

$\delta_{\text{TMS}}^{\text{CDCl}_3}$ 1.08 (s, 3), 1.17 (s, 3), 1.63 (m, 3), 1.80–3.20 (br m, 5), and 4.90–5.60 (br m, 3).

1,3-Dimethylsemibullvalene (23). A solution containing 1.09 g (8.3 mmol) of **22** and 2.95 g (16.6 mmol) of *N*-bromosuccinimide in 40 ml of carbon tetrachloride was refluxed for 2 hr and cooled to 0°. The succinimide was removed by filtration and the filtrate evaporated to leave 2.42 g (100%) of a pale yellow lachrymatory oil. This oil was dissolved in 50 ml of ether and 25 g of 0.8% lithium amalgam was added portionwise under argon. After 1.2 hr, the analysis showed no remaining dibromide. The excess amalgam and mercury were separated by decantation and the filtrate was evaporated at atmospheric pressure. The residual liquid was chromatographed on silica gel (pentane elution) to yield 672 mg (61%) of **23** as a colorless liquid. Final purification was achieved by preparatory vpc: $\delta_{\text{TMS}}^{\text{CDCl}_3}$ 1.11, (s, 3), 1.58 (m, 3), 2.64 (m, 1), 3.06 and 3.28 (m, 1 H each), 4.35, 4.69, and 5.03 (m, 1 H each); *m/e* calcd 132.0939, obsd 132.0940.

1,3-Dimethylcyclooctatetraene (24). Freshly prepared **23** (250 mg, 1.90 mmol) was pyrolyzed as previously described at 445° (35 mm). Vpc analysis of the yellow pyrolysate (195 mg, 78%) revealed a composition of 89% of **24** and 11% of unreacted **23**. Preparative scale isolation (3 ft \times 0.25 in 5% OV-11 on Chromosorb G) gave pure **24**; see text for pmr data; *m/e* 132.0939, obsd 132.0940.

Anal. Calcd for $\text{C}_{10}\text{H}_{12}$: C, 90.85; H, 9.15. Found: C, 91.10; H, 8.97.

Method for Obtaining Pmr Spectra of Anions in ND_3 . Approximately 0.5 ml of ND_3^{53} was vacuum transferred to a small reaction vessel equipped with a miniaturized glass-encased magnetic stirring bar. Freshly cut potassium metal was introduced into the reaction vessel after removal of the serum cap under a positive nitrogen pressure. In practice, nitrogen was simply allowed to flow over the surface of the solid ND_3 during this operation. The cap was replaced and the ND_3 was slowly allowed to thaw by

gradual removal of the liquid nitrogen cooling bath and replacement with a Dry Ice-isopropyl alcohol bath. Substrate was injected by syringe into the resulting dark blue solution with simultaneous frequent agitation of the reaction mixture by means of an external magnet. When the reduction was complete, the mixture was frozen in the liquid nitrogen bath and the serum cap removed under nitrogen and replaced with a pmr tube side arm containing a plug of glass wool in the upper portion. After regaining partial vacuum (40 cm) the reaction vessel was inverted by rotation about the standard taper 10/30 joint and the tube rapidly cooled to -78° . The contents of the reaction vessel upon thawing collected above the glass wool plug. Filtration through the plug was achieved by rapidly removing the Dry Ice-isopropyl alcohol bath and replacing it with the liquid nitrogen bath. The tube was sealed *in vacuo* in the customary fashion after degassing the sample and the solid in the pmr tube was carefully thawed by swabbing with cold Dry Ice-isopropyl alcohol solution. The pmr spectra were then recorded in precalibrated cold probes.

Electrochemical Measurements. Polarographic studies in purified, dry tetrahydrofuran solution were carried out on a specially designed vacuum-line electrochemical cell allowing all preparations and measurements to be carried out under conditions of rigorous exclusion of air and moisture.⁵⁴ Details of procedure have been previously described.⁴² Techniques for purifying solvents and background electrolytes and experimental procedures were identical with those utilized in our earlier work.^{42, 43, 55}

Acknowledgment. This research was supported in part with funds provided by the National Science Foundation. The authors are grateful to Professors L. B. Anderson and T. Kuwana for helpful discussions and necessary advice. Without access to Professor Anderson's equipment, the electrochemical phase of this study would not have been possible.

(54) J. L. Mills, R. Nelson, S. Shore, and L. B. Anderson, *Anal. Chem.*, **43**, 157 (1971).

(55) (a) L. A. Paquette, L. B. Anderson, J. F. Hansen, S. A. Lang, Jr., and H. Berk, *J. Amer. Chem. Soc.*, **94**, 4907 (1972); (b) L. B. Anderson, M. J. Broadhurst, and L. A. Paquette, *ibid.*, **95**, 2198 (1973).

(53) Prepared by reaction of magnesium nitride and deuterium oxide according to the directions of V. I. Melczynski, *Angew. Chem.*, **74**, 32 (1962). Several vacuum transfers of the ND_3 were made to guarantee maximum dryness of the solvent; the last transfer was effectively a distillation over elemental sodium.

Thermally Induced Degenerate Skeletal Rearrangement and Isomerization Reactions of Cyclooctatetraenes

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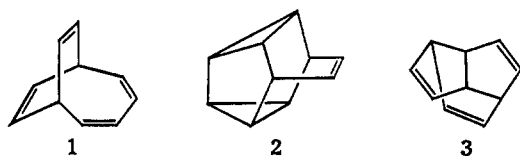
Abstract: Thermal rearrangements in the gas phase at 395° and above of various cyclooctatetraenes are herein reported to lead to [8]annulene \rightarrow [8]annulene isomerization or degenerate rearrangement depending upon substitution. In particular, attention has been given to the four isomeric dimethylcyclooctatetraenes, a doubly labeled (deuterium) derivative of the 1,2-dimethyl compound, benzocyclooctatetraene and its nonaromatic tetrahydro counterpart, various monosubstituted derivatives with wide-ranging electronic demands ($\text{R} = \text{COOCH}_3$, C_6H_5 , CH_3), and the parent hydrocarbon itself (in the form of the 1,4-dideuterio structure). The results are rationalized in mechanistic terms which stress the importance of the valence isomeric bicyclo[4.2.0]octatrienes and orbital symmetry control. The rearrangements are held to occur predominantly through intramolecular Diels-Alder cyclization of the bicyclic trienes with formation and subsequent ($\sigma_2 + \sigma_2 + \pi_2$) opening of intermediate tetracyclo[4.2.0.0^{2,8}.0^{5,7}]octenes and/or [1,5]-sigmatropic shift within these same trienes. Other possibilities are weighed in light of predicted "one-pass" bond reorganizations and considered less likely or inoperative. The relationship of the various schemes to known thermochemistry is discussed.

The phenomenon of degenerate structural rearrangement continues to be a source of fascination for chemists. In addition to providing much fundamental information about the structure and behavior of both neutral molecules and ions, processes involving the interchange of constituent atoms and bonds with regeneration of the same gross structure are mechanisti-

cally intriguing as well. No generalized reaction scheme accommodates this group of reactions; rather, a broad spectrum of pathways has been uncovered. Bullvalene¹

(1) G. Schröder and J. F. M. Oth, *Angew. Chem., Int. Ed. Engl.*, **6**, 414 (1967); W. von E. Doering, *et al.*, *Tetrahedron*, **23**, 3943 (1967); G. Schröder, *Chem. Ber.*, **97**, 3140 (1964); W. von E. Doering and W. R. Roth, *Tetrahedron*, **19**, 715 (1963).

and hypostrophene,² for example, owe their fluxional behavior to repetitive Cope rearrangement of divinylcyclopropane and divinylcyclobutane units, respectively. Circumambulatory degenerate rearrangements of cyclopentadienes³ and 1,3-cyclooctadienes⁴ proceed, in contrast, *via* sequential [1,5]-sigmatropic shifts; cyclopolyenyl cations are capable of related self-interconversion.⁵ Because of its fully saturated nature, the 9-homocubyl cation must necessarily automerize *via* consecutive 1,2-alkyl shifts, which it does readily.⁶ In some instances as with 1, an intramolecular Diels-Alder mechanism is responsible for such behavior.⁷ The degenerate thermal valence isomerization of snoutene (2) may possibly involve [$2_s + \sigma 2_a + \pi 2_a$] bond reorganization.⁸ In yet other instances such as with lumibullvalene (3), diradical intermediates seemingly intervene.⁹



As a class, the $(CH)_{10}$ hydrocarbons hold a notable position of being particularly prone to degenerate rearrangement.¹⁰ This facet of their chemistry may be ascribed to the richly varied possibilities for $p\pi$ - $p\pi$ interaction in the many isomers.¹¹ We were surprised to realize upon initiation of the work described in this paper that no substance of molecular formula $(CH)_8$ other than semibullvalene had yet been reported capable of structural self-interconversion. Knowledge of the propensity of annulated bicyclo[4.2.0]octatrienes for thermal rearrangement,¹² however, made investigation of the behavior of cyclooctatetraenes (to which the former are related by valence isomerization) under similar conditions an interesting and important extension of this chemistry.

