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.

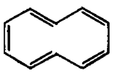
The *trans*-9,10-Dihydronaphthalene–Cyclodecapentaene Valence Bond Isomer System[1]

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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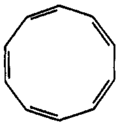
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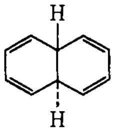
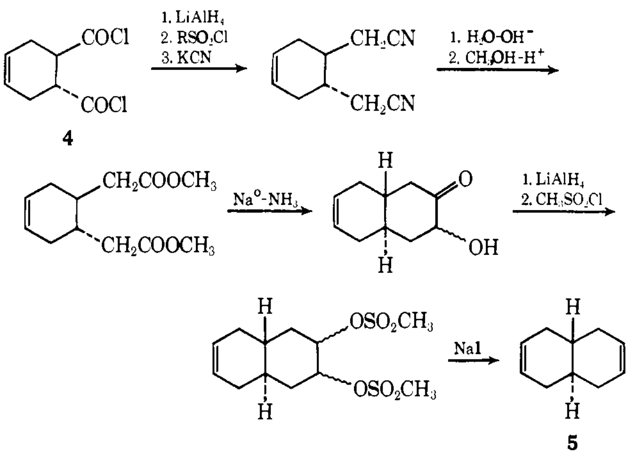


3

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



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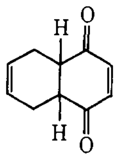
[1] The essentials of this work were originally described in a Communication to the Editor: E. E. van Tamelen and T. L. Burkoth, *J. Amer. Chem. Soc.*, **89**, 151 (1967).

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

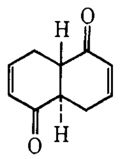
[3] For a review of earlier work in this area, see E. E. van Tamelen, *Angew. Chem.*, **77**, 759 (1965); *Angew. Chem., Int. Ed. Engl.*, **4**, 738 (1965).

[4] K. Mislow, *J. Chem. Phys.*, **20**, 1489 (1952).

[5] H. Winicov, Ph.D. Dissertation, University of Wisconsin, 1961.

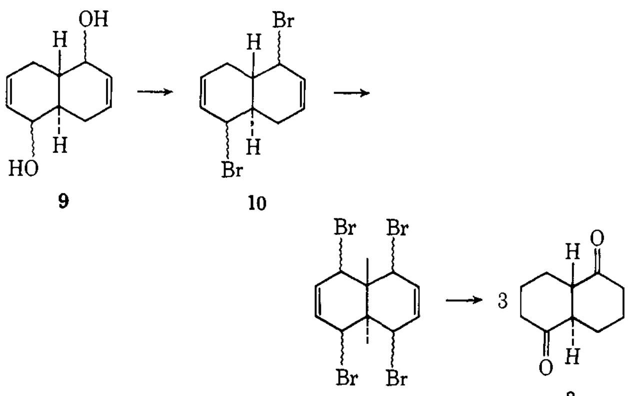


6



7

some useful product in the trans series were unavailing.[6,7] Accordingly, attention was turned to the known *trans*-1,4,5,8,9,10-hexahydronaphthalene-1-5-dione (**7**),[9] a dienedione which offered reaction outlets in the trans series similar to options open and already exercised in the predecessing cis series.[2]



9 **10** **11** **8**

The reduction of this compound, anticipated to be a laboratory operation bordering on the trivial, became a near impossibility for want of a suitable solvent. Reaction with lithium aluminum hydride in hexamethylphosphoramide (which itself appears to react slowly with lithium aluminum hydride) afforded only diketone **8**, the product of 1,4 reduction. The result of a reduction attempt using a slurry of sodium borohydride in methanol was recovered starting material. Either the aluminum isopropoxide–isopropyl alcohol method used for reduction of **6** or simply stirring a slurry of the dienedione in a solution of lithium aluminum hydride in ether provided a mixture of ten spots by tlc, some of which could be oxidized to starting material. Reduction with sodium borohydride in an ethyl alcohol–isopropyl alcohol mixture (a method used successfully by Büchi, *et al.*,[10] for reduction of an α,β-unsaturated aldehyde to an allylic alcohol) gave no product which was oxidizable back to starting material. This synthetic route was rescued from early failure by the successful reduction device of soxhlet extraction of the dienedione **7** into a slurry of a 100-fold molar excess of lithium aluminum hydride in refluxing ether.

The dienediol **9** was found to be a mixture of at least two isomeric components. By a crude recrystallization procedure it was possible to isolate material (mp 212–214°) corresponding to one spot on tlc. The structure **9** was supported by ir, nmr, and elemental analysis. It was observed that the two-spot mixture of diols could be oxidized with Jones reagent solely to starting dienedione **7** (by tlc). Although the diol mixture was not particularly amenable to analysis by nmr, benzoylation (83% yield) afforded a readily soluble sample of dibenzoates featuring aromatic protons as an internal reference for integration. The dibenzoate of **9** exhibited strong bands at 5.82, 8.0, and 9.15 μ. The nmr spectrum had signals at δ 8.1 (4 H, complex multiplet), 7.1 (6 H, complex multiplet), 5.7 (4 H, broadened singlet), 5.55 (2 H, broad singlet), and an allylic methylene–methine envelope at 1.8–2.8 (6 H).

A third piece of evidence for the isomeric nature of the diols from the reduction mixture was provided by the result of the next reaction in the synthesis, namely, conversion to dibromide with hydrobromic acid. The replacement was performed separately on one-spot material (tlc) and also on crude reduction product, with the result that an identical two-spot mixture (tlc) of dibromides was obtained in each case. The crude product, a clear oil after filter chromatography on Florisil, could be crystallized from pentane at −78° to give a white solid, mp 60–64° (a single spot on tlc). This material, shown by nmr and analysis to be *trans*-1,5-dibromo-1,4,5,8,9,10-hexahydronaphthalene (**10**), was stable under nitrogen in the freezer but rapidly blackened at room temperature. Its nmr spectrum featured a broad singlet at δ 4.8 (2 H), assigned to protons both allylic and on carbon bearing bromine. The observation of only one such signal militates against allylic rearrangement during introduction to halogen. As in the case of the diol mixture above, evidence for the diastereoisomeric relationship of the two dibromides, suggested by the tlc of the crude product, was provided by separate execution of the next synthetic step. Treatment of one-spot dibromide (tlc) and crude two-spot material under the conditions for bromination with *N*-bromosuccinimide gave identical three-spot (tlc) mixtures of proposed tetrabromides **11**.

