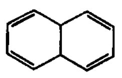
The *cis*-9,10-Dihydronaphthalene–Cyclodecapentaene Valence Bond Isomer System

Eugene E. van Tamelen*[1] and Betty C. T. Pappas

Contribution from the Department of Chemistry, University of Wisconsin, Madison, Wisconsin 53706. Received September 30, 1970

Abstract: In connection with an overall program concerned with valence bond isomers of $(4n + 2)$ π-electron systems, there was carried out a rational synthesis of *cis*-9,10-dihydronaphthalene (**4**), the first (κ^1) valence bond isomer of 1,3,5,7,9-cyclodecapentaene and also the central energy level and structural reference compound in the rapidly proliferating series of (CH)$_{10}$ compounds. The hydrocarbon **4** was characterized by means of its ultraviolet and nmr spectra as well as by catalytic reduction to *cis*-decalin. Although stereochemically suitable for thermal ring expansion to a monocycle, the *cis*-dihydronaphthalene **4** was not appreciably converted to a cyclodecapentaene, either at room or elevated temperatures. On the basis of the foregoing, 1,3,5,7,9-cyclodecapentaene (**2** or **3**) was predicted to be a relatively unstable $(4n + 2)$ π electron case which would require special circumstances for direct detection or isolation. In related work, 1,4,9,10-tetrahydronaphthalene was prepared and studied.

First formalized and tendered in 1963,[2] the concept of valence bond isomerism of aromatic, $(4n + 2)$ π-electron systems as a viable and fruitful area of research was exemplified initially by the preparation and study of selected diverse cases,[3] including that of 9,10-dihydronaphthalene (**1**). Of interest because of its relationship to the valence bond isomeric 1,3,5,7,9-cyclodecapentaene system **2** (trans,cis,trans,cis,cis)-**3** (all cis) (or trans,cis,cis,cis,cis), the 9,10-dihydronaphthalene molecule was first obtained in the cis form **4**,[4,5] and some years later as the trans type **5**.[6] Parent *cis*-9,10-dihydronaphthalene, not only the first 9,10-dihydronaphthalene ever to be prepared but also the κ^1-forerunner[7] in the important (CH)$_{10}$ series, is the subject of this full account.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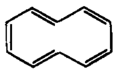
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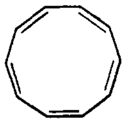
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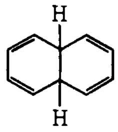

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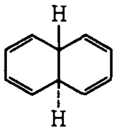

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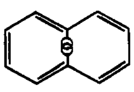
For decades there has been in evidence a strong undercurrent of interest in cyclodecapentaene,[5,8] after benzene the next higher homolog in the cyclic $(4n + 2)$ π-electron series, for which aromatic character would be anticipated. In 1952, Mislow treated the t,c,t,c,c isomer **2**,[9] concluding on the basis of a consideration of van der Waals' radii, bond lengths, and angles that a severe 1,6-hydrogen interaction (**6**) would prevent molecular coplanarity and thereby correspondingly diminish the π-electron overlap required for aromatic stabilization. On the other hand, it was observed by others that aromatic character—as evidenced, for example, by nmr behavior—can be discerned in cases which involve considerable distortion of the $(4n + 2)$ π-electron framework from planarity.[8c,10,11] Although the all-cis geometrical isomer **3** would be free from "internal" hydrogen interactions, it would suffer from in-plane distortion of bond angles—144° in a regular decagon, as contrasted with the normal 120° considered to be "strainless." Since in both cases reliable quantitative estimates of the opposing factors were not available, it was in fact not possible, at the outset of this work, to predict with confidence the stability level of a cyclodecapentaene. Hence, acquisition of evidence bearing on this matter was set up as a primary goal.[12]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Prelog, in emphasizing the hypothetical valence bond isomeric relationship of 9,10-dihydronaphthalene and cyclodecapentaene,[8b] presaged the crucial role the former entity would play in the search for the aromatic counterpart. Since the two structures differ only in respect to electronic structure and bond angle makeup, it is attractive to conjecture that the appropriate bicyclic stereoisomer would act as a penultimate intermediate and proceed to the cyclodecapentaene. Alternatively, if an easily negotiable energy barrier between the two structures is assured, lack of conversion of bicycle to monocycle would signify instability of the parent aro-

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(1) Address correspondence to this author at: Department of Chemistry, Stanford University, Stanford, Calif.

(2) Abstracts, 18th American Chemical Society National Organic Symposium, Columbus, Ohio, June 16–20, 1963.

(3) For the synthesis and identification of the first valence bond isomers of benzene, see E. E. van Tamelen and S. P. Pappas, *J. Amer. Chem. Soc.*, **84**, 3789 (1962); **86**, 3297 (1963).

(4) Preliminary communication: E. E. van Tamelen and B. C. T. Pappas, *ibid.*, **85**, 3296 (1963).

(5) Review: E. E. van Tamelen, *Angew. Chem.*, 77, 759 (1965); *Angew. Chem., Int. Ed. Engl.*, 4, 738 (1965).

(6) Preliminary communication: E. E. van Tamelen and T. L. Burkoth, *J. Amer. Chem. Soc.*, **89**, 151 (1967).

(7) For nomenclature convention, see ref 5.

(8) (a) W. Baker in "Perspectives in Organic Chemistry," A. Todd, Ed., Interscience, New York, N. Y., 1956, p 39; (b) V. Prelog, p 127; (c) W. Baker and J. F. W. McOmie, "Non-Benzenoid Aromatic Compounds," D. Ginsburg, Ed., Interscience, New York, N. Y., 1959, p 477; (d) E. Vogel, *Angew. Chem., Int. Ed. Engl.*, **2**, 1 (1963).

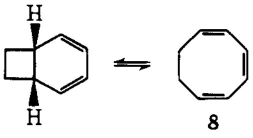
(9) K. Mislow, *J. Chem. Phys.*, 20, 1489 (1952).

(10) D. J. Cram, C. S. Montgomery, and G. R. Knox, *J. Amer. Chem. Soc.*, **88**, 515 (1966).

(11) F. Sondheimer, *Proc. Roy. Soc. London, Ser. A*, **297**, 173 (1967).

(12) For further discussion of this and related matters, see the treatment of cyclodecapentaene chemistry by T. L. Burkoth and E. E. van Tamelen in "Non-Benzoid Aromatics," Academic Press, New York, N. Y., 1969, p 63.

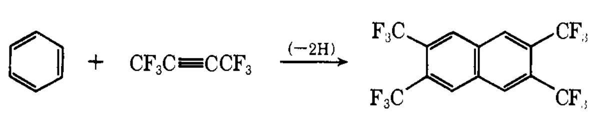
matic structure. In this connection, Cope had earlier reported[13] the facile thermal interconversion of *cis*-bicyclo[4.2.0]octa-2,4-diene (**7**) and *cis,cis,cis*-1,3,5-cyclooctatriene (**8**), thereby not only demonstrating the



7 **8**

ready feasibility of the type change in question, but also revealing the permissiveness of the cis stereochemistry in this thermal process. The proposed valence bond isomer route to the cyclodecapentaene environs offered in addition the advantage of better stereochemical and positional control than might be encountered in attempting stepwise incorporation of π bonds into a cyclodecane framework. In view of the foregoing, there was launched a rational synthesis of *cis*-9,10-dihydronaphthalene.

At the time our investigations began, several formulas possessing the σ–π electronic structure of a 9,10-dihydronaphthalene system had appeared in the literature. Krespan, McKusick, and Cairns[14] interpreted the synthesis of 2,3,6,7-tetrakis(trifluoromethyl)naphthalene (**9**)



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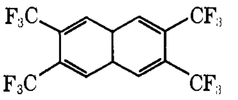
from benzene and hexafluoro-2-butyne as proceeding through a 9,10-dihydronaphthalene intermediate, **10**,



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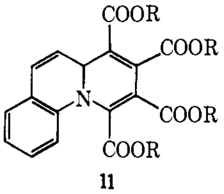
which—not isolated or otherwise perceived—would dehydrogenate and generate naphthalenoid product. In a reinspection of the 1:2 quinoline–acetylenedicarboxylic ester adducts originally described by Diels and Alder, van Tamelen, Aldrich, Bender, and Miller[15] considered two possible alternative structures for the "labile" isomers, namely the quinolizine (**11**) and the azacyclodecapentaene (**12**). Nuclear magnetic resonance, ultraviolet, and infrared spectral studies on the quinoline as well as the quinaldine series of adducts revealed that either the planar or nonplanar ten-membered cyclic structure is ruled out, implying also that corresponding formulations for the adducts of acetylenedicarboxylic ester with pyridine and other heterocyclic bases are also untenable. Similarly, nmr studies demonstrated that the "stable" isomers (obtained from the "labile" adducts by heating or by acid treatment) also are not azacyclodecapentaenes, but possess structures arising from proton shift.[15,16]



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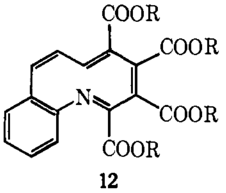