In actuality, COT is recognized to be labile in the liquid phase at temperatures as low as 25°. Slow dimerization is observed. This process can be thermally accelerated, whereupon four dimers can be obtained depending on the level of external heating.¹³ At

significantly higher temperatures, COT is subject to fragmentation with formation of benzene, styrene, acetylene, and ethylene along with polymers and other unidentified volatile hydrocarbons.¹⁴ Under more controlled conditions, the successful gas phase rearrangement of COT to dihydropentalene is realizable;¹⁵ also, the thermally induced isomerizations of the 1,3,5,7-tetramethyl¹⁶ and octamethyl derivatives¹⁷ to semibullvalenes have been achieved. These latter reactions have been postulated to occur *via* bicyclo[3.3.0]octadienediyls, intermediate species apparently involved also in the thermal isomerization of 5,6- to 5,11-disubstituted dibenzocyclooctatetraenes.¹⁸

The thermochemistry of certain halocyclooctatetraenes has likewise come under study. The conversion of BrCOT and 1,4-Br₂COT to *trans*- β -bromostyrenes is rapid at 70–180°. These deep-seated structural changes have been accounted for in terms of sequential valence isomerization, ionic halogen shift, and conrotatory cyclobutene ring opening.¹⁹ In contrast, the fully substituted nature of Cl₈COT lends itself more readily to bicyclo[3.3.0]octadiene formation.²⁰

Despite the extraordinary richness of this [8]annulene chemistry, no indication can be found either of skeletal rearrangement to isomeric cyclooctatetraenes or of degenerate thermal behavior.²¹ Understandably, experimental evaluation of such phenomena requires not only appropriate levels of suitable substitution such that processes which would otherwise go unnoticed would now be unveiled, but also convenient experimental assessment of such structural changes. We now provide details of a rather comprehensive study showing that variously derivatized cyclooctatetraenes as well as the parent hydrocarbon itself do indeed possess the fascinating capability for structural self-interconversion.²²

Results

Dimethylcyclooctatetraenes. At the outset, recourse was made to dialkyl substitution and attention was given specifically to the four possible dimethyl isomers. The preparation of these hydrocarbons has been detailed in the preceding paper.²³ Gas-phase pyrolysis of

(2) J. S. McKennis, L. Brener, J. S. Ward, and R. Pettit, *J. Amer. Chem. Soc.*, **93**, 4957 (1971); L. A. Paquette, R. F. Davis, and D. R. James, *Tetrahedron Lett.*, 1615 (1974).

(3) W. C. Herndon and J. M. Manion, *J. Org. Chem.*, **33**, 4504 (1968); V. A. Mironov, V. S. Peshegorova, T. M. Foderva, and A. A. Akkrem, *Tetrahedron Lett.*, 3997 (1968); S. McLean and P. Haynes, *Tetrahedron*, **21**, 2329 (1965); W. R. Roth, *Tetrahedron Lett.*, 1009 (1964).

(4) D. S. Glass, R. S. Boikess, and S. Winstein, *Tetrahedron Lett.*, 999 (1966); W. R. Roth, *Justus Liebigs Ann. Chem.*, **671**, 25 (1964).

(5) For a current listing of pertinent references, see W. J. Hehre, *J. Amer. Chem. Soc.*, **94**, 8909 (1972).

(6) P. v. R. Schleyer, J. J. Harper, G. L. Dunn, V. J. DiPasquo, and J. R. E. Hoover, *J. Amer. Chem. Soc.*, **89**, 698 (1967); J. C. Barborak and R. Pettit, *ibid.*, **89**, 3080 (1967); R. E. Leone, J. C. Barborak, and P. v. R. Schleyer, "Carbonium Ions," Vol. IV, Wiley-Interscience, New York, N. Y., 1973, p 1837 ff.

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

(8) L. A. Paquette and J. C. Stowell, *J. Amer. Chem. Soc.*, **93**, 2459 (1971).

(9) L. A. Paquette and M. J. Kukla, *J. Amer. Chem. Soc.*, **94**, 6874 (1972); L. A. Paquette, M. J. Kukla, and J. C. Stowell, *ibid.*, **94**, 4920 (1972).

(10) For additional examples, refer to L. T. Scott and M. Jones, Jr., *Chem. Rev.*, **72**, 181 (1972).

(11) For a complete listing, consult A. T. Balaban, *Rev. Roum. Chim.*, **11**, 1097 (1966).

(12) L. A. Paquette, R. E. Wingard, Jr., and J. M. Photis, *J. Amer. Chem. Soc.*, **96**, 5801 (1974); L. A. Paquette and R. E. Wingard, Jr., *ibid.*, **94**, 4398 (1972).

(13) For a discussion of the preparation of these dimers and their structure proofs, see G. Schröder, "Cyclooctatetraen," Verlag Chemie, Weinheim/Bergstr., 1965.

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

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

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

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

(18) M. Stiles and U. Burckhardt, *J. Amer. Chem. Soc.*, **86**, 3396 (1964); M. Stiles, 19th National Organic Chemistry Symposium, Tempe, Ariz., June, 1965, p 62.

(19) A. C. Cope and M. Burg, *J. Amer. Chem. Soc.*, **74**, 168 (1952); R. Huisgen and W. E. Konz, *ibid.*, **92**, 1402 (1970); W. E. Konz, W. Hecht, and R. Huisgen, *ibid.*, **92**, 4104 (1970).

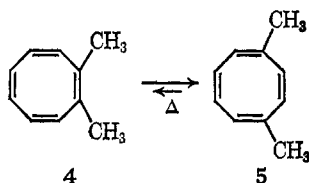
(20) A. Roedig, G. Bonse, and R. Helm, *Chem. Ber.*, **106**, 2156 (1973); see also A. Roedig and R. Helm, *Tetrahedron Lett.*, 2137 (1969).

(21) This statement relates to structurally unconstrained cyclooctatetraenes and is not meant to include, for example, dibenzo derivatives where two of the four double bonds are involved predominantly in benzenoid stabilization.¹⁸

(22) For preliminary reports of portions of this work, see L. A. Paquette, R. H. Meisinger, and R. E. Wingard, Jr., *J. Amer. Chem. Soc.*, **94**, 9224 (1972); L. A. Paquette and M. Oku, *ibid.*, **96**, 1219 (1974).

(23) L. A. Paquette, S. V. Ley, R. H. Meisinger, R. K. Russell, and M. Oku, *J. Amer. Chem. Soc.*, **96**, 5806 (1974).

1,2-Me₂COT (**4**) under nitrogen in a quartz tube packed with quartz chips at 395–590° (18–30 mm) (contact time 1–3 sec) proved to be remarkably free of polymer formation. Vpc analysis of the pyrolysate denoted the recovery of significant amounts of a cyclooctatetraene fraction together with aromatic products, with the latter being produced in increasing amounts paralleling the input of added heat to the system. Expanded scale 100-MHz pmr spectra of the recovered polyolefin mixtures revealed a progressive diminution in the intensity of the δ 1.68 and 1.82 methyl singlets due to **4** and a concomitant enhancement of a third singlet at 1.72. This new peak represented above 80% of the total methyl absorption after thermal activation at 590°. Because the three remaining isomers all exhibit methyl signals in this vicinity,²³ reliance could not be placed on pmr spectroscopy for product composition analysis. To achieve maximum accuracy it became necessary after much experimentation to resort to a combination of vpc and quantitative infrared techniques.²³ Product characterization in this manner revealed that **4** experiences *initial* rearrangement to **5** and that formation



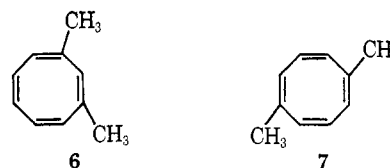
of the 1,3- and 1,5-dimethyl isomers takes place only at more elevated temperatures (Table I).

Table I. Polyolefin Product Composition Data for the Thermal Rearrangement of the Dimethylcyclooctatetraenes (Gas Phase, Flow System, 18 mm)

Hydro-carbon	Temp, °C	Recovery, % ^a	1,2 (4), %	1,3 (6), %	1,4 (5), %	1,5 (7), %
4	395	71	100			
	435	70	95		5	
	450	63	91		9	
	465	58	84	3	11	2
	500	40	34	25	23	17
	525	29	20	29	27	24
5	435	75			100	
	450	68	4	5	83	8
	465	60	6	19	61	14
	500	42	12	27	34	27
	525	33	12	26	30	32
6	480	83		100		
	525	49	8	27	51	14
7	395	80				100
	415	77			8	92
	435	70			14	86
	465	66	3	7	19	71
	480	53	6	12	22	60
	500	51	8	23	29	40
	525	38	12	29	35	24

^a Values relate to cyclooctatetraenes isolated upon vpc purification and do **not** include aromatic products.

When **5** was heated under entirely comparable conditions, rearrangement was not seen to operate until a temperature of 450° was attained or exceeded, at which point isomerization to **4** was evidenced. Significantly, however, **6** and **7** were formed concomitantly (Table I). Therefore, although the 1,2 to 1,4 rearrangement is



reversible, **5** is seemingly capable of more direct conversion to the remaining isomers than is **4**.

To allow for characterization of the aromatic components, **4** and **5** were both pyrolyzed at 600° (where the level of fragmentation is high) and the volatile material was carefully separated by preparative scale vpc methods. Composition analysis measurements were conducted on a 24 ft × 0.125 in. Hi-Pac column at 35° and determination of relative abundances was achieved by electronic integration corrected for detection coefficients. The data are compiled in Table II. The

Table II. Benzenoid Aromatic Product Composition Data from Pyrolysis of **4** and **5** (Gas Phase, Flow System, 600° (25 mm))

Benzenoid aromatic	From 4, %	From 5, %
Benzene	1.3	2.6
Toluene	96.2	70.5
<i>o</i> -Xylene	1.3	21.6
<i>p</i> -Xylene	1.1	5.4

absence of *m*-xylene, whose presence could have been determined at quite low concentrations (0.1%), at this temperature is of particular significance. In less exhaustive experiments conducted at lower temperatures, the formation of small amounts of *m*-xylene was indicated. This temperature dependence is believed to be of mechanistic significance (see Discussion).

In experiments with **6**, it was discovered that all isomers were generated concurrently but that formation of the 1,4-dimethyl derivative was kinetically dominant (Table I). Importantly, the reactivity of **7** is such that high levels of regioselectivity are encountered at 415–435° with rearrangement initially leading uniquely to **5**. Only when the temperature range was extended to 465° and above did **4** and **6** make their appearance.

Our conviction that at least certain of these disubstituted hydrocarbons were experiencing further extensive, but degenerate and therefore invisible, carbon atom transposition was vindicated when the doubly labeled **9** became available. The successful synthesis of this COT was achieved readily by deuterium exchange and photolysis of the known bridged sulfone **8**.²⁴ Pyrolysis at 395° for short contact times did not result in scrambling of the isotope to the other ring positions. At 510°, however, 13% of the available deuterium had migrated from its original C₃,C₈ position in **9** to C₄,C₇; no measurable change in protium content at C₅,C₆ could be detected.²⁵ To assess quantitatively the location and extent of deuterium migration, recourse was made to formation of TCNE adducts. Earlier observations had established that 1,2-Me₂COT (**4**) reacts with TCNE by way of a single valence isomer to

(24) L. A. Paquette, R. H. Meisinger, and R. E. Wingard, Jr., *J. Amer. Chem. Soc.*, **95**, 2230 (1973); L. A. Paquette, R. E. Wingard, Jr., and R. H. Meisinger, *ibid.*, **93**, 1047 (1971).

(25) Mass spectral analysis of this and many other pyrolysates indicated that no measurable loss of deuterium occurs during the gas phase rearrangement reactions.

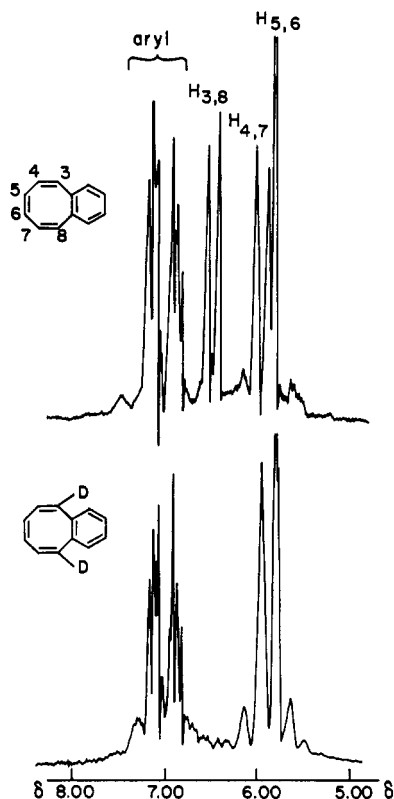
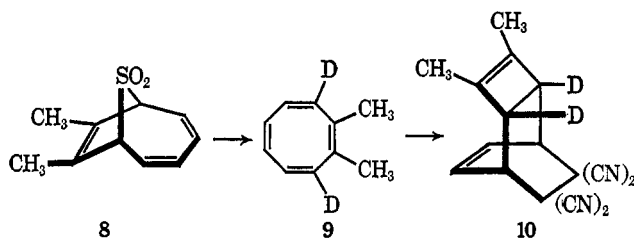


Figure 1. The partial pmr spectra (100 MHz) of benzocyclooctatetraene and its 3,8-dideuterio derivative (15).

give unlabeled 10 in which the well-separated chemical



shifts of the several pairs of protons [$\delta_{\text{TMS}}^{\text{CD}_3\text{COCD}_3}$ 1.55 (s, 6), 3.08 (m, 2), 3.95 (m, 2), and 6.47 (m, 2)] lend themselves conveniently to integration. With utilization of the single methyl signal as internal standard, the incursion of degenerate rearrangement was diagnosable without difficulty.

Annulated Cyclooctatetraenes. Because the degenerate rearrangement of 9 was accompanied by substantial structural isomerization, we were not able to achieve measurable migration of deuterium (with its attendant carbon atom) to the most remote (C_5, C_6) ring positions prior to translocation of the methyl substituents. However, following the discovery that 1,2-tetramethylenecyclooctatetraene is rather stable to pyrolysis, attention was turned to the labeled counterpart 11¹² in anticipation that this hydrocarbon would serve as a more convenient substrate with which to examine such degenerate processes. Gas-phase experiments with 11 (89% isotopically labeled) provided immediate indication of nondestructive skeletal isomerization as gauged by conversion of the various pyrolysates to TCNE adduct 12 and quantitative integration of the individual pmr signals (Table III). Because higher temperatures were now utilizable without incur-

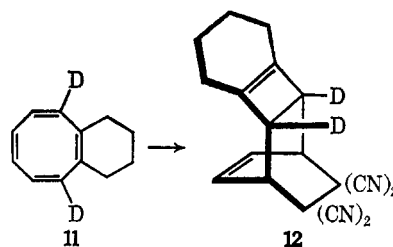


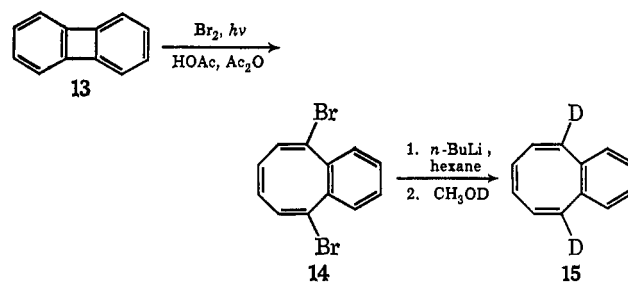
Table III. Hydrogen Distribution in 12 Prepared from Samples of 11 Pyrolyzed at Various Temperatures^a

Temp, °C	Hydrogen content		
	Cyclobutene ring	Bridge-head	Olefinic
Before pyrolysis	0.21	1.99	2.00
545	0.31	1.85	2.03
575	0.70	1.70	1.80
610	0.94	1.66	1.60

^a Determined by careful integration of 100-MHz nmr spectra.

sion of complicating side reactions, the stepwise shift of deuterium first to C_4, C_7 and then to C_5, C_6 was made clearly evident.

To gain some indication of the effect which structural perturbation as in benzocyclooctatetraene would contribute to the thermal isomerization, the 3,8- d_2 derivative 15 (i.e., tetradehydro 11) was synthesized. In 15,



one double bond from the polyolefinic quartet is effectively "frozen out" such that π -bond shifting and all but two valence isomerization processes become high energy and therefore less likely mechanistic options. Photobromination of biphenylene (13) gave 3,8-dibromobenzocyclooctatetraene (14),²⁶ which upon halogen-metal interconversion with *n*-butyllithium and deuteration by addition of methanol-*O-d* was converted uneventfully to 15.²⁷ Owing to the well-separated chemical shifts of the pairs of peripheral olefinic protons in the parent hydrocarbon²⁸ (Figure 1), direct quantitative integration of pmr spectra without recourse to the preparation of adducts was possible in this case. This was somewhat fortunate, since 15 proved to be very sluggish in its reactivity toward TCNE. As revealed in Table IV, gas-phase pyrolysis of 15 at 565° and above resulted in migration of deuterium first to C_4, C_7 and subsequently to C_5, C_6 . The need for such elevated temperatures led to competitive fragmentation of acetylene and formation of 1,4-dideuterionaphthalene (16).

Monosubstituted Cyclooctatetraenes. Just as the thermal cleavage of methyl-substituted cyclobutanes has

(26) J. W. Barton and K. E. Whitaker, *J. Chem. Soc. C*, 1663 (1968).

(27) J. W. Barton, T. A. Chandri, P. Gaskin, and K. E. Whitaker, *J. Chem. Soc., Perkin Trans. 1*, 717 (1972).

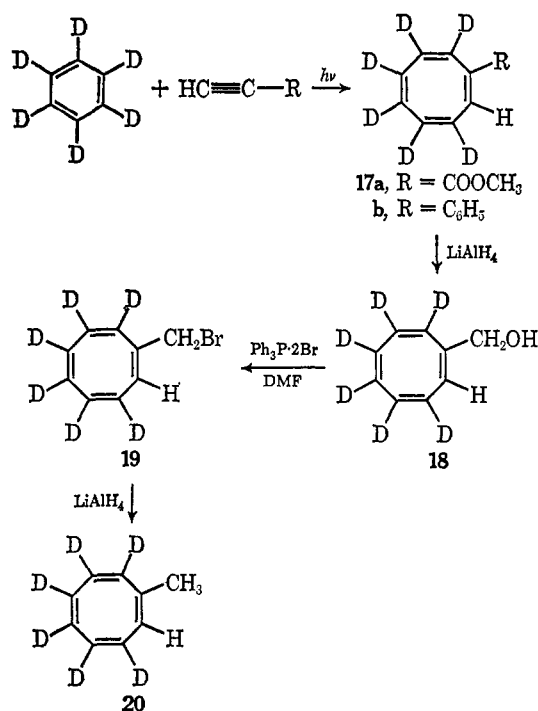
(28) H. E. Zimmerman, R. S. Givens, and R. M. Pagni, *J. Amer. Chem. Soc.*, **90**, 6096 (1968).

Table IV. Hydrogen Distribution in Benzocyclooctatetraene Arising from Pyrolysis of **15**

Temp, °C	Hydrogen content			Recovery, %	16, %
	H _{3,8}	H _{4,7}	H _{5,6}		
Before pyrolysis	0.13	2.00	2.00		
565	0.13	2.00	2.00	46	
625	0.29	1.85	2.00	22	4 ^a
675	0.67	1.57	1.88	5	10 ^a

^a Uncharacterized higher boiling materials are also obtained (5–20%).

suggested to certain investigators that the alkyl groups may play a more significant role than merely that of stereochemical markers,²⁹ so the thermal interconversion of disubstituted cyclooctatetraenes could be facilitated by the presence of two ring appendages. In rigorous terms, therefore, extension of the preceding study to cyclooctatetraenes monosubstituted with groups of widely varying electronic features was in order. In this instance, attack on the problem took the form of assessing the migration of C₈ and its hydrogen away from C₁ to which the R group is bonded in the hexadeuterio derivatives **17** and **20**.



Irradiation of methyl propiolate in benzene-*d*₆ under nitrogen with 2537-Å light from a Rayonet photochemical reactor gave ester **17a**.^{30,31} PhCOT-2,3,4,5,6,7-*d*₆ (**17b**) was similarly prepared in one step by the photoaddition of phenylacetylene to deuterium-labeled benzene.³⁰ Reduction of **17a** with lithium aluminum hydride afforded alcohol **18**, bromination of which with triphenylphosphine dibromide in dimethyl-

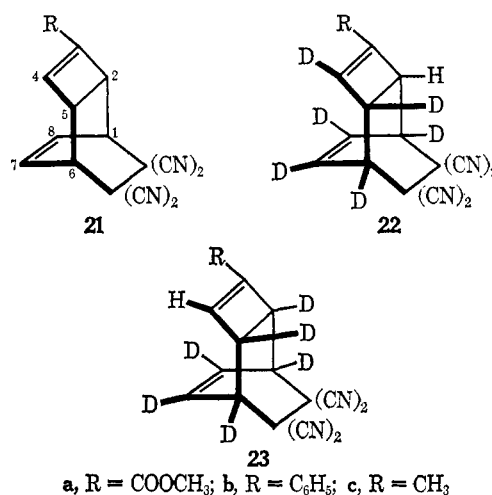
(29) J. E. Baldwin and P. W. Ford, *J. Amer. Chem. Soc.*, **91**, 7192 (1969); A. T. Cocks, H. M. Frey, and I. D. R. Stevens, *J. Chem. Soc., Chem. Commun.*, 458 (1969); A. T. Cocks and H. M. Frey, *J. Chem. Soc. A*, 1671 (1969); J. A. Berson, D. C. Tompkins, and G. Jones, II, *J. Amer. Chem. Soc.*, **92**, 5799 (1970).

(30) The undeuterated compounds have been prepared previously: D. Bryce-Smith and J. E. Lodge, *Proc. Chem. Soc., London*, 333 (1961).

(31) The analogous preparation of the ethyl ester has been reported: F. A. L. Anet, A. J. R. Bourn, and Y. S. Lin, *J. Amer. Chem. Soc.*, **86**, 3576 (1964).

formamide²³ led in 84% yield to **19**.³² When subjected to hydride reduction, **19** underwent facile conversion to **20**.³³

In experiments preliminary to the thermal activation studies, we determined that the unlabeled counterparts of these cyclooctatetraenes undergo cycloaddition with TCNE with formation only of those adducts in which the R group is situated at a trigonal cyclobutene carbon (**21a–c**).³⁴ In addition to such favorable regioselectivity, the pmr spectra of these adducts were seen to consist generally of well-resolved multiplets. Consequently, the feasibility of locating the unique hydrogen in the deuterated [8]annulenes prior to and after pyrolysis had been demonstrated. However, because the labeled substrates are capable of valence isomerization to *two different* bicyclo[4.2.0]octatriene tautomers which would ultimately lead to **22** and **23** by processes controlled by



various H/D isotope effects,³⁵ allowance must be made for this partitioning.

The pyrolysis data for **17a** are summarized in Table V.

Table V. Thermally Induced Protium Scrambling in **17a** as Derived from the TCNE Adducts

Temp, °C	Relative protium content			
	H _{1,6}	H ₂	H ₄	H _{7,8}
Before heating	0.00	0.56	1.00	0.00
455	0.00	0.55	1.00	0.00
495	0.18	0.55	1.00	0.09
530	0.48	0.63	1.00	0.40
550	1.04	0.64	1.00	0.93

Quantitative analysis was performed by manual planimeter integration of suitably expanded 100-MHz pmr spectra of the individual TCNE adducts. All values are normalized to the area of H₄ which, for convenience, has been given a relative intensity of 1.00. Values for H₅ were not obtainable in this particular example because of the close proximity of its chemical shift to that of the methoxyl signal. Inspection of these data reveals again the propensity for degenerate rearrangement as

(32) For an alternative preparation of the unlabeled bromide, see A. C. Cope, R. M. Pike, and R. F. Rugen, *J. Amer. Chem. Soc.*, **76**, 4945 (1954).

(33) F. A. L. Anet, *J. Amer. Chem. Soc.*, **89**, 2491 (1967).

(34) Similar positional specificity has been noted in the phenylcyclooctatetraene-maleic anhydride cycloaddition: R. Huisgen, F. Mietzsch, G. Boche, and H. Seidl, *Chem. Soc., Spec. Publ.*, No. 19, 3 (1964).

(35) Full details of our study in this area will be reported elsewhere.

demonstrated by the migration of protium around the ring relative to the carbomethoxy group.

Comparable pyrolysis data have been obtained for methyl derivative **20** (Table VI). That the lone ring

Table VI. Thermally Induced Protium Scrambling in **20** as Derived from the TCNE Adducts

Temp, °C	Relative protium content			
	H _{1,6}	H _{2,5}	H ₄	H _{7,8}
Before heating	0.00	0.50	0.50	0.00
465	0.00	0.49	0.51	0.00
495	0.00	0.50	0.50	0.00
535	0.11	0.40	0.43	0.07
580	0.21	0.32	0.31	0.16
610	0.31	0.18	0.19	0.32
Statistical	0.28	0.28	0.14	0.28

hydrogen is entirely capable of migrating from its initial position one carbon removed from the methyl substituent to all other positions of the ring is most dramatically revealed in the 610° experiment. By comparison with the theoretical values for complete scrambling (last entry in the table), it can be seen that the statistical distribution is almost attained.²⁵ The lower value for the protio content at C₂,C₅ is almost certainly a manifestation of the well-documented preference of a hydrogen for attachment to an sp² rather than an sp³-hybridized center during TCNE cycloaddition.

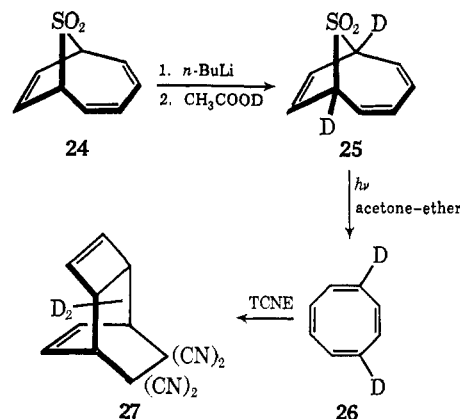
On being heated at 445–548° (0.7–1.2 mm), **17b** underwent comparable degenerate rearrangement (Table VII). This observation is taken as convincing evidence

Table VII. Thermally Induced Protium Scrambling in **17b** as Derived from the TCNE Adducts

Temp, °C	Relative protium content						
	H ₁	H ₂	H ₄	H ₅	H ₆	H ₇	H ₈
Before heating	0.00	0.47	0.53	0.00	0.00	0.00	0.00
445	Tr	0.47	0.53	Tr	Tr	Tr	Tr
495	0.06	0.27	0.30	0.08	0.10	0.11	0.07
548	0.15	0.16	0.16	0.16	0.15	0.10	0.11

that a styrene part structure does not deter operation of the mechanistic pathway(s) which leads to positional isomerization.

The Parent Hydrocarbon. Because all eight carbon atoms in the unsubstituted cyclooctatetraene molecule are formally identical, analysis of any structural rearrangement which returns the original [8]annulene ring system is made less facile. The effect of mono- and disubstitution has been shown to lend itself conveniently to regiospecific trapping during TCNE addition. The parent hydrocarbon has no capability to achieve similar control. Notwithstanding, several experimental options do exist and we chose to examine the thermal chemistry of 1,4-dideuteriocyclooctatetraene (**26**) in an effort to shed light on the question of automerization. Should deuterium isotope effects, as anticipated,³⁵ gain importance during the reaction of TCNE with **26**, then one might expect to view a well-defined deuterium-labeling pattern in **27**. In point of fact, integration of the expanded scale 100-MHz pmr absorptions corresponding to the four different pairs of protons in **27** revealed a highly reproducible deuterium isotope



distribution (Table VIII). It should be cautioned that

Table VIII. Thermally Promoted Deuterium Scrambling in **26** as Derived from Pmr Analyses of **27**

Temp, °C	Relative deuterium content, % ^a			
	C _{1,6}	C _{2,5}	C _{3,4}	C _{7,8}
Before heating	28.5	25.8	9.2	36.5
520 (30 mm)	25.9	23.8	17.2	33.1

^a Values represent an average of duplicate runs.

no information is available on the extent to which the various possible bicyclo[4.2.0]octatriene-*d*₂ valence isomers enter into competitive reaction with TCNE. However, because this point is irrelevant to the question of degenerate rearrangement, we considered it safe to proceed on the assumption that alteration of the 1,4 relationship of the pair of deuterium atoms by thermal activation would be demonstrable in deviations from the "normal" distribution exhibited by **26** during conversion to **27**. With this assumption one can make the further inference, crucial to the success of these experiments, that such migrations of deuterium will in fact be diagnosable upon ultimate conversion to **27**. As reflected in Table VIII, no difficulties were encountered in demonstrating experimentally that cyclooctatetraene itself can indeed partake of structural ring interconversion without aromatization.

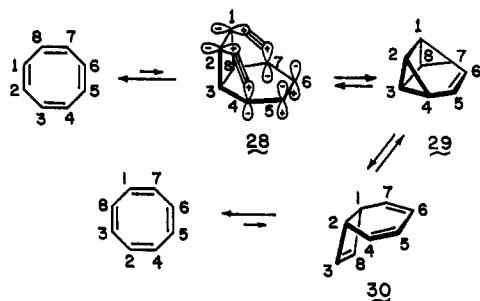
Discussion

With the propensity of a variety of cyclooctatetraenes for thermal [8]annulene → [8]annulene rearrangement established, the question now arises as to how these interesting isomerizations take place. A number of mechanistic hypotheses may be advanced which differ phenomenologically in rather distinct ways. As will be shown, circumstantial experimental evidence disfavors the title rearrangements occurring chiefly through certain of the proposed pathways. The various options are discussed below in order of decreasing probability of their actual involvement.

According to the first alternative, prior valence isomerization of the cyclooctatetraene to one or more bicyclo[4.2.0]octatrienes (e.g., **28**) is followed by intramolecular ($\pi_4s + \pi_2s$) cycloaddition to give a tetracyclo[4.2.0.0^{2,8}.0^{5,7}]octene intermediate (**29**) and ultimate ($\sigma_2s + \sigma_2s + \pi_2s$) bond relocation in this *cis*²-bishomobenzene intermediate. The new bicyclo[4.2.0]octatriene arising in this manner (**30**) can ring open to return a cyclooctatetraene which must inescapably possess a

carbon framework different from that of the starting [8]annulene (see Scheme I). A relevant aspect of this

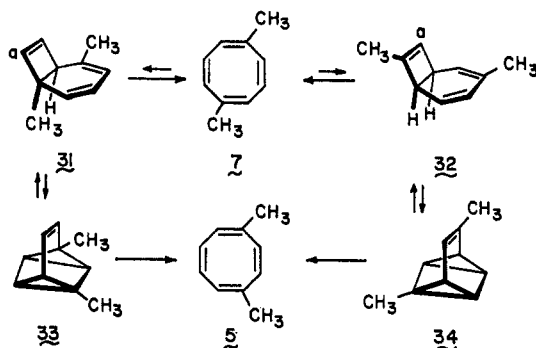
Scheme I



scheme is the awareness that the two key steps, namely $28 \rightarrow 29$ and $29 \rightarrow 30$, are permitted to occur thermally in a fashion which conserves orbital symmetry.

An argument in support of this proposal is founded upon the behavior of 1,5-Me₂COT (7). As a consequence of its symmetry, 7 can give rise in preliminary isomerization only to the two bicyclooctatrienes 31 and 32 (Scheme II). Although the equilibrium constants

Scheme II



of the $7 \rightleftharpoons 31$ and $7 \rightleftharpoons 32$ conversions are unknown, knowledge of these data is not necessary for the present purposes. This is due to the subtly parallel manner in which 31 and 32 can undergo further chemical change along the tetracyclooctene reaction channel. As illustrated, passage through either 33 or 34 results in convergence uniquely to 1,4-Me₂COT (5). As a consequence of this identity, the isomerization is seen to be independent of which triene is the favored reactant.

When the data for the thermal activation of 7 are examined, a decided preference for *initial* isomerization is witnessed. In Table IX, we have compiled a listing of those dimethylcyclooctatetraenes which result upon one-time rearrangement of the four isomers through the various mechanisms under consideration. Only in the case of the Diels–Alder pathway is the 1,5 to 1,4 rearrangement seen to be unique. The possibility exists that selective isomerizations in other reaction manifolds could be kinetically preferred by reason of alkyl substitution such that a single new cyclooctatetraene would be produced. Definitive statements on the extent of their operation could thereby be precluded. As relates to 7, such a phenomenon could arise if both 31 and 32 would experience positionally selective [1,5]-sigmatropic shift such that the cyclobutene carbon atoms labeled “a” would act exclusively as the pivot. Because these rearrangements would return 7 and consequently be degenerate, their operation would pass unrecognized. Such exclusivity is unlikely, however, since literature

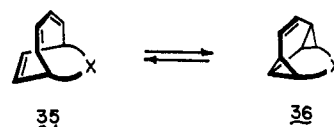
Table IX. Hypothetical Rearrangement Pathways and Predicted “One-Pass” Rearrangement Products for the Four Dimethylcyclooctatetraenes

Mechanism	Possible product composition after one rearrangement ^a			
	1,2-Me ₂	1,3-Me ₂	1,4-Me ₂	1,5-Me ₂
Diels–Alder	1,3; 1,4	1,2; 1,4	1,2; 1,3; 1,5	1,4
[1,5]-Sigmatropic shift	1,4	1,5	1,2	1,3
Bicyclo[3.3.0]octa-dienediyl formation	1,5	1,3	1,3; 1,5	1,2; 1,4
Antara–antara				
Cope	<i>b</i>	<i>b</i>	1,5	1,4
($\pi 2_a + \pi 2_a$) ring formation	1,3	1,2; 1,4	1,3	1,4
($\pi 2_a + \pi 2_a + \pi 2_a$) cyclization	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>

^a Degenerate processes are not indicated. ^b Degenerate reactions only.

precedent suggests that both possible [1,5] shifts in 31 and 32 should be nearly isoenergetic.^{36,37}

Additional basis for the feasibility of the intramolecular Diels–Alder mechanism is derived from a number of sources. Of perhaps most direct relevance is the finding that preformed bicyclo[4.2.0]octatrienes do experience thermal isomerization to annulated cyclooctatetraenes by this pathway under comparable conditions.¹² In more general terms, adjoining the two components of a Diels–Alder reaction in a bishomo-conjugative way^{24,38} as in 35 is unquestionably very conducive to intramolecular bonding with formation of the tetracyclic isomer 36.^{15,39–41} As Goldstein has noted,⁴¹ however, because the cyclopropane strain in 36 (*ca.* 55 kcal/mol) is much larger than the otherwise



exothermic cycloaddition (*ca.* 33 kcal/mol), compounds of type 36 are frequently only transient intermediates. However, a few have been characterized at low temperatures,⁴⁰ and 38 has recently been discovered to be more thermodynamically stable than 37.⁴¹

(36) R. B. Woodward and R. Hoffmann, “The Conservation of Orbital Symmetry,” Academic Press, New York, N. Y., 1970; G. Maier, Valenzisomerisierungen,” Verlag Chemie, Weinheim/Bergstr., Germany, 1972.

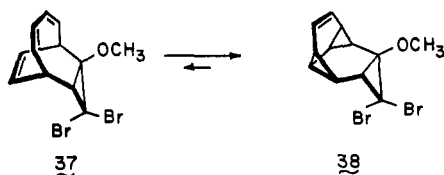
(37) Given this assumption, 1,3-Me₂COT should be formed in readily detectable quantities (see Table IX) but it is not seen until higher temperatures are employed.

(38) L. A. Paquette, R. H. Meisinger, and R. E. Wingard, Jr., *J. Amer. Chem. Soc.*, **94**, 2155 (1972).

(39) T. S. Cantrell and H. Shechter, *J. Amer. Chem. Soc.*, **89**, 5877 (1967); H. Tsuruta, K. Kurabayashi, and T. Mukai, *ibid.*, **90**, 7167 (1968); J. A. Berson, R. R. Boettcher, and J. J. Vollmer, *ibid.*, **93**, 1540 (1971); H. Prinzbach, W. Auge, and M. Basbudak, *Helv. Chim. Acta*, **54**, 759 (1971); T. A. Antkowiak, D. C. Sanders, G. B. Trimitsis, J. B. Press, and H. Shechter, *J. Amer. Chem. Soc.*, **94**, 5366 (1972).

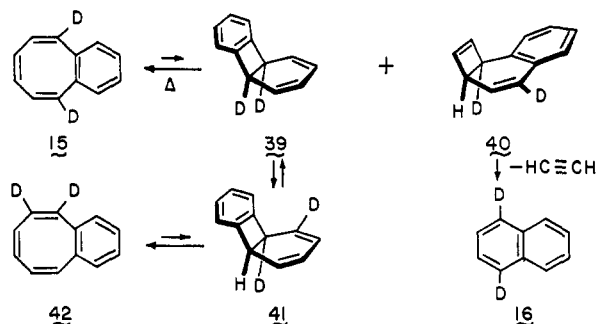
(40) S. Masamune, R. T. Seidner, H. Zenda, and M. Wiesel, N. Nakatsuka, and G. Bigam, *J. Amer. Chem. Soc.*, **90**, 5286 (1968); R. T. Seidner, N. Nakatsuka, and S. Masamune, *Can. J. Chem.*, **48**, 187 (1970); W. Grimme, H.-J. Riebel, and E. Vogel, *Angew. Chem., Int. Ed. Engl.*, **7**, 823 (1968); J. S. McConaghy, Jr., and J. J. Bloomfield, *Tetrahedron Lett.*, 1121 (1969); J. Altman, E. Babad, M. B. Rubin, and D. Ginsburg, *ibid.*, 1125 (1969); W. von Philipsborn, J. Altman, E. Babad, J. J. Bloomfield, D. Ginsburg, and M. B. Rubin, *Helv. Chim. Acta*, **53**, 725 (1970).

(41) M. J. Goldstein and S. A. Kline, *Tetrahedron Lett.*, 1085, 1089 (1973).



According to the second mechanistic alternative, these isomerizations involve [1,5]-sigmatropic rearrangement of a trigonal cyclobutene carbon in the same bicyclo[4.2.0]octatrienes and subsequent disrotatory ring opening of the newly formed triene. The workability of this pathway is suggested by the degenerate behavior of benzocyclooctatetraene. Because of benzo ring fusion, the 3,8-dideuterio derivative **15** is probably restricted (due to conservation of aromaticity) in the accessible energy range to valence isomerization with formation of **39** and **40** (Scheme III). Should maintenance of benze-

Scheme III

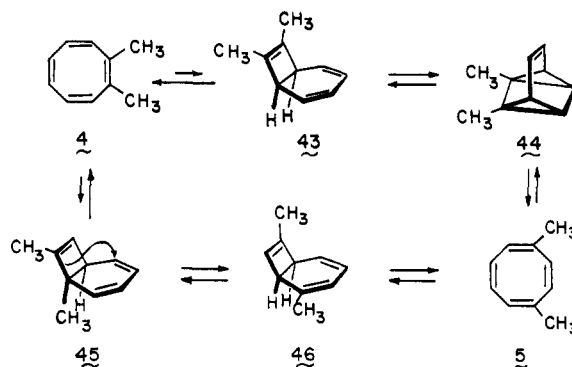


noid resonance persist, then neither **39** nor **40** is capable of Diels–Alder reactivity. [1,5]-Sigmatropic shift in **40** leads to no new structure but fragmentation would produce 1,4-dideuterionaphthalene (**16**) which is in actuality isolated at the more elevated temperatures (Table IV). Such symmetry allowed migration in **39** gives rise by way of **41** to the isotopically rearranged structure **42**. Repetition of this process would ultimately introduce isotopic label at C₅, C₆. This would account for the greater relative difficulty in achieving migration of deuterium to these positions as compared to C₄, C₇.

At this point, some mention of the behavior of 1,2-Me₂COT (**4**) is warranted. Its thermal chemistry is such as to provide 1,4-dimethyl isomer **5** initially (Table I). If viewed as the result of exclusive operation of the Diels–Alder mechanism, then isomerization to **43** and closure to tetracyclooctene **44** would have to be ruled kinetically dominant. Other possible valence isomers do not encompass comparable selectivity. In contrast, should the isomerization of **4** be based upon the [1,5]-sigmatropic shift mechanism, then **45** is required to be the bicyclooctatriene of kinetic consequence. Additionally, unidirectional pivoting (depicted in Scheme IV) is required for conversion to **5**.

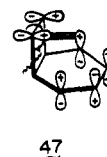
On the basis of the positional selectivity which is encountered in the reaction of **4** with TCNE, there is no doubt that valence isomerization of this cyclooctatetraene to **43** does operate. However, such cycloadditions are conducted in refluxing ethyl acetate solution and need not reflect possible equilibration of **4** with a far greater number of bicyclo[4.2.0]octatriene isomers, especially in the gas phase at higher temperatures. Actually, little of a quantitative or conclusive nature can be said on this point (the Curtin–Hammett

Scheme IV



principle applies as well). What is known is that the 3,8-dideuterio derivative (**9**) is capable of degenerate rearrangement at a rate estimated to be qualitatively somewhat slower than that of the process which leads to methyl migration. Although neither of the two pathways shown in Scheme IV accounts for the degenerate behavior, these experimental observations can be rationalized by simple extension of the original concepts. For example, should **43** be capable of partitioning between conversion to **44** and [1,5]-sigmatropic shift, our findings would be accommodated. Alternatively, were **45** to enjoy the latitude of [1,5] migration of either trigonal cyclobutene carbon, competitive conversion to **5** and return to skeletally rearranged **4** would result.

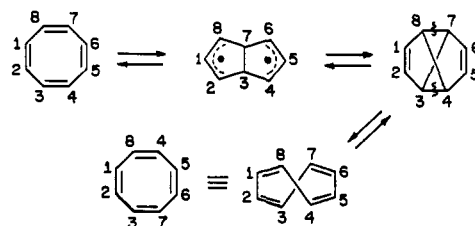
Detailed analysis of the thermal behavior of **4**–**7** (Table I) in light of predicted “one-pass” rearrangement products (Table IX) is most consistent with an overall predominance of the Diels–Alder mechanism. Perhaps the concerted [1,5] migration alternative is somewhat less favored because of the orbital symmetry requirement that the sp²-hybridized cyclobutene carbon migrate with retention rather than “opposite-face” bonding through the antisymmetric p orbital as in **47**. This im-



position forces the potential migratory center to maintain an ungainly spatial relationship to the migration terminus, a factor not present in the competing ($\pi_4s + \pi_2s$) transition state (**28**).

The third alternative mechanism outlined in Scheme V, which raises the possibility of bicyclo[3.3.0]octa-

Scheme V

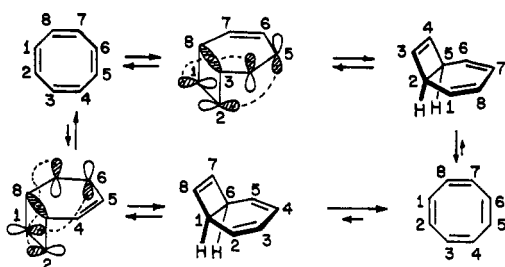


dienediyl intervention, improperly discriminates between the “one-pass” products (Table IX). Stiles and coworkers¹⁸ have provided convincing evidence that the thermal bond reorganizations of 1,2:5,6-dibenzocyclooctatetraenes are mediated by such a process. This

mechanistic selectivity undoubtedly arises because of the high level of benzo fusion which effectively lessens the cyclooctatetraene-like nature of the central eight-membered ring by reducing the number of potentially reactive double bonds to two. An examination of the behavior of labeled benzocyclooctatetraene **15** reveals that its degenerate thermal chemistry cannot be accounted for in terms of this pathway. Transitory passage through its more stable bicyclo[3.3.0]octadienediyl isomers simply does not eventuate in migration of deuterium away from C₃, C₈ to the remaining olefinic sites.

As outlined in Scheme VI, bicyclo[4.2.0]octatrienes

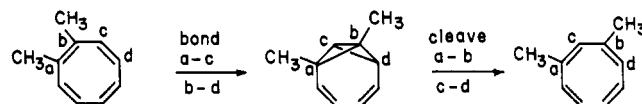
Scheme VI



are also hypothetically capable of symmetry allowed *antara-antara* Cope rearrangement. Such intramolecular cycloreactions would necessitate suprafacial rupture of the central σ bond and antarafacial utilization of one cyclohexadienyl and the cyclobutenyl π bonds. Although claims⁴² and counterclaims⁴³ of the operation of such ($2_s + \pi 2_a + \pi 2_a$) bond relocations are to be found in bicyclo[3.2.0]hepta-2,6-diene and bicyclo[4.2.0]octa-2,7-diene thermochemistry, the one point of agreement is that *trans,trans* [3,3]-sigmatropic reactions, or helix Cope rearrangements,⁴⁴ are normally kinetically noncompetitive. With specific reference to the Me₂COT's, it is to be noted that adherence by the 1,2 and 1,3 isomers to this mechanism leads only to degenerate skeletal rearrangement, whereas the 1,4 and 1,5 isomers are capable only of mutual interconversion (Table IX). Consequently, neither this pathway nor the mechanistically related⁴³ conrotatory valence isomerization of the cyclobutene moiety (to give *trans,trans*-1,2,5,6-cyclooctatetraene intermediates) are regarded to be of high relevance in the present context.

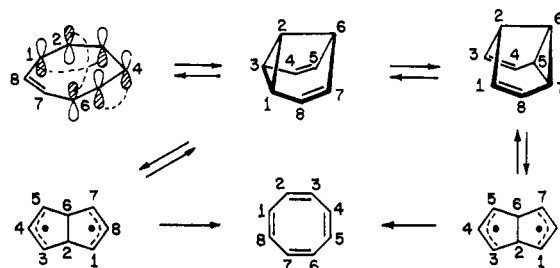
There are at least two other ways in which the cyclooctatetraene ring system can undergo isomerization. One such possibility consists of symmetry allowed ($\pi 2_a + \pi 2_s$) ring closure to a tricyclo[5.1.0.0^{2,8}]octa-3,5-diene, a ring system which has escaped synthesis to this date,⁴⁵ and subsequent retrograde ($\sigma 2_a + \sigma 2_s$) cleavage in the opposite sense. This route (see Scheme VII) differs in the predictive sense (Table IX) from experimental observation and is consequently removed from further consideration. Additionally, cyclooctatetraenes are subject in principle (and practice^{16,17}) to sym-

Scheme VII



metry allowed ($\pi 2_a + \pi 2_a + \pi 2_s$) cyclization to semi-bullvalenes, a ring system now recognized to be capable of thermal fragmentation with regeneration of the [8]-annulene framework.⁴⁶ However, as a glance at Scheme VIII will show, this two-step process is incap-

Scheme VIII



able of providing peripheral carbon atom scrambling and is inadequate for the present purposes.

Expectedly, as the temperature of the pyrolysis chamber is increased, more extensive skeletal rearrangement is encountered. The percentage of conversion to benzenoid products is also progressively enhanced. The composition of these aromatic fractions was examined most closely in the case of the 1,2- and 1,4-Me₂COT's (Table II). At very high temperatures (600°) benzene, toluene, *o*-xylene, and *p*-xylene, but no *m*-xylene, were produced. With less intense heat, traces of *m*-xylene were found. These observations suggest that, under the conditions of high temperature where the 1,3- and 1,5-Me₂COT's are being formed in quantity, these polyolefins escape from the heated confines before experiencing loss of acetylene to give *m*-xylene. Seemingly, therefore, fragmentation is competitive with "one-pass" rearrangement under the conditions employed by us. At lower temperatures where the residence time is certainly longer, some cleavage of the rearranged cyclooctatetraenes could arise and probably does to a small extent. These conversions are not considered well understood, however, and a more thorough investigation could be enlightening.

In summary, we share the view that the evidence is rather convincing that cyclooctatetraenes as a class of compounds are capable of thermally induced nondestructive skeletal rearrangement and that these isomerizations occur chiefly by intramolecular Diels-Alder (k_i) and [1,5]-sigmatropic shift (k_{ii}) mechanisms. Which pathway gains dominance is seemingly a function of structure, but product composition analysis of the unconstrained dimethyl derivatives examined herein suggests k_i generally to exceed k_{ii} .

Experimental Section

Melting points are corrected and boiling points are uncorrected. Proton magnetic resonance spectra were obtained on Varian A60-A, Varian HA-100, and Jeolco MH-100 spectrometers; apparent splittings are given in all cases. Infrared spectra were determined on Perkin-Elmer Model 137 and 467 instruments. Mass spectra were recorded on an AEI-MS9 spectrometer at an ionization poten-

(42) T. Miyashi, M. Nitta, and T. Mukai, *Tetrahedron Lett.*, 3433 (1967); *J. Amer. Chem. Soc.*, **93**, 3441 (1971).

(43) J. E. Baldwin and M. S. Kaplan, *J. Chem. Soc., Chem. Commun.*, 1560 (1970); 1354 (1969); *J. Amer. Chem. Soc.*, **93**, 3969 (1971); **94**, 669 (1972).

(44) J. J. Gajewski in "Mechanisms of Molecular Migrations," Vol. 4, B. S. Thyagarajan, Ed., Wiley-Interscience, New York, N. Y., 1971, pp 32-35.

(45) For a recently documented attempt, see P. Janse-van Vuuren, R. J. Fletcher, J. Meinwald, and R. E. Hughes, *J. Chem. Soc., Chem. Commun.*, 883 (1970).

(46) L. A. Paquette, R. K. Russell, and R. E. Wingard, Jr., *Tetrahedron Lett.*, 1713 (1973).

tial of 70 eV. Elemental analyses were performed by the Scandinavian Microanalytical Laboratory, Herlev, Denmark. Preparative vpc work was done on a Varian Aerograph A90-P3 instrument equipped with a thermal conductivity detector. All quantitative vpc analyses were performed with a Hewlett-Packard Model 5750 instrument in the flame ionization mode equipped with a Hewlett-Packard Model 3370A integrator. Peak response corrections were made in all cases. Appropriate controls excluded the possibility of rearrangement during vpc analysis under the stated conditions.

General Pyrolysis Procedure. Pyrolyses were conducted in the gas phase in a flow system⁸ by passing the vapor through a quartz tube packed with quartz chips at the stipulated temperatures under an atmosphere of nitrogen at reduced pressure. Under these conditions, the contact time was *ca.* 1–3 sec. The resultant crude pyrolysates, which were collected at -70° and usually recovered in 90–100% mass balance, were initially separated into aromatic and cyclooctatetraene components by preparative vpc on column A.⁴⁷ The cyclooctatetraene fraction was then analyzed quantitatively by vpc and infrared methods as outlined in the preceding paper.²⁸ Care was taken to avoid loss of material during all manipulations. The mixture of aromatic hydrocarbons so isolated was analyzed on column B⁴⁷ at 35° .

7,8-Dimethyl-9-thiabicyclo[4.2.1]nona-2,4,7-triene 9,9-Dioxide-1,6-*d*₂. A stirred solution of 545 mg (2.78 mmol) of **8**²⁴ in 25 ml of deuterium oxide and 100 ml of distilled dioxane was treated portionwise at 0° under dry nitrogen with 1.12 g (10 mmol) of potassium *tert*-butoxide. The resultant yellow solution was stirred at ambient temperature in the absence of oxygen for 10 days, at which time pmr analysis indicated almost complete exchange. After a total of 11 days, the solution was poured into 250 ml of ether, washed with water (3×50 ml) and brine, dried, and evaporated *in vacuo*. The resultant white solid was thoroughly dried on a vacuum pump to afford 436 mg (80%) of the dideuterated sulfone which was directly photolyzed.

1,2-Dimethylcyclooctatetraene-3,8-*d*₂ (9). A solution of 426 mg (2.14 mmol) of the predescribed sulfone in 100 ml of acetone and 300 ml of ether (previously deaerated with dry nitrogen) was irradiated with a 200-W Hanovia lamp fitted with a Corex filter housed in a water-cooled quartz immersion well. After 30 min, the solution was carefully concentrated to a small volume at reduced pressure and 20° , whereupon the remaining solvent was removed by distillation at atmospheric pressure. Preparative isolation from column A⁴⁷ at 110° afforded 76 mg (26%) of **9** which was identified by conversion to its TCNE adduct (**10**).

3,4-Dimethyl-9,9,10,10-tetracyanotricyclo[4.2.2.0^{2,5}]deca-3,7-diene. A solution containing 158 mg (1.20 mmol) of **4** and 1.28 g (10.0 mmol) of tetracyanoethylene in 10 ml of ethyl acetate was refluxed for 7 hr. The initial deep red color was rapidly discharged. Upon cooling, the solution was diluted with ethyl acetate, washed numerous times with 10% sodium bisulfite solution, water, and brine, dried, and evaporated. The crude product (305 mg) was recrystallized from methylene chloride–ether to give 152 mg (52%) of adduct: mp $256\text{--}257^\circ$ dec; $\delta_{\text{TMS}}^{\text{acetone-}d_6}$ 1.55 (s, 6 H, CH_3), 3.08 (m, 2 H, cyclobutenic sp³ C–H), 3.95 (m, 2 H, bridgehead), and 6.47 (m, 2 H, olefinic).

Anal. Calcd for $\text{C}_{16}\text{H}_{12}\text{N}_4$: C, 73.83; H, 4.65. Found: C, 73.51; H, 4.73.

3,4-Dimethyl-9,9,10,10-tetracyanotricyclo[4.2.2.0^{2,5}]deca-3,7-diene-2,5-*d*₂ (10). Heating 20 mg (0.149 mmol) of **9** and 256 mg (2.00 mmol) of tetracyanoethylene at reflux in ethyl acetate (5 ml) for 5 hr, followed by work-up as above with additional chromatography on Florisil (5 g, elution with ether), furnished 25 mg (64%) of crystalline **10**. Trituration with ether gave 12 mg of white crystals, pmr analysis of which revealed it to contain 95% of two D atoms (signal at δ 3.08 almost totally absent).

Thermal Activation of Benzocyclooctatetraene-3,8-*d*₂ (15). A 168-mg sample of **15** was pyrolyzed as predescribed at 675° (25 mm). Under these excessive conditions, considerable decomposition occurred in the pyrolysis chamber. The collected pyrolysate (150 mg) gave the appearance of being polymeric. However, preparative vpc isolation from column A⁴⁷ at 135° furnished 8 mg (5%) of rearranged **15** (see Table IV) and 15 mg (10%) of 1,4-dideuterionaphthalene (**16**), identified by its pmr spectrum and vpc retention time.

Methyl Cyclooctatetraenecarboxylate-2,3,4,5,6,7-*d*₆ (17a). A

(47) The following vpc columns were employed in the course of this work: A, 5.5 ft \times 0.25 in. 5% SE-30 on 60–80 mesh Chromosorb G; B, 24 ft \times 0.125 in. Hi-Pac column; C, 8 ft \times 0.25 in. 5% OV-11 on 60–80 mesh Chromosorb W.

solution containing 6 ml of methyl propiolate in 120 ml of benzene-*d*₆ was irradiated in a Rayonet reactor (2537 Å) through quartz optics for six 20-hr periods. Additional portions (2 ml) of methyl propiolate were added each time the apparatus was cleaned with chlorosulfonic acid to remove the opaque polymer which arose during reaction. The benzene-*d*₆ was recovered by distillation at atmospheric pressure and the residue was subjected to molecular distillation ($90\text{--}130^\circ$ (0.02 mm)). In this way 1.75 g of **17a** was isolated as a clear yellow liquid: $\delta_{\text{TMS}}^{\text{CDCl}_3}$ 3.71 (s, 3 H, OCH_3), 6.0 and 6.95 (br s, 1 H total, olefinic).

Phenylcyclooctatetraene-2,3,4,5,6,7-*d*₆ (17b). A solution of 500 mg (4.90 mmol) of phenylacetylene in 120 ml of benzene-*d*₆ contained in a quartz tube was flushed with nitrogen (4 min) and irradiated for seven 12-hr periods. Cleaning of the tube with chlorosulfonic acid and addition of 0.40 ml of phenylacetylene were performed between periods. Removal of benzene-*d*₆ was followed by chromatography on silica gel (80 g, elution with pentane) to give 490 mg of **17b**.

Hydroxymethylcyclooctatetraene-2,3,4,5,6,7-*d*₆ (18). To a stirred suspension containing 8.28 g (0.218 mol) of lithium aluminum hydride in 200 ml of ether was added dropwise a solution containing 3.66 (21.8 mmol) of **17a** in 100 ml of ether at 0° during 45 min. The mixture was stirred at 25° for several hours, at which time it was cooled to 0° and treated cautiously with 40 ml of water and 350 ml of 10% sulfuric acid solution. The organic layer was separated and the aqueous phase was extracted several times with ether. The combined organic layers were washed with brine, dried, and concentrated. Distillation of the residue afforded 1.93 g (64%) of **18** as a pale yellow liquid: bp $64\text{--}73^\circ$ (0.05 mm); $\delta_{\text{TMS}}^{\text{CCl}_4}$ 3.0 (br s, 1 H, hydroxyl), 3.85 (s, 2 H, $-\text{CH}_2\text{O}-$), and 5.66 (s, 1 H, olefinic).

Cyclooctatetraenylmethyl-2,3,4,5,6,7-*d*₆ Bromide (19). To a solution of triphenylphosphine dibromide [from 14.62 g (55.8 mmol) of triphenylphosphine and 8.85 g (55.3 mmol) of bromine] in 100 ml of freshly distilled dimethylformamide was added dropwise with stirring a solution of 1.933 g (13.8 mmol) of **18** in 25 ml of dimethylformamide over a 1-hr period at 25° under nitrogen. Upon completion of the addition, the mixture was stirred for 3 hr, poured into 500 ml of ice-water, and extracted with hexane (5×200 ml). The combined organic layers were washed with ice-water and brine, dried, and evaporated. The residue was triturated with hexane, filtered to remove some residual triphenylphosphine oxide, and evaporated *in vacuo* to yield 2.33 g (84%) of **19** as a clear yellow liquid: $\delta_{\text{TMS}}^{\text{CDCl}_3}$ 3.9 (s, 2 H, $-\text{CH}_2-$) and 5.9 (br m, 1 H, olefinic).

Methylcyclooctatetraene-2,3,4,5,6,7-*d*₆ (20). To a stirred suspension of lithium aluminum hydride (2.19 g, 60.0 mmol) in 75 ml of anhydrous ether was added dropwise a solution of **19** (2.325 g, 11.55 mmol) in 50 ml of the same solvent during 30 min. The mixture was heated at reflux for 12 hr, cooled to 0° , treated with sufficient 10% sulfuric acid to dissolve all salts, and extracted with ether. The combined organic layers were washed with water and brine, dried, and freed of solvent by distillation at atmospheric pressure. Fractionation of the residue furnished 952 mg (67%) of **20**: bp $71\text{--}72^\circ$ (30 mm); $\delta_{\text{TMS}}^{\text{CDCl}_3}$ 1.75 (s, 3, CH_3) and *ca.* 5.8 (br s, 1 H, olefinic).

3-Carbomethoxy-9,9,10,10-tetracyanotricyclo[4.2.2.0^{2,5}]deca-3,7-diene (21a). A solution of methyl cyclooctatetraenecarboxylate (138 mg, 0.85 mmol) and tetracyanoethylene (1.28 g, 10.0 mmol) in 5 ml of dioxane was heated at reflux for 5 hr and processed as before to yield 154 mg (62%) of **21a**: mp $187\text{--}188^\circ$ dec (from methylene chloride–ether); $\delta_{\text{TMS}}^{\text{acetone-}d_6}$ 3.38 (t, $J_{2,5} = J_{3,6} = 4.0$ Hz, 1, H_5), 3.55 (t, $J_{2,5} = J_{1,2} = 4.0$ Hz, 1, H_2), 3.68 (s, 3, OCH_3), 4.05–4.22 (m, 2, $\text{H}_{1,6}$), 6.37–6.51 (m, 2, $\text{H}_{7,8}$), and 6.63 (s, 1, H_4).

Anal. Calcd for $\text{C}_{16}\text{H}_{10}\text{N}_4\text{O}_2$: C, 55.20; H, 3.47. Found: C, 65.82; H, 3.53.

The hexadeuterio derivative was prepared in an analogous fashion except for the fact that ethyl acetate was employed as solvent and the heating period was extended to 14 hr.

3-Phenyl-9,9,10,10-tetracyanotricyclo[4.2.2.0^{2,5}]deca-3,7-diene (21b). A solution of phenylcyclooctatetraene (360 mg, 2.0 mmol) and tetracyanoethylene (1.28 g, 10.0 mmol) in 10 ml of ethyl acetate was heated at reflux for 5 hr. The predescribed work-up gave 358 mg (58%) of **21**, which after several recrystallizations from acetone–ether had mp $262\text{--}263.5^\circ$ dec: $\delta_{\text{TMS}}^{\text{acetone-}d_6}$ 3.32 (t, $J_{2,6} = 3.5$ Hz, 1, H_5), 3.71 (t, $J_{2,5} = J_{1,2} = 3.5$ Hz, 1, H_2), 3.71 (t, $J_{2,5} = J_{1,2} = 3.5$ Hz, 1, H_2), 3.92–4.16 (m, 1, H_6), 4.30–4.48 (m, 1, H_1), 6.21 (s, 1, H_4), 6.21–6.60 (m, 2, $\text{H}_{7,8}$), and 7.20–7.50 (m, 5, aryl).

Anal. Calcd for $\text{C}_{20}\text{H}_{17}\text{N}_4$: C, 77.90; H, 3.92. Found: C, 78.00; H, 4.05.

The hexadeuterio derivative was prepared in analogous fashion.

3-Methyl-9,9,10,10-tetracyanotricyclo[4.2.2.0^{2,5}]deca-3,7-diene

(21c). A solution of methylcyclooctatetraene (198 mg, 1.68 mmol) and tetracyanoethylene (1.28 g, 10.0 mmol) in 10 ml of ethyl acetate was refluxed for 4.5 hr, cooled and processed in the manner outlined earlier. Chromatography of the crude adduct on Florisil and recrystallization from methylene chloride-ether gave 252 mg (61%) of 21c: mp 203–204.5°; $\delta_{\text{TMS}}^{\text{acetone-d}_6}$ 1.63 (s, 3 H, CH_3), 3.04–3.32 (m, 2 H, cyclobutene $\text{sp}^3 \text{CH}$), 3.80–4.12 (m, 2 H, bridgehead), 5.63 (s, 1 H, cyclobutene), and 6.32–6.54 (m, 2 H, olefinic).

Anal. Calcd for $\text{C}_{15}\text{H}_{10}\text{N}_4$: C, 73.15; H, 4.09. Found: C, 73.01; H, 4.12.

The labeled derivative was obtained similarly except for extension of the heating period to 9 hr.

9-Thiabicyclo[4.2.1]nona-2,4,7-triene-1,6- d_2 9,9-Dioxide (25). To a stirred solution of 9-thiabicyclo[4.2.1]nona-2,4,7-triene 9,9-dioxide (3.36 g) in 250 ml of anhydrous tetrahydrofuran at -70° under nitrogen was added 40 ml of *n*-butyllithium (2 *M*) during 15 min. The deep purple solution was stirred for an additional 10 min and treated in one portion with 10 ml of acetic acid-*O-d* (95% d_1). The tetrahydrofuran was removed by evaporation under reduced pressure and 20 ml of water was added. Extraction with methylene chloride was followed by washing of the combined

organic layers with water and brine. Drying and evaporation of solvent afforded 2.17 g of 25.

Cyclooctatetraene-1,4- d_2 (26). A solution containing 1.00 g of 25 in 400 ml of acetone-ether (1:3) was irradiated as before for 2 hr. Removal of the solvent left a yellow oil which was purified by vpc chromatography on column C.⁴⁷ There was obtained 250 mg of 26; *m/e* calcd 106.0752, found 106.0753.

9,9,10,10-Tetracyanotricyclo[4.2.2.0^{2,5}]deca-3,7-diene- d_2 (27). A solution containing 53 mg of 26 and 640 mg of tetracyanoethylene in 10 ml of ethyl acetate was refluxed for 8 hr and processed in the usual manner. There was obtained after column chromatography on Florisil 78 mg of 27, mp 248° (lit. for unlabeled adduct mp 249°).

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Conformational Analysis. CII. Levopimaric Acid and Related Steroidal Dienes^{1,2}

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Abstract: Force field calculations suggest that the conformation of levopimaric acid and configurationally related steroidal dienes such as cholesta-2,4-diene may best be discussed in terms of a conformationally mobile system in which the diene ring can adopt a "levopimaric like" or a "cholesta-2,4-diene like" conformation. The energies of these conformations vary with the number and positioning of substituents, and the resulting equilibria are discussed for a number of model compounds. Previously reported circular dichroism data are discussed in terms of relative populations calculated for these conformers. The effects of substituents appear to be important in determining the amplitudes of the circular dichroism curves.

X-Ray crystallography³ has shown that levopimaric acid (1a) exists in a folded conformation in the crystalline state, with the C9–C10 bond in a quasi-axial orientation with respect to the diene ring. Investigation of the optical rotatory dispersion⁴ of levopimaric acid (1a) and cholesta-2,4-diene (2a) had previously led to the suggestion that levopimaric acid exists in this folded conformation in solution, in contrast to the extended conformation deduced for the configurationally related cholesta-2,4-diene (2a), in which the C10–C9 bond is quasi-equatorial. Supporting evidence for the latter conclusion had been obtained from nmr,^{4,5} surface film,⁶ and photochemical⁷ studies.

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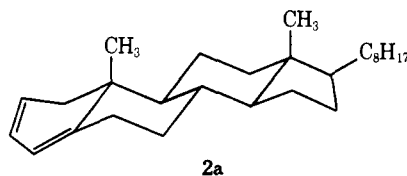
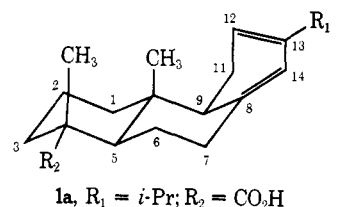
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Burgstahler, *et al.*,⁸ have investigated the effect of substituents on the circular dichroism of the $\pi \rightarrow \pi^*$ band at ca. 270 nm of levopimaric acid and configurationally related steroidal 2,4-dienes with varying substitution patterns (see Table I). The sign and magnitude of the Cotton effect showed a marked dependence on the substitution.

The degree to which this dependence reflects conformational changes is not clear *a priori*, and an independent assessment of the effect of substituents on the

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