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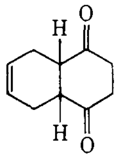
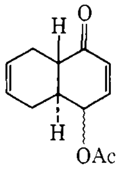
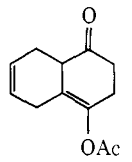
(6) These attempts include several different approaches. It was hoped that *cis*-enedione (i) might be enol acetylated and isomerized to ii;



i

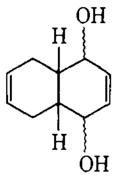


ii



iii

however, enol acetate (iii) was the only observable end product of such attempts. Also, ketol v, secured by selective oxidation of iv, could



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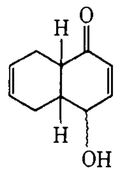
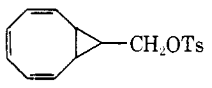


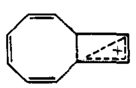
v

not, as the *O*-benzoate, be isomerized to a *trans*-hydronaphthalene by appropriate base—either starting material was recovered or a complex mixture resulted.

(7) In a plan designed to utilize a cyclobutonium ion vii precursor for $C_{10}H_{10}$ hydrocarbons, the bicyclo[6.1.0]nonatrienecarbinyl tosylate (vi)



vi



viii

was subjected to ionizing conditions. In a solution of lithium perchlorate in THF with potassium carbonate,[8] tosylate vi generated hydrocarbon, including naphthalene and *trans*-1-phenylbuta-1,3-diene, in a total 5% yield. With DMF–lithium perchlorate and potassium carbonate, vi at room temperature gave rise to naphthalene (10%), *trans*-1-phenylbuta-1,3-diene (30%), and two unidentified alcohols (6%).

(8) S. Winstein, S. Smith, and D. Darwish, *J. Amer. Chem. Soc.*, **81**, 5513 (1959).

(9) W. S. Johnson, J. D. Bass, and K. L. Williamson, *Tetrahedron*, **19**, 861 (1963).

(10) G. Büchi and J. D. White, *J. Amer. Chem. Soc.*, **86**, 2884 (1964).

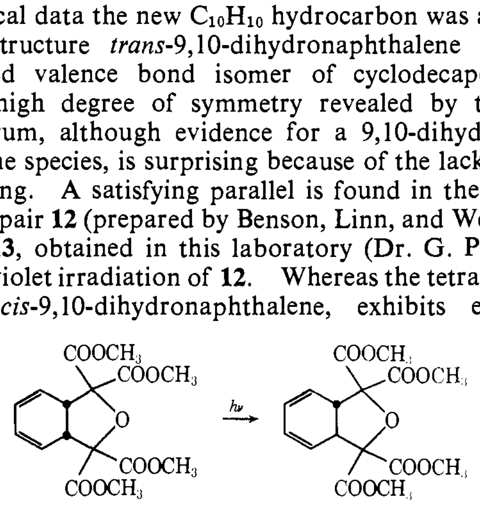
The mixture of tetrabromo species **11** did not yield to any means of purification, although fast column chromatography on Florisil permitted the enrichment of each of the three spots (tlc) in certain fractions. Lithium amalgam debrominations of tetrabromides, which were enriched in one of the three components (tlc) by rapid column chromatography on Florisil, were performed with assay by glpc. Such experiments showed that the highest R_f spot of the tetrabromide mixture afforded hydrocarbon material exhibiting one peak on glpc. This new hydrocarbon exhibited in methanol maximal uv absorption at 276 mμ[11,12] and revealed surprisingly simple nmr behavior in that two virtually unsplit signals appeared at δ 5.9 (4 H) and 2.8 (1 H). The only observable product of air oxidation was naphthalene, as detected by nmr and reinjection on glpc. The lifetime of this hydrocarbon at room temperature and in solution protected from atmospheric oxygen by means of the usual precautions is so short that preparation of a sample for elemental analysis or the undertaking of any quantitative reduction studies is precluded.

When the new hydrocarbon was collected from glpc in which the chromatograph detector temperature was elevated to 250° from the usual collection temperature of 150°, reinjection showed that a new compound had been formed. This thermal product was collected and identified as *cis*-1-phenylbuta-1,3-diene by comparison of its glpc retention time and uv spectrum, and by coinjection with authentic material prepared by the method of Jones and Scott.[13]

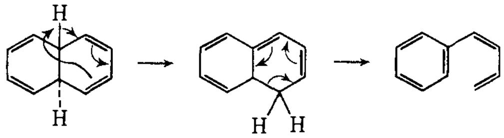
Reduction studies on the new hydrocarbon were at first enigmatic. Hydrogenation over prereduced Adams' catalyst apparently gave in early runs (T. L. B.) only *cis*-decalin, identified by glpc retention time and coinjection with authentic material. Later experiments (R. H. G.) involved formation of *cis*- and *trans*-decalins in a ratio of 6:94, not dissimilar from that (15:85) observed by Jones, Reich, and Scott[14] (and prior personal communication from Professor Jones). With diimide followed by Pd/C-catalyzed hydrogenation, Masamune and coworkers[12] observed only *trans*-decalin (>90%). These varying results may be due to Pt-promoted isomerization (the extent of which depends on individual experimental differences) at some reduction level to a $\Delta^{1(9)}$ intermediate, which, on further hydrogenation, is converted to cis fused product.

Diimide (generated *in situ* by acidification of sodium azodicarboxylate) reduction of **3** furnished in good yield a product which exhibited glpc behavior characteristic of *cis*-decalin. In separate experiments, the reduction product was not reduced further by additional exposure to diimide. At first thought to be *cis*-decalin, the diimide reduction product exhibited other properties incompatible with that structure. The nmr spectrum revealed olefinic signals at τ 5.2–5.6 (2 H) in addition to methine–methylene resonances at 1.0–2.2 (14 H). Further, catalytic reduction (Pd/C) yielded *trans*-decalin. The structure of the material in question was demonstrated conclusively as *trans*-$\Delta^{1(2)}$-octalin by comparison with an authentic specimen synthesized by base-induced decomposition of 1-decalone *p*-toluenesulfonylhydrazone. Why *trans*-$\Delta^{1(2)}$-octalin is not reduced by diimide is not apparent.

On the basis of the above chemical behavior and physical data the new $C_{10}H_{10}$ hydrocarbon was assigned the structure *trans*-9,10-dihydronaphthalene (**3**), the desired valence bond isomer of cyclodecapentaene. The high degree of symmetry revealed by the nmr spectrum, although evidence for a 9,10-dihydronaphthalene species, is surprising because of the lack of spin splitting. A satisfying parallel is found in the cis and trans pair **12** (prepared by Benson, Linn, and Webster[15]) and **13**, obtained in this laboratory (Dr. G. Parry) by ultraviolet irradiation of **12**. Whereas the tetraester **12**, like *cis*-9,10-dihydronaphthalene, exhibits extensive splitting in the vinyl and methine regions (δ 6.1–5.9, 5.8–5.5, and 4.02–3.98, all multiplets in the integrated ratio of 2:2:2), isomer **13** revealed singlets in the vinyl (6.1, 4 H) and methine (3.50, 2 H) regions. The thermal reorganization of *trans*-9,10-dihydronaphthalene (**3**) to *cis*-1-phenylbuta-1,3-diene is also quite readily rationalized. Such a rearrangement might occur by a 1,5 suprafacial hydrogen shift (sigmatropic change of order [1, 5])[16] to **14**, predicted to be a thermally permitted process, followed by the known retro Diels–Alder reaction to give observed product.



