parent tricyclo[4.2.2.0^{2,5}]deca-3,7,9-triene molecule.[23a]

The Ag$^+$-catalyzed conversion of benzobasketene (**5**) to benzosnoutene (**19**) finds analogy in the isomerization of other 1,8-bishomocubanes under these conditions.[27-29] Due to the excessive temperatures required to convert **19** to **20**, and the recognized susceptibility of **8** to hydrogen shifts under these conditions, we see that the significant chemical change is the conversion of benzosnoutene into *cis*-4b,8a-dihydrophenanthrene (**8**). Unlike the situation with snoutene (**28**) itself which undergoes twofold degenerate rearrangement more rapidly than isomerization to *cis*-9,10-dihydronaphthalene (**29**),[3c] **19** is incapable of degenerate valence



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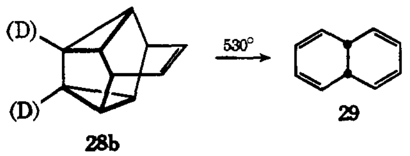
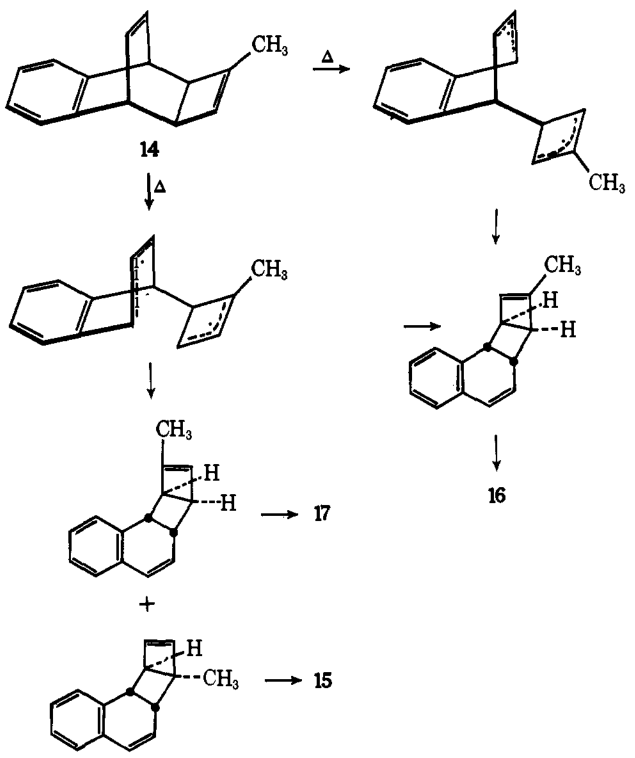


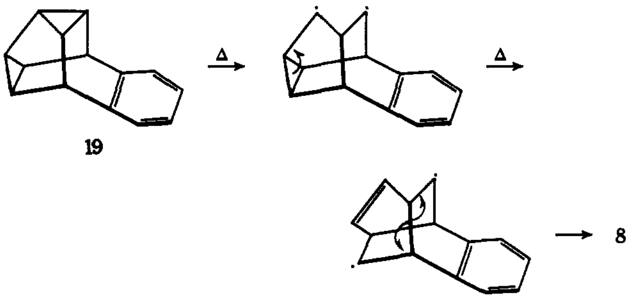
28b **29**

isomerization. However, the formally analogous processes which give rise to **8** and **29** are most readily explained by the mechanism depicted in Scheme II. In view of the recently established fact that *cis*-9,10-dihydronaphthalene (**29**) is capable of degenerate rearrangement in its own right,[3d] it now appears that **19** and **28** share a common isomerization pathway which does not involve 7-(2-cyclopropen-1-yl)-1,3,5-cycloheptatriene intermediates.[3c] In this regard, it is of interest that the

Scheme I



Scheme II



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(21) (a) C. D. Nenitzescu, M. Avram, I. I. Pogany, G. D. Mateescu, and M. Farcasiu, *Acad. Repub. Pop. Rom., Stud. Cercet. Chim.*, **11**, 7 (1963); (b) W. von E. Doering and J. W. Rosenthal, *J. Amer. Chem. Soc.*, **88**, 2078 (1966); (c) M. Avram, C. D. Nenitzescu, and E. Marica, *Chem. Ber.*, **90**, 1857 (1957).

(22) G. Maier, *ibid.*, **102**, 3310 (1969).

(23) (a) E. Vedejs, *Tetrahedron Lett.*, 4963 (1970); (b) E. Vedejs, *Chem. Commun.*, 536 (1971).

(24) H. H. Westberg, E. N. Cain, and S. Masamune, *J. Amer. Chem. Soc.*, **91**, 7152 (1969).

(25) J. A. Berson and E. J. Walsh, Jr., *ibid.*, **90**, 4730 (1968).

(26) The isolation of very small amounts of 4-methylphenanthrene cannot be correlated satisfactorily with either mechanism. At the present time, the mode of formation of this hydrocarbon is not understood.