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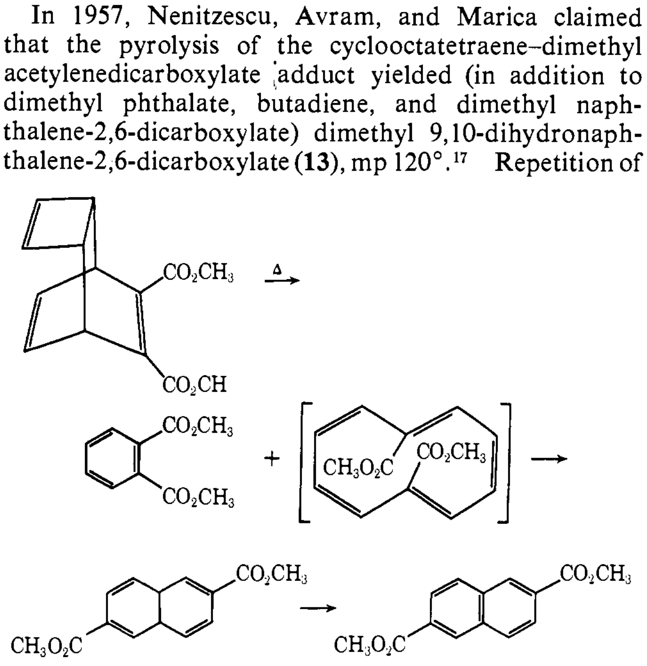
In 1957, Nenitzescu, Avram, and Marica claimed that the pyrolysis of the cyclooctatetraene–dimethyl acetylenedicarboxylate adduct yielded (in addition to dimethyl phthalate, butadiene, and dimethyl naphthalene-2,6-dicarboxylate) dimethyl 9,10-dihydronaphthalene-2,6-dicarboxylate (**13**), mp 120°.[17] Repetition of the pyrolysis in our laboratories provided a mixture of products from which there could be separated a dihydronaphthalenedicarboxylic ester fraction, obtained as a solid of mp *ca.* 119–120° by fractional crystallization from methanol. After repeated heating and crystallizing of this material with methanol, there remained only naphthalene-2,6-dicarboxylic ester, mp 186–187°. A 60 MHz nmr spectrum of the material of mp 119–120° revealed three main peak areas: τ 2.0–3.0 (five peaks, *ca.* 4 H, benzenoid and olefinic), 6.09 and 6.17 (two singlets, 6 H, -COOCH$_3$), 7.24 (sextuplet, *ca.* 4 H, -CH$_2$CH$_2$-). These data, fortified by ultraviolet spectral results, suggested that the dihydronaphthalene-2,6-carboxylic ester does not possess structure **13**, but rather the constitution **14**.[18] Concurrently, Cookson, Hudec, and Marsden found[19] that the Nenitzescu pyrolysis gave rise to both the 3,4-dihydronaphthalene diester **14** as well as the 1,2-dihydro isomer **15**. In neither reinvestigation was there any evidence for the presence of the 9,10-dihydro type. Thus, at the commencement of our efforts to secure parent 9,10-dihydronaphthalene, no example of this structural class had in fact been obtained.



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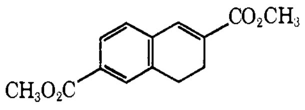

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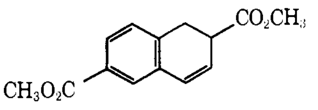

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The simple plan utilized for the synthesis of *cis*-9,10-dihydronaphthalene depends on the secure approach of

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[13] A. C. Cope, A. C. Haven, F. L. Rampand, and E. R. Trumbull, *J. Amer. Chem. Soc.*, 74, 4867 (1952).

[14] C. G. Krespan, B. C. McKusick, and T. L. Cairns, *ibid.*, **82**, 1515 (1960); **83**, 3428 (1961).

[15] E. E. van Tamelen, P. E. Aldrich, P. Bender, and G. Miller, *Proc. Chem. Soc.*, 309 (1959).

[16] R. M. Acheson and G. A. Taylor, *ibid.*, 186 (1959).

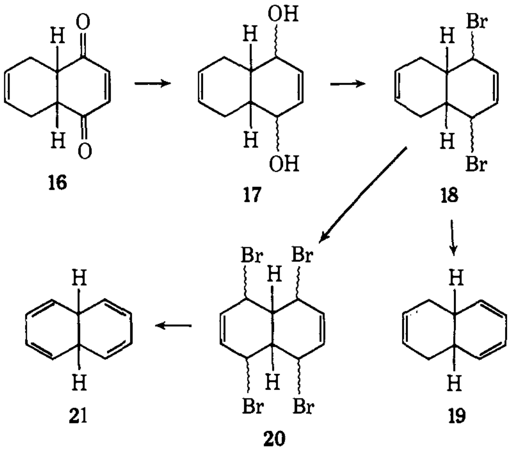
[17] C. D. Nenitzescu, M. Avram, and E. Marica, *Chem. Ber.*, **90**, 1857 (1957).

[18] B. C. T. Pappas, Ph.D. Dissertation, University of Wisconsin, 1963.

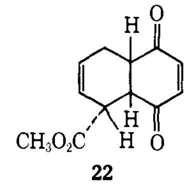
[19] R. Cookson, J. Hudec, and M. Marsden, *Chem. Ind.* (*London*), 21 (1961).

having intact the correct carbon skeleton at the outset and subsequently adjusting the oxidation level by such controlled means as to place unambiguously the required four olefinic links. Thus, the *p*-benzoquinone-1,3-butadiene adduct **16** was utilized as the starting material for the series of transformations shown in Chart I.

Chart I



Several potential methods were available for the reduction of the adduct **16** to the dienediol **17**. Since treatment of a closely analogous compound, *cis*-1,4-diketo-5-carbomethoxy-$\Delta^{2,6}$-hexalin (**22**), with alumi-



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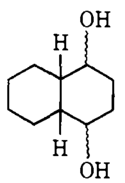
num isopropoxide–isopropyl alcohol had been found to result in carbonyl reduction with maintenance of the cis ring juncture,[20] it was expected that the ring juncture of **16** would remain intact under like reduction conditions. Reaction of the cis adduct **16** with an excess of freshly distilled aluminum isopropoxide in dry isopropyl alcohol afforded, after purification by chromatography, a 60–65% yield of the desired 1,4-dihydroxy-$\Delta^{2,6}$-*cis*-hexalin (**17**). Only one isomer was isolated in pure form from the semicrystalline chromatographed product. Recrystallization from ether–petroleum ether yielded analytically pure material of mp 165–166°. Catalytic reduction of this dienediol under atmospheric pressure resulted in the uptake of 2 mol equiv of hydrogen, yielding a 1,4-dihydroxy-*cis*-decalin (**23**), mp 154.5–



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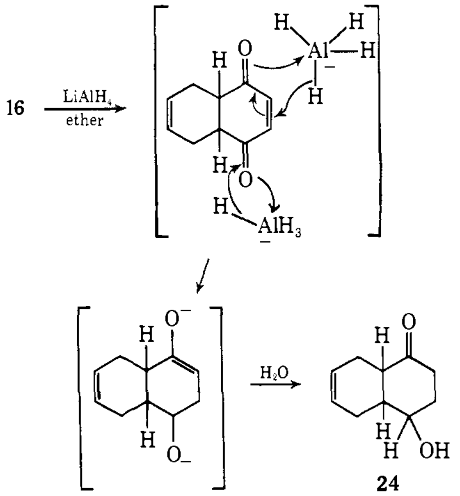
155°, of unknown stereochemistry.

The reactions of the Diels–Alder adduct with lithium aluminum hydride in ether and with sodium borohydride in methanol were also investigated. Reduction of adduct with lithium aluminum hydride in ether did not yield dienediol, but instead an oil which exhibited bands at 2.87, 2.98, and 5.80 μ in the infrared region. A 2,4-dinitrophenylhydrazone and an impure *p*-nitrobenzoate could be obtained from the crude oil. This evidence suggests that the reduction product is 4-hydroxy-Δ^6-octalone-1 (**24**), probably generated by 1,4



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addition of lithium aluminum hydride to the α,β-unsaturated ketone system with prior or subsequent 1,2 reduction of the other carbonyl group. The enolate formed by 1,4 addition of hydride would be stable to further reduction, and the hydroxy ketone is liberated upon hydrolysis.[21]

Reaction of the Diels–Alder adduct **16** with sodium borohydride gave a still different product. An excess of sodium borohydride in methanol led to the formation of an oily alcohol which defied purification but did provide a crystalline ditosylate. The same ditosylate could be made from the sodium borohydride reduction product of *cis*-1,4-diketo-Δ^6-octalin (**25**), prepared by zinc and acetic acid reduction of the cis adduct **16**. Again, no effort was made to establish the stereochemistry of this enediol.

A variety of methods for replacing the hydroxyl groups of 1,4-dihydroxy-$\Delta^{2,6}$-*cis*-hexalin (**17**) with halogen atoms were assayed. The reaction of the diol with phosphorous trichloride in ether provided a low yield of an ether-soluble oil which exhibited phosphate ester bands in the infrared region. Slightly impure starting material was isolated when the diol was allowed

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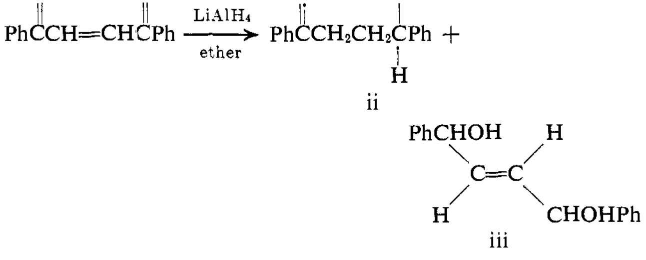
[20] R. B. Woodward, F. E. Bader, H. Bickel, A. J. Frey, and R. W. Kierstad, *Tetrahedron*, 1 (1958).