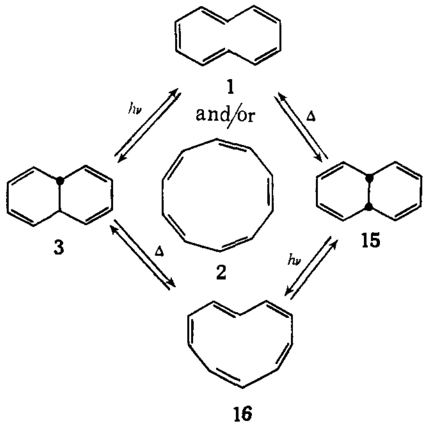
12 **13**



3 **14**

The possibility of conversion of *trans*-9,10-dihydronaphthalene (**3**) to cyclodecapentaene could now be tested. In Chart II, predictions, based on the Wood-

Chart II



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[11] The value 231 mμ reported by van Tamelen and Burkoth[1] must be regarded as incorrect, and the source of this error remains undiscovered. The value 276 mμ is in agreement with that reported by Masamune, *et al.*[12]

[12] S. Masamune, R. T. Seidner, H. Zenda, M. Wiesel, N. Nakatsuka, and G. Bigam, *J. Amer. Chem. Soc.*, **90**, 5286 (1968).

[13] M. Jones, Jr., and L. T. Scott, *ibid.*, **89**, 150 (1967).

[14] M. Jones, Jr., S. D. Reich, and L. T. Scott, *ibid.*, **92**, 3118 (1970).

[15] R. E. Benson, W. J. Linn, and O. W. Webster, *ibid.*, **85**, 2032 (1963).

[16] R. B. Woodward and R. Hoffmann, *ibid.*, **87**, 2511 (1965); **88**, 2078 (1966).

ward–Hoffmann rules, for permitted valence bond isomerizations of *cis*- and *trans*-9,10-dihydronapthalene are summarized. In the trans case photoinduced isomerization is predicted to be a conrotatory[16] process, each mode of conrotation affording either *all-cis*- (**2**)- or *cis,trans,cis,cis,trans*-cyclodecapentaene (**1**). The prediction for thermal opening is, on the other hand, a disrotatory process of which the product is the tetra-*cis*,-mono-*trans*-cyclodecapentaene (**16**).

The photolysis of *trans*-9,10-dihydronaphthalene was performed initially under the simplest conditions: material was photolyzed as a solution in pentane at room, or slightly higher, temperature, using a quartz uv cuvette as a photolysis cell. The irradiation was carried out in a Rayonet photochemical reactor with lamps having their maximum output at 2537 Å. After 5 min the starting material was apparently completely consumed. A great general increase in absorbance occurred, particularly in end absorption and in the region 240–280 mμ. The development of very sharp, intense maxima at 334, 317, 304, and 290 mμ (optical density 0.84, 0.78, 0.47, and 0.25) was particularly striking. The reaction mixture was found to be distillable under reduced pressure, and also to be stable to reflux for 1.0 hr in heptane (100°). Photolysis for an additional 10 min caused the intensity of the sharp, long-wavelength maxima to be halved. Analysis of the mixture resulting from 5-min photolysis (glpc) showed a complex mixture of 12 apparent components.

Because *trans*-9,10-dihydronaphthalene is difficultly available by the above synthesis route, structural assignments to room temperature photolysis products were made largely on the basis of uv spectra, glpc retention times, and coinjection with authentic material.

The glpc trace of the crude photoproduct on a DC550 column is shown schematically in Figure 1a, and that on a STAP column in Figure 1b. The peaks in close clusters were poorly resolved. In working with the STAP column, naphthalene (peak 11) was shown to be present as a contaminant in the major species (peak 10). The compound corresponding to peak 10 was collected and proved to be bullvalene (**17**) by comparison of glpc behavior, uv spectrum, as well as coinjection with authentic material obtained from Doering and Rosenthal.[17]

When the uv spectrum of the poorly resolved trio of peaks 4, 5, and 6 (DC550) was taken, broad absorption including a maximum at 247 mμ was observed. A carefully collected sample of peak 6 provided a uv spectrum virtually superimposable with that of authentic *cis*-9,10-dihydronaphthalene (**15**). The identity of this compound was confirmed by coinjection with an authentic sample prepared by the method of Pappas.[2]

Coinjection of 1,2-dihydronaphthalene with the photomixture on both DC550 and STAP columns served as tentative proof for the presence of this species in the mixture as peaks 9 (DC550) and 7 (STAP). The material could not be obtained in sufficient quantity or purity for further substantiation by uv. Likewise the structure 1,4-dihydronaphthalene was tentatively assigned to peak 10 (DC550) and peak 9 (STAP), but due to the trace quantities involved even the coinjection results must be regarded as tentative.

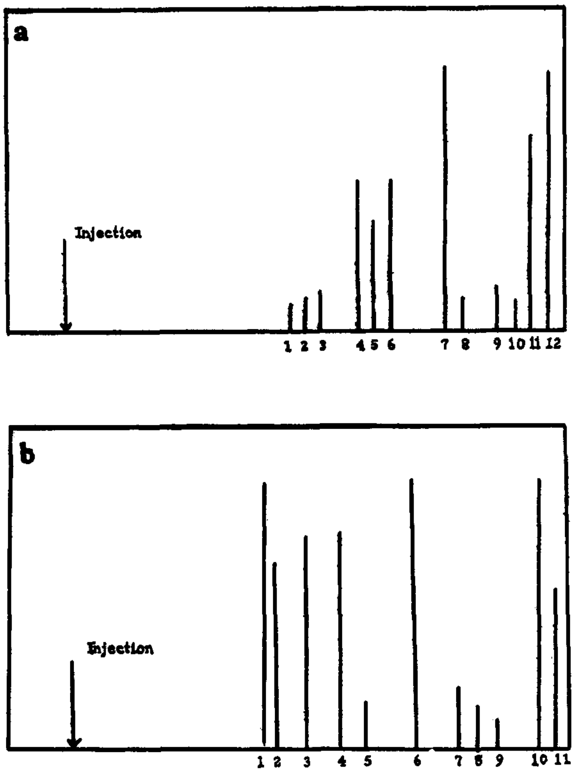

Figure 1. Glpc behavior of products of room temperature photolysis of **3** on (a) 0C550 and (b) STAP.