(27) (a) L. A. Paquette and J. C. Stowell, *J. Amer. Chem. Soc.*, **92**, 2584 (1970); (b) W. G. Dauben, M. G. Buzzolini, C. H. Schallhorn, D. L. Whalen, and K. J. Palmer, *Tetrahedron Lett.*, 787 (1970).

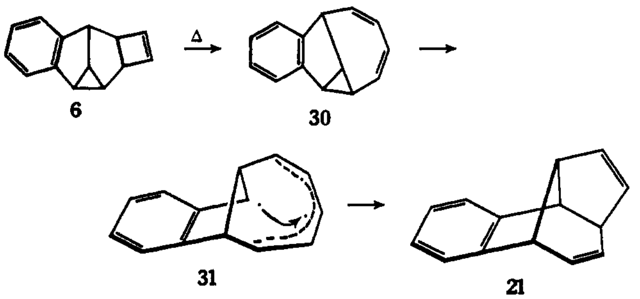
(28) L. A. Paquette, *J. Amer. Chem. Soc.*, **92**, 5765 (1970).

(29) The intrinsic mechanistic details of such skeletal bond reorganizations are to be discussed separately: L. A. Paqeutte and R. S. Beckley, paper in preparation; L. A. Paquette and J. S. Ward, paper in preparation.

positioning of the benzene ring in **19** is not suitable for assisting the sequential homolytic fission of either of the two "edge" cyclopropyl bonds. This conclusion is borne out by the experimental data since a higher temperature is required for isomerization.

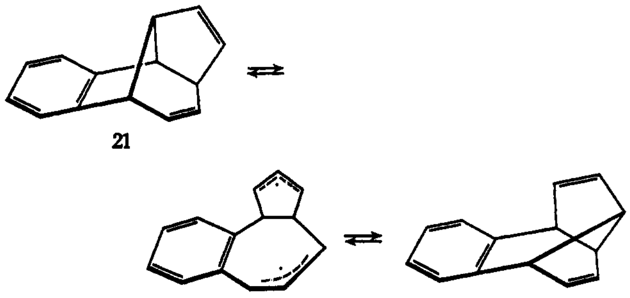
Turning to the case of **6**, we see that it represents a benzosemibullvalene system in which the 3 and 4 positions are bridged by a cyclobutene moiety. Initial opening of the central cyclobutene single bond in symmetry-disallowed (and therefore stepwise) ${}_{\pi}2_s + {}_{\sigma}2_s$ fashion leads directly to 8,9-benzotricyclo[5.3.0.0^{2,10}]decatriene (**30**), a molecule previously recognized[17] to be convertible to **21** at somewhat lower temperatures (330°, Scheme III). In the rearrangement of **30**, stabilized diradical **31** is very likely generated; subsequent σ bond formation by the indicated π diradical recombination pathway gives rise to **21**, the isomer with lesser inherent strain energy.

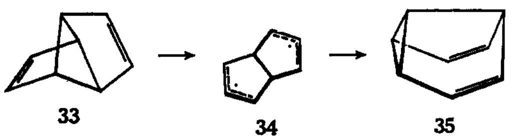
Scheme III



The interconversion of **21** and **22** can be explained on the basis of a nonconcerted 1,3 shift involving diradical **32** (Scheme IV). In this connection, we wish to call particular attention to the important quantitative difference in the temperature required for the **30** → **31**, **21** → **32**, and **22** → **32** bond cleavage reactions, specifically as they contrast with the ease with which tricyclo[3.3.0.0^{2,6}]octa-3,7-diene (**33**) undergoes closely analogous conversion to semibullvalene (**35**).[30] If such transformations are treated in the manner suggested recently by Goldstein and Hoffmann,[31] it is seen that the transition states of the first three bond cleavage processes can be represented by the formal zwitterionic representation **36**, whereas **34** may be described by formalism **37**. In view of the stabilized interactions enjoyed by 3^+3^- pericyclic structures such as **37** and the destabilization generally anticipated for 3^+5^- interacting ribbons of type **36**,[31] reactions such as those leading to **31** and **32** should be disfavored and apparently are.

Scheme IV

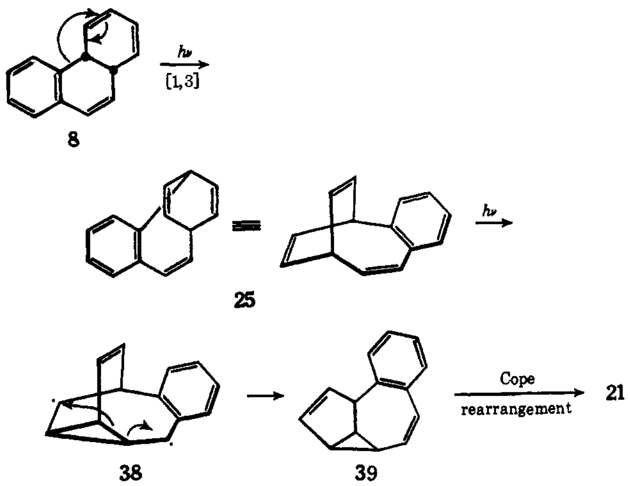




The isolation of lesser quantities of *cis*-4b,8a-dihydrophenanthrene from the pyrolysis of **21** and **22** can be construed as evidence supporting the capability of diradicals **31** and **32** for ring opening to benzo[10]annulene at the requisite elevated temperatures. However, this intriguing possibility has no supporting documentation at the present time.