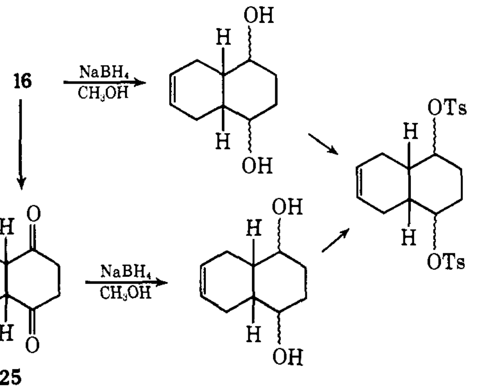
[21] Similarly, the reduction of *cis*- and *trans*-dibenzoylethylenes (i) with an excess of lithium aluminum hydride in ether has been reported to give 88% of 1,4-diphenyl-4-hydroxy-1-butanone (ii) and 10% of the trans unsaturated glycol iii.[22] The formation of ii was postulated to be



$$\text{PhC(=O)CH=CHC(=O)Ph} \xrightarrow[\text{ether}]{\text{LiAlH}_4} \underset{\text{ii}}{\text{PhC(=O)CH}_2\text{CH}_2\text{CH(OH)Ph}} + \underset{\text{iii}}{\text{PhCHOH(H)C=C(H)CHOHPh}}$$

the result of independent 1,4- and 1,2-hydride additions to the α,β-unsaturated ketone system and to the carbonyl group, respectively.

[22] R. Lutz and J. Gillespie, Jr., *J. Amer. Chem. Soc.*, 72, 2002 (1950).



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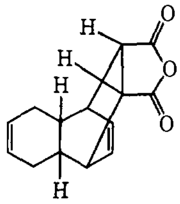
to stand 50 hr with a 0.15 N solution of dry hydrogen chloride in ether. Replacement of the hydroxyl groups with halogen was finally accomplished satisfactorily by stirring the diol with an excess of 48% aqueous hydrogen bromide and an equal volume of petroleum ether for 3–4 hr at room temperature. From the hydrocarbon layer there could be isolated an 85–90% yield of a mixture containing three isomeric dibromides, as indicated by tlc (silica gel). Column chromatography on Florisil, or recrystallization from petroleum ether, permitted isolation of a 21% yield of crystalline 1,4-dibromo-$\Delta^{2,6}$-*cis*-hexalin (**18**), mp 81–82°, which was characterized by elemental analysis as well as infrared, ultraviolet, and nmr spectra. A small amount of a second isomeric dibromide, mp 65–67°, could also be isolated. The structure 1,2-dibromo-$\Delta^{3,6}$-hexalin has been tentatively assigned to this substance on the basis of elemental analysis, and infrared, ultraviolet, and nmr spectra.

With the 1,4-dibromo-$\Delta^{2,6}$-*cis*-hexalin (**18**) in hand, it became of interest to find a suitable method of debromination, which could then be used ultimately for the preparation of *cis*-9,10-dihydronaphthalene itself. Prior to investigating the debromination of diene dibromide, model experiments with 1,4-dibromocyclohex-2-ene were carried out. Although this dibromide has been reported to undergo reaction with sodium in boiling xylene to give 1,3-cyclohexadiene, an experiment using zinc was claimed to have failed.[23] The reaction of diene dibromide with sodium and xylene was not practical due to expected difficulties in separating the product, *cis*-1,4,9,10-tetrahydronaphthalene, from the solvent, xylene. Therefore, the reaction of 1,4-dibromocyclohex-2-ene with zinc was repeated. It was found that, upon refluxing a methanolic solution of 1,4-dibromocyclohex-2-ene over zinc for 2.5 hr, a 38% yield (calculated on the basis of the ultraviolet spectrum of the reaction product) of 1,3-cyclohexadiene was formed. Similar results could be obtained with potassium iodide in ethanol or acetone.

Reaction of 1,4-dibromo-$\Delta^{2,6}$-*cis*-hexalin (**18**) with zinc in boiling methanol afforded, after work-up, a cyclohexane solution of a single substance (tlc) with a maximum in the ultraviolet at 262 mμ. In a more convenient procedure, treatment of 1,4-dibromo-$\Delta^{2,6}$-*cis*-hexalin with 4 mol equiv of 0.5% lithium amalgam[24] in ether also gave the product with an ultraviolet maximum at 262 mμ. In order to characterize the triene, ether was replaced by benzene, and an excess of maleic anhydride in benzene was added. After being allowed to stand 11 days at room temperature, the reaction mixture gave rise to a 21% yield of a pure adduct **26**. The structure assigned to this adduct was supported by nmr and infrared spectra and elemental analysis.



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The pure triene **19** could be isolated by means of gas chromatography, which also demonstrated the formation of only one product in the lithium amalgam-induced reaction. The triene (43% yield) was collected in a receiver immersed in a Dry Ice–methanol bath, and the structure was verified by an elemental analysis and by the nmr characteristics of the triene. Furthermore, a solution of **19** in cyclohexane could be catalytically hydrogenated to *cis*-decalin, the identity of which was established by infrared and nmr spectra as well as glc retention times.

Efforts were now directed toward functionalization of the 5 and 8 positions of 1,4-dibromo-$\Delta^{2,6}$-*cis*-hexalin (**18**). This was accomplished by the reaction of **18** with 2 mol equiv of *N*-bromosuccinimide in refluxing carbon tetrachloride in the presence of a catalytic amount of benzoyl peroxide. Thin-layer chromatography on silica gel of the product solution revealed the presence of at least four compounds in the product mixture. The spot with the highest R_f value (0.50) was attributed to the starting dibromide. A spot with R_f = 0.42 was not investigated further, but two spots which had R_f values of 0.36 and 0.31 and which could never be completely resolved were found to represent a mixture of material with the composition $C_{10}H_{10}Br_4$. An oily mixture of the two isomeric tetrabromides could be isolated in 20–30% yield by preparative tlc on silica gel or by column chromatography on Florisil. The infrared, ultraviolet, and nmr spectra as well as the elemental analyses were consistent with the structure 1,4,-5,8-tetrabromo-$\Delta^{2,6}$-*cis*-hexalin for the isomers, **20**. A small amount of a crystalline hexabromide, analyzing for $C_{10}H_{10}Br_6$, could also be isolated from the *N*-bromosuccinimide reaction mixture. Although this material could be recrystallized to a constant melting point, the nmr spectrum could not be interpreted as representing a single compound.

The oily mixture of tetrabromides was sensitive to air but, if used soon after its preparation, could be utilized for further reaction to give *cis*-9,10-dihydronaphthalene. Preparative runs were carried out by stirring the mixture of tetrabromides with 8 mol equiv of 0.5% lithium amalgam in ether; the reaction was stopped after about 2 hr, or when the intensity of the developing ultraviolet maximum at 247 mμ remained constant. Vpc analysis of the solution indicated the formation of four volatile products, besides naphthalene. Three of these peaks corresponded in retention times to *cis*-decalin, *trans*-decalin, and *cis*-1,4,9,10-tetrahydronaphthalene. The major product, having the longest retention time, was collected and characterized as *cis*-9,10-dihydronaph-

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(23) N. A. Domnin and A. S. Beletskaya, *Zh. Obshch. Khim.*, **24**, 1636 (1954).

(24) R. Criegee and G. Louis, *Chem. Ber.*, **90**, 417 (1957).

thalene by elemental analysis and ultraviolet and nmr spectra, as well as its conversion to *cis*-decalin by catalytic hydrogenation.

The nmr spectrum (60 MHz) of *cis*-9,10-dihydronaphthalene has two peak areas in the ratio 4:1, the first an A_2B_2 quartet at τ 4.11, 4.28, 4.50, and 4.67, and the second, a broad singlet at τ 6.75 (Figure 1).

In view of the readily induced thermal interconversion of *cis*-bicyclo[4.2.0]octa-2,4-diene and 1,3,5-cyclooctatriene, cited above, it appeared at this point that the cis geometry of the 9,10-dihydronaphthalene in hand should permit pyrolytic transformation to a cyclodecapentaene—provided that the thermodynamics of the system are favorable. However, as foreshadowed by the quinoline–acetylenedicarboxylic ester studies, transformation of the 9,10-dihydronaphthalene to a cyclodecapentaene by a thermal process was not realized. Insofar as room temperature equilibrium is concerned, the excellent agreement between the observed nmr spectrum and that expected for 9,10-dihydronaphthalene would seem to rule out any contribution of the ten-membered carbocycle. Also, heating of dilute carbon tetrachloride solutions of the $C_{10}H_{10}$ hydrocarbon under nitrogen for 10–15 min at 150, 195, and 220° resulted in formation of naphthalene, the conversion being essentially complete at the highest temperature. As indicated by nmr and gas chromatographic analysis, disproportionation products were not formed in any of the pyrolysis experiments carried out under the conditions described.[25,26,29] Thus, in terms of a thermally induced change, there is no overt tendency for formation of cyclodecapentaene. Assuming an energy barrier between **1** and **2**–**3** that is realizable under the conditions of the experiments described, we conclude that the thermal stability of cyclodecapentaene is of comparatively minor moment and is completely outweighed by that of naphthalene and hydrogen, formed in a thermodynamically and kinetically preferred process at higher temperatures. It thus appears that either steric interference of (potential) 1,6-"internal" hydrogens in the t,c,t,c,c isomer, or internal strain in the all-cis isomer, is sufficient to prevent observation of a cyclodecapentaene in the reaction system studied, and it seems likely that these adverse factors do win out over the 10π-electron stabilization inherent in a nearly or completely planar monocyclic cyclodecapentaene.