An intensely uv absorbing material seemed to be located in a shoulder on peak 7 (DC550) and somewhere in the unresolved trio of peaks 7, 8, and 9 (STAP). A photolysis mixture, estimated at 15–20 mg total weight, was placed on a silver nitrate–silica gel column and eluted with pentane and pentane–ether mixtures. The fractions were measured directly by uv spectral and glpc means. A pure sample of the uv-active material was obtained from one fraction after reinjection and collection from glpc (STAP). The uv spectrum displayed λ_{max} 334, 317, 304, 290, 277 (s), and 265 (s) mμ (optical density: 0.85, 0.80, 0.49, 0.26, 0.14, and 0.09). There was insufficient material for analysis by nmr, but a uv spectrum was found in the literature[18,19] which sufficed to identify the compound as *all-trans*-deca-1,3,5,7,9-pentaene.

Another component, after separation by silver nitrate–silica gel column chromatography, was identified on the basis of its uv spectrum as *cis*-1-phenylbuta-1,3-diene. The isolation of this species was complicated by the presence of another hydrocarbon with similar uv absorption and similar retention on the silver nitrate activated column. The presence of *cis*-1-phenylbuta-1,3-diene was finally proven by further purification through glpc and comparison with authentic material by means of uv and glpc.

During the course of this investigation two other research groups reported complementary work which permitted the identification of another photolysis product in the mixture. As mentioned previously, Doering and Rosenthal[17] reported that the photolysis of *cis*-9,10-dihydronaphthalene generated bullvalene, ac-

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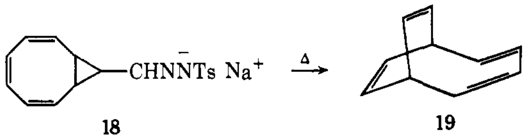
[17] W. von E. Doering and J. W. Rosenthal, *J. Amer. Chem. Soc.*, **88**, 2078 (1966).

[18] A. D. Mebane, *ibid.*, **74**, 5227 (1952).

[19] F. Sondheimer, D. A. Ben Efraim, and R. Wolovsky, *ibid.*, **83**, 1675 (1961).

companied by naphthalene and two other unidentified hydrocarbons. The identity of one of these was established by Jones and Scott,[18] who, in an effort to synthesize bicyclo[6.2.0]deca-2,4,6,9-tetraene, pyrolyzed the sodium salt of the tosylhydrazone of bicyclo[6.1.0]-nona-2,4,6-triene-9-carboxaldehyde (**18**). In place of the desired tetraene, Jones and Scott isolated the bicyclic isomer **19** as the major product along with *cis*-1-phenylbuta-1,3-diene, 1,2-dihydronaphthalene, and *cis*- and *trans*-9,10-dihydronaphthalene. The latter product was identified by them on the basis of data supplied by this laboratory. The tetraene **19** was found to be identical with one of the hydrocarbons produced by irradiation of **15**.[20]

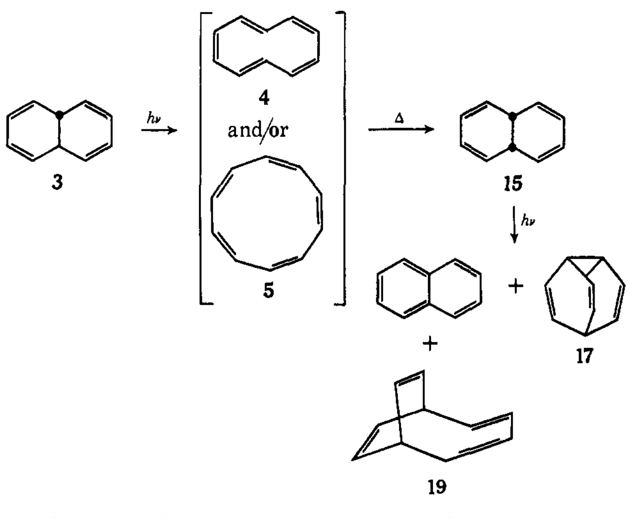


18 **19**

Authentic tetraene **19**, prepared according to the method of Jones and Scott,[18] was found to be identical (uv and glpc behavior) with one of the photolysis products of *trans*-9,10-dihydronaphthalene, hydrocarbon comprising in major part peak 7 (DC550) and peak 6 (STAP). In addition it was found to be an impurity in *cis*-1-phenylbuta-1,3-diene isolated by column chromatography on silver nitrate–silica gel.

The appearance of *cis*-9,10-dihydronaphthalene and its photoproducts bullvalene, naphthalene, and bicyclo-[4.2.2]deca-2,4,7,9-tetraene, in major amount (estimated 50%), upon photolysis of *trans*-9,10-dihydronaphthalene suggested its formation by a thermal, disrotatory process from a transient cyclodecapentaene (**1** or **2**), itself formed in a conrotatory event from excited state *trans*-9,10-dihydronaphthalene (Chart III).

Chart III



On the strength of this surmise and with the aim of preserving the unstable isomer under modified conditions, low-temperature photolysis experiments were initiated.

The technique employed for photolysis at low temperature involved freezing 9,10-dihydronaphthalene at uv sample concentration in a glass composed of ether, isopentane, and ethyl alcohol (EPA) at −190° in a quartz uv cuvette. The cuvette was suspended in a quartz, dewar jacketed tube through which liquid nitrogen was rapidly distilled in order to provide cooling. This apparatus was arranged in a (slightly modified) Rayonet photochemical reactor and irradiated for 2 min. The entire apparatus was transferred without warming to a slightly modified Cary 14 uv spectrophotometer, and a uv spectrum was recorded. Broad absorption between 240 and 280 mμ, with several inflections, was observed, and no maximum attributable to *cis*-9,10-dihydronaphthalene was apparent. The sample was then allowed to warm momentarily to room temperature, then recooled to −190° whereupon a peak at 247 mμ, diagnostic for *cis*-9,10-dihydronaphthalene, was apparent in the uv spectrum. The remainder of the spectrum was qualitatively unaltered, but analysis by plotting of a simple difference spectrum showed that in addition to generation of the maximum at 247 mμ maxima at 265, 275, and 285 had apparently been destroyed. In several repetitions of this experiment the positions of the generated and destroyed maxima were constant but no quantitative relationship could be established.

To gain further supporting evidence for a thermally unstable cyclodecapentaene (**1** or **2**) as the source of the *cis*-9,10-dihydronaphthalene (**15**) a trapping experiment was performed. The low-temperature photolysis was repeated exactly as described above, but the reaction product was transferred with a minimum of warming to a diimide reduction medium precooled to −78°. The elusive cyclodecapentaene was converted to cyclodecane in an estimated (glpc) yield of 40%. The cyclodecane, isolated by means of glpc, was identified by (1) glpc coinjection with authentic material and (2) comparison of its mass spectral fragmentation pattern with that of authentic material. After room temperature photolysis of *trans*-9,10-dihydronaphthalene only a trace amount of cyclodecane is obtained by diimide reduction.