The photoisomerization of **8** to **25** can be formulated as a concerted ${}_{\sigma}2_s + {}_{\pi}2_s$ (1,3-sigmatropic shift) reaction (Scheme V). The most attractive excited state pathway leading from **25** to **21** is initial di-π-methane rearrangement to benzotricyclo[5.3.0.0^{2,10}]decatriene **39** and subsequent thermal Cope rearrangement.[17] Photochemical rearrangements of this type are well known.[2a,32] Diradical **38** is also *a priori* capable of rearrangement to benzobullvalene, but apparently does not do so because benzobullvalene undergoes photochemical conversion to **21** only slowly under these conditions.[33]

Scheme V



Lastly, the thermal retrogression of **25** to **8** may occur by a precedented[3b] intramolecular ${}_{\pi}2_s + {}_{\pi}4_s$ cycloaddition and subsequent electrocyclic bond reorganization. However, because the first step of this pathway requires in the present instance temporary destruction of benzenoid aromaticity, it is possible that 1,3-vinyl or 1,3-benzo shifts are competitive. Whatever the pathway, it is clear that **8** is the thermodynamic well into which all benzo $(CH)_{10}$ isomerizations eventually tumble.

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(30) (a) J. Meinwald and D. Schmidt, *J. Amer. Chem. Soc.*, **91**, 5877 (1969); (b) J. Meinwald and H. Tsuruta, *ibid.*, **91**, 5877 (1969); (c) H. E. Zimmerman, J. D. Robbins, and J. Schantl, *ibid.*, **91**, 5878 (1969).

(31) M. J. Goldstein and R. Hoffmann, *ibid.*, **93**, 6193 (1971).

(32) (a) H. E. Zimmerman and A. C. Pratt, *ibid.*, **92**, 6259 (1970), and earlier papers by the Zimmerman group; (b) L. A. Paqeutte and G. R. Krow, *ibid.*, **90**, 7149 (1968).

(33) We are grateful to Professor E. Vedejs for providing us with details of his experience with the photochemistry of benzobullvalene.

Experimental Section

Benzyne Addition to 7,8-Dichlorobicyclo[4.2.0]octa-2,4-diene. A solution of anthranilic acid (7.14 g, 0.052 mol) in 40 ml of acetone was added dropwise over a 3-hr period to a refluxing solution of *cis*- and *trans*-7,8-dichlorobicyclo[4.2.0]octa-2,4-dienes[6,34] (8.76 g, 0.050 mol) and isoamyl nitrite (6.21 g, 0.053 mol) in 150 ml of methylene chloride. This was heated an additional hour and then evaporated *in vacuo* to give a black residue of tarry appearance. This material was taken up in ether coated on alumina, and chromatographed on alumina (elution with methylene chloride–pentane 1:1) to give 5.03 g (40%) of white crystals of mixed isomers **2** and **3** melting at 125–175°.

A sample (100 mg) rich in the lower melting isomer was chromatographed on Woelm neutral alumina and eluted with 5% methylene chloride in pentane. The isomer to elute first was recrystallized twice from ethanol to furnish pure **3** as white crystals, mp 134–135°; $\delta_{TMS}^{CDCl_3}$ 7.13 (s, 4, aryl), 6.5–6.8 (m, 2, olefinic), 4.0–4.6 (m, 4, diallylic methine and >C*H*Cl), and 2.7–3.0 (m, 2, methine).

Anal. Calcd for $C_{14}H_{12}Cl_2$: C, 66.95; H, 4.82. Found: C, 67.36; H, 4.89.

Another sample (100 mg) rich in the higher melting isomer was similarly chromatographed on alumina. The isomer to elute last was recrystallized from ethanol to give pure **2** as white crystals, mp 182–183°; $\delta_{TMS}^{CDCl_3}$ 7.18 (s, 4, aryl), 6.72 (t, J = 4.5 Hz, 2, olefinic), 4.0–4.3 (m, 4, diallylic methine and >C*H*Cl), and 2.67–2.90 (m, 2, methine).

Anal. Calcd for $C_{14}H_{12}Cl_2$: C, 66.95; H, 4.82. Found: C, 67.03, H, 4.86.

***anti*-7,8-Benzotricyclo[4.2.2.0^{2,5}]deca-3,7,9-triene (4).** A mixture of 26.75 g (0.15 mol) of anthracene in 250 ml of anhydrous tetrahydrofuran was placed in a dry 500-ml flask equipped with a glass-covered stirring bar. Sodium metal (3.46 g, 0.15 g-atom) cut into small pieces was added and the mixture was stirred at room temperature for 20 hr, after which time no undissolved sodium or anthracene could be detected. The dark blue solution was cooled in an ice bath and 12.55 g (0.050 mol) of a mixture of **2** and **3** was added under nitrogen during 10 min. The ice bath was removed and the mixture was stirred for an additional 20 min. Water (2.5 ml) was cautiously added dropwise until the intense color was discharged. The solvent was removed *in vacuo* and the residue was chromatographed on alumina. Pentane elution gave a semisolid hydrocarbon fraction (mixture of **4** and 9,10-dihydroanthracene) which was fractionally sublimed at 80° (10 mm) to give 9.01 g of **4** containing *ca.* 5% of 9,10-dihydroanthracene (vpc analysis). The residue of the sublimation was 3.14 g of nearly pure 9,10-dihydroanthracene (nmr analysis). The product was resublimed to afford 8.52 g (94.5%) of **4**, mp 44–51°. Further purification by preparative scale vpc 5 ft × 0.25 in. column packed with SF-96 (5%) on Chromosorb G, 165° gave **4** as a white solid, mp 51–52°; $\delta_{TMS}^{CDCl_3}$ 7.11 (m, 4, aryl), 6.22 (3 lines, 2, olefinic), 6.05 (s, 2, cyclobutenyl, 3.6–3.9 (m, 2, diallylic methine), and 2.65 (m, 2, methine).

Anal. Calcd for $C_{14}H_{12}$: C, 93.29; H, 6.71. Found: C, 92.87; H, 6.88.

Sensitized Photolysis of 4. A solution of 500 mg of **4** in 300 ml of acetone under nitrogen was irradiated with a 450-W Hanovia lamp through Pyrex for 90 min. The solvent was carefully evaporated and the residual oil was subjected to preparative scale vpc separation (same column as above). There was obtained 125 mg (25%) of **5**, 135 mg (27%) of **6**, and 30 mg (6%) of **7**.

The benzobasketene (**5**) was recrystallized from hexane to afford white crystals, mp 57–58°; $\delta_{TMS}^{CDCl_3}$ 7.32 (s, 4, aryl), 4.17 (m, 2, benzylic), 3.46 (m, 2, remote cyclobutyl), and 3.00 (m, 4, cyclobutyl).

Anal. Calcd for $C_{14}H_{12}$: C, 93.29; H, 6.71. Found: C, 92.98; H, 6.80.

Benzosemibullvalene derivative **6** was obtained as a colorless oil, $\delta_{TMS}^{CDCl_3}$ 7.06 (m, 4, aryl), 6.21 (d, J = 2.5 Hz, 1, olefinic), 5.96 (m, 1, olefinic), 3.55 (d, J = 5.0 Hz, 1, H_1), 3.10 (m, 1, H_2 or H_5), 2.99 (d, J = 2.5 Hz, 1, H_5 or H_2), 2.69 (m, 1, H_7), 2.35 (dd, J = 6.0 and 8.0 Hz, 1, H_8), and 1.97 (dd, J = 6.0 and 8.0 Hz, 1, H_6). Double irradiation showed that H_1 and H_7 were spin coupled, J = 5.0 Hz.

Anal. Calcd for $C_{14}H_{12}$: C, 93.29; H, 6.71. Found: C, 93.19; H, 6.74.

Dihydro derivative **7** was likewise a colorless oil; $\delta_{TMS}^{CDCl_3}$ 6.7–7.4 (m, 4, aryl), 3.4 (d, J = 5.0 Hz, 1, cyclopropyl), and 1.5–3.0 (m, 9, methine and methylene protons).

Anal. Calcd for $C_{14}H_{14}$: C, 92.26; H, 7.94. Found: C, 92.18; H, 7.90.

Sensitized Photolysis of 6. A solution of 16.5 mg of **6** in 10 ml of acetone was irradiated through Pyrex with a 450-W Hanovia lamp for 10 hr. The progress of the reaction was followed by vpc; after this length of time, virtually complete conversion to a second compound was noted. The crude yellow oil was purified by preparative vpc (above column at 150°) to yield 1 mg of colorless oil. An infrared spectrum showed this substance to be **7**.

Diimide Reduction of 6. A solution of 52 mg (0.28 mmol) of **6** and 1.0 g (5.5 mmol) of potassium azodicarboxylate in 20 ml of methanol was placed in a 50-ml three-necked flask equipped with a reflux condenser and dropping funnel. Dropwise addition of 1 ml (16 mmol) of acetic acid initiated an exothermic reaction which refluxed briefly. The mixture was allowed to stir for 30 min during which time the yellow color of the solution had faded. Water (50 ml) was added and the product was extracted into ether (3 × 50 ml). The combined ether layers were washed with saturated sodium bicarbonate solution and brine, dried, and evaporated. Molecular distillation of the residual oil afforded 50 mg (95%) of **7**, with infrared and nmr spectra identical with those obtained on the previous samples.

