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# Syntheses and Thermal Isomerizations of Bicyclo[3.2.2]nona-2,6,8-triene and Its Benzo Analog[1,2]

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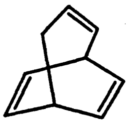
A convenient synthesis of bicyclo[3.2.2]nona-2,6,8-triene (**1**) was devised starting from the cycloheptatriene-maleic anhydride adduct. Benzo[*f*]bicyclo[3.2.2]nona-2,6,8-triene (**2**) was prepared starting from benzo[*f*]bicyclo[3.2.2]nona-3,6,8-trien-2-one. Heating **1** in *n*-hexane at 160—180°C gave almost quantitatively 3-vinylcycloheptatriene (**9**) besides a trace of 7-vinylcycloheptatriene (**10**). It was found however that **10** undergoes thermal isomerization into **9** under milder conditions. The result from **1** is thus rationalized by the existence of an equilibrium between **1** and **10** preceding the conversion of **10** into **9**. On the other hand, benzo analog **2** does not isomerize in a similar manner and instead, is transformed by heating at 270—290°C into benzobarbaralane (**14**) and hydrobenzindene (**15**). The contrast in behavior is discussed.

Despite the great interest involved, relatively little is known about bicyclo[3.2.2]nona-2,6,8-triene (**1**), a highly unsaturated polycyclic $C_9H_{10}$ hydrocarbons, perhaps because of the difficulty in synthesizing it.[3]



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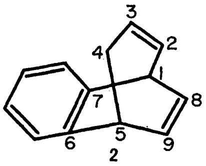

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Synthesis of **1** has been achieved independently by three groups,[3a–c] through multi-step processes and/or by ones involving troublesome purification procedures. During the course of studies on the cycloaddition reactions of cycloheptatriene,[4] we found a simple syntheses of **1**. This paper deals with the synthesis and

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[1] Presented at the IUPAC Symposium of Nonbenzenoid Aromatic Compounds in Sendai, August, 1970.

[2] The numbering used is shown in the charts. Compounds in which the substituent on the aliphatic ring is directed toward the benzene ring are difined as *endo*; those in which the substituent is directed away from the benzene ring are defined as *exo*.

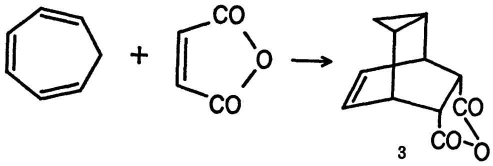
[3] a) M. Jones and S. D. Reich, *J. Amer. Chem. Soc.*, **89**, 3935 (1967); b) J. Daub and P. v. R. Schleyer, *Angew. Chem. Int. Ed. Engl.*, **7**, 468 (1968); c) J. B. Grutzner and S. Winstein, *J. Amer. Chem. Soc.*, **90**, 6562 (1968); d) S. W. Staley and D. W. Reichard, *ibid.*, **91**, 3998 (1969).

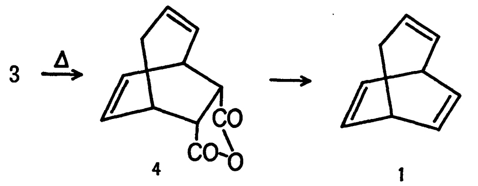
[4] T. Tsuji, S. Teratake, and H. Tanida, This Bulletin, **42**, 2033 (1969).

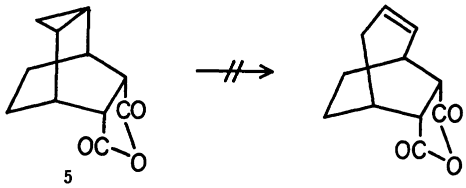
thermal rearrangement of **1** and a benzo variant, benzo[*f*]bicyclo[3.2.2]nona-2,6,8-triene (**2**). The thermal behavior of unsaturated polycyclic hydrocarbons is typically a unimolecular reaction, and as such can frequently give important data for testing the theories of such processes.[5] In this connection and because of our interest in such reactions,[6] thermolyses of the present [3.2.2]triene systems were investigated.

## Results and Discussion

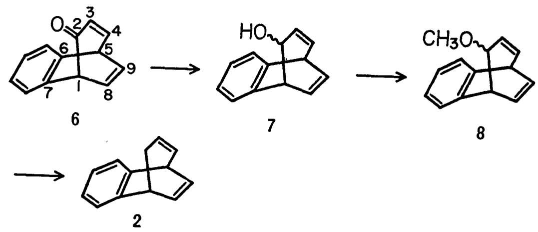
*Synthesis.* The cycloaddition of cycloheptatriene to maleic anhydride was reported by Alder and Jacobs[7] to produce a single adduct, tricyclo[3.2.2.0$^{2,4}$]non-6-ene-8,9-dicarboxylic anhydride (**3**). The photosensitized addition with the same materials has also been found by Schenk *et al.* to form mainly the same adduct, together with two other minor compounds.[8,9] Conversion of **3** into bicyclo[3.2.2]nona-2,6-diene-8,9-dicarboxylic anhydride (**4**) with opening of the cyclopropane ring was accomplished by heating **3** in chlorobenzene at 220°C. Such a relatively easy cleavage of cyclopropane was not observed with a similar treatment of the dihydro derivative of **3** (**5**).[10] Electrolytic bisdecarboxylation, principally by applying the reported procedure,[12] was carried out on **4** to obtain **1**, the physical properties of which were consistent in all respects with the reported data.[3a–c)