As surmised earlier and as revealed by the above set of experiments, parent cyclodecapentaene is a species which, although capable of being generated and trapped under appropriate conditions, is highly unstable. Formally a 10π electron cyclic system, the monocyclic hydrocarbon (**2** or **3**) very readily undergoes valence bond isomerization to *cis*-9,10-dihydronaphthalene and exhibits no aromatic stability in the traditional sense of the word. Questions concerning the geometry, conformation, and electronic character of the species prepared herein remain unknown and subjects for future investigation. Although it seems very unlikely that *parent* cyclodecapentaene *per se* will ever be gotten in hand under ambient conditions, its isolation in the form of a transition metal complex would appear to be a reasonable possibility. Nevertheless, this study has resulted in the first generation and direct detection of a parent cyclodecapentaene, and confirmation that the energy of stabilization due to delocalization in the 10π-electron system is outweighed by the destabilizing effect of strain and/or nonbonded internal hydrogen repulsion in the molecular framework.

More recently, other studies involving *trans*-9,10-dihydronaphthalene–cyclodecapentaene systems have been reported. Grohmann and Sondheimer[21] have achieved the synthesis of mono-*trans*-1,2:3,4:7,8-tri-

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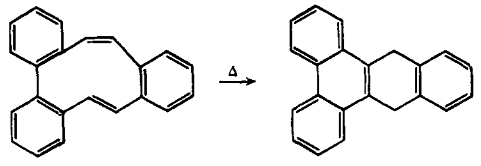
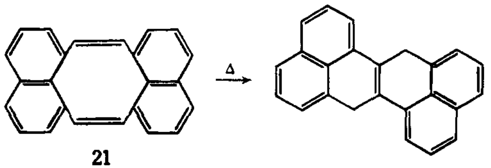
(20) W. von E. Doering and J. W. Rosenthal, *Tetrahedron Lett.*, 349 (1967).

(21) K. Grohmann and F. Sondheimer, *J. Amer. Chem. Soc.*, **89**, 7119 (1967).

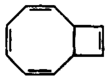
benzcyclodecapentaene (**20**) by the bis ylide route. By similar means, Mitchell and Sondheimer[22] secured the dinaphthcyclodecapentaene **21**. Both substances were observed to undergo thermal rearrangements, **20** to the 9,10-dihydroanthracene **22**, and **21** to the dihydro **23**. Also, other sources of *trans*-9,10-dihydronaphthalene have been uncovered: both pyrolysis (*vide supra*) and photolysis[23] of the tosylhydrazone anion **18** yield the hydrocarbon, in addition to a variety of isomers. Furthermore, the *trans*-dihydronaphthalene is produced in a thermal isomerization from the *cis*-bicyclo[6.2.0]decatetraene,[24] and also in low-temperature pyrolytic and photolytic reactions, respectively, from the unisolated precursors *all-cis-* and mono-*trans*-cyclodecapentaene (**16**).[24]



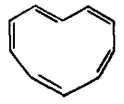
20 **22**



21 **23**



24



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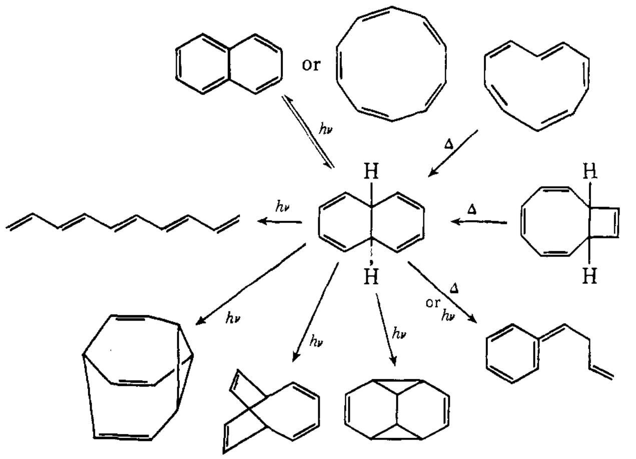
All reported preparations and reactions of *trans*-9,10-dihydronaphthalene are shown in Chart IV. After the completion and publication in preliminary form of the Stanford *trans*-9,10-dihydronaphthalene–[10]annulene work, Masamune and Seidner reported[24] that they were unable to detect cyclodecapentaene conversion from **3** and that at the temperature (−190°) stated in the Stanford publication, **3** was completely recovered after irradiation attempts. These authors found that at distinctly higher temperatures (−110 to −60°), however, *cis*-9,10-dihydronaphthalene (**15**) and photolysis products of **15** were generated. Since **15** would be formed by initial photolytic conversion of **3** to [10]annulene (**1** or **2**) (in accordance with the Woodward–Hoffmann rules) followed by the postulated interconversion[24] of **1, 2, 16,** and **15**, the Masamune and Seidner results do reveal *initial* formation in high yield of [10]annulene from **3**, in accordance with our findings. There remains only the discrepancy in the experiments carried out at −190°.

Chart IV



In a reinvestigation of the low-temperature photolysis work, it was discovered that the consumption of starting material **3** is inversely related to its concentration, as shown in Table I. Thus, a very poor quantum yield in reaction **3** → **1** or **2** would account for the disparity in results: at extremely low concentrations, a reasonable conversion is possible, while at much higher molarity levels, only a small per cent of starting material is consumed. At appropriately low concentrations, formation of [10]annulene can be accomplished at a temperature sufficiently low to permit its preservation and reduction to cyclodecane. However, at the higher concentrations used by Masamune and Seidner, conversion of **3** to **1** or **2** will proceed measurably only under such conditions that the annulene cannot be retained, but is transformed *in situ* to **15** and **15**-derived isomers, observed as the only products in their experiments. It should be mentioned that the irradiation medium used at Stanford (ether–isopentane–ethanol) differed from that used at Alberta (perdeuteriotetrahydrofuran), and of course variations in personnel and in other factors such as lamp types and age would be involved.

Table I. Dependence of *trans*-9,10-Dihydronaphthalene Consumption on Concentration, Irradiation at −190°

Starting concn, *M*	Starting material consumed, %
$3.5\text{–}4.5 \times 10^{-1}$	0[a]
$2.5 \times 10^{-2\Delta}$	3
$1.5\text{–}4.0 \times 10^{-3}$ [c]	8–15
6×10^{-4}	22
$\leqslant 1.5\text{–}3 \times 10^{-4}$ [b]	$\geqslant 40$

[a] See ref 13. [b] Estimated concentration, ref 1. [c] Estimated concentration.

In the repetition of the 1967 Stanford experiments,[1] most of the original equipment was no longer available. Despite this complication, the results were reasonably satisfactory, and sufficient to clarify the issue. In the subsequent runs (in contrast to the earlier experiments) thermal isomerization of cyclodecapentaene to **15** apparently competed strongly with hydrogenation of the monocycle, with the result that mixtures of *cis*-decalin and cyclodecane were obtained after the concluding reduction operation, in addition to *trans*-decalin, originating from starting material **3**. Such variations from run to run undoubtedly were due to use of differing diimide reduction procedures—a lower initial reduction rate would have the effect of markedly enhancing the competing thermal conversion of [10]annulene (**1** or **2**) to **15**, precursor of *cis*-decalin. Based on starting material

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[22] R. H. Mitchell and F. Sondheimer, *J. Amer. Chem. Soc.*, **90**, 530 (1968).