***cis*-4b,8a-Dihydrophenanthrene (8).** A 200-mg sample of **4** was passed through a quartz tube (28 cm × 16 mm) packed with quartz chips maintained at 550° (1 mm) with a slow stream of nitrogen. There was collected in the cold (−70°) trap 198 mg of a pale yellow oil. Vpc and nmr analysis indicated that essentially one pure substance had been produced with a small amount of phenanthrene and a trace of naphthalene. The pyrolysis product was purified by chromatography on silica gel–silver nitrate (15%); attempted purification by preparative scale vpc resulted in disproportionation (see below). Elution with benzene brought out phenanthrene; continued elution with benzene and ether–benzene gave **8** which was finally molecularly distilled at 60° (0.1 mm); $\lambda_{max}^{isooctane}$ 248 nm (ϵ 15,000); $\delta_{TMS}^{CDCl_3}$ 6.9–7.3 (m, 4, aryl), 6.45 (dd, J = 9.5 and 2.5 Hz, 1, H_{10}), 5.45–6.05 (m, 5, olefinic), 3.70 (m, 1, H_{4b}), and 3.28 (m, 1, H_{8a}). Triple resonance at 100 MHz showed $J_{H_{4b}-H_{8a}}$ to be 11 Hz.

Anal. Calcd for $C_{14}H_{12}$: C, 93.29; H, 6.71. Found: C, 93.38; H, 6.65.

Oxidation of 8. To a solution of 103 mg of **8** (as crude pryolysate) in 2 ml of benzene was added 252 mg of dichlorodicyanobenzoquinone. A green color and a precipitate appeared immediately and the solution became warm. After 5 min, this mixture was poured onto a column of alumina (12 cm × 8 mm) and elution was performed with benzene. There was obtained 89 mg of white solid, mp 80–89°, which when recrystallized once from ethanol melted at 96–98° (67 mg). The infrared and nmr spectra were identical with those of phenanthrene.

***cis-as*-Octahydrophenanthrene (10). A. Hydrogenation of 8.** A 54-mg sample of **8** dissolved in 4 ml of ethyl acetate was hydrogenated at atmospheric pressure over 5% palladium on carbon. Filtration of the catalyst, evaporation, and distillation gave 36 mg of colorless liquid. Vpc analysis showed one major and several minor components. Separation of the main component afforded 16 mg of *cis-as*-octahydrophenanthrene (**10**); $\delta_{TMS}^{CDCl_3}$ 7.04 (s, 4, aryl), 2.5–3.0 (m, 3, benzylic), and 1.1–2.1 (m, 11, methine and methylenes).

B. Hydrogenation of 1,2,3,4,9,10-Hexahydrophenanthrene (11). Catalytic reduction of 20 mg of **11**[11] in 1 ml of ethyl acetate over Adams' catalyst at 1 atm and 25° furnished 19 mg of colorless oil, identical in all respects with the sample of **10** prepared above.

Disproportionation of 8. A freshly prepared 200-mg sample of **8** was heated at 150° in a sealed evacuated glass tube for 3 hr. Gas chromatography of the resulting semisolid showed two major and two very minor peaks. The major products were isolated by preparative vpc to give 64 mg of phenanthrene and 63 mg of *cis*-1,2,4a,10a-tetrahydrophenanthrene (**12**), a colorless liquid; $\lambda_{max}^{isooctane}$ 260 (ϵ 7850) and 267 sh nm (7700); $\delta_{TMS}^{CDCl_3}$ 6.8–7.2 (m, 4), 6.36 (dd, 1), 5.45–5.95 (m, 3), 3.39–3.58 (m, 1), 2.59–3.00 (m, 1), 2.90–3.15 (m, 2), and 1.58–2.84 (m, 2). Triple resonance at 100 MHz gave $J_{H_{4a}-H_{10a}}$ as 8.0 Hz.

Anal. Calcd for $C_{14}H_{14}$: C, 92.26; H, 7.74. Found: C, 92.36; H, 7.73.

***anti*-3-Chloro-7,8-benzotricyclo[4.2.2.0^{2,5}]deca-3,7,9-triene (13).** A mixture of **2** and **3** (2.51 g, 10 mmol) was added cautiously over a 10-min period to a mixture of potassium hydroxide (1.98 g of 85%, 30 mmol) and 10 ml of triethylene glycol at 180°. The mixture was heated for an additional 15 min at 180–190°, cooled, and poured into 100 ml of water. The resulting precipitate was filtered, dried,

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(34) R. Pettit and J. Henery, *Org. Syn.*, 50, 36 (1970).

and sublimed (54°, 0.15 mm) to give 1.98 g (92%) of **13** as a white powder, mp 55–56.5°; $\delta_{\mathrm{TMS}}^{\mathrm{CDCl_3}}$ 6.9–7.3 (m, 4, aryl), 6.16–6.35 (m, 2, olefinic), 5.85 (s, 1, cyclobutene olefinic), 3.5–4.0 (m, 2, diallylic methine), 2.83 and 2.53 (t, J = 3.5 Hz, 1 H each, cyclobutene methine).

Anal. Calcd for $C_{14}H_{11}Cl$: C, 78.32; H, 5.16. Found: C, 78.52; H, 5.16.

***anti*-3-Methyl-7,8-benzotricyclo[4.2.2.0^{2,5}]deca-3,7,9-triene (14).** Methyllithium in ether (57.5 ml, 92 mmol) was added to cuprous iodide (8.75 g, 46 mmol) in 50 ml of dry ether at 0° under nitrogen. After 15 min, 1.98 g (9.2 mmol) of **13** was added and the mixture was stirred at room temperature for 24 hr. Water was added dropwise cautiously under nitrogen until gas evolution ceased, and then 50 ml more of water was added. The ether layer was separated and the water layer was extracted with ether. The combined organic layers were evaporated and the semisolid residue was extracted with pentane. The pentane extract was evaporated and the residue was molecularly distilled at 140–145° (15 mm) to give 1.27 g (71%) of **14** as a colorless oil. Analytically pure **14** was obtained by preparative vpc; $\delta_{\mathrm{TMS}}^{\mathrm{CDCl_3}}$ 7.0–7.4 (m, 4, aryl), 6.19–6.39 (5 lines, 2, olefinic), 5.81 (m, 1, cyclobutene olefinic), 3.60–3.93 (m, 2, diallylic methine), 2.4–2.65 (m, 2, cyclobutene methine), and 1.64 (m, 3, methyl).

Anal. Calcd for $C_{15}H_{14}$: C, 92.74; H, 7.26. Found: C, 92.57; H, 7.26.

Thermal Rearrangement of 14. A 200-mg sample of **14** was passed through a packed quartz tube at 550° (1.5 mm) as above with a slow stream of nitrogen to give 195 mg of pale yellow oil. Part (160 mg) of this oil was stirred with 250 mg of dichlorodicyanoquinone in 2 ml of benzene. Chromatography on a small column of alumina (benzene elution) furnished 150 mg of hydrocarbons. Gas chromatographic analysis indicated the presence of naphthalene (7%), phenanthrene (18%), methylphenanthrenes (61%), and two unknown substances (2 and 1%, respectively), in addition to recovered **14** (10%). The methylphenanthrene fraction was collected and examined at 1% concentration in CCl_4 using TMS sideband calibration. Four methyl peaks were observed at 253.8 (2-methyl isomer, 61%), 260.4 (3-methyl isomer, 19%), 273.5 (1-methyl isomer, 17%), and 313.5 (4-methyl isomer, 3%); the chemical shift values are expressed in Hz at 100 MHz downfield from TMS.[35,36]

Benzosnoutene (19). A. Rearrangement of 5 on Silica Gel–Silver Nitrate. A 65-mg sample of **5** was chromatographed on silver nitrate (5% by weight). Elution with pentane gave 59 mg of white solid, recrystallization of which from pentane gave pure **19**, mp 105–106.5°. No benzobasketene was present. A sample of **19** was gas chromatographed at 150° and recovered unchanged, mp 105–106.5°; $\delta_{\mathrm{TMS}}^{\mathrm{CDCl_3}}$ 7.05–7.35 (m, 4, aryl), 3.62 (m, 2, benzylic), 2.35 (m, 2, remote cyclopropyl), and 1.71 (m, 4, cyclopropyl).

Anal. Calcd for $C_{14}H_{12}$: C, 93.29; H, 6.71. Found: C, 93.38; H, 6.85.

B. Silver Fluoroborate Catalysis. A solution of 15 mg of **5** in 0.25 ml of $CDCl_3$ was treated with 2 mg of silver fluoroborate. Repeated nmr scans showed a gradual decrease in the absorptions due to **5** accompanied by gradual appearance of peaks due to **19**. No extraneous peaks were seen. The reaction was approximately 75% complete after 30 min.[37]

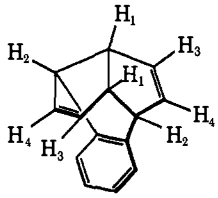
Pyrolysis of 19. A 50.6-mg sample of **19** was pyrolyzed (vapor phase) at 615° (2 mm) under nitrogen in the flow system previously described. Vpc analysis of the condensate showed a small amount of unreacted **19**, two major products, and very small quantities of several minor products. The major components were collected (6 ft × 0.25 in. column packed with 5% SF-96 on Chromosorb G at 165°). The product of longest retention time (5.7 mg) was phenanthrene (**9**). The other significant product was found to be 3,4-dihydrophenanthrene (**20**, 15.3 mg), mp 32–34°; $\delta_{\mathrm{TMS}}^{\mathrm{CDCl_3}}$ 7.1–8.2 (m, 6), 5.92–6.72 (m, 2), 2.75–3.4 (m, 2), and 2.1–2.65 (m, 2).[38]

Anal. Calcd for $C_{14}H_{12}$: C, 93.29; H, 6.71. Found: C, 93.14; H, 6.64.

High Temperature Thermal Rearrangement of *cis*-4b,8a-Dihydrophenanthrene (8). A 30-mg sample of **8** was introduced in the gas phase into the same pyrolysis apparatus maintained at 600°. Nitrogen was the carrier gas and the system was evacuated to 1.5 mm. The yellowish semisolid which was collected (21 mg) was shown by nmr and vpc analysis to consist of an approximate 1:1 mixture of 3,4-dihydrophenanthrene (**20**) and phenanthrene (**9**).

Pyrolysis of Benzobasketene (5). Benzobasketene (84 mg) was pyrolyzed as above at 350° (3 mm) in a slow stream of nitrogen. A vpc trace of the condensate (75 mg) showed that three products (ratio 1.5:2.3:1.0) had been formed. The components were separated by preparative scale gas chromatography (6 ft × 0.25 in. column packed with 5% XF-1150 at 155°) and shown to be unreacted **5**, **4**, and **8**, respectively.

Pyrolysis of 8,9-Benzotetracyclo[5.2.1.0^{2,5}.0^{6,10}]deca-3,8-diene (6). When an 112-mg quantity of **6** was pyrolyzed at 386° (3 mm) in the predescribed fashion, there was produced a mixture of four new components. Purification of these hydrocarbons by preparative vpc at 130° (5% SF-96 column) furnished 40.7 mg (36%) of **21**, the spectral parameters of which matched those reported by Vedejs for **21**.[17] The second component (7.9 mg, 7%) was assigned structure **22**, mp 50–51.5° (from methanol); $\lambda_{\max}^{\mathrm{C_2H_5OH}}$ 251 (ϵ 650) and 259 nm (660); $\delta_{\mathrm{TMS}}^{\mathrm{CDCl_3}}$ 3.04 (dd, $J_{1,2}$ = 2.5 Hz, $J_{1,3}$ = 2.0 Hz, H_1), 3.26 (m, H_2), 5.43 (dd, $J_{2,4}$ = 3.0 Hz, $J_{2,3}$ = 6.0 Hz, H_4), 6.21 (dd, H_4), and 6.90 (m, 4, aryl). The coupling constants were obtained by appropriate spin decoupling measurements at 100 MHz.



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Anal. Calcd for $C_{14}H_{12}$: C, 93.29; H, 6.71. Found: C, 93.03; H, 6.69.

The third component (7.4 mg) was identified as **8**, but the fourth component (6.0 mg) was not characterized due to limited quantities. Unfortunately, the 200-MHz nmr spectrum of "X" was not sufficiently resolved to permit an unequivocal assignment to be made.[39] The isomeric nature of "X" follows from its mass spectrum, *m/e* 180.0941 (calcd 180.0939).

Pyrolysis of 21. The hydrocarbon (43 mg) was pyrolyzed in the gas phase at 425° (3 mm) in a nitrogen atmosphere and furnished 40 mg of a yellow oil. This three-component mixture was separated into its components on the SF-96 column to give **22**, **8**, and recovered **21** in the ratio of 1.27:2.15:1.00.

Pyrolysis of 22. In the flow system described previously, 12 mg of **22** was pyrolyzed at 425° (2 mm) to yield a quantitative mass return. Preparative gas chromatography identified the various components as recovered **22**, isomeric counterpart **21**, "X," and dihydrophenanthrene **8** in the ratio of 21:67:1.0:1.5, respectively.

Sensitized Photoisomerization of 8. A solution of 120 mg of **8** in 8 ml of acetone was photolyzed through Pyrex with a 450-W Hanovia immersion lamp. The progress of the reaction was followed by vpc employing a sample of cyclododecane as an internal standard. After 6 hr, an apparent photostationary state of **8** and **25** of approximately 1:2 was realized. Continued irradiation revealed no further change in this ratio; however, polymerization began to set in. The product was isolated by preparative vpc at 155° on the XF-1150 column to give **25** (25 mg) as a colorless oil; $\lambda_{\max}^{\mathrm{isooctane}}$ 252 sh (ϵ 5300), 260 (7900), 270 (9800), and 280 nm (6600); $\lambda_{\max}^{\mathrm{C_2H_5OH}}$ 253 sh (ϵ 5400), 261 (7900), 270 (9600), and 279 sh (6700); $\delta^{\mathrm{CDCl_3}}{}_{\mathrm{TMS}}$ 3.3 (m, 1, methine), 3.9 (m, 1, methine), 5.9 (apparent t, 4, olefinic), 6.2 (apparent d, 2, olefinic), and 7.2 (m, 4, aryl).

Anal. Calcd for $C_{14}H_{12}$: C, 93.29; H, 6.71. Found: C, 93.07; H, 6.97.

Ozonolysis of 2,3-Benzobicyclo[4.2.2]deca-2,4,7,9-tetraene (25). Ozone was bubbled through a solution of **25** (53 mg) in 60 ml of CH_2Cl_2—CH_3OH (1:1) cooled to −78° for 10 min. To this solution was added 2 ml of 30% hydrogen peroxide, 2 ml of water, and 2 ml of formic acid and the mixture was refluxed for 3 hr. Solvent removal *in vacuo* furnished a yellowish semisolid. Esterification

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(35) We are grateful to Professor Ouellette for making available to us the authentic methylphenanthrenes or suitable precursors of these hydrocarbons.

(36) This product distribution differs somewhat from that reported in our earlier communication,[4] but represents a reproducible set of values. The newer analyses were conducted at 100 MHz rather than at 60 MHz as before.

(37) A more detailed kinetic analysis of this rearrangement will be reported elsewhere.

(38) The nmr spectra of 1,2- and 3,4-dihydrophenanthrenes at 40 MHz have been reported: C. Reid, *J. Mol. Spectrosc.*, **1**, 18 (1957).

(39) We thank Professor E. Wenkert for kindly recording this spectrum.

with diazomethane afforded a yellow oil which was purified by vpc at 160° (SF-96 column) to give 6 mg of dimethyl homophthalate (**27**).[40] An unidentified minor component (3 mg) was also isolated.

Pyrolysis of 2,3-Benzobicyclo[4.2.2]deca-2,4,7,9-tetraene (25). Thermal rearrangement of 17.7 mg of **25** in the gas phase at 395° (2 mm) (N_2 atmosphere) yielded 15.3 mg of pale yellow oil. Vpc analysis showed this material to consist of **8** and **25** in the ratio of 1.0:1.17, respectively. Separation of the isomers was achieved on the SF-96 column at 150° and the two components were characterized by their nmr spectra.

Photolysis of 25. A solution of 29 mg of **25** in 8 ml of acetone containing cyclododecane as an internal standard was photolyzed with a 450-W Hanovia lamp through Pyrex glass. After 1 hr, the starting material was seen to be converted cleanly to a single product of shorter retention time (SE-30 column). This photoproduct was purified by preparative vpc at 155° (XF-1150 column) and shown by nmr analysis to be 21.

Acknowledgment. The authors wish to thank Dr. Stanley A. Lang, Jr., for his generous assistance with the 100-MHz spectra.

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[40] For an infrared comparison, refer to Sadtler Infrared Prism Spectrum No. 7616.

Stable Carbocations.[1] CXXXIII. Bicyclononyl and Methylbicyclooctyl Cations

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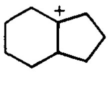
Abstract: The 2-methyl-2-bicyclo[3.2.1]octyl cation (**3**) is formed from several bicyclononyl precursors under long-lived ion conditions. Ion **3** is found to undergo irreversible thermal transformation to the 1-bicyclo[4.3.0]nonyl (8-hydrindyl) cation (**1**), which is also generated directly from bicyclo[4.3.0]nonyl precursors. The tertiary bridgehead 1-bicyclo[3.2.2]nonyl cation (**2**) is stable in SbF_5–SO_2ClF solution at temperatures below −50°. The proton and carbon-13 nmr spectra of ions **1**, **2**, and **3** are reported. The mechanism of the transformation of ion **3** to ion **1** is also discussed.

The solvolyses of bicyclononyl systems including bicyclo[3.2.2]nonyl,[2–5] bicyclo[2.2.2]octanecarbinyl,[6] bicyclo[3.3.1]nonyl,[7] bicyclo[4.2.1]nonyl,[8] hydrindyl,[7,9–11] methyl-substituted cyclohexenylethyl,[9–14] and 2-methylbicyclo[3.2.1]octyl derivatives[15,16] have been reported to give products *via* the classical (carbenium) ions **1–3** and nonclassical (carbonium) ions **4–5**.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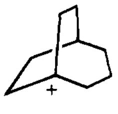
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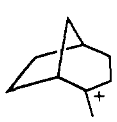
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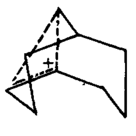
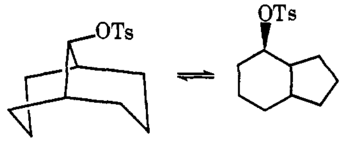
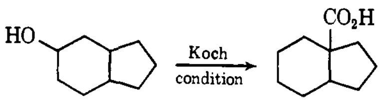

4


5

In their relevant studies Foote and Woodward[7] have reported on internal return of bicyclo[4.3.0]nonyl and 9-bicyclo[3.3.1]nonyl tosylates in acetic acid solvent, as well as the observation of *cis*- and *trans*-hydrindyl products. Aluminum chloride catalyzed isomerization[14,1,7] and the Koch reaction[18] of bicyclononyl systems also reveal the stability of bridgehead cations in these systems.





Bartlett's[19a] and Doering's studies[19b] indicated that bridgehead cations were extremely unstable. How-

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