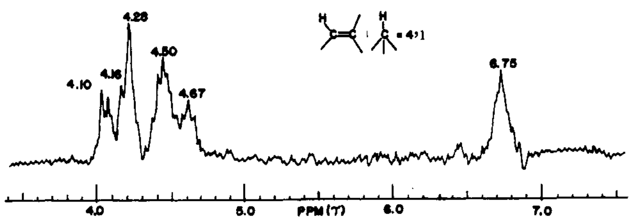
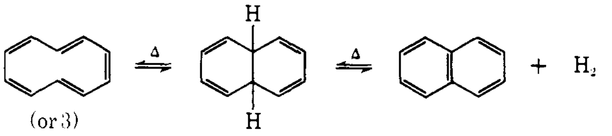
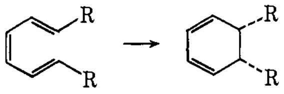


Figure 1.



The thermal stereospecific ring closure of 1,3,5-trienes to 1,3-cyclohexadienes (**27**) was rationalized in 1965 by Woodward and Hoffmann in terms of conservation of orbital symmetry at the highest occupied level, **28**.[30] The reverse reaction is subject to similar control.



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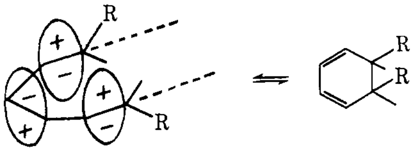

28

It is evident that various ring-opening and -closing phenomena conform to this pattern, including the bicyclo[4.2.0]octadiene–cycloocta-1,3,5-triene case, as well as the even more facile interconversion of the bicyclo[4.2.0]octatriene and cycloocta-1,3,5,7-tetraene (**29**).[31] In regard to the 9,10-dihydronaphthalene–cyclodeca-1,3,5,7,9-pentaene system, it is the cis bicyclic isomer—not the trans—which should be, in principle, conver-

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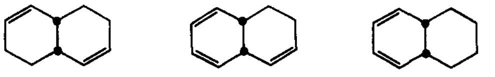
(25) Apparently the course of dehydrogenation is highly dependent on the nature of the medium. W. E. Doering and J. W. Rosenthal (*J. Amer. Chem. Soc.*, **88**, 2078 (1966)) initially reported that at 396° in a flow system, *cis*-9,10-dihydronaphthalene is converted to a 4:2:1 ratio of 1,4-dihydronaphthalene, 1,2-dihydronaphthalene, and naphthalene. Later, Doering and Rosenthal stated (*ibid.*, **89**, 4534 (1967)) that the starting hydrocarbon is subject to a disproportionation process in cyclohexane at 95°, giving products iv, v, vi, and naphthalene in the ratio 0.23:0.56:0.067:1.00. In another, concurrent study, Doering and Rosenthal (*Tetrahedron Lett.*, 349 (1967)) found that in a pyrolysis reaction at 245°, *cis*-9,10-dihydronaphthalene is generated from bicyclo-[4.2.2]decatetraene, and is accompanied only by naphthalene (20:80 ratio of $C_{10}H_{10}$ and $C_{10}H_8$ products).



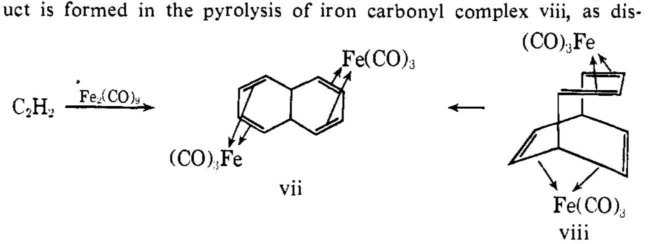
iv v vi

(26) An abortive attempt was made to prepare a $Mo(CO)_3$ complex of cyclodecapentaene by the reaction of $Mo(CO)_6$ with *cis*-9,10-dihydronaphthalene. There was observed formation in small yield of product—too unstable to permit isolation—the yellow color of which suggested that 1,3-diene, rather than 1,3,5-triene, ligands were present. A reported precedent,[27] namely the formation of a cyclononatetraene complex by reaction of 8,9-dihydroindene with $Mo(CO)_6$, has proved erroneous,[28] the product being in fact a dimer comprising two 4,5-dihydroindene complex moieties.

(27) R. B. King and F. G. A. Stone, *J. Amer. Chem. Soc.*, **85**, 3296 (1963).

(28) R. B. King, *Chem. Commun.*, 986 (1967).

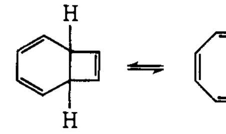
(29) E. Weiss, W. Hubel, and R. Merenyi, *Chem. Ber.*, **95**, 1155 (1962), described the isolation in trace amount of a substance $C_{10}H_{10}$-$Fe_2(CO)_6$ from the reaction products generated during high-pressure acetylene polymerization in the presence of $Fe_2(CO)_9$. The same product is formed in the pyrolysis of iron carbonyl complex viii, as discovered by G. N. Schrauzer, P. Glockner, and R. Merenyi, *Angew. Chem., Int. Ed. Engl.*, **3**, 509 (1964). On the basis of ultimate and nmr spectral analysis, the former workers assigned structure vii to the substance in question. The stereochemistry of vii has not been determined.



vii viii

(30) R. B. Woodward and R. Hoffmann, *J. Amer. Chem. Soc.*, **87**, 395 (1965). See also E. Havinga and J. L. M. A. Schlatmann, *Tetrahedron*, **16**, 151 (1961), and H. C. Longuet-Higgins and E. W. Abrahamson, *J. Amer. Chem. Soc.*, **87**, 2045 (1965).

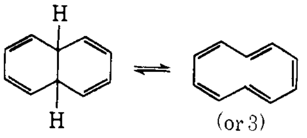
(31) E. Vogel, H. Kiefer, and W. R. Roth, *Angew. Chem.*, **76**, 432 (1964); *Angew. Chem., Int. Ed. Engl.*, **3**, 442 (1964).



29

tible to the all-cis or 1,3-bis-trans monocycle.[5] Thus, on theoretical grounds, there is a reaction path available for the formation of a cyclodecapentaene in a simple thermal process, and the absence of such change in our experiments again supports the conclusion that the simple monocyclic cyclodecapentaene does not possess high stability.

In 1967 we were able to demonstrate[6] that the cyclodecapentaene produced by low-temperature photolysis of *trans*-9,10-dihydronaphthalene does in fact undergo very rapid thermal reorganization to *cis*-9,10-dihydronaphthalene—irreversibly, as far as could be determined. Thus, with this experimental observation available, the 9,10-dihydronaphthalene–cyclodecapentaene equilibrium was clearly established as lying far on the side of the bicyclic component (**30**).



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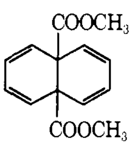
Serious attempts to generate a cyclodecapentaene by irradiation of *cis*-9,10-dihydronaphthalene were not made by us in the early 1960's because suitable (low temperature) spectral equipment was not available at the time, and also because photochemical generation of the sought *all-cis*- or *trans,cis,trans,cis,cis*-cyclodecapentaene called for *trans*-9,10-dihydronaphthalene as the starting material. Consequently, subsequent to the completion of the work described above, we concentrated efforts on the synthesis and study of the *trans*-dihydronaphthalene.[6] However, from other laboratories, a number of interesting findings featuring *cis*-9,10-dihydronaphthalene chemistry were reported. In 1964, Vogel and coworkers[32] revealed that the diester **31** at 90° is converted to a mixture of isomeric 9,10-dihydronaphthalenedicarboxylic esters, whereas at 150° dehydrogenation accompanies isomerization, and 1,5-, 2,6-, and 1,2-naphthalenedicarboxylic esters are formed. In a somewhat similar case, Zimmerman and Grunewald reported[33] that pyrolysis of the barrelene–dicyanoacetylene adduct **32** induces formation of both 1,2- and 2,3-dicyanonaphthalene. In both studies, generation of the observed products may involve appearance of transient *cis*-9,10-dihydronaphthalenes and cyclodecapentaenes (**33**–**34**) which could ring close in various positional modes before final dehydrogenation to the naphthalene system. In the same year, Vogel and Roth demonstrated[34] that the cyclodecapentaene nucleus is stabilized if a methylene unit replaces the opposed 1,6 hydrogens in parent bis-*trans*-cyclodecapentaene, thereby bridging C-1 and C-6 in the cyclic framework, **35**. Furthermore, oxygen or nitrogen can replace the methano bridge, and the heterobridged species can be obtained.[35,36] Chemical and spectral studies reveal that these versions of cyclodecapentaenes, existence of which is enforced by the 1,6 bridge, indeed display behavior expected of a 10π-electron aromatic moiety.[37] The (cis) valence bond isomer **37** is never observed, the strain inherent in the three-membered ring apparently precluding any observable contribution of this form, and instead causing the energy balance to be tipped strongly on the cyclodecapentaene side.



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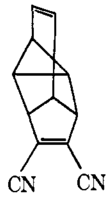

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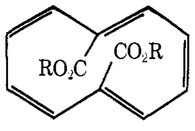

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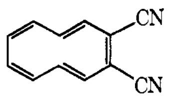

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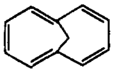

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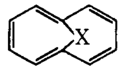

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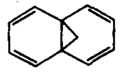

37

In 1969, Masamune and Seidner described[38] low-temperature ultraviolet photolyses of *cis*-9,10-dihydronaphthalene, experiments very similar in concept and execution to those employed earlier by van Tamelen and Burkoth[6] in the conversion of *trans*-9,10-dihydronaphthalene to a cyclodecapentaene. The cis isomer was found to generate at −60° a product which (1) was thermally transformed at higher temperatures to *trans*-9,10-dihydronaphthalene and (2) was hydrogenated to cyclodecane, the results which are exact counterparts of our experiments with *trans*-9,10-dihydronaphthalene. On the basis of nmr spectral observations made directly on unisolated photolysis products, the mono-*trans*-cyclodecapentaene was implicated in the above experiments.

Compilation and consideration of the various $(CH)_{10}$ isomer conversions and interconversions reported to date by various laboratories lead to the relationships in Chart I. Of the many changes observed, nearly all conform to the Woodward–Hoffmann pattern, and the body of results constitutes an elegant and compelling demonstration of the utility and value of the orbital symmetry construct. Two exceptions are noteworthy: the thermal conversions of bullvalene (**38**) and bicyclo[4.2.2]deca-2,4,7,9-tetraene (**39**) to *cis*-9,10-dihydronaphthalene (**4**). However, in keeping with this inconformity is the drastic thermal treatment apparently needed for the transformations cited. It is also of interest that *cis*-9,10-dihydronaphthalene represents a "thermal sink" into which nearly all the isomers tend to

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[32] E. Vogel, W. Meckel, and W. Grimme, *Angew. Chem.*, 76, 786 (1964); *Angew. Chem., Int. Ed. Engl.*, 3, 643 (1964).

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

[34] E. Vogel and H. D. Roth, *Angew. Chem.*, 76, 145 (1964); *Angew. Chem., Int. Ed. Engl.*, 3, 228 (1964).

[35] E. Vogel, M. Biskup, W. Pretzer, and W. A. Böll, *ibid.*, 76, 785 (1964); 3, 642 (1964).

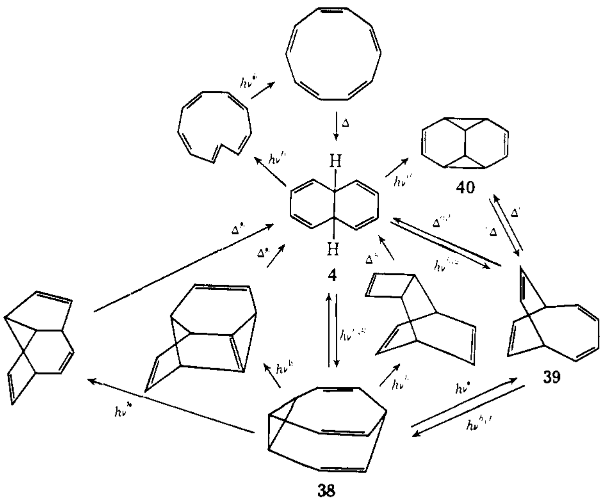
[36] F. Sondheimer and A. Shani, *J. Amer. Chem. Soc.*, 86, 3168 (1964).

[37] E. Vogel and W. A. Böll, *Angew. Chem.*, 76, 784 (1964); *Angew. Chem., Int. Ed. Engl.*, 3, 642 (1964).

[38] S. Masamune and R. T. Seidner, *Chem. Commun.*, 542 (1969).

fall, either by W–H allowed or disallowed processes. Those isomers (**39** and **40**) which thermally change to products other than *cis*-9,10-dihydronaphthalene (**4**) are forbidden by the W–H rules to give **4**, and, with the exception of the transformation referred to above, all observed thermal conversions to **4** are permitted processes. Extrication from and avoidance of the *cis*-9,10-dihydronaphthalene energy minimum can be managed by various photolytic means—irradiations of bullvalene and **4** open up pathways to diverse higher energy structures, as shown. Not all such products necessarily derive from these aforementioned starting materials in simple, one-stage photochemical events, as might be concluded from Chart II; for example, the photolytic conversion of **4** to bullvalene is not direct but proceeds *via* **39**.[39,40]

Chart II



[a] Woodward–Hoffmann forbidden. [b] Reference 38. [c] Reference 6. [d] S. Masamune, C. G. Chin, K. Hojo, and R. T. Seidner, *J. Amer. Chem. Soc.*, **89**, 4804 (1967). [e] M. Jones, Jr., and B. Fairless, *Tetrahedron Lett.*, 4881 (1968). [f] Reference 40. [g] Reference 39. [h] M. Jones, Jr., *J. Amer. Chem. Soc.*, **89**, 4236 (1967). [i] H. P. Löffler and G. Schroder, *Angew. Chem.*, **80**, 758 (1968); *Angew. Chem., Int. Ed., Engl.*, **7**, 736 (1968). [j] M. Jones, Jr., and L. T. Scott, *J. Amer. Chem. Soc.*, **89**, 150 (1967).

Experimental Section

Melting points are uncorrected and were taken on a Reickert hot-stage apparatus equipped with a microscope, unless otherwise stated. The infrared spectra were measured on a Baird infrared recording spectrometer (Model B) in 0.1-mm cells or as potassium bromide pellets. A Cary recording spectrometer (Model 11MS) was used for ultraviolet spectra (1-cm quartz cells). The nuclear magnetic resonance spectra were obtained on a Varian A-60 spectrometer. The solvents used were either of "reagent grade" quality or purified by standard methods. Petroleum ether refers to the fraction boiling between 60 and 68°.

Pyrolysis of the Diels–Alder Adduct of Cyclooctatetraene and Dimethyl Acetylenedicarboxylate. The procedure followed was that described by Nenitzescu.[17] Cyclooctatetraene, 23 g (0.221 mol), and dimethyl acetylenedicarboxylate, 28 g (0.197 mol), were kept at 150–155° for 8 hr. The adduct was distilled through an insulated 6-in. Vigreux column to give 24 g, bp 100–117° (0.3 mm) (lit.[17] bp 140–150° (2 mm)), of a clear, colorless liquid.

The adduct (27.0 g) was heated quickly to the boiling point with a free flame at which point a rapid evolution of gas took place. The residue was cooled and extracted with cold ether to leave 4.8 g of crystalline 2,6-dicarbomethoxynaphthalene. The ether extract was evaporated and the residue was fractionally distilled. Four fractions were taken: 8.2 g, bp 95–105° (0.35 mm), which consisted of dimethyl phthalate; two intermediate fractions, 1.480 g, bp 105–140° (0.35 mm), and 0.484 g, bp 140–144° (0.35 mm); and 9.485 g, bp 144–159° (0.4–0.6 mm), which was partially crystalline and represented the dihydronaphthalene product. The latter was triturated with petroleum ether to give 2.7 g of crystalline material, recrystallized from methanol to afford 2.1 g, mp 107–114°, of colorless crystals. These were fractionally recrystallized from methanol in an attempt to isolate the material melting at 120° reported[17] to be 2,6-dicarbomethoxy-9,10-dihydronaphthalene. Isolation of material having a fairly sharp melting point in the 120° range was possible, but upon recrystallization the melting point rose sharply and eventually a small amount of 2,6-dicarbomethoxynaphthalene could be isolated.

An ultraviolet spectrum of material with mp 120–130° showed maxima at 301 (ϵ 16,570), 293 (ϵ 18,040), 241 (ϵ 19,000), and 233 mμ (ϵ 22,400). 2,6-Dicarbomethoxynaphthalene, mp 186–187°, has ultraviolet maxima at 348 (ϵ 2470), 333 (ϵ 2220), 294 (ϵ 13,900), 283 (ϵ 14,410), and 241 mμ (ϵ 90,800).

***cis*-1,4-Dihydroxy-$\Delta^{2,6}$-hexalin (17).** Freshly distilled aluminum isopropoxide (105 g, 0.515 mol) and 500 ml of isopropyl alcohol (distilled from calcium hydride), were added to a three-necked, 2-l. flask fitted with a dropping funnel, nitrogen gas inlet, and an outlet. The mixture was heated and swirled on a steam bath under nitrogen until the aluminum isopropoxide had dissolved. The outlet was removed and a distillation apparatus was attached; the assemblage was protected from atmospheric moisture by means of a calcium chloride drying tube attached to the distillation receiver. The nitrogen inlet was closed off and the solution was brought to the boiling point. When slow distillation had commenced addition of the cis adduct **16** (23.0 g, 0.142 mol) in 80 ml of isopropyl alcohol was begun. Acetone began at once to distill from the reaction mixture, as evidenced by formation of a yellow precipitate when a drop of the distillate was treated with 2,4-dinitrophenylhydrazone reagent. Addition of the cis adduct **16** was complete after 1 hr, and slow distillation was allowed to continue for an additional 6 hr. Isopropyl alcohol was added through the dropping funnel when needed so as to keep the reaction vessel volume between 300 and 500 ml. The reaction mixture was then allowed to stand overnight at room temperature. The solvent was distilled off under reduced pressure and the residue was allowed to foam, which made the subsequent dissolution in 1 l. of ice-cold 2 *N* hydrochloric acid much easier. The resulting cloudy, aqueous solution was extracted with ether (three 350-ml portions). The combined extracts were washed with saturated sodium chloride solution, dilute sodium bicarbonate solution, and again saturated sodium chloride solution. After drying over anhydrous sodium sulfate and filtration, the ether was removed *in vacuo* to leave a light red oil, 20.1 g, which had bands in the infrared (10%, chloroform) at 2.73, 2.90, and 6.03 μ.

The oil was dissolved in 5–10 ml of benzene and chromatographed on a Florisil column (d = 5.75 cm, l = 29.5 cm) set up with petroleum ether. Elution with petroleum ether, 2 l., caused the separation of a yellow band. Further elution with benzene–petroleum ether (50:50, 60:40, 70:30, 80:20), 8.5 l., brought down the yellow band, but when a portion of these fractions was evaporated under reduced pressure, decomposition occurred to leave a black residue. Elution with benzene, 5 l., cleared the column of the last traces of the yellow material. The alcoholic product was then eluted with ether, 6 l., to give a total of 14.2 g (60%) of oily crystals. Several recrystallizations from ether–petroleum ether gave analytically pure 1,4-dihydroxy-$\Delta^{2,6}$-hexalin (**17**), mp 165.6–165.7°, which had end absorption in the ultraviolet region, $\epsilon_{210}^{\mathrm{CH_3OH}}$ 560, $\epsilon_{220}^{\mathrm{CH_3OH}}$ 60.

Anal. Calcd for $C_{10}H_{14}O_2$ (166.21): C, 72.26; H, 8.49. Found: C, 71.75; H, 8.65.

For further reaction with hydrobromic acid, the diol purified only by chromatography could be triturated with ether and the solid thereby obtained (mp 124–147°) used without further purification. Oily diol obtained from the filtrate could also be used for further reaction with hydrobromic acid; however, the yields of the dibromide were somewhat lower.

1,4-Dihydroxy-*cis*-decalin (23). A solution of 1,4-dihydroxy-$\Delta^{2,6}$-*cis*-hexalin (**17**) (71.1 mg, 0.428 mmol), mp 160–162°, in 20 ml of methanol was hydrogenated at room temperature and atmospheric pressure over 35 mg of prereduced platinum oxide. After 10 min absorption had ceased and 22.6 ml (calcd: 21.4 ml) of hydrogen had been taken up. The catalyst was removed by filtration and the filtrate was evaporated under a stream of nitrogen. The residue (71.3 mg), mp 147–150°, was recrystallized from ether–petroleum ether to give analytically pure material, mp 154.5–155°.

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(39) W. v. E. Doering and J. W. Rosenthal, *J. Amer. Chem. Soc.*, **88**, 2078 (1966).

(40) W. v. E. Doering and J. W. Rosenthal, *Tetrahedron Lett.*, 349 (1967).

The compound had no absorption in the ultraviolet, and there was a strong band in the infrared (Nujol mull) at 2.98 μ.

Anal. Calcd for $C_{10}H_{18}O_2$ (170.24): C, 70.54; H, 10.66. Found: C, 70.43; H, 10.57.

4-Hydroxy-Δ^6-octalone-1 (**24**). Under an atmosphere of dry nitrogen, a solution of *cis*-1,4-diketo-$\Delta^{2,6}$-hexalin (**16**) (1.51 g, 9.33 mmol), in 20 ml of ether, was added dropwise to a well-stirred solution of lithium aluminum hydride, 0.746 g (19.65 mmol) dissolved in 30 ml of ether. The addition proceeded with little evolution of heat, and a thick precipitate formed toward the end of the addition. The reaction mixture was stirred 1.5 hr following completion of addition of the diketone. The excess lithium aluminum hydride was destroyed by careful addition of ethyl acetate. Then a saturated solution of anhydrous sodium sulfate was added until the precipitate appeared wet. About 2.5 g of anhydrous magnesium sulfate was added and the solution was stirred an additional 10 min. The precipitated brown mass was filtered and washed well with ether. The ether solution was dried over anhydrous sodium sulfate. After filtration, the ether was removed by distillation at reduced pressure to give 1.40 g of a light red oil. This crude product exhibited bands at 2.87, 2.98, and 5.82 μ in the infrared and low-extinction end absorption in the ultraviolet.

From 91.9 mg of crude oil, 84.2 mg of an orange, crystalline 2,4-dinitrophenylhydrazone could be isolated, mp 185–195°. Two recrystallizations from ethanol afforded well-formed crystals, mp 208–209°. An infrared spectrum of the purified material (5% in chloroform) showed bands at 2.80, 3.04, 6.05, and 6.15 μ.

An impure *p*-nitrobenzoate of mp 105–160° could also be made from the crude oil by standard methods.

1,4-Dihydroxy-Δ^6-octalin. The cis adduct **16** (2.6115 g, 0.0161 mol) in 150 ml of methanol was added quickly to a stirred solution of sodium borohydride, 5.2871 g (0.1398 mol) in 100 ml of methanol, under a nitrogen atmosphere. The reaction mixture was kept at 0–10° by immersion of the reaction flask in an ice bath. After addition of the diketone the reaction mixture was stirred for 3 hr at 0° and then allowed to come to room temperature. The solvent was removed under reduced pressure and water was added to dissolve the pink, oily residue. The water solution was extracted with ether (three 75-ml portions) and the ether was dried over anhydrous sodium sulfate, filtered, and removed under reduced pressure. The residual pink oil was sublimed at 70° (0.4 mm) to give 2.390 g of a colorless oil which exhibited bands in the infrared (10% chloroform) at 2.80, 2.94, 6.02, and 8.05 μ and had end absorption in the ultraviolet, $\epsilon_{213}^{\mathrm{MeOH}}$ 332.

1,4-Dihydroxy-Δ^6-octalin. Under an atmosphere of nitrogen, *cis*-1,4-diketo-Δ^6-octalin (**25**) (1.0021 g, 0.00619 mol) dissolved in 25 ml of methanol was added quickly to a well-stirred solution of sodium borohydride, 2.3175 g (0.0613 mol) in 50 ml of methanol. The slightly cloudy reaction mixture was stirred 5 hr at room temperature and the methanol was removed under reduced pressure to give a colorless, crystalline residue. To this residue was added 100 ml of water. The resulting clear solution was extracted with ether (three 75-ml portions) and the ether was washed with water. The ether extract was dried over anhydrous magnesium sulfate and filtered and the solvent was removed *in vacuo* to give 597 mg of a nearly colorless oil. This was sublimed at 70° (0.4 mm) to give 521 mg of a clear, colorless, viscous oil which exhibited bands in the infrared region at 2.80, 2.90, 6.08, and 8.0 μ (10% chloroform).

The ditosylate was prepared from 129.1 mg of 1,4-dihydroxy-Δ^6-octalin prepared from **25**, and 642.9 mg of *p*-toluenesulfonyl chloride. The weight of the crude product was 226.1 mg, mp 112–113°. The ditosylates of products resulting from reduction with sodium borohydride of either *cis*-1,4-diketo-Δ^6-octalin (**25**) or the cis adduct **16** were proved to be identical by comparison of infrared and ultraviolet spectra and by a mixture melting point determination.

1,4-Dibromo-$\Delta^{2,6}$-*cis*-hexalin (**18**). A mixture of finely powdered 1,4-dihydroxy-$\Delta^{2,6}$-*cis*-hexalin (**17**) (1.948 g, 0.01171 mol), mp 150–157°, 43 ml of 48% hydrobromic acid, and 50 ml of petroleum ether was vigorously stirred at room temperature for 3–4 hr. At the end of this time the mixture was transferred to a separatory funnel; the hydrocarbon layer was washed with water, dilute sodium bicarbonate solution, and saturated sodium chloride solution. After drying over anhydrous sodium sulfate, the filtered solution was evaporated on a rotary evaporator from a water bath (25°) under reduced pressure, to give 3.022 g (88%) of a light yellow oil.

Thin-layer chromatography on silica gel with 10:1 cyclohexane–benzene revealed the product to be a three-component mixture. The slowest moving spot had the most intense color, while the faster moving spots were poorly resolved.

A portion of the product, 2.80 g, was dissolved in petroleum ether and passed over a short Florisil column with 200 ml of petroleum ether to give 2.62 g of a colorless oil, which was chromatographed on Florisil (d = 3.5 cm, l = 36 cm). Elution with 10-ml portions of petroleum ether provided no clean separation, but after standing in the refrigerator for 2 days crystallization occurred in the later fractions. The crystals were triturated with petroleum ether and collected by filtration with suction to give 375 mg (1%), mp 70–78°, of a single material corresponding to the slowest moving spot on thin-layer silica gel. Recrystallization from petroleum ether provided analytically pure material, mp 81–82°.

Anal. Calcd for $C_{10}H_{12}Br_2$: C, 41.12; H, 4.14; Br, 54.73. Found: C, 41.20; H, 4.21; Br, 55.05.

The dibromide **18** exhibited bands in the infrared at 3.20, 3.55, 3.42, and 6.02 μ (10%, chloroform) and end absorption in the ultraviolet region, 210 (ε 8230) and 220 mμ (ε 7120), in cyclohexane.

The dibromide could be obtained in an alternative manner. After filtration over the short Florisil column with petroleum ether, the solvent volume was reduced to 10–15 ml, and the solution was seeded and allowed to stand at −10° for several days. Yields of 20–23% of crude crystalline dibromide could be obtained in this way.

1,2-Dibromo-$\Delta^{3,6}$-hexalin. From the earlier chromatography fractions during the isolation of **18**, an isomeric dibromide, mp 65–67°, coud be isolated in small yield. This dibromide corresponds to the fastest moving spot on thin-layer silica gel. This material had infrared absorption (15%, chloroform) at 3.30, 3.42, 3.51, and 6.05 μ and end absorption in the ultraviolet at 220 mμ (4830) in cyclohexane. The proton resonance spectrum was compatible with the structure 1,2-dibromo-$\Delta^{3,6}$-hexalin.

Anal. Calcd for $C_{10}H_{12}Br_2$: C, 41.12; H, 4.14; Br, 54.73. Found: C, 41.31; H, 4.35; Br, 54.32.