[23] S. Masamune, C. G. Chin, K. Hojo, and R. T. Seidner, *ibid.*, **89**, 4804 (1967). Samples of *trans*-9,10-dihydronaphthalene prepared according to the Jones and Scott[13,14] and the Masamune, *et al.*, procedures were shown to be indistinguishable from those secured by the procedure described in this paper (comparisons made by vpc, uv, and nmr means).

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

photochemically utilized (8–22%), the yields of *cis*-decalin and cyclodecane in several of the later runs fell in the ranges 67–87% and 12–33%, respectively.

Experimental Section

All melting points were taken on a Büchi melting point apparatus or a microscope hot stage, and are uncorrected.

Analyses were carried out at the Stanford University Microanalytical Laboratory by E. Meier and J. Consul.

The infrared (ir) spectra were recorded on a Perkin-Elmer Model 421 grating spectrometer. The ultraviolet (uv) spectra were taken with a Bausch and Lomb spectronic 5050 or with a Cary Model 14 M recording spectrometer. All nuclear magnetic resonance (nmr) spectra were recorded with a Varian A-60 spectrometer with tetramethylsilane as an internal reference. The solvent was deuteriochloroform unless otherwise noted. Mass spectra were determined on an AEI Model MS-9 mass spectrometer using a heated inlet system.

Gas–liquid partition chromatography (glpc) was accomplished on two F&M series 700 instruments equipped with a power proportioning temperature programmer. Flame ionization was the means of detection for qualitative work, and thermal conductivity (helium eluent), for preparative work. The columns, $^1/_8$-in. diameter copper or $^1/_4$-in. diameter aluminum, were prepared to specifications recorded in the experiment by packing with vibration and gravity feeding before coiling. Support materials were purchased from Varian-Aerograph or Applied Science Laboratories; solid supports were 100–120 mesh and hexamethylchlorodisiliazane treated.

The substrates for column chromatography were: silica gel, 100–200 mesh, Davison Chemical; Florisil, Floridin Co. Preparative thin-layer chromatography (tlc) was done on Merck silica gel GF_{254}, 1 mm thick. Analytical tlc was carried out on Merck silica gel H coated (as a chloroform suspension) by immersion of microscope slides. All chromatography solvents were distilled before use. One commonly used drying agent was Linde Molecular Sieve type 5A (designated: molecular sieve).

Preparation of Lithium Amalgam. In our hands the preparation of 0.5% lithium amalgam by Criegee[25] proved impractical in that steel bombs were relatively expensive, and also short lived. Another method was developed which is simple and effective but only roughly quantitative. However, *this method is dangerous unless executed with caution.*

Reagent grade mercury was placed in a round-bottomed, long-necked distillation flask supplied with a clamp as a handle. The mercury was brought to its boiling point by heating over an open flame with swirling. At this point, the flask was rested on an asbestos pad while a small sliver of clean lithium was cut, then added with shaking to the mercury. The heating of the mercury followed by the *important, short cooling period* during lithium cutting was repeated until the approximate amount of lithium was added. The addition of lithium causes a type of detonation each time (including vaporization of small amounts of both lithium and mercury). This detonation grows less vigorous as the lithium content rises. The entire operation is perfectly safe if performed in a hood, behind a shield, and with suitable asbestos gloves and safety glasses.

The amalgam produced by this method varied in its physical appearance from a very crystalline solid to a semicrystalline liquid, probably owing to differences in the lithium content. Such preparations were effective in reducing allylic bromides, using the normally large excess quantities employed.

***trans*-1,4,5,8,9,10-Hexahydronaphthalene-1,5-diol (9).** A 500-ml round-bottomed flask, equipped with soxhlet extractor, magnetic stirrer, and reflux condenser, was heated in an oven and cooled under a fast sweep of dry nitrogen. Sodium-dried ether (400 ml) was transferred to the flask by means of a syringe needle, under a positive pressure of dry nitrogen. To the ether was added 2.50 g of lithium aluminum hydride (66.0 mmol) under a fast nitrogen sweep. Likewise, 1.935 g of *trans*-1,4,5,8,9,10-hexahydronaphthalene-1,5-dione (**7**) (12.0 mmol), in an extraction thimble, was placed into the soxhlet extractor under a fast flow of nitrogen. The nitrogen flow was modified to a slight positive pressure of nitrogen, and the ether was brought to reflux and maintained thus for ~15 hr. After this time the reaction flask was cooled with ice, and the excess lithium aluminum hydride was decomposed during approximately 1 hr by dropwise addition of water with vigorous stirring and continued cooling. The resulting aqueous layer was then separated, acidified with 10% sulfuric acid, saturated with sodium chloride, and extracted continuously with ether for 36 hr. The two ether portions, when combined, dried over magnesium sulfate, and filtered, could be concentrated on a rotary evaporator to afford 1.861 g (94%) of the *trans*-dienediol (**9**) as a white microcrystalline solid. This material was found to give two unresolved spots on tlc with ethyl acetate as eluent. Several recrystallizations from methyl alcohol provided a pure sample of material corresponding to the upper tlc spot. This material, mp 212–214° with sublimation, exhibited absorption in the ir consistent with the structure **9**, having a broad OH band centered at 3.0 μ and a weak band at 6.05, indicating unsaturation. The nmr spectrum in perdeuteriodimethyl sulfoxide contained vinyl absorption at δ 5.59 (4 H, singlet), two exchangeable protons at 4.61 and 4.71, a broad signal at 3.73 (2 H), another broad signal at 2.32 (2 H), and a complex envelope 1.3–2.0 (4 H).

Due to the low solubility of diol **9**, the process of recrystallization was inefficient and involved a great loss of material. Crude two-spot material (tlc) was subsequently employed for reaction with hydrobromic acid.

Anal. Calcd for $C_{10}H_{14}O_2$: C, 72.26; H, 8.49. Found: C, 71.56; H, 8.60.

***trans*-1,5-Dibromo-1,4,5,8,9,10-hexahydronaphthalene (10).** The method of Pappas[2] was employed to replace the hydroxyl groups of the *trans*-dienediol (**9**) with bromine. To an ice-cold, magnetically stirred suspension of 705 mg of diol **9** (4.25 mmol) in 20 ml of spectral grade cyclohexane was added 18 ml of 48% aqueous hydrobromic acid. The mixture, allowed to warm quickly to room temperature, turned a blue color, which changed over ~5 min to greenish brown. After stirring at room temperature for 3.5 hr, the organic layer was separated, and the aqueous layer was extracted with five 10-ml portions of pentane. The combined organic portions were extracted with five 10-ml portions of water, extracted with two 10-ml portions of saturated aqueous sodium bicarbonate, dried briefly over magnesium sulfate, filtered, and concentrated to a viscous yellow oil on a rotary evaporator. This yellow oil was placed on a Florisil column (h = 30 cm, d = 0.7 cm) and eluted with 70 ml of pentane. Concentration on a rotary evaporator afforded 885 mg (71%) of a clear oil. Inspection by tlc (eluting with 10:1 hexane–benzene) indicated two compounds, the upper spot predominating. Although this oil would not crystallize on standing at −20° for several days, addition of a small amount of pentane and scratching at −70° caused precipitation of a white solid. This material could be crudely recrystallized at low temperatures to mp 60–64° dec and exhibited one spot (upper) on tlc. The nmr spectrum of this material was complex, as expected, and consistent with the assigned structure **10**: complex vinyl region δ 5.5–6.2 (4 H), broad singlet at 4.8 (2 H), allylic protons on carbon bearing bromine, and a complex allylic methylene and methine envelope at 2.0–3.0 (6 H). Subsequent brominations with *N*-bromosuccinimide were performed on the clear, oily mixture of two-spot (tlc) dibromides (**10**).

Anal. Calcd for $C_{10}H_{12}Br_2$: C, 41.12; H, 4.14; Br, 54.73. Found: C, 41.65; H, 4.36; Br, 54.5.

***N*-Bromosuccinimide Bromination of 10.** A mixture of the *trans*-diene dibromides (**10**), 885 mg (3.03 mmol), *N*-bromosuccinimide, 1.10 g (6.25 mmol), and 3 grains of benzoyl peroxide in 60 ml of carbon tetrachloride were refluxed together for 10 min. The reaction mixture was then cooled, filtered through sintered glass with light suction, and concentrated to ~5 ml on a rotary evaporator at room temperature. The concentrate, including some crystals of succinimide which precipitated during concentration, were placed on a 0.8 × 40 cm Florisil column and eluted with 70 ml of 30–60° boiling petroleum ether. Concentration on a rotary evaporator at room temperature provided 961 mg of a light yellow oil (70% based on tetrabromination). Analysis of this oil by tlc (elution with hexane–benzene, 10:1) showed three main spots (designated spots 1, 2, 3, spot 1 being least polar) plus a faint forerunning spot (so designated) and several minor post-running spots (discarded). There was no discernible effect on this product mixture on varying the amount of *N*-bromosuccinimide.

The above oily mixture was placed on another Florisil column (1.18 × 30 cm). Elution was accomplished with 30–60° boiling petroleum ether, and fractions of 15 ml were collected (Table II). Only minimal separation was achieved, a consequence of the need to place the material on the column in benzene–petroleum ether due to crystallization. The combined material from fractions 4, 5, and 6 was a white microcrystalline solid. Although after trituration with benzene it exhibited one fine spot on tlc, its behavior on heating (wide melting point range and low reproducibility) suggested a mixture of stereoisomers. The general behavior, solubility, as

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[25] R. Criegee and G. Louis, *Chem. Ber.*, 90, 417 (1957).

Table II

Fraction	Content (tlc)	Wt, mg
2	Traces of everything but mainly spots 1, 2, and forerunner	307
3	Spots 2 and 3 with a trace of 1	144
4, 5, 6	Mainly spot 3	200

well as retention factor on tlc, suggested a hexa- or higher bromide, but no suitable solvent was found to permit substantiation of this guess by means of nmr.

After removal of the least soluble component from the mixture, the material from fraction 2 (307 mg) was rechromatographed on Florisil (1.60 × 23 cm), the material being applied to the column by a small amount of 60–68° boiling petroleum ether. Elution was accomplished with 60–68° boiling petroleum ether and fractions of 5–7 ml were taken (Table III). Although the separation was inadequate for collection of good physical data on the compounds indicated by the tlc spots, several observations were made. The nmr spectra of the fractions listed were both poor and uninterpretable. The nmr spectrum of material from fractions 1–5 contained aromatic protons, indicating elimination of hydrogen bromide. The material in fraction 6 appears least stable, as determined by tlc and visual inspection, an observation compatible with a species containing four allylic bromine atoms. Each fraction was subjected separately to dehalogenation with lithium amalgam as described below, and the products were analyzed by glpc. Only the material in fraction 6 (spot 1) was observed to give rise to *trans*-9,10-dihydronaphthalene under such treatment. Unfortunately, the yield of material of such purity (63 mg) was only 4.5%.

Table III

Fraction	Content (tlc)	Wt, mg
1–5	Mainly forerunner plus some spot 1	39
6	Mainly spot 1 with trace spot 2 and forerunner	63
7	Mainly spot 2 with trace spot 1	35
8	Mainly spot 2 with trace spot 3	34
9–12	Spot 3	60

It was also found that dehalogenation of the crude (3 spot) mixture of bromides gave rise to a hydrocarbon which was all but inseparable from *trans*-9,10-dihydronaphthalene by glpc. This impurity was observed to arise from spot 2 and its presence necessitated chromatographic semiisolation of spot 1. In practice this was done by means similar to that described above, but by a single chromatography on Florisil taking 3–5 ml fractions. Since the retention factor of the desired tetrabromo species seemed to vary considerably with the amount of so-called hexabromo species, the fractions were analyzed by tlc before combining for debromination. All material from such a chromatography up to and including spot 1, but not including material corresponding to spot 2, was employed for debromination. The yield of spot 1 material is unlikely to have ever exceeded 5%. In addition, the increased length of time involved in chromatography of more than 1 g of crude bromides resulted in drastic reductions in yield.

***trans*-9,10-Dihydronaphthalene (3).** A solution of 63 mg of *trans*-diene tetrabromide (**11**), as prepared above (spot 1 and some forerunner), in 3 ml of sodium-dried ether, was placed in a 25-ml round-bottomed flask equipped with a magnetic stirrer. The solution was degassed by means of a stream of argon. Several spatulas of freshly prepared lithium amalgam were added during the final degassing. The flask was then sealed by means of a serum cap and stirred for 1.5 hr. Liquid mercury was observed very early in the reaction, and the ether assumed a slight greenish cast as the reaction progressed. After 1.5 hr, 10 ml of degassed pentane was introduced by means of a syringe. The resulting white precipitate of lithium bromide was collected on sintered glass. The filtrate was quickly concentrated on a rotary evaporator at room temperature to $\sim$50 μl and then sealed under argon by means of a serum cap and cooled to $-78°$. Material so prepared was analyzed by glpc, and it was generally observed that any additional handling resulted in increased formation of naphthalene. Even in the cold and under argon the desired *trans*-9,10-dihydronaphthalene (**3**) seemed to decompose to naphthalene. Therefore, in subsequent experiments, this reaction was performed as above, and the material isolated in one injection by glpc was then used directly.

The final conditions for glpc analysis were very strictly controlled. A $^1/_4$ in. × 6 ft column of 10% DC550 on acid-washed Chromosorb G was employed. The injection port temperature was 130° and the detector temperature was 150°. The oven was programmed from ambient to 200° at 5°/min. The trace in the above reaction showed four main peaks in the ratio of 2:1:2:1. The first peak was shown to be *trans*-9,10-dihydronaphthalene (**3**). The second peak, overlapping the first, varied drastically in amount from reaction to reaction depending on the purity of the starting bromides. The third peak was shown to be naphthalene by retention time, uv comparison, and coinjection of glpc. The fourth peak, due to its long retention time and its apparent production during the sodium in alcohol reduction of naphthalene[26] (preparation of Δ^1 and Δ^2 dialins as glpc reference compounds), is likely to be a dinaphthyl or dihydrodinaphthyl species. The retention times of the four peaks were 20, 21, 25.5, and 34.5 min, respectively. The desired first peak was collected in a glass capillary cooled with Dry Ice, and washed immediately into a reaction flask, uv cell, or nmr tube. This collector was apparently sufficiently degassed by the glpc helium stream. A yield of this hydrocarbon (only estimated due to lack of success in reproducing tares of the capillary glpc collectors), based on glpc peak size and nmr spectral data, is $\sim$15%. The half-life, in solution and with reasonable precaution to exclude air, is estimated at 10 min. The only detectable product of decomposition by glpc and nmr is naphthalene. Under similar conditions the isomer *cis*-9,10-dihydronaphthalene lasted $\sim$2 hr.

The second peak on glpc was not investigated other than to record its uv and nmr (by subtraction) spectra. This peak, surely due to a hydrocarbon on the basis of its glpc retention time, could be shown to arise from tetrabromide fractions enriched in spot 2 by column chromatography on Florisil. The uv spectrum showed maximal absorption at 260 mμ (methyl alcohol) and the nmr spectrum contained signals at δ 5.82 (1 H, multiplet), 5.62 (1 H, multiplet), 2.13 (2 H, broad singlet), and 1.8 (1 H, multiplet).

Catalytic Reduction of *trans*-9,10-Dihydronaphthalene (T. L. B.) (3). Platinum oxide, 90 mg, was placed in a 25-ml three-necked flask equipped with a magnetic stirrer, and covered carefully with 10 ml of spectrograde methyl alcohol without dispersing it. The flask was then equipped with a serum cap, mercury bubbler, and hydrogen inlet. The system was swept for 1.0 hr, without stirring, under a slow stream of hydrogen. The mixture was then stirred for an additional hour to prereduce the catalyst. Several milligrams of *trans*-9,10-dihydronaphthalene, as produced above, was collected from glpc, washed carefully into an argon-degassed vial with 5 ml of spectral grade methyl alcohol, and transferred to the reduction flask by means of syringe. The reaction was stirred for 15 min at room temperature. The reaction mixture was then filtered on sintered glass with a pad of Celite, diluted with 10 ml of distilled water, and extracted with three 10-ml portions of pentane. The combined pentane extracts were dried briefly over magnesium sulfate, filtered, and concentrated to $\sim$50 μl on a rotary evaporator at room temperature. Analysis of this material by glpc ($^1/_8$ in. × 10 ft, 10% DC550 on acid-washed Chromosorb G, program, ambient to 200° at 10°/min) indicated only *cis*-decalin, the presence of which was proven by nmr analysis. Later runs (R. H. G) gave product which was analyzed on polypropylene glycol-silver nitrate, indicating 94:6 ratio of trans–cis isomers.

Diimide Reduction of *trans*-9,10-Dihydronaphthalene to *trans*-Δ^1-Octalin. Several milligrams of *trans*-9,10-dihydronaphthalene were injected into a slurry of 1.0 g of potassium diazodicarboxylate in 5 ml of methanol and 1 ml of water which had been degassed by an argon stream for 1 hr. To this mixture was added a solution of 0.7 ml of acetic acid in 2 ml of methanol, and the system was stirred under argon overnight. The product was then isolated by pentane–water extraction, dried (MgSO$_4$), and concentrated to *ca.* 0.1 ml. This crude product was then purified with a 1-m 10% Carbowax 20M on Chromosorb P glpc column and trapped in a glass loop at $-78°$.

The above product was analyzed by nmr, which revealed an aliphatic region from τ 1.0 to 2.2 and a complex vinyl region from 5.2 to 5.6, as opposed to an aliphatic region from 1.2 to 1.8 in *cis*-decalin. The ir contained peaks at 3020, 2925, 2855, 1445, and 668 cm^{-1}.

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[26] H. Hock and F. Depke, *Chem. Ber.*, **83**, 326 (1950).

***trans*-Δ^1-Octalin.** A 1.0-g sample of *trans*-1-decalone (98% trans by glpc) was heated to 60° for 2.5 hr with 1.5 g of *p*-toluenesulfonylhydrazine and 22 ml of ethanol. The crude product was isolated by ether extraction, washing with water, drying ($MgSO_4$), and concentration. This product was then dissolved in a solution of base (prepared by addition of 1.0 g of sodium to 25 ml of ethylene glycol) and slowly heated to 160° until N_2 evolution slackened. The product was cooled and diluted with water, and the hydrocarbon was extracted into pentane.

A concentrate of the above crude product was fractionated on a 3.5-m 10% Carbowax 20M on Chromosorb P column (glpc) and the desired component was separated. Repurification on a 1-m 10% DC550 on Chromosorb G column gave pure *trans*-Δ^1-octalin. This component comprised 20% of the original crude mixture, while $\Delta^{1(9)}$-octalin comprised the remaining 80%.

Analysis by nmr of this product showed an aliphatic region from τ 1.0 to 2.2 and a complex vinyl region from 5.2 to 5.6 which appeared virtually identical with that of the diimide reduction product of *trans*-9,10-dihydronpahthalene previously described. Infrared analysis showed absorptions at 3020, 2920, 2855, 1445, and 669 cm^{-1}.

A crude diimide reduction product of *trans*-9,10-dihydronaphthalene prepared as previously described was dissolved in 6 ml of ethanol and stirred with 30 mg of 5% palladium-on-charcoal under an argon stream for 40 min. At this point, a hydrogen flow was introduced, and the system was stirred under the hydrogen stream for 30 min. The hydrogen was then blown out with argon and the system was opened. The product was isolated by pentane–water extraction, concentrated, and analyzed by glpc with a 4% polypropylene glycol–silver nitrate on Chromosorb G column 1 m in length. This method showed the presence of less than 1% of *cis*-decalin with the remainder of the product being *trans*-decalin.

Thermolysis of *trans*-9,10-Dihydronaphthalene (3). The behavior of *trans*-9,10-dihydronaphthalene upon being heated was studied employing the gas chromatograph as a flow thermolysis system. Material from the lithium amalgam debromination of the *trans*-diene tetrabromide (**11**) was treated under slightly altered glpc conditions, *i.e.*, the detector block temperature was raised to 235°. When the peak corresponding to *trans*-9,10-dihydronaphