

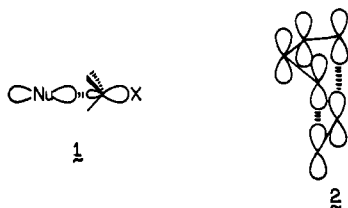
Perpendicularly Oriented π Systems. Thermal Activation of Annulated Bicyclo[4.2.0]octatrienes and Establishment of the Tetracyclo[4.2.0.0^{2,8}.0^{5,7}]octene Pathway of Bond Relocation

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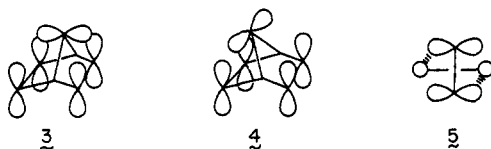
Contribution from the Department of Chemistry, The Ohio State University, Columbus, Ohio 43210. Received March 19, 1974

Abstract: The thermolysis of a number of annulated bicyclo[4.2.0]octatrienes leads to structural rearrangement with formation of 1,2-bridged cyclooctatetraenes. Strong evidence for the intermediacy of tetracyclo[4.2.0.0^{2,8}.0^{5,7}]octenes was obtained by making recourse to dideuterated and dimethyl substituted derivatives. An alternative [1,5]-sigmatropic shift mechanism is apparently not competitive and reasons are given for kinetic preference of the Diels–Alder pathway. The implications of bracketing strain and cyclobutene ring substitution on the critical flexing of the cyclobutene ring toward the conjugated diene moiety are discussed. In synthetic terms, these transformations represent a convenient preparative source of unusually constructed cyclooctatetraenes.

Elucidation of the mechanistic features of a host of chemical reactions of which the S_N2 displacement and Diels–Alder cycloaddition are but two examples has provided evidence suggesting that end-on-end orbital interaction as in **1** and **2** is highly preferred to initial bonding arrangements that deviate significantly from



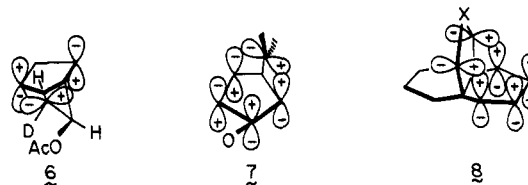
the 180° alignment. That such partiality for in-plane overlap should not be attributed exclusively to steric interactions is suggested *inter alia* by the structure of the 7-norbornadienyl cation which is known to distort away from the symmetrical conformation having near perpendicular overlapping lobes (**3**) to the unsymmetrical structure **4**.² An increased awareness of this state of affairs developed when it became clear that examples of the symmetry allowed thermal $\pi_2 + \pi_2$ dimerization of ethylenes where perpendicular approach is mandatory (*cf.* **5**)³ are indeed few.⁴ The generalized concept of



in-plane overlap of interacting lobes has served as a guiding principle in many mechanistic applications, stereoelectronic control in the halogenation of cyclo-

alkanones and in the alkylation of cyclic enolate anions serving as time-worn examples.⁵

Certain recent investigations have documented evidence showing that steric inhibition of the seemingly favored “end-for-end” orbital construct does not preclude the incursion of chemical change. Stereochemical analysis of the thermally promoted bicyclo[3.2.0]hept-2-ene \rightarrow norbornene transformation by Berson and coworkers⁶ has led to the suggestion that **6** is the intermediate of consequence. In comparable fashion, [1,4]-sigmatropic rearrangement of zwitterionic species derived from 6,6-disubstituted bicyclo[3.1.0]hexan-3-ones seemingly proceeds *via* intermediate **7**.⁷ Also,



the bishomoconjugative rearrangement of tricyclic and bicyclic α -halo ketones and sulfones has been attributed to intramolecular $\pi_4 + \pi_2$ capture of intermediates of general type **8** and subsequent bond relocation in the resulting *cis*-bishomobenzene cycloadducts.⁸

Current theoretical understanding of bicycloaromaticity is founded upon through-space interactions of perpendicular or nearly perpendicular π systems.⁹ The sign discontinuity in the basis set of atomic orbitals present in the neutral hydrocarbons barrelene (**9**),¹⁰ bicyclo[4.2.2]deca-2,4,7,9-tetraene (**10**),¹¹ and [4.4.2]-

(5) H. O. House, “Modern Synthetic Reactions,” 2nd ed, W. A. Benjamin, Menlo Park, Calif., 1972, pp 469–473 and 587–594.

(6) J. A. Berson, *Accounts Chem. Res.*, **1**, 152 (1968).

(7) T. M. Brennan and R. K. Hill, *J. Amer. Chem. Soc.*, **90**, 5614 (1968); H. E. Zimmerman and D. S. Crumrine, *ibid.*, **90**, 5612 (1968); H. E. Zimmerman, D. S. Crumrine, D. Döpp, and P. S. Huyffer, *ibid.*, **91**, 434 (1969).

(8) L. A. Paquette, R. E. Wingard, Jr., and R. H. Meisinger, *J. Amer. Chem. Soc.*, **93**, 1047 (1971); L. A. Paquette, R. H. Meisinger, and R. E. Wingard, Jr., *ibid.*, **94**, 2155 (1972); **95**, 2230 (1973).

(9) M. J. Goldstein, *J. Amer. Chem. Soc.*, **89**, 6357 (1967); M. J. Goldstein and R. Hoffmann, *ibid.*, **93**, 6193 (1971).

(10) H. E. Zimmerman and R. M. Paufer, *J. Amer. Chem. Soc.*, **82**, 1514 (1960); H. E. Zimmerman, G. L. Grunewald, R. M. Paufer, and M. A. Sherwin, *ibid.*, **91**, 2330 (1969).

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

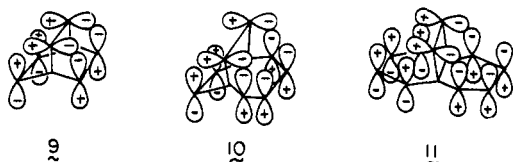
(1) National Institutes of Health Predoctoral Fellow, 1969–1971; University Dissertation Fellow, 1971.

(2) P. R. Story and M. Saunders, *J. Amer. Chem. Soc.*, **82**, 6199 (1960); **84**, 4876 (1962); P. R. Story, L. C. Snyder, D. C. Douglass, E. W. Anderson, and R. L. Kornegay, *ibid.*, **85**, 3630 (1963); G. A. Olah and A. M. White, *ibid.*, **91**, 6883 (1969); R. K. Lustgarten, M. Brookhart, and S. Winstein, *ibid.*, **94**, 2347 (1972).

(3) R. B. Woodward and R. Hoffmann, “The Conservation of Orbital Symmetry,” Academic Press, New York, N. Y., 1970, pp 68–76.

(4) K. Kraft and G. Koltzenburg, *Tetrahedron Lett.*, 4357, 4723 (1967).

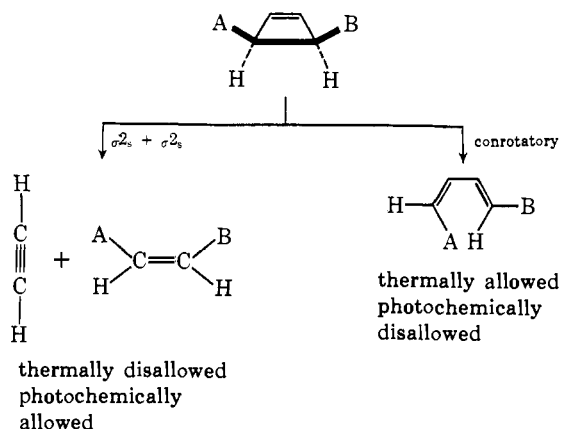
propellapentaene (**11**)¹² results in the operation of some electronic delocalization but no attendant stabilization.¹³ The chemical properties of such molecules are consequently of considerable interest. In this paper, we describe an extension of our investigation of un-



saturated propellane chemistry to a study of the thermal (and photochemical) activation of **11** and related tricyclic hydrocarbons possessing the bicyclo[4.2.0]octatriene part structure.¹⁴ Because little was known about this valence isomeric form of cyclooctatetraene,¹⁵ encompassing as it does the near perpendicular arrangement of $p\pi$ electrons of interest, it seemed desirable to gain some insight into those orbital interactions which develop upon thermal and photochemical excitation.

Results and Discussion

Owing to the unique structural features embodied in annulated bicyclo[4.2.0]octatrienes such as **11**, thermally allowed conrotatory rupture of the weak doubly allylic C-C bond cannot obtain readily. For reasons of orbital symmetry, photochemical cleavage in this mode is disallowed. Therefore, major perturbation of the precise point at which cyclobutene ring openings normally occur prevails in such molecules. Because of this, the real possibility existed that cyclobutene ring cleavage in $\sigma_2 + \sigma_2$ fashion to give acetylenic and olefinic fragments, normally an energetically inaccessible reaction pathway, might now be favored. The situation is illustrated in the scheme which indicates further that



stereochemical retention at all four termini, unrecognizable of course in the acetylene, can take place *concertedly* only from the first excited state.¹⁶ When trans-

(12) L. A. Paquette and J. C. Phillips, *J. Amer. Chem. Soc.*, **91**, 3973 (1969); L. A. Paquette, J. C. Phillips, and R. E. Wingard, Jr., *ibid.*, **93**, 4516 (1971).

(13) For reports dealing with the photoelectron spectra of **9** and **11**, see E. Haselbach, E. Heilbronner, and G. Schröder, *Helv. Chim. Acta*, **54**, 153 (1971); R. Gleiter, E. Heilbronner, L. A. Paquette, G. L. Thompson, and R. E. Wingard, Jr., *Tetrahedron*, **29**, 565 (1973).

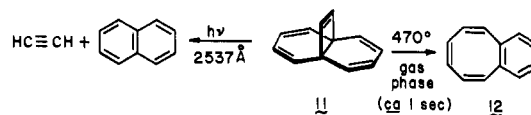
(14) For a preliminary report, consult L. A. Paquette and R. E. Wingard, Jr., *J. Amer. Chem. Soc.*, **94**, 4398 (1972).

(15) (a) E. Vogel, H. Kiefer, and W. R. Roth, *Angew. Chem.*, **76**, 432 (1964); (b) H. E. Zimmerman and H. Iwamura, *J. Amer. Chem. Soc.*, **92**, 2015 (1970).

(16) Such considerations are presently restricted to stereochemical retention in both components for two reasons. First, in our systems

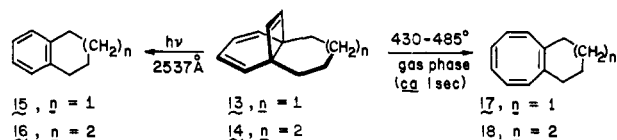
lated into chemical reactivity terms, this analysis can be taken to mean that the cyclobutene ring in **11** and its derivatives should be susceptible to fragmentation only under conditions of photochemical excitation. On the other hand, cleavage should not be favored under pyrolysis conditions and an alternative lower energy process should be followed if available. Our findings fully confirm these expectations.

That [4.4.2]propellapentaene (**11**) is subject to ready photoinduced aromatization was immediately revealed upon irradiation of ether solutions of the hydrocarbon at 25° with 2537-Å light; rapid formation of naphthalene and acetylene ensued. Gas-phase pyrolysis of **11** at 470° (2.5 mm) in a flow system (contact time *ca.* 1 sec) under nitrogen resulted instead in skeletal rearrange-



ment to benzocyclooctatetraene (**12**) which was isolated in 53% yield.

The behavior of propellatrienes **13** and **14** proved to be entirely comparable. Thus, exposure to a 2537-Å light source led again with loss of acetylene to the formation of tetralin (**15**) and benzocycloheptene (**16**), respectively. In contrast, passage of these unsaturated



propellanes through the quartz pyrolysis chamber under closely comparable conditions gave rise in greater than 95% conversion to the 1,2-annulated cyclooctatetraenes **17** (60% isolated) and **18** (47% isolated). The identities of these products were established by direct vpc and spectral comparisons with authentic samples.⁸

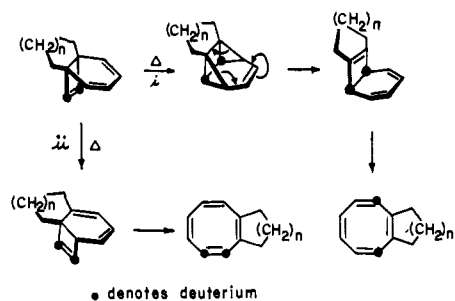
Several hypothetical mechanisms can be advanced in explanation of these thermochemical rearrangements.

Intuitively, one might expect that those pathways in which continuous orbital overlap can be maintained throughout the bond relocation process might be most favored. In this context, two hypothetical mechanisms were considered most plausible. The first is triggered by intramolecular $\pi_4 + \pi_2$ (Diels-Alder) cycloaddition leading to a tetracyclo[4.2.0.0^{2,8}.0^{5,7}]octene intermediate, followed by six-electron reorganization within this newly formed bishomobenzene. Alternatively, isomerization could be initiated by [1,5]-sigmatropic shift of a trigonal cyclobutene carbon atom and completed by disrotatory opening of the newly formed bicyclo[4.2.0]octatriene. Other alternatives involving Cope rearrangement of the cyclobutene double bond or its $\sigma_2 + \pi_2 + \pi_2$ bond relocation appear prohibited because of obvious Bredt's rule difficulties.

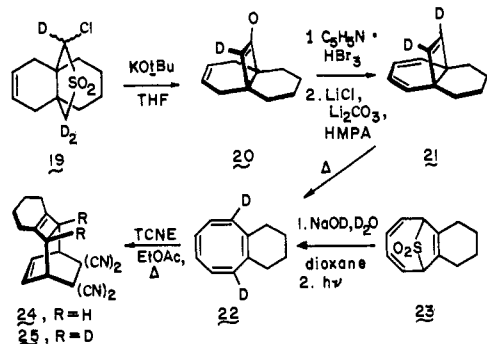
The preferred mechanistic hypotheses are illustrated in Scheme I which describes further how deuterium labeling of the sp^2 -hybridized cyclobutene centers

the developing olefin fragment is an aromatic ring system requiring mandatory *cis* geometry in the double bond being created. Second, formation of the acetylene unit *via* a $\sigma_2 + \sigma_2$ retrograde cycloaddition is not possible unless rotation of the π bond also operates. The ensuing $\sigma_2 + \sigma_2 + \pi_2$ process should be still more energy demanding and is therefore probably not a truly viable alternative.

Scheme I



would permit in principle a distinction to be made between the pair of alternatives. Whereas the cycloaddition pathway would lead to cyclooctatetraene product with olefinically bound deuterium at C₃ and C₈, the course of the [1,5]-sigmatropic shift process is such as to locate the isotopic labeling at C₃ and C₄. Mechanistic differentiation was achieved by thermal rearrangement of **21**. Access to this hydrocarbon was gained by a modification of our earlier synthesis¹² and involved initial hydrogen–deuterium exchange in the protio analog of α -chloro sulfone **19** with NaOD in dioxane–D₂O at reflux.¹⁷ When treated with freshly sublimed potassium *tert*-butoxide in anhydrous tetrahydrofuran, **19** underwent ready Ramberg–Bäcklund rearrangement¹⁸ to **20**. Mass spectral analysis of **20** revealed it to be 92% dideuterated. Bromination–dehydrobromination of **20** gave **21** (92% d₂) which on pyrolysis as before yielded only **22** (91% d₂). Because the olefinic protons of **17** at 60 and 100 MHz appear as closely spaced overlapping multiplets, specific location of the deuterium atoms in **22** was not readily achievable by pmr techniques. Suggestive evidence that the 3,8-d₂ derivative had been produced was derived by spectral comparison with an authentic sample of **22** prepared in unequivocal fashion by deuterium exchange and photol-



ysis of the known⁸ bridged sulfone **23**.¹⁹ Confirmation of this labeling pattern was derived by conversion of both **17** and **22** to their respective tetracyanoethylene adducts. This dienophile was selected because it reacts preferentially with that valence isomer of the cyclooctatetraene having the cycloalkane ring fused to the cyclobutene moiety and does so under relatively mild conditions (refluxing ethyl acetate solution, 3 hr). While the pmr spectrum of **24** exhibits a trio of well-

(17) L. A. Paquette and J. C. Philips, *Tetrahedron Lett.*, 4645 (1967).

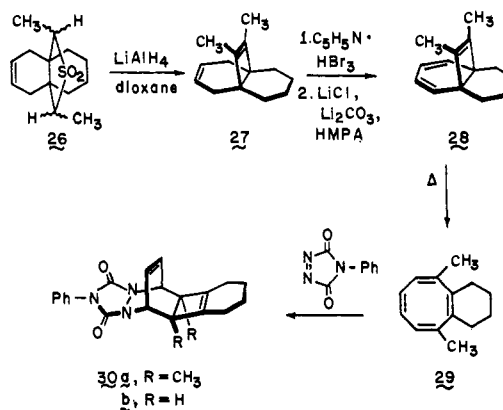
(18) L. A. Paquette, "Mechanisms of Molecular Migrations," Vol. I, B. S. Thyagarajan, Ed., Interscience, New York, N. Y., 1968, pp 121–156; L. A. Paquette, *Accounts Chem. Res.*, 1, 209 (1968); F. G. Bordwell, *ibid.*, 3, 281 (1970).

(19) For other examples of related photochemical sulfur dioxide extrusion reactions, see ref 8 and L. A. Paquette, S. V. Ley, R. H. Meisinger, R. K. Russell, and M. Oku, *J. Amer. Chem. Soc.*, 96, 5806 (1974).

separated multiplets for the three pairs of relevant protons [$\delta_{\text{TMS}}^{\text{CD}_2\text{Cl}_2}$ 6.42 (m, 2), 3.65 (m, 2), and 3.33 (m, 2)], the absorption at δ 3.33 was essentially lacking in **25** (except for the *ca.* 10% protium impurity carried through from **19**).

These findings implicate exclusive operation of the $\pi_4s + \pi_2s$ bond reorganization mode (path i). Seemingly, the ease of initial conversion to the tetracyclooctene intermediate will depend in part upon the capability of the cyclobutene carbon atoms to flex somewhat in the direction of the adjoining diene unit. In an attempt to address this question, we proceeded to examine the thermal chemistry of 11,12-dimethyl[4.4.2]-propella-2,4,11-triene (**28**) and of [4.3.2]propella-2,4,10-triene (**31**). If steric effects play a meaningful role, one might expect the barrier for closure in **28** to be higher than that for the parent system. Likewise, Dreiding models of **31** indicated that the trimethylene bridge noticeably restricts this critical molecular motion. On the other hand, if incipient ring strain is the major deterrent to closure, then placement of alkyl groups upon the cyclobutene ring could likely facilitate the skeletal rearrangement.

Convenient synthetic entry to the first of these hydrocarbons (**28**) was gained by initial conversion of 12-thia[4.4.3]propell-3-ene 12,12-dioxide to the epimeric mixture of α, α' -dimethyl sulfones **26**. When exposed to the action of lithium aluminum hydride in refluxing dioxane, **26** was converted into dimethylpropelladiene **27** (37% yield). This unusual yet rather general²⁰ preparative route to dimethylcyclobutenes consists formally of a 1,2-alkyl shift from sulfur to carbon with ultimate elimination of the heteroatom. Its mechanism is unknown, but the overall process bears close analogy to the transformation of 2,5-diphenyltetrahydrothiophene 1,1-dioxide to 1,2-diphenylcyclobutene (40%) in the presence of ethereal ethylmagnesium bromide²¹ and of tetrahydrothiophene 1,1-dioxide to cyclobutene (0.5%) under the same conditions.²² In light of the behavior of thietane 1,1-dioxides toward Grignard reagents and other bases,²³ the grossly reasonable



possibility exists that carbanionic intermediates are involved.

(20) J. M. Photis and L. A. Paquette, *J. Amer. Chem. Soc.*, 96, 4715 (1974).

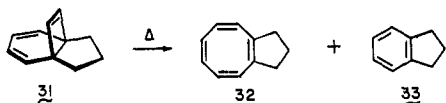
(21) A. Zielski, Ph.D. Thesis, University of Minnesota, 1966.

(22) E. Jancis, Ph.D. Thesis, University of Minnesota, 1967.

(23) R. M. Dodson and G. Klose, *Chem. Ind. (London)*, 1203 (1963); R. M. Dodson, P. D. Hammen, E. H. Jancis, and G. Klose, *J. Org. Chem.*, 36, 2698 (1971); R. M. Dodson, P. D. Hammen, and J. Y. Fan, *ibid.*, 36, 2703 (1971); R. M. Dodson and J. Y. Fan, *ibid.*, 36, 2708 (1971).

Under conditions (430°) where **13** was found to experience 60–70% conversion to **17**, dimethyl derivative **28** was completely unreactive. At 470°, **28** underwent partial (*ca.* 50%) rearrangement to **29** and to small amounts of an unidentified second substance. Control experiments revealed this second product to be derived from further thermal rearrangement of **29** and consequently it was not given further attention. The ultraviolet spectrum of **29** displays only end absorption. In the pmr, this hydrocarbon shows two sets of olefinic resonances (2 H each) at δ 5.67 (m) and 5.34 (m), a six-proton methyl singlet at 1.53, and a broad multiplet of area 8 at 1.4–2.4 due to the methylene groups. On the basis of these data, the material appeared to be symmetrically substituted. This conclusion was substantiated and the relative location of the methyl groups established by conversion of **29** to its *N*-phenyltriazolinedione (PTAD) adduct (**30a**). The resulting white solid exhibits a pmr spectrum (see Experimental Section) having absorptions entirely compatible with ($\pi_4 + \pi_2$) addition to that symmetrical bicyclic valence tautomer of **29** having alkyl substitution uniquely on the cyclobutene ring. 1,2-Tetramethylenecyclooctatetraene (**13**) behaved analogously in the presence of PTAD and provided the closely related molecule **30b**. The preferred direction of approach of PTAD to the valence isomer of **13** can be surmised on the basis of extensive analogy to be that involving bonding to the unencumbered surface of the tricyclic intermediate with ultimate product geometry being that illustrated in **30b**. In the case of **29** where methyl groups have replaced the two angular hydrogens and the option now rests between the related accessibilities to this surface or to that from which the cyclobutene ring projects, a distinction cannot be made with comparable confidence. Consequently, although the stereochemistry of **30a** remains uncertain, the gross spectral features clearly require that its precursor be **29**.

Thermal rearrangement of propellatriene **31**, available from a companion study,²⁴ proved to be unusually difficult. Only when temperatures in excess of 600° were attained did reaction occur. Under these conditions, low yields of **32** and **33** were realized and, in fact, indan predominated by a factor of 2. These findings



suggest that the added rigidity conferred upon the tricyclic bicyclo[4.2.0]octatriene as the bracketing strain is progressively enhanced effectively deters the capability of the cyclobutene sp^2 carbons to alter their relative position sufficiently to enter into tetracyclo[4.2.0.0^{2,8}.0^{5,7}]-octene formation.

Pathway i of Scheme I clearly serves to explain our experimental observations. In particular, it accommodates in logical orbital-symmetry allowed fashion the overall molecular change whereby the cyclobutene sp^2 -hybridized centers become inserted into the C_1C_2 and C_5C_8 σ bonds. The (qualitative) rate-retarding effects of the methyl groups in **28** and the impact of trimethylene bridging as in **31** are subtle structural changes which

(24) L. A. Paquette, R. E. Wingard, Jr., and R. K. Russell, *J. Amer. Chem. Soc.*, **94**, 4739 (1972).

can be rationalized in terms of tetracyclo[4.2.0.0^{2,8}.0^{5,7}]-octene intervention.

The intramolecular juxtaposition of the two components of a $\pi_4 + \pi_2$ cycloaddition in the indicated near-orthogonal fashion, a bishomoconjugative alignment as it were,³ somewhat unexpectedly leads to rather facile intramolecular bonding despite the requirement that two cyclopropane rings are produced. We have been unable to gain evidence for token competition from the [1,5]-sigmatropic shift process (pathway ii). In view of a number of recent developments in this field, bishomoconjugative Diels–Alder reactivity can no longer be regarded as a chemical curiosity. The weight of evidence in our companion examination of the thermal chemistry of cyclooctatetraenes also favors a similar reaction manifold in certain instances and further discussion of this point is deferred to the accompanying paper.²⁵

In conclusion, we note that the fate of unsaturated propellanes in thermal and photochemical reactions is seemingly controlled significantly by orbital symmetry effects.

Experimental Section

Melting points are corrected while boiling points are uncorrected. Pmr spectra were recorded with Varian A-60A and HA-100 spectrometers and apparent splittings have been cited in all cases. Preparative scale vpc isolations were performed with the aid of Varian Aerograph A-90P gas chromatographs. Microanalyses were performed by the Scandinavian Microanalytical Laboratory, Herlev, Denmark.

General Photolysis Procedure. A solution of 65 mg (0.38 mmol) of **13**¹² in 4 ml of ether contained in a quartz test tube was irradiated with a bank of 2537 Å lamps in a Rayonet reactor for 1–1.5 hr. Vpc analysis of the reaction mixture indicated complete loss of starting material and formation of a single product. The solvent was distilled carefully through a short helices-packed column and the residue was purified by preparative vpc isolation (column A,²⁶ 110°) to give 35 mg (61%) of tetralin, identified by its infrared and pmr spectra. Naphthalene obtained from **11** was similarly characterized while benzocycloheptene (**16**) was identified by comparison with an authentic sample.²⁷

Pyrolysis of [4.4.2]Propella-2,4,7,9,11-pentaene (11). A 45-mg (0.29 mmol) sample of **11**¹² was slowly volatilized in a stream of nitrogen and carried through the quartz chip-packed quartz reactor²⁸ heated at 470° under 2.5 mm of pressure. The residence time was approximately 1 sec. The volatile effluent product was collected in a U-tube trap cooled to –78°. The only product was isolated in pure form by preparative vpc isolation (column B,²⁶ 80°); there was obtained 24 mg (53%) of benzocyclooctatetraene (**12**), identical in all respects with an authentic sample.²⁹

Pyrolysis of [4.4.2]Propella-2,4,11-triene (13). Pyrolysis of 60 mg (0.38 mmol) of **13**¹² at 430° (2.5 mm) under comparable conditions and isolation of the only product from column B at 90° afforded 36 mg (60%) of annulated cyclooctatetraene **17**, identified by its characteristic spectral features (ir, pmr, uv).⁸

Pyrolysis of Bicyclo[5.4.2]trideca-7,9,11,13-tetraene (14). An 87-mg (0.51 mmol) sample of **14**¹² was pyrolyzed as above at 485° (2.5 mm). Vpc analysis of the pyrolysate again showed a single component to be present. Isolation from column B²⁶ at 100° furnished 41 mg (47%) of **18**; $\lambda_{\text{max}}^{\text{isooctane}}$ 285 sh nm (ϵ 123); ir and pmr identical with an authentic sample.⁸

(25) L. A. Paquette, M. Oku, W. E. Heyd, and R. H. Meisinger, *J. Amer. Chem. Soc.*, **96**, 5815 (1974).

(26) The following vpc columns were employed in the course of this work: A, 10 ft \times 0.25 in. 10% Carbowax 20M on 60–80 mesh Chromosorb W; B, 4 ft \times 0.25 in. 5% SF-96 on 60–80 mesh Chromosorb G; C, 5.5 ft \times 0.25 in. 5% Carbowax 20M on 60–80 mesh Chromosorb G.

(27) Prepared by us according to the general procedure of N. L. Allinger and E. S. Jones, *J. Org. Chem.*, **27**, 70 (1962).

(28) For a description of the apparatus, see L. A. Paquette and J. C. Stowell, *J. Amer. Chem. Soc.*, **93**, 2459 (1971).

(29) L. Friedman and D. F. Lindow, *J. Amer. Chem. Soc.*, **90**, 2329 (1968).

11-Chloro-12-thia[4.4.3]propell-3-ene 12,12-Dioxide-11,13,13-*d*₃ (19). A vigorously stirred solution of 10.00 g (38.2 mmol) of 11-chloro-12-thia[4.4.3]propell-3-ene 12,12-dioxide³⁰ and 10 g of dry sodium hydroxide was heated at reflux for 72 hr in a medium consisting of deuterium oxide (75 g) and dioxane (200 ml, freshly distilled from CaH₂). The cooled solution was diluted with ether (500 ml) and the aqueous layer separated. The ethereal solution was washed with water (2 × 150 ml) and brine (150 ml), dried, and evaporated. The resulting brownish oil was chromatographed on silica gel (elution with ether-petroleum ether 2:3) to give 10.0 g of 19 as a white crystalline solid: $\delta_{\text{TMS}}^{\text{CDCl}_3}$ 5.57–5.78 (m, 2, olefinic) and 1.3–2.8 (m, 12, methylenes).

[4.4.2]Propella-2,4,11-triene-11,12-*d*₂ (21). To an ice cold magnetically stirred solution of 19 (10.0 g, 37.9 mmol) in 250 ml of tetrahydrofuran (distilled from LiAlH₄) was added under nitrogen 33.5 g (0.299 mol) of potassium *tert*-butoxide (freshly sublimed at 140° (0.05 mm)). The slurry was allowed to warm to room temperature and refluxed for 4 hr. After cooling to 0°, the mixture was diluted with water (250 ml) and extracted with pentane (3 × 500 ml). The combined extracts were washed with water (4 × 600 ml) and brine, dried, and carefully distilled through a short metal helix-packed column. Molecular distillation of the residue (30° (0.1 mm)) afforded 4.97 g (81%) of [4.4.2]propella-3,11-diene-11,12-*d*₂ (20) as a colorless oil: $\delta_{\text{TMS}}^{\text{CDCl}_3}$ 5.75 (m, 2, olefinic), 1.87 (m, 4, allylic), and 1.57 (br s, 8, methylenes).

To a solution of 20 (4.97 g, 30.7 mmol) in 150 ml of carbon tetrachloride-acetic acid (1:1) was added 9.82 g (30.7 mmol) of pyridinium hydrobromide perbromide in one portion and stirring was continued for 12 hr at room temperature. The mixture was diluted with ether (400 ml) and water (300 ml), the aqueous phase removed, and the ethereal solution washed with water, 0.5 *N* sodium hydroxide solution (2 × 100 ml), water, and brine. The dried solution was evaporated (no heat) to leave a quantitative yield of the 3,4-dibromide as a clear oil. This oil was dissolved in 250 ml of dry hexamethylphosphoramide, 12.0 g (0.30 mol) of lithium chloride and 22.2 g (0.30 mol) of lithium carbonate (both predried *in vacuo*) were added, and the mixture was heated at 95–100° under nitrogen for 21 hr. After cooling, the solution was diluted with water (250 ml) and extracted with pentane (3 × 400 ml). The combined organic layers were washed with water (5 × 250 ml) and brine. The dried solution was passed through a column of neutral alumina (activity I) and the solvent evaporated carefully through a metal helix-packed column. The last traces of solvent were removed at 20° (20 mm) to leave 3.16 g (64.3%) of 21 as a clear oil: $\delta_{\text{TMS}}^{\text{CDCl}_3}$ 5.64 (AA'BB', 4, olefinic) and 1.54 (br s, 8, methylenes); *m/e* calcd 160.1223, obsd 160.1221.

Pyrolysis of 21. A 315-mg sample (1.97 mmol) of 21 was passed slowly through the quartz reactor at 380° (2.5 mm) with a slow stream of nitrogen as above (residence time *ca.* 1 sec). Vpc examination of the pale yellow condensate denoted that conversion to 22 had occurred to the extent of 43%. The rearranged hydrocarbon was isolated (column B, 25° 90°), 95 mg (30% without accounting for recovered 21): $\delta_{\text{TMS}}^{\text{CDCl}_3}$ 5.65–5.92 (m, 4, olefinic) and 1.5–2.5 (br m, 8, allylic and saturated methylenes); *m/e* calcd 160.1223, obsd 160.1221.

Independent Synthesis of 22. Freshly sublimed potassium *tert*-butoxide (11.2 g, 0.10 mol) was introduced portionwise into a magnetically stirred solution containing 693 mg (3.12 mmol) of sulfone 23⁸ in 125 ml of dioxane-D₂O (4:1) and the reaction mixture was allowed to stir at room temperature with protection from the atmosphere for 11 days. The contents were poured into ether (250 ml), washed with water (2 × 150 ml) and brine, and dried. The solvent was removed *in vacuo* to afford 463 mg (66.5%) of white crystalline solid: $\delta_{\text{TMS}}^{\text{CDCl}_3}$ 5.90 (s, 4, olefinic), 2.13 (br s, 4, allylic), and 1.74 (br s, 4, methylenes).

A solution of this labeled sulfone (463 mg, 7.07 mmol) in 300 ml of ether and 100 ml of acetone was irradiated under nitrogen with a 200-W Hanovia lamp through Vycor optics for 30 min. Vpc analysis (column B, 25° 90°) indicated formation of a single product. Preparative isolation on this column yielded 82 mg (25%) of 22; *m/e* calcd 160.1223, obsd 160.1220; the pmr spectrum was identical with that of the above pyrolysis product.

Tetracyanoethylene Adduct of 1,2-Tetramethylenecyclooctatetraene (24). A solution of 714 mg (4.52 mmol) of 1,2-tetramethylenecyclooctatetraene⁸ and 4.51 g (35.3 mmol) of tetracyanoethylene in 50 ml of ethyl acetate was heated at reflux under nitrogen

for 3 hr. During this period a color change from deep red to dark brown was evidenced. The contents were diluted with 200 ml of ethyl acetate-benzene (1:1) and this solution was washed with 10% sodium bisulfite solution (10 × 50 ml), water, and brine. The dried organic layer was evaporated *in vacuo* to give 1.18 g of yellowish solid. Recrystallization from methylene chloride-ether afforded 840 mg (65%) of adduct 24, mp 237–239° dec: $\delta_{\text{TMS}}^{\text{CDCl}_3}$ 6.42 (m, 2, olefinic), 3.65 (m, 2, bridgehead), 3.33 (m, 2, cyclobutyl), and 1.5–1.8 (br m, 8, methylenes).

Anal. Calcd for C₁₈H₁₄N₄: C, 75.50; H, 4.93. Found: C, 75.07; H, 4.91.

Tetracyanoethylene Adduct of 22. A solution of 22 (62 mg, 0.38 mmol) and tetracyanoethylene (1.28 g, 10.0 mmol) in 12.5 ml of ethyl acetate was heated at reflux under nitrogen for 5 hr and subsequently processed as above. After chromatography and recrystallization from methylene chloride, there was obtained 45 mg (40%) of 25: $\delta_{\text{TMS}}^{\text{CDCl}_3}$ 6.42 (m, 2, olefinic), 3.65 (m, 2, bridgehead), and 1.5–1.8 (br m, 8, methylenes). The peak at δ 3.33 was 8–10% of the original intensity as expected from protio contamination evidenced in the pmr spectra of the precursors.

11,13-Dimethyl-12-thia[4.4.3]propell-3-ene 12,12-Dioxide (26). To a solution of 12-thia[4.4.3]propell-3-ene 12,12-dioxide³⁰ (7.0 g, 0.0310 mol) in 100 ml of dry tetrahydrofuran cooled to –78° under nitrogen was added 50 ml of 1.3 *M tert*-butyllithium in pentane (0.065 mol) *via* syringe. After stirring for 15 min at –78°, this solution was treated slowly with 30 ml of methyl iodide again *via* syringe. The mixture was allowed to warm to 25° and partitioned between ether and water. The organic phase was separated, washed three times with water, dried, and evaporated. The residue (7.4 g, 94%) solidified, mp 85–95°, and was used without further purification; *m/e* calcd 254, obsd 254.

11,12-Dimethyl[4.4.2]propella-3,11-diene (27). To a refluxing, stirred mixture of 10.5 g (0.276 mol) of lithium aluminum hydride and 200 ml of dry dioxane was added dropwise a solution of crude 26 (7.0 g, 0.0276 mol) dissolved in 50 ml of the same solvent. After 50 hr, the slurry was cooled and treated cautiously with 50 ml of saturated aqueous sodium sulfate (dropwise). The precipitated salts were filtered and washed repeatedly with ether. The combined filtrates were washed with water, dried, filtered, and evaporated with care. Distillation of the residue gave 1.91 g (37%) of 27, bp 90° (0.1 mm), mp 56–58° (after purification through column C): $\delta_{\text{TMS}}^{\text{CDCl}_3}$ 5.55 (m, 2, olefinic), 1.78 (m, 4, allylic), 1.43 (s, 6, methyls), and 1.38 (pseudosinglet, 8, methylenes).

Anal. Calcd for C₁₄H₂₀: C, 89.29; H, 10.71. Found: C, 89.19; H, 10.66.

11,12-Dimethyl[4.4.2]propella-2,4,11-triene (28). Treatment of 3.2 g (0.017 mol) of 27 with 6.0 g (0.0187 mol) of pyridinium hydrobromide perbromide in CCl₄-HOAc as described previously (2.5-hr reaction period) afforded the desired dibromide. This unpurified product was added in one portion to a mixture of 7.15 g (0.17 mol) of dry lithium chloride and 12.6 g (0.17 mol) of lithium carbonate in 150 ml of anhydrous hexamethylphosphoramide and heated at 90–95° for 18 hr. Work-up as described above afforded an oil, distillation of which gave 2.3 g (73%) of 28 as a colorless liquid, bp 42° (0.15 mm): $\delta_{\text{TMS}}^{\text{CDCl}_3}$ 5.10–5.80 (m, 4, olefinic), 1.53 (s, 6, methyls), and 1.47 (pseudosinglet, 8, methylenes). The proton-decoupled Fourier transform cmr spectrum of 28 exhibited six peaks in agreement with the molecular symmetry: 8.44, 18.24, 28.65, 47.43, 120.88, 133.08, and 141.52 ppm.

Anal. Calcd for C₁₄H₁₈: C, 90.26; H, 9.74. Found: C, 89.74; H, 9.65.

Pyrolysis of 28. A 166-mg sample (0.89 mmol) of 28 was pyrolyzed as before at 500° (2.5 mm) and the pyrolysate was purified by preparative vpc isolation from column C²⁶ operating at 130°. There was obtained 126 mg (76%) of 29 as a colorless oil: $\delta_{\text{TMS}}^{\text{CDCl}_3}$ 5.67 (m, 2, olefinic), 5.34 (m, 2, olefinic), 1.78 (s, 6, methyls), and 1.4–2.4 (br m, 8, methylenes).

Anal. Calcd for C₁₄H₁₈: C, 90.26; H, 9.74. Found: C, 90.38; H, 9.65.

***N*-Phenyltriazolinedione Adduct of 29.** A solution of 140 mg (0.81 mmol) of *N*-phenyltriazolinedione and 150 mg (0.81 mmol) of unpurified pyrolysis product (containing 70% of 29) in 5 ml of ethyl acetate was stirred at room temperature for 2 hr and then heated at reflux for the same period of time. Methanol was added and heating was continued until the red color had changed to pale orange. The solvents were evaporated and the semisolid residue was chromatographed on Florisil. Ether elution afforded 90 mg (44% after correction for purity) of 30a as a white solid, mp 182–184° (from hexane): $\delta_{\text{TMS}}^{\text{CDCl}_3}$ 7.42 (m, 5, aryl), 6.20 (m, 2, olefinic),

(30) L. A. Paquette, R. E. Wingard, Jr., J. C. Philips, G. L. Thompson, L. K. Read, and J. Clardy, *J. Amer. Chem. Soc.*, **93**, 4508 (1971).

4.62 (m, 2, >CHN<), 1.35–1.9 (br m, 8, methylenes), and 1.30 (s, 6, methyls).

Anal. Calcd for $C_{22}H_{23}N_3O_2$: C, 73.10; H, 6.41; N, 11.63. Found: C, 72.92; H, 6.35; N, 11.60.

N-Phenyltriazolinedione Adduct of 24. Treatment of 200 mg (1.27 mmol) of somewhat impure 1,2-tetramethylenecyclooctatetraene (**24**) with 443 mg (2.53 mmol) of *N*-phenyltriazolinedione in ethyl acetate as predescribed afforded after chromatography 350 mg (83%) of **30b**, mp 209–211° (from benzene–hexane): $\delta_{TMS}^{CDCl_3}$ 7.50 (m, 5, aryl), 6.32 (m, 2, olefinic), 5.04 (m, 2, >CHN<), 3.17 (m, 2, 4-ring methine), and 1.3–1.9 (br m, 8, methylenes).

Anal. Calcd for $C_{20}H_{19}N_3O_2$: C, 72.05; H, 5.74; N, 12.61. Found: C, 71.97; H, 5.77; N, 12.64.

Thermal Rearrangement of [4.3.2]Propella-2,4,10-triene (31). An

80-mg sample of **31**³¹ was pyrolyzed as before at 615° (5 mm) in a stream of nitrogen. Vpc analysis of the pyrolysate revealed two products to be present in a 2:1 ratio and no starting material remaining. Both hydrocarbons were collected from column B at 70°; the major component was characterized as indan (**33**) on spectral grounds (m/e calcd 118.0782, obsd 118.0781) while the minor component was characterized as 1,2-trimethylenecyclooctatetraene (**32**) by its pmr spectrum.^{24, 31}

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(31) R. K. Russell, full experimental details in preparation.

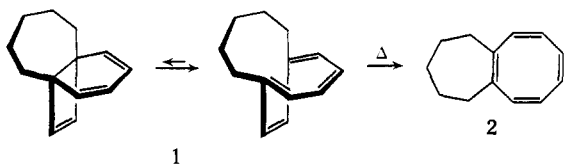
Directed Syntheses of the Isomeric Dimethylcyclooctatetraenes and a Study of Their Polarographic and Alkali Metal Reduction

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Abstract: The 1,2-, 1,3-, 1,4-, and 1,5-dimethylcyclooctatetraenes have been prepared conveniently in isomerically pure fashion by methods which hold promise of considerable generality. Evidence is presented that these hydrocarbons undergo alkali metal reduction in ND_3 at -50 to -58° with formation of planar or essentially planar dianions. The pmr spectra of these solutions reveal the diatropic nature of these species and show that symmetrical ion pairing prevails. When subjected to polarographic reduction (dry THF, TBAP electrolyte), the polyolefins were found to exhibit reduced electron affinities compared to the parent $(CH)_8$ system because of the inductive contributions from the pair of methyl substituents. The waves were non-Nernstian with n_{app} values between 1 and 2; the irreversibility of the reductions was established by cyclic voltammetry on the 1,5-dimethyl derivative down to -78° . Coulometric studies confirmed the fractional electron uptake. These data point to rapid subsequent reaction of the product of electrochemical reduction. Interestingly, the $E_{1/2}$ values are a linear function of the distance separating the methyl groups. This effect is believed to have its origin chiefly in steric parameters. The significance of these results as well as questions raised by the investigation are discussed.

Discovery² of the clean, unimolecular rearrangement of unsaturated propellanes such as **1** to 1,2-bridged cyclooctatetraenes by way of intramolecular ($\pi_4s + \pi_2s$) cycloaddition prompted study of the thermal



activation of cyclooctatetraenes themselves.³ To allow for detection of structural bond reorganizations in these COT thermolyses, initial recourse to dialkylated derivatives and specifically to the four possible dimethyl isomers seemed highly desirable.⁴ In his recent treatise on COT chemistry, Schröder⁵ notes, however, that

(1) University Dissertation Fellow, 1973–1974.

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

(3) L. A. Paquette, M. Oku, W. E. Heyd, and R. H. Meisinger, *J. Amer. Chem. Soc.*, **96**, 5815 (1974).

(4) 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).

(5) G. Schröder, "Cyclooctatetraen," Verlag Chemie, Weinheim/Bergstr., Germany, 1965.

synthetic entry to isomeric disubstituted COT's has been realized only in the diphenyl series and this by way of a highly unselective process. Cope and Moore⁶ allowed phenyllithium to react with phenylcyclooctatetraene and separated the resulting isomeric tetraenes in very low yield by tedious countercurrent distribution techniques.

Because of anticipated difficulties (subsequently realized, *vide infra*) in separation of the four Me_2COT 's, processes of this sort were clearly undesirable and we therefore sought to develop synthetic methodology which would provide each hydrocarbon uncontaminated by isomeric impurities. Simple approaches to these compounds have now been developed which hold promise as general synthetic methods, particularly for 1,3-, 1,4-, and 1,5-functionalized derivatives. In design, the preparative routes avoid the problems engendered by the susceptibility of the cyclooctatetraene ring to rearrangement by approaching the end product in an indirect way and liberating the $(CH)_8$ nucleus in the final step.

We felt that an examination of the polarography and

(6) A. C. Cope and W. R. Moore, *J. Amer. Chem. Soc.*, **77**, 4939 (1955).