1,3-Cyclohexadiene. A mixture of 1,4-dibromocyclohex-2-ene (220.2 mg, 0.917 mmol) and purified zinc dust (1.4 g, 21.4 mg-atom) in 5 ml of methanol was refluxed for 2.5 hr. The mixture was then cooled and filtered. An ultraviolet spectrum of the filtrate, $\lambda_{\max}^{\mathrm{MeOH}}$ 257 mμ, indicated a 38% yield of 1,3-cyclohexadiene.

A mixture of 1,4-dibromocyclohex-2-ene, 234.2 mg (0.00100 mol), and potassium iodide, 355.6 mg (0.00200 mol), in 9 ml of absolute ethanol was refluxed 30 min with stirring. At the end of the reaction the color of elemental iodine was present as well as a finely divided precipitate. The reaction mixture was cooled and 0.5 ml of glacial acetic acid was added. Addition of 5 ml of 2 *M* sodium thiosulfate produced a homogeneous, colorless solution to which 20 ml of distilled water was added. The solution was extracted with spectral grade isooctane (two 30-ml portions) and the combined extracts were washed with dilute sodium hydroxide solution and water. The washed extract was dried over calcium chloride for 3 hr. After filtration an ultraviolet spectrum indicated the presence of 22 mg (28%) of 1,3-cyclohexadiene: $\lambda_{\max}^{\mathrm{isooctane}}$ 257 mμ (ε 8000). The reaction could also be carried out using dry acetone was solvent. Four hours at reflux afforded, after work-up, an isooctane solution containing 35% of the theoretical amount of 1,3-cyclohexadiene.

***cis*-1,4,9,10-Tetrahydronaphthalene** (**19**). 1,4-Dibromo-$\Delta^{2,6}$-*cis*-hexalin (**18**) (307.9 mg, 1.05 mmol), lithium amalgam,[24] 0.5% (6.10 g, 4.4 mmol), and 2 ml of ether were placed in a 10-ml round-bottomed flask and the flask was closed with a rubber syringe cap. The reaction mixture was magnetically stirred at room temperature for 2 hr. The flask contents were diluted with 5 ml of spectral grade cyclohexane and filtered. The filtrate was evaporated under a thin stream of nitrogen to a volume of 3–4 ml and refiltered. Thin-layer chromatography on silica gel with 10:1 petroleum ether–benzene showed only one spot when the plate was developed with iodine. Vapor phase chromatography on a packed column also demonstrated the formation of a single volatile product with a retention time of 13.3 min.

For isolation purposes, the filtrate was carefully evaporated to a volume of 275 μl. Portions of 60–70 μl each were injected into the gas chromatogram and collected in a glass receiver immersed in a Dry Ice–methanol bath. About 15 mg of 1,4,9,10-tetrahydronaphthalene was collected from each of the four portions to give a total of 60 mg (43%). The compound has ultraviolet absorption at $\lambda_{\max}^{\mathrm{ether}}$ 262 mμ (ε 3250).

Anal. Calcd for $C_{10}H_{12}$: C, 90.85; H, 9.15. Found: C, 91.00; H, 9.09.

A crude solution of about 25 mg of *cis*-1,4,9,10-tetrahydronaphthalene in 20 ml of spectral grade cyclohexane was hydrogenated over 100 mg of prereduced platinum oxide at room temperature and atmospheric pressure. Hydrogen uptake ceased after 10 min, when 13.2 ml of hydrogen had been absorbed (theoretical for 25 mg of **19** is 14.2 ml). Following filtration of the catalyst and careful evaporation of the solvent under a thin stream of nitrogen to a volume of 100 μl, the product was isolated by means of vapor-phase chromatography. Ten milligrams of a single product having the same retention time as *cis*-decalin was collected. An infrared spectrum (10%, carbon tetrachloride) and one of authentic *cis*-decalin were identical. The crude reaction product had no absorption in the ultraviolet region above 220 mμ.

Maleic Anhydride Adduct of *cis*-1,4,9,10-Tetrahydronaphthalene (26). 1,4-Dibromo-$\Delta^{2,6}$-*cis*-hexalin (**18**) (63.8 mg, 0.219 mmol), lithium amalgam,[24] 0.5% (1.29 g, 0.930 mmol), 2 ml of ether (previously dried over sodium), and a magnetic stirrer were placed in a 10-ml round-bottomed flask stoppered with a rubber syringe cap. The course of the reaction was followed by ultraviolet studies. The reaction mixture was stirred vigorously at room temperature for 3 hr, after which time the extinction at 262 mμ remained constant. The reaction mixture was filtered through a sintered glass funnel with suction and the residue on the filter was washed with benzene. Addition of 4 ml of benzene to the filtrate caused precipitation of lithium salts, which were filtered off, and the filtrate was evaporated to a volume of 3 ml. More benzene (1–2 ml) was added and the solution was evaporated again under nitrogen and filtered a final time. To the filtrate (2 ml) was added a solution of maleic anhydride. 65.9 mg (0.673 mmol) in benzene, and the total volume of the resulting solution was reduced to 2 ml. After 11 days at room temperature the solvent was removed under a stream of nitrogen and the residue was dried under a water pump vacuum for 1 hr. The residue, 58.2 mg, was sublimed at 25° (20 mm) to give 21.5 mg of maleic anhydride, mp 52–53°, and then at 90° (0.05 mm) to give 23.0 mg, mp 192–196°, of the adduct **26**. The adduct exhibited bands in the infrared (KBr) at 1846 and 1767 cm^{-1}. Recrystallization from ether–petroleum ether gave colorless prisms, mp 196–197°.

Anal. Calcd for $C_{14}H_{14}O_3$: C, 73.02; H, 6.12. Found: C, 73.08; H, 6.06.

1,4,5,8-Tetrabromo-$\Delta^{2,6}$-*cis*-hexalin (20). A mixture of 1,4-dibromo-$\Delta^{2,6}$-*cis*-hexalin (**18**) (79.5 mg, 0.272 mmol), *N*-bromosuccinimide (88.4 mg, 0.492 mmol), and 2 grains of benzoyl peroxide in 5 ml of carbon tetrachloride was refluxed together for 16 min, at the end of which time the reaction mixture tested negative with starch–iodide paper. The reaction mixture was cooled, filtered through sintered glass with suction, and then passed over a 5-cm Florisil column (d = 1 cm) with 200 ml of petroleum ether. The hydrocarbon solution was evaporated to dryness on a rotary evaporator (bath at 25°) under reduced pressure to give 103 mg of a colorless oil. Tlc analysis on silica gel with 10:1 petroleum ether–benzene followed by development with iodine showed the presence of at least five compounds, the fastest moving of which (R_f 0.50) was the starting material. Two spots of R_f 0.36 and 0.31 were subsequently shown to correspond to a mixture of tetrabromides. A small spot having R_f 0.43 was not investigated further. The slowest moving spot, $R_f \sim 0.25$, may correspond to a hexabromide.

Preparative thin-layer chromatography of 96 mg of the product and isolation of the material located in the area corresponding to R_f values 0.29–0.38, by extraction of the silica gel with ether, afforded 60 mg of a colorless oil, which had end absorption in the ultraviolet region, 220 mμ (ϵ 13,400), isooctane. An analytical sample was prepared by sublimation at 90° (0.5 mm).

Anal. Calcd for $C_{10}H_{20}Br_4$: C, 26.70; H, 2.24; Br, 71.06. Found: C, 26.83; H, 2.24; Br, 71.10.

The tetrabromide fraction could also be isolated by column chromatography using Florisil as adsorbent and petroleum ether as eluent. Fraction contents were determined by thin-layer chromatography.

A nuclear magnetic resonance spectrum was obtained from twice-chromatographed *N*-bromosuccinimide–dibromide reaction product in the following way. From 110.0 mg of **18** and 135.1 mg of *N*-bromosuccinimide, 164.6 mg of crude tetrabromide was isolated. This was chromatographed on a Florisil column (d = 1.3 cm, l = 20 cm) with petroleum ether. Thirty-three fractions of 3–5 ml were taken. Fractions 18–33 (33.4 mg) contained mainly the tetrabromide. This was rechromatographed on Florisil (d = 1 cm, l = 15 cm) with petroleum ether. Thirty-two fractions of 3–5 ml each were taken, of which fractions 18–32 (18.5 mg) contained only the two spots corresponding to the tetrabromide mixture. A nuclear magnetic resonance spectrum of this material in 0.35 ml of deuteriochloroform showed three main peak areas, in the ratio 4:4:2: a singlet at τ 4.02, a multiplet centered at 5.12 (289 Hz), and a multiplet centered at 6.75 (195 Hz).

The preparation of the tetrabromide could not be conveniently scaled up as too much decomposition occurred on larger Florisil columns. Optimum conditions were found to involve chromatography of about 620 mg of crude tetrabromide (obtained from 400 mg of the dibromide **18**) on a Florisil column having a diameter of 2 cm and a length of 25 cm. In this case, 81 fractions of 5–8 ml were taken and fractions 35–81 (177.6 mg) were found by thin layer chromatography to contain mainly the tetrabromide mixture. Product of this purity was used for later experiments.

From the later chromatography fractions could be isolated a small amount of highly crystalline, colorless material, which after recrystallization from ether–petroleum ether had mp 181–182°. Thin-layer chromatography on silica gel showed a streaked spot with a low R_f value ($\sim$ 0.25) with 10:1 petroleum ether–benzene.

Anal. Calcd for $C_{10}H_{10}Br_6$: C, 19.70; H, 1.65; Br, 78.65. Found: C, 19.65; H, 1.67; Br, 78.75.

The hexabromide has a wide maximum in the ultraviolet region at 217 mμ (ϵ 10,600), ether. The nuclear magnetic resonance spectrum, 15% in deuteriochloroform, was complex and yielded no further definitive information.

Treatment of the hexabromide with lithium amalgam, 0.5% in ether, did not give *cis*-9,10-dihydronaphthalene.

***cis*-9,19-Dihydronaphthalene (21).** A mixture of 1,4,5,8-tetrabromo-$\Delta^{2,6}$-*cis*-hexalin (**20**) (157.0 mg, 0.349 mmol) and lithium amalgam, 0.5% (3.92 g, 2.83 mmol), in 1 ml of ether was placed in a 10-ml round-bottomed flask. The flask was stoppered with a rubber syringe cap and cooled briefly in ice. Vigorous stirring at room temperature caused immediate formation of liquid mercury. The reaction course was followed by ultraviolet analysis fo 1-μl portions which were removed from the reaction flask at 20–30-min intervals and diluted to 3 ml with methanol. After 2 hr the maximum appearing at 247 mμ remained at constant intensity. The flask contents were diluted with 3 ml of spectral grade cyclohexane and filtered through sintered glass with suction. Evaporation of the filtrate under a thin stream of nitrogen to a volume of 2 ml caused the precipitation of lithium salts. The mixture was refiltered and the clear filtrate carefully reduced in volume to 100 μl. Gas chromatographic analysis under the conditions previously described for *cis*-1,4,9,10-tetrahydronaphthalene showed a major product with a retention time of 16.7 min. Also present are small peaks corresponding in retention times to *cis*- and *trans*-decalins, 7.7 and 5.7 min, respectively, and a shoulder at 13.3 min, the retention time of *cis*-1,4,9,10-tetrahydronaphthalene. The major peak was collected ($\sim$5 mg) and the collector tube was washed out with 0.35 ml of carbon tetrachloride. A nuclear magnetic resonance spectrum of this sample is consistent with the assigned structure of *cis*-9,10-dihydronaphthalene. *cis*-9,10-Dihydronaphthalene (**21**) has an absorption maximum in the ultraviolet at $\lambda_{max}^{cyclohexane}$ 247 mμ (ϵ 4500–9000) and a shoulder at $\lambda_{sh}^{cyclohexane}$ 240 mμ (ϵ 4300–8600).

Anal. Calcd for $C_{10}H_{10}$: C, 92.26; H, 7.74. Found: C, 91.75; H, 8.19.

A solution of *cis*-9,10-dihydronaphthalene (**21**) (2.5 mg, in 8 ml of methanol) was hydrogenated over prereduced platinum oxide (59.2 mg) at 25° and atmospheric pressure. Hydrogen absorption ceased after 2 min, when an amount of hydrogen (1.80 ml) equivalent to 2.4 mg of **21** had been taken up. The reaction mixture was filtered and the fitrate was diluted with water. The aqueous solution was extracted with spectral grade cyclohexane and the hydrocarbon extract was washed with saturated calcium chloride solution. After standing overnight over anhydrous calcium chloride the solution was filtered and the filtrate was evaporated under a thin stream of nitrogen to a volume of 0.5 ml. Ultraviolet analysis (of either the methanolic filtrate or the cyclohexane extract) showed that the absorption at 247 mμ had disappeared, leaving only the spectrum of naphthalene, of the same low intensity in the spectrum of the starting material. Vapor phase chromatographic analysis of the product solution gave a single peak which had the same retention time as *cis*-decalin.

Pyrolysis of *cis*-9,10-Dihydronaphthalene (21). *cis*-9,10-Dihydronaphthalene, 3 mg, was dissolved in 0.45 ml of carbon tetrachloride and a nuclear magnetic resonance spectrum was taken. The solution was transferred to a pear-shaped glass bomb of 1.5-ml volume. The bomb contents were frozen by immersion in a Dry Ice–trichloroethylene bath, alternately evacuated and filled with nitrogen, and then sealed off *in vacuo*. The bomb was heated at

150° for 10 min. After cooling to room temperature, it was broken open and the contents were transferred to the nmr tube used originally. Using the same settings as for the spectrum of the starting material, the nmr spectrum indicated a decrease in vinylic proton absorption centered at 337 Hz and an increase in aromatic absorption centered at 459 Hz. The same procedure was repeated twice more, the pyrolysis temperatures being increased to 195° for 10 min and 220° for 15 min. Each successive nmr spectrum showed less vinylic and more aromatic absorption until after the final pyrolysis at 220° only the aromatic pattern centered at 459 Hz was clearly discernible. A nuclear magnetic resonance spectrum of 4 mg of naphthalene in 0.4 ml of carbon tetrachloride was identical with that of the 220° pyrolysis product.

Gas chromatographic analysis of the pyrolysis products indicated about 10% *cis*-9,10-dihydronaphthalene was left after 10 min at 195°, and none was evident after 15 min at 220°.

Acknowledgment. This research was supported by the Petroleum Research Fund (Grant No. 589-C), administered by the American Chemical Society.

The *trans*-9,10-Dihydronaphthalene–Cyclodecapentaene Valence Bond Isomer System[1]

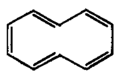
E. E. van Tamelen,* T. L. Burkoth, and R. H. Greeley

Contribution from the Department of Chemistry, Stanford University, Stanford, California 94305.

Received February 25, 1971

Abstract: The first synthesis of *trans*-9,10-dihydronaphthalene (**3**) is described. Low-temperature photolysis of this key compound in the $C_{10}H_{10}$ family produces cyclodeca-1,3,5,7,9-pentaene, parent member and the first monocycle in the [10]annulene group to be detained and studied. Thermal isomerization of the latter leads to *cis*-9,10-dihydronaphthalene, while reduction affords cyclodecane.

Completion of the *cis*-9,10-dihydronaphthalene study[2,3] left little doubt that the parent cyclodeca-1,3,5,7,9-pentaene system (**1** or **2**) is, on account of adverse steric or strain factors inherent in the $C_{10}H_{10}$ nucleus,[4] so intrinsically unstable that only fleeting existence would be expected at or near room temperature. Further, it became evident that observation, detention, or capture of the elusive species would require special chemical, spectral, and/or physical methods.



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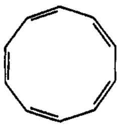

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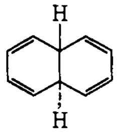

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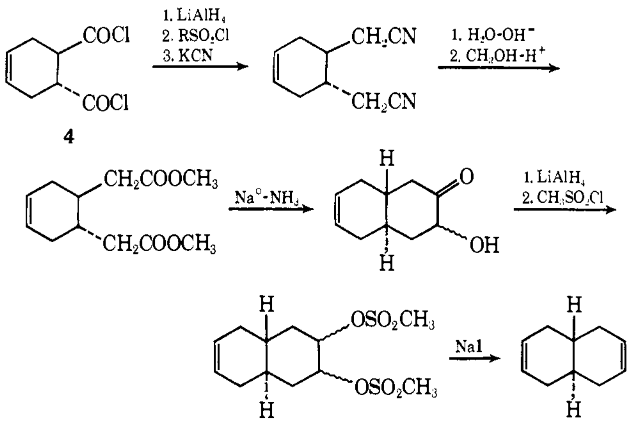
Thus, in our pursuit of the tantalizing monocycle, we initiated a synthetic program designed to provide *trans*-9,10-dihydronaphthalene (**3**), a case especially suitable for the low-temperature photolytic conversion to the valence bond isomer cyclodecapentaene. Herein we describe the successful completion of this project.

In view of the practicality of fashioning a *trans*-9,10-dihydronaphthalene synthesis along lines successfully used in the construction of the cis isomer,[2] we set out to prepare a hydronaphthalene which would be suitable for the halogenation–dehalogenation sequence constituting the final steps in the elaboration of the $C_{10}H_{10}$ system. By reason of earlier synthesis studies[5] carried out in this connection, a route to *trans*-1,4,5,8,9,10-hexahydronaphthalene (**5**) was available, starting with the butadiene–fumaryl dichloride adduct **4**, and involving the steps shown in Chart I. Unfortunately, and as feared, the *N*-bromosuccinimide reaction with diene **5** was not controllable, and no pure component could be isolated from the complex bromination mixture. Lithium amalgam dehalogenation of the crude reaction product provided at least half a dozen hydrocarbons, including naphthalene and two congeners tentatively identified as 1-phenyl-*cis*-1,3-butadiene and *trans*-5,8,9,10-tetrahydronaphthalene. The above experience taught that a synthesis based on the *cis*-9,10-dihydronaphthalene approach, in order to be successful, should also be stepwise in the later stages.

Chart I



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In view of the foregoing, efforts were made to secure a specific dibromo substitution product of *trans*-hexahydronaphthalene **5**, which could be further halogenated at allylic methylene sites and ultimately converted to *trans*-9,10-dihydronaphthalene. All attempts to transform the *cis*-1,3-butadiene–quinone adduct **6** to

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(1) The essentials of this work were originally described in a Communication to the Editor: E. E. van Tamelen and T. L. Burkoth, *J. Amer. Chem. Soc.*, **89**, 151 (1967).

(2) E. E. van Tamelen and B. C. T. Pappas, *ibid.*, **85**, 3296 (1963).

(3) For a review of earlier work in this area, see E. E. van Tamelen, *Angew. Chem.*, **77**, 759 (1965); *Angew. Chem., Int. Ed. Engl.*, **4**, 738 (1965).

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