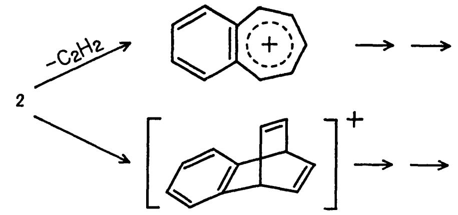






Essentially the same route reported for the preparation of bicyclo[3.2.1]octa-2,6-diene[13] and **1**[3c] was applied for the synthesis of **2**. Lithium aluminum hydride reduction of benzo[*f*]bicyclo[3.2.2]nona-3,6,8-trien-2-one (**6**) (prepared by the addition of benzyne to tropone)[14] gave a mixture of the *endo*- and *exo*-alcohols (**7**), which were methylated with dimethyl sulfate. *endo*- and *exo*-ethers (**8**) were treated with sodium-potassium alloy in dimethoxyethane and then quenched with methanol to yield **2** as crystals from **6** in 43% yield. The UV, IR, NMR, and mass spectral data are consistent with the indicated structure for **2** (see Experimental). The NMR pattern of the aliphatic moiety is very similar to that of **1**[3c] and shows the $C_3$ vinyl proton at an unusually high field $\tau$ 5.71. Since all the peaks reported for 2-methylnaphthalene,[15a] and benzobicyclo[2.2.2]octatriene[15b,c] but no other peaks were observed in the mass spectrum of **2**, it is considered that the fragmentation of **2** begins with the formation of the benzotropyrilium ion and the benzobicyclo[2.2.2]octatriene ion (*m/e* 154).





*Thermal Isomerization of Bicyclo*[*3.2.2*]*nonatriene* (**1**). When a solution of **1** in *n*-hexane was heated in a degassed sealed ampoule in the temperature range 160—180°C, the reaction mixture initially showed an almost quantitative formation of 3-vinylcycloheptatriene (**9**)[3b] besides a trace of 7-vinylcycloheptatriene (**10**).[16] Further heating of the mixture resulted in a

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[5] A review, H. M. Frey, "Advances in Physical Organic Chemistry," Vol. 4, V. Gold Ed., Academic Press, New York, N. Y. (1966), pp. 147—193.

[6] H. Tanida and Y. Hata, *J. Amer. Chem. Soc.*, **91**, 6775 (1969).

[7] K. Alder and G. Jacobs, *Chem. Ber.*, **86**, 1528 (1953).

[8] G. O. Schenk, J. Kuhls, and C. H. Krauch, *Ann. Chem.*, **693**, 20 (1966).

[9] Alder and Jacobs[7] originally assigned the *endo* configuration to the dicarboxylic anhydride group in **3**, while Schenk and his coworkers[8] suggested the *exo* configuration on the grounds that treatment of **3** with a basic iodine-potassium iodide solution did not cause iodolactonization. We re-examined the thermal cycloaddition reaction of cycloheptatriene with maleic anhydride and configuration of the adduct. From our preliminary results we prefer the *endo* configuration. Details of our re-examination will be reported soon.

[10] A bond-breaking process in simple cyclopropanes requires an activation energy as high as ~63 kcal.[11] Therefore, the result from **5** would be more common.

[11] B. S. Rabinowitch, E. W. Schlag, and K. Wiberg, *J. Chem. Phys.*, **28**, 504 (1958); B. S. Rabinowitch and E. W. Schlag, *J. Amer. Chem. Soc.*, **86**, 5996 (1960).

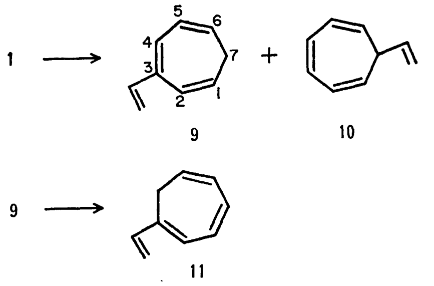
[12] P. Radlick, R. Klem, S. Spurlock, J. J. Sims, E. E. van Tamelen, and T. Whitesides, *Tetrahedron Lett.*, **1968**, 5117; H. H. Westberg and H. J. Dauben, Jr., *ibid.*, **1968**, 5123.

[13] J. M. Brown, *Chem. Commun.*, **1967**, 638.

[14] J. Ciabattoni, J. E. Crowley, and A. S. Kende, *J. Amer. Chem. Soc.*, **89**, 2778 (1967).

[15] a) "Catalog of Mass Spectral Data," American Petroleum Institute, Research Project 44, Carnegie Institute of Technology, Pittsburgh, Pennsylvania, Ref. 1, spectra Nos 855; b) R. G. Miller and M. Stiles, *J. Amer. Chem. Soc.*, **85**, 1798 (1963); c) T. Goto, A. Tatematsu, Y. Hata, R. Muneyuki, H. Tanida, and K. Tori, *Tetrahedron*, **22**, 2213 (1966).

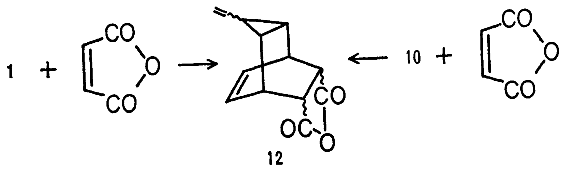
[16] R. B. King and F. G. A. Stone, *J. Amer. Chem. Soc.*, **83**, 3590 (1961).



hydrogen shift transforming **9** into 1-vinylcycloheptatriene (**11**). The structure of **11** was determined principally by the NMR spectrum which shows a doublet at $\tau$ 7.46 ($J$=7.0 Hz) arising from two methylene protons at $C_7$.[17] The 7-vinyl isomer **10** was independently synthesized and subjected to thermal isomerization. It was observed that **10** isomerizes into a 1:9 mixture of **1** and **9** in the temperature range 120—140°C, and that the products are the same as those from the thermolysis of **1**, although the reaction proceeded at lower temperatures. No isomerization of **1** thus formed was confirmed under the present conditions. The results are therefore compatible with an equilibrium between **1** and **10** preceding the conversion of **10** into **9**. A further support of this view was

$$\mathbf{1} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathbf{10} \xrightarrow{k_2} \mathbf{9}$$

provided by a trapping experiment. Thermolysis of **1** in the presence of maleic anhydride produced a tricyclic adduct bearing a vinylcyclopropane moiety (**12**), which was identical with the product obtained from the cycloaddition of **10** with maleic anhydride in boiling dioxane.



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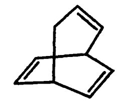
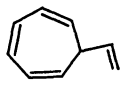
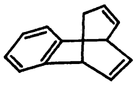
The rates of disappearance of **1** and **10** ($k_t$ and $k'_t$, respectively) on thermolysis were determined by use of vpc. Good first-order kinetics was observed in all runs. The rate constants thus observed are listed in Table 1, with the kinetic parameters derived at 159.2°C. Since it was confirmed experimentally that the concentration of **10** did not exceed 1.4% of the total of reaction components through all the reaction period, it is not unreasonable to approximate a steady state on **10**. Thus we obtain

$$k_t = k_1k_2/(k_{-1}+k_2) \text{ and } k_t' = k_{-1} + k_2$$

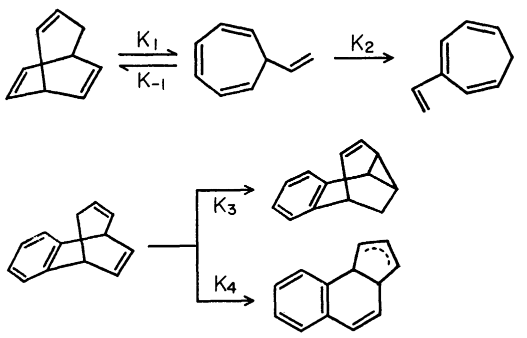
where $k_1$ and $k_{-1}$ are the interconversion rates between **1** and **10**, and $k_2$ is the rate of conversion of **10** into **9**. The constants, $k_1$, $k_{-1}$, and $k_2$, in Table 2 are thus calculated and the derived kinetic parameters produce a free energy diagram as shown in Fig. 1. The energy barrier $\Delta F^{\neq}$ for the interconversion between **1** and **10** at 159.2°C is 35.0 kcal/mol from **1** and 33.2 kcal/mol from **10**.

TABLE 1. RATE CONSTANTS OF THERMOLYSIS[a)]

| Compound | Temp °C | $k$, sec$^{-1}$ | $\Delta H^{\neq}$, kcal | $\Delta S^{\neq}$ cal/deg |
|---|---|---|---|---|
|  | 159.2 | $1.70\times10^{-5}$ | 34.3[b)] | −1.8[b)] |
| | 180.2 | $1.13\times10^{-4}$ | | |
|  | 119.7 | $3.61\times10^{-5}$ | | |
| | 140.0 | $2.49\times10^{-4}$ | | |
| | 159.2 | $1.30\times10^{-3}$ | 29.8[b)] | −3.5[b)] |
|  | 268.5 | $1.18\times10^{-4}$ | 46.8[d)] | 5.5[d)] |
| | 289.8 | $6.36\times10^{-4}$ | | |

a) Carried out with 0.1N solution in $n$-hexane.
b) Calculated at 159. 2°C.
c) Calculated by Arrhenius plots.
d) Calculated at 268. 5°C.

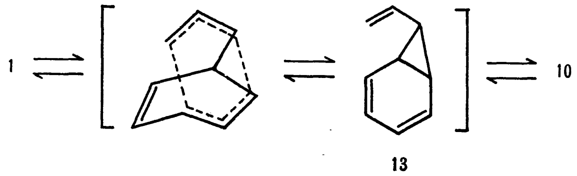
TABLE 2. ANALYSIS OF OBSERVED RATE CONSTANTS[a)]



| Process | Temp °C | $k$, sec$^{-1}$ | $\Delta H^{\neq}$, kcal | $\Delta S^{\neq}$, cal/deg |
|---|---|---|---|---|
| $k_1$ | 159.2 | $1.94\times10^{-5}$ | 34.1[b)] | −1.9[b)] |
| | 180.2 | $1.28\times10^{-4}$ | | |
| $k_{-1}$ | 119.7 | $2.89\times10^{-6}$ | | |
| | 140.0 | $2.49\times10^{-5}$ | | |
| | 159.2 | $1.58\times10^{-4}$[a)] | 33.4[b)] | 0.49[b)] |
| $k_2$ | 119.7 | $3.32\times10^{-5}$ | | |
| | 140.0 | $2.24\times10^{-4}$ | | |
| | 159.2 | $1.15\times10^{-3}$[c)] | 29.5[b)] | −4.5[b)] |
| $k_3$ | 268.5 | $8.43\times10^{-5}$ | 48.3[d)] | 10.8[d)] |
| | 289.8 | $4.79\times10^{-4}$ | | |
| $k_4$ | 268.5 | $3.37\times10^{-5}$ | 43.8[d)] | −1.4[d)] |
| | 289.8 | $1.57\times10^{-4}$ | | |

a) For calculations of $k_1$, $k_{-1}$, and $k_2$, see Text.
b) Calculated at 159. 2°C.
c) Calculated by Arrhenius plots.
d) Calculated at 268. 5°C.

A mechanism which accommodates all the results is



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[17] Cycloheptatrienes having no substituent at $C_1$ and $C_6$ show a triplet due to the protons at $C_7$. Refer to R. Roth, *Angew. Chem. Int. Ed. Engl.*, **2**, 688 (1963); A. P. ter Borg and H. Kloosterziel, *Rec. Trav. Chem., Pays-Bas*, **82**, 741 (1963).

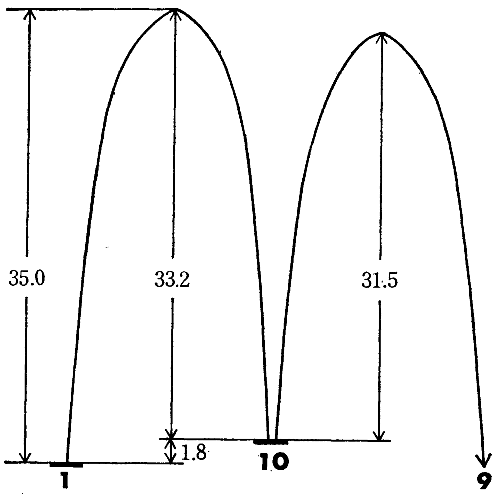
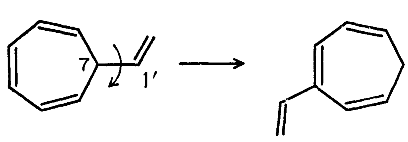
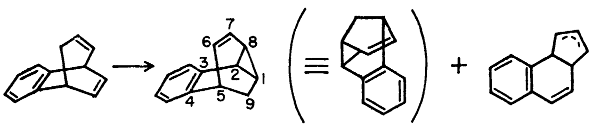


Fig. 1.

the Cope rearrangement (a [3,3]sigmatropic rearrangement) passing through *cis*-7-vinylnorcaradiene (**13**) as a transition state or an intermediate. The rearrangement of *cis*-6-vinylbicyclo[3.1.0]hex-2-ene to bicyclo-[3.2.1]octa-2,6-diene[18] and the formation of bicyclo-[3.2.2]nona-3,6,8-trien-2-one by treatment of cyclohepta-2,4,6-trienylacetyl chloride with triethylamine, presumably by a Cope rearrangement of the cyclohepta-2,4,6-trien-7-yl ketene intermediate,[19] are thought to be related precedents, although they are one-way reactions corresponding to the $k_{-1}$ process and not interconversion as in the present case. The isomerization of **10** into **9** is an example of the familiar 1,5-hydrogen shift. It is noted that the kinetic parameters ($\Delta H^{\neq}=29.5$ kcal, $\Delta S^{\neq}=-4.5$ cal/deg at 159.2°C) are comparable with those reported for the thermal isomerization of 1,4-bis(7-cycloheptatrienyl)benzene into 1,4-bis(3-cycloheptatrienyl)benzene ($\Delta H^{\neq}=29.8$ kcal, $\Delta S^{\neq}=-3.9$ cal/deg at 140°C),[20] but not with those for the isomerization of 7-phenylcycloheptatriene into 3-phenylcycloheptatriene ($\Delta H^{\neq}=26.9$ kcal, $\Delta S^{\neq}=-11.7$ cal/deg: for which the specific temperature has not been reported).[21] The 7 substituents in these molecules have freedom of rotation around the $C'_1$–$C_7$ axis, but it is somewhat restricted after the hydrogen has shifted, because the $\pi$-electrons in the substituents now come to conjugation with the unsaturation in the ring. The observed entropy decrease is compatible with this decreasing freedom of motion in the molecules.



*Thermolysis of Benzobicyclo[3.2.2]nonatriene(2).* The thermal transformtion of **2** in *n*-hexane was monitored by vpc at two temperatures, 268.5°C and 289.8°C and found to give mainly benzo[3,4]barbaralane (**14**) and the hydrobenzindene (**15**) (in total, 95%), with a trace of an unidentified compound. The ratios of **14** and **15** were 2.5:1 at 268.5°C and 3.0:1 at 289.8°C.[22] Rates and kinetic parameters are summarized in Tables 1 and 2. The two major products, **14** and **15**, were isolated by vpc. The structure of **14** was assigned on the basis of spectral evidence. The presence of two vinyl protons and the absence of a double bond conjugated with benzene were indicated by NMR and UV, respectively. The 100 MHz NMR data obtained using double and triple resonance techniques are in line with the structure **14** (see Experimental). Also, the NMR demonstrated that **14** possess a fixed structure, and not a fluxional character like barbaralane.[23] Conceivable alternatives to structures **14**, **16**, **17**, and **18** were ruled out by NMR. The methylene protons appear as a triplet at a field higher than usually expected for allylic protons and show no coupling with the vinyl protons. These facts eliminate structure **16.** The identical coupling constants ($J=7.6$ Hz) between $H_1$ and $H_2$, $H_1$ and $H_8$, and $H_2$ and $H_8$ support the existence of a three-membered ring, but not that of structure **17** or **18**. The UV maximum at 268 m$\mu$ ($\varepsilon$ 8500) observed in product 15 indicates the presence of a double bond conjugated with a benzene ring. The NMR spectrum of **15** exhibits a doublet of doublets at $\tau$ 3.8 assignable to a vinyl proton adjacent to a benzene ring. Catalytic hydrogenation over palladium on carbon resulted in the uptake of 2 moles of hydrogen to yield the known 2,3,3a$\beta$,4,5,9b$\beta$-hexahydro-1*H*-benz[*e*]-indene.[24] Consequently, the structure of **15** was determined to be either 3a,9b-dihydro-3*H*-benz[*e*]indene or its double-bond isomer, 3a,9b-dihydro-1*H*-benz[*e*]-indene.



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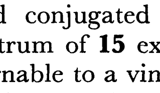

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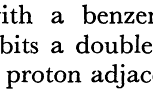

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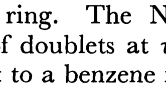

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The formation of **14** can be explained by postulating an intramolecular ene reaction[25] through such a six-membered transition state as **19**, which involves one of the allylic hydrogens. Concerning the formation of

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[18] J. M. Brown, *Chem. Commun.*, **1965**, 226; C. Cupas, W. E. Wattes, and P. v. R. Schleyer, *Tetrahedron Lett.*, **1964**, 2503.

[19] M. J. Goldstein and B. G. Odell, *J. Amer. Chem. Soc.*, **89**, 6356 (1967).

[20] R. W. Murry and H. L. Kaplan, *ibid.*, **88**, 3527 (1966).

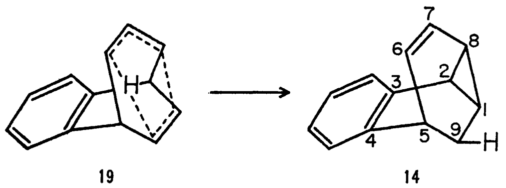
[21] A. P. ter Borg and H. Kloosterziel, *Rec. Trav. Chem., Pays-Bas*, **82**, 741 (1963).

[22] It was found that the reverse reaction from **14** to **2** takes place at a sufficiently slow rate compared with that of **2**→**14**, and is insignificant. Such a reverse reaction was not found for **15**, which decomposed very slowly on further heating.

[23] U. Biethan, H. Klusacek, and H. Musso, *Angew. Chem. Int. Ed. Engl.*, **6**, 176 (1967); W. V. E. Doering, B. M. Ferrier, E. T. Fossel, J. H. Hartenstein, M. Jones, Jr., G. Klumpp, P. M. Rubin, and M. Saunders, *Tetrahedron*, **23**, 3943 (1967).

[24] R. Muneyuki and H. Tanida, *J. Amer. Chem. Soc.*, **90**, 656 (1968).

[25] As an excellent review, *cf.* H. M. R. Hoffmann, *Angew. Chem.*, **81**, 597 (1969).



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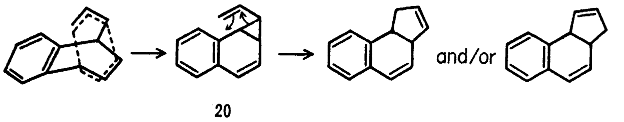
15, we have considered the Cope rearrangement leading to the *cis*-7-vinyl-2,3-benzonorcaradiene transition state or intermediate, followed by a vinylcyclopropane-cyclopentene rearrangement. A pair of *exo*- and *endo*-2-methoxy derivatives of **2** (**8**) were prepared in order to get stereochemical information on the migrating $C_4$ site (inversion or retention). It was found however that epimerization of the methoxyl group takes place at a temperature (190°C) below that at which the thermolysis occurs, and on thermolysis at ~230°C both epimers gave almost the same complex product mixtures. These findings can be understood by proposing an equilibrium between **2** and the norcaradiene intermediate (**20**)[26] preceding the product formation, which is analogous to the equilibrium between **1** and **10**. A rotation of the vinyl group in **20** followed by the return to **2** results in the epimerization. A resonable explanation for the present results is to assume the following reaction schema.



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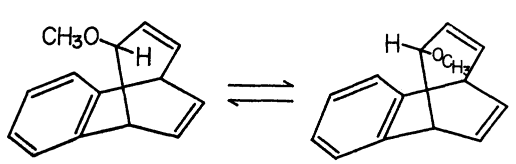

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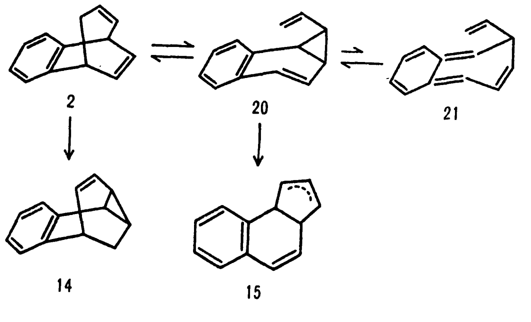

The question arises, why do the parent (**1**) and the benzo (**2**) compounds react differently? Transformation of **20** into the cycloheptatriene intermediate (**21**) must involve loss of aromaticity of the benzene ring which is thermodynamically unfavored. Such an unfavorable factor is not present in the reaction of **1**. As a result, the thermal isomerization of **2** must proceed by a different mechanism, requiring a temperature higher than that for **1**.

## Experimental

All melting points were taken in sealed capillaries and are corrected. Infrared spectra were determined with a Nippon Bunko IR-S spectrometer, ultraviolet spectra with a Beckman DK-2A spectrometer, and NMR spectra with a Varian Associates A-60A and/or HA-100. Mass spectra were taken on a Hitachi RMU-6 mass spectrometer. Vpc analysis was carried out on a Hitachi-Perkin-Elmer gas chromatograph F-6D equipped with a hydrogen flame ionization detecter using one of the following columns: (A) 1 m×3mm, stainless steel column packed with 5% XE 60 on Chromosorb W; (B) 1 m×3 mm stainless steel column packed with 5% SE on the same support; (C) 2 m×3 mm stainless steel column packed with 5% diethylene glycol succinate polyester on the same support. Helium was used as a carrier gas. Preparative vpc was carried out with a Yanagimoto gas chromatograph GCG, equipped with 6 m×14 mm stainless steel column, packed with 20% Silicon 550 on the Chromosorb W.

*Bicyclo[3.2.2]nona-2,6-dien-8,9-dicarboxylic Anhydride (4).* A solution of 10 g of the cycloheptatriene-meleic anhydride adduct (**3**) in 70 m*l* of chlorobenzene was placed in a heavy-walled glass ampoule, cooled to −70°C and sealed. The ampoule was placed in a steel bomb and heated at 220°C for 17 hr. The reaction mixture was cooled, decolorized by treatment with charcoal, filtered, and concentrated under reduced pressure. The residue was extracted with warm carbon tetrachloride. The solution was decolorized again, filtered and cooled to separate 4.5 g crystalline **4**. Concentration of the mother liquor gave 1.0 g of **4** (in total, 55% yield), homogeneous on vpc. Recrystallizaton from carbon tetrachloride afforded a pure sample; mp 136—138°C (lit,[8] mp 138—139°C); IR ($CCl_4$): 3060 (C=C), 1868, 1780, and 1223 $cm^{-1}$ (C=O); NMR ($CDCl_3$): $\tau$ 7.60 (m, 2H at $C_4$), 6.9 (broad m, 2H at $C_1$ and $C_5$), 6.52 (d-d, $J$=9.3 and 2Hz, 1H at $C_8$ or $C_9$), 6.23 (d-d, $J$=9,3 and 2 Hz, 1H at $C_8$ or $C_9$), 4.6 (d-t-d, $J$=10.2, 3.2, and 1 Hz, 1H at $C_3$), 4.1 (d-d-t, $J$=10.2, 8.0, and 2.3 Hz, 1H at $C_2$), 3.9 (d-d-d, $J$=8.8, 6.6 and 1.5 Hz, 1H at $C_6$), 3.57 (d-d-d, $J$=8.8, 6.7, and 1.5 Hz, 1H at $C_7$).

Found: C, 69.82; H, 5.27%. Calcd for $C_{11}H_{10}O_3$: C, 69.46; H, 5.30%.

*Bicyclo[3.2.2]nona-2,6,8-triene (1).* A solution of 3.0 g of **4** and 4 m*l* of triethylamine in 100 m*l* of 85% pyridine-water was placed under nitrogen atmosphere in an electrolysis apparatus equipped with two stationary electrodes made of platinum gauze, nitrogen inlet tube, and glass tube for cooling, and maintained below room temperature with strirring. Electrolysis was conducted for 300 min at 70 V. During the reaction, the current fell from 1.0 A to 0.20 A, and then remained constant. The dark reaction mixture was diluted with 300 m*l* of saturated sodium chloride solution and extracted three times with 200 m*l* of pentane. The combined pentane extract was washed twice with 20 m*l* of dilute hydrochloric acid, then 200 m*l* of water, and dried over sodium sulfate. Evaporation of the solvent and distillation of the residue at 61—62°C (45 mmHg) gave 367 mg of **1** (19.7%), which was homogeneous on vpc (column C) and had physical properties identical with the reported data.[3a-c)]

*Benzo[f]bicyclo[3.2.2]nona-2,6,8-triene (2).* To a stirred suspention of 500 mg of lithium aluminum hydride in 50 ml of ether was added at −20°C a solution of 5.0 g of the ketone **6**[14)] in 100 m*l* of ether. After the mixture had been stir-

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26) The vinyl-unsubstituted derivative of **20** has been found to be a stable compound. W. V. E. Doering and M. J. Goldstein, *Tetrahedron*, **5**, 53 (1959).

red for 2.5 hr, the usual work-up gave 5.0 g of an alcohol mixture **7**. A solution of 5.0 g of **7** and 5.0 g of methyl iodide in 50 m*l* of dimethoxyethane was cooled to −15°C and stirred for 15 min during the additon of 750 mg of sodium hydride. The reaction proceeded with evolution of hydrogen gas. After further addition of 1.0 g of methyl iodide, the reaction mixture was warmed to room temperature, stirred for 3.0 hr, and then poured into water. After extraction with ether, evaporation of the solvent and distillation at 96—98°C (0.1 mmHg) gave 4.2 g of a crude ether. Further purification by elution chromatography over 100 g of Merck standard alumina using ether gave 3.6 g of **8**.

To a stirred solution of 3.6 g of **8** in 36 m*l* of dimethoxyethane, 3 m*l* of sodium-potassium alloy (1:5) was added at −10°C and the mixture was stirred for 4 hr. The reddish brown solution was poured into 50 m*l* of could methanol and diluted with water. After extraction with ether and washing with water, evaporation of the ether left 2.3 g of residue. Sublimation of the residue under reduced pressure afforded 2.0 g of **2**, mp 58—59°C. Total yield from **6** was 43%. IR ($CS_2$): 3026 and 1632 $cm^{-1}$ (C=C); $\lambda_{max}^{hexane}$ m$\mu$ (log $\varepsilon$): 265 (377) and 272 (397); NMR ($CCl_4$): $\tau$ 7.75 (m, 2H at $C_4$), 6.55 (m, 2H at $C_1$ and $C_5$), 5.1 (d-t-d, $J$=10.5, 3.8, and 1 Hz, 1H at $C_3$), 3.98 (d-d-t, $J$=10.5, 8, and 2 Hz, 1H at $C_2$), 3.77 (d-d-d, $J$=8,7, and 1.5 Hz, 1H at $C_9$), 3.37 (d-d-d, $J$=8,7 and 1.5 Hz, 1H at $C_8$), and 3.0 (aromatic 4H); mass spectrum (70 eV) *m/e* 168, 167, 165, 154, 153, 152, 141, 128, 115, 102, 89, 83, 76, 63, 51, 39.

Found: C, 92.80; H, 7.17%. Calcd for $C_{13}H_{12}$: C, 92.81; H, 7.19%.

*Thermolysis of 1.* A 0.1 N solution of **1** in *n*-hexane was degassed, sealed in an ampoule and placed in a constant temperature bath controlled in the range 160—180°C. Analysis of the thermolysis products was carried out by vpc (column C at 50°C with a flow pressure of 1 kg/cm$^2$) and showed the formation of three products, whose retention times were 4 min, 8 min, and 8 min 30 sec, while that of **1** was 5 min 20 sec. The peak at 4 min was identical with that of independently synthesized **10**. The peak at 8 min was identified as **9**, which was obtained as the main product on thermolysis of **10** as reported by Daub and Schleyer.[3b)] The peak at 8 min 30 sec did not appear at the initial stage of pyrolysis, but increased gradually as the reaction proceeded by further isomerization of the initially formed **9**. This isomerization product was assigned as 1-vinylcycloheptatriene (**11**) on the basis of its NMR spectra,[17)] $\tau$ 7.46 (d, $J$=7.0 Hz, 2H at $C_7$).

Thermolysis was followed by vpc using dodecane as an interanl standard, and integration of the component peaks was carried out with a planimeter. After correction for the relative sensitivity of the detector, decreases in the concentration of **1** were determined by comparing the peak area of **1** with that of the standard. With this technique the yield of **9** was quantitative, at least for the half-life of the reaction. Vpc of the infinity ampoule (more than the 10 half-lives) showed complete disappearance of **1** and two peaks corresponding to **9** and **11** with areas of approximately 2:3. Thermolysis rates determined by following the decrease of **1** for two half-lives, were shown to be first-order.

*Thermolysis of 10.* The reaction was carried out at a temperature in the range 120—140°C and gave quantitatively a mixture of **1** and **9** in the ratio 1:9. Formation of **11** was not observed up to the three half-lives, and no rearrangement of **1** was observed under the present conditions. The rates of conversion of **10** into **1** and **9** were determined by the same technique employed for **1** and gave first-order constants.

*3-Vinyltricyclo[3.2.2.0$^{2,4}$]nona-6-ene-8,9-dicarboxylic Anhydride (12).* (a) A mixture of 100 mg of **1** and 100 mg of maleic anhydride in 10 m*l* of *n*-hexane was sealed in a degassed ampoule and heated at 160°C overnight. Vpc analysis of the reaction mixture on column A at 180°C with a flow pressure of 1.0 kg/cm$^2$ showed three peaks with retention times of 2 min 30 sec, 3 min 20 sec, and 3 min 40 sec with areas in the ratios 2:1:20. Evaporation of the solvent and recrystallization from ligroin gave 120 mg of **12**, mp 168—169°C, corresponding to the main peak with a retention time of 3 min 20 sec; IR ($CHCl_3$): 1865 and 1780 $cm^{-1}$ (C=O), NMR ($CDCl_3$): $\tau$ 8.76 (m, 3H at $C_2$, $C_3$, and $C_4$), 6.76 (t, $J$=2 Hz, 2H at $C_8$ and $C_9$), 6.45 (m, 2H at $C_1$ and $C_5$), 4.2—5.2 (m, vinyl 3H), and 4.05 (d-d, $J$=5 and 3.5 Hz, 2H at $C_6$ and $C_7$).

Found: C, 71.99; H, 5.59%. Calcd for $C_{13}H_{12}O_3$: C, 72.21; H, 5.59%.

The minor peak, having a retention time of 3 min 20 sec, was identical with that of the product obtained from the reaction of **9** with maleic anhydride.

(b) A solution of 300 mg of **10** and 250 mg of maleic anhydride in 20 m*l* of dioxane was refluxed for 2 hr. After the usual work-up, recrystallization from carbon tetrachloride gave 450 mg of **12**, identical with the main product in procedure (a).

*Thermolysis of 2.* A solution of 900 mg of **2** in 40 m*l* of *n*-hexane was placed in an ampoule, cooled to −70°C, purged with nitrogen and sealed. The ampoule was heated at 230°C for 140 hr in the absence of light. After evaporation of the solvent, 900 mg of the residue was subjected to preparative vpc at a column temperature of 200°C with a flow rate of 300 m*l*/min of helium gas. The chromatogram showed three peaks with retention times of 50, 63, and 72 min with areas in the ratio 1:2:5. The fraction (63 mg) corresponding to the peak with a retention time of 50 min was identical with the starting material (**2**). Collection of the second peak, at 63 min, gave 130 mg of the hydrobenzindene (**15**): bp 80°C (0.3 mmHg), $n_D^{25}$ 1.5987; $\lambda_{max}^{hexane}$ m$\mu$ ($\varepsilon$): 260 (8080) and 268.5 (8500); NMR ($CCl_4$): $\tau$ 5.8—8.0 (complex signals due to aliphatic 4H), 4.3 (m, vinyl 3H), 3.8 (d-d, $J$=10 and 2 Hz, benzylic vinyl 1H) and 3.0 (m, aromatic 4H)].

Found: C, 92.80; H, 7.17%. Calcd for $C_{13}H_{12}$: C, 92.81; H, 7.19.

The third fraction, at 72 min, was collected to give 301 mg of benzobarbaralane (**14**), bp 76—78°C (0.25 mmHg), $n_D^{24.3}$ 1.6037; $\lambda_{max}^{hexane}$ m$\mu$ ($\varepsilon$): 255 (692), 269.5 (550) and 276.5 (484); NMR ($CDCl_3$): $\tau$ 8.56 (t, $J$=2.3 Hz, 2H at $C_9$), 7.95 (t-d-d, $J$=7.6, 5.3, and 1.2 Hz, 1H at $C_8$), 7.82 (t-t, $J$=7.6 and 2.3 Hz, 1H at $C_1$), 7.45 (t, $J$=7.6 Hz, 1H at $C_2$), 6.78 (d-t-d, $J$=6.9, 2.3, and 1.4 Hz, 1H at $C_5$), 4.40 (d-d-d, $J$=9.6, 5.3, and 1.4 Hz, 1H at $C_7$), 4.20 (d-d-d, $J$= 9.6, 6.9, and 1.2 Hz, 1H at $C_6$), and 3.0 (m, aromatic 4H); the mass spectrum was identical with that of **2**.

Found: C, 92.67; H, 7.24%. Calcd for $C_{13}H_{12}$: C, 92.81; H, 7.19%.

Kinetic measurements were carried out with a 0.1 N solution of **2** in *n*-hexane using a vpc technique on column B at 100°C under a pressure of 1.0 kg/cm$^2$. Retention times of **2**, **15**, and **14** were 20, 34, and 41 min, respectively. Pentamethylbenzene, whose retention time was 8 min, was used as an internal standard. Extrapolation of the product compositions to zero time gave kinetically controlled ratios for **14** and **15**, of 2.5 at 268.5°C and 3.0 at 289.8°C, respectively. The decreasing rate of **2** was followed up to two half-lives and shown to be first-order.

*2,3,3aβ,4,5,9bβ-Hexahydro-1*H*-benz[*e*]indene.* A solution of 40 mg of **15** in 10 m*l* of methanol was hydrogenated at atmospheric pressure and room temperature over 5% palladium on carbon. Uptake ceased after absorption of 11 m*l* of hydrogen. After the usual work-up, the hydrogenated product (37 mg), boiling at 80—82°C (1 mmHg), $n_D^{21.0}$ 1.5532, was found to be identical with the reported compound.[24]

Found: C, 90.40; H, 9.31%. Calcd for $C_{13}H_{16}$: C, 90.64; H, 9.36%.

Endo- *and* exo*-2-methoxybenzo*[f]*bicyclo*[3.2.2]*nona-3,6,8-triene.* A 7:3 mixture of the *endo*- and *exo*-2-methoxy compounds (**8**) was separated by preparative tlc using silica gel G (E. Merck Co.) as an adsorbent, and developing with ether-pentane (1:4). Collection and vacuum distillation of the more mobile fraction gave 580 mg of the *endo* compound, bp 115°C (0.25 mmHg), $n_D^{25}$ 1.5758. Vpc (column C at 150°C with a flow pressure of 1 kg/cm$^2$) showed a single peak with a retention time of 8 min: IR ($CCl_4$): 1632 cm$^{-1}$ (C=C) and 1100 cm$^{-1}$ (C–O), NMR ($CCl_4$): $\tau$ 6.73 (s, 3H of $CH_3O$), 6.1—6.6 (m, 3H of $C_1$, $C_2$, and $C_5$), 5.1 (d-t, *J*=10.2 and 2.5 Hz, 1H at $C_3$), 3.90 (d-d-d, *J*=10.2, 7.8, and 1 Hz, 1H at $C_4$), 3.70 (d-d-d, *J*=8.0, 6.4, and 1 Hz, 1H at $C_8$), 3.26 (d-d-d, *J*=8.0, 5.5, and 1 Hz, 1H at $C_9$) and 3.0 (m, aromatic 4H).

Found: C, 84.79; H, 7.05%. Calcd for $C_{14}H_{14}O$: C, 84.81; H, 7.12%.

The less mobile fraction gave 270 mg of the *exo* compound, bp 103°C (0.17 mmHg), $n_D^{24}$ 1.5729. Vpc showed it to be homogeneous with a retention time of 6 min 30 sec: IR ($CCl_4$): 1631 (C=C) and 1100 cm$^{-1}$ (C–O), NMR ($CCl_4$): $\tau$ 6.67 (s, 3H of $CH_3O$), 6.40 (m, 2H at $C_1$ and $C_5$), 6.10 (m, 1H at $C_2$), 5.03 (d-m, *J*=10.8 Hz, 1H at $C_3$), 3.86 (d-d-t, *J*=10.8, 5.0, and 1.0 Hz, 1H at $C_4$), 3.72 (d-d-d, *J*=9.0, 8.0, and 1.5 Hz, 1H at $C_8$), 3.30 (d-d-d, *J*=9.0, 6.0, and 1.5 Hz, 1H at $C_9$), and 3.0 (m, aromatic 4H).

Found: C, 84.43; H, 7.08%. Calcd for $C_{14}H_{14}O$: C, 84.81; H, 7.12%.

*Thermolysis of 8.* A 0.1 N solution of the exo or endo methoxy compounds (two separate experiments) was degassed, sealed in an ampoule and heated at 190°C for 17 hr. Epimerization between the two alcohols was observed by vpc. Orientations of the methoxyl groups were determined by measurement of infrared hydroxyl bands in the corresponding saturated alcohols, which were obtained by hydrogenation of the two double bonds in **7**.

Benzo[*f*]bicyclo[3.2.2]nona-3,6,8-trien-2(*endo*)-ol had mp 91—91.5°C. Found: C, 84.65; H, 6.64%. Calcd for $C_{13}H_{12}O$: C, 84.75; H, 6.57%. The *exo* epimer had mp 109—109.5°C. Found: C, 84.91; H, 6.62%.

Benzo[*f*]bicyclo[3.2.2]non-6-en-2(*endo*)-ol had mp 52—53°C. Found: C, 83.09; H, 8.52%. Calcd for $C_{13}H_{16}O$: C, 82.93; H, 8.57%. IR ($CCl_4$): 3618 (free OH) and 3583 cm$^{-1}$ (associated OH). The *exo* epimer had mp 95—96°C. Found: C, 82.90; H, 8.57%. IR ($CCl_4$): 3620 cm$^{-1}$ (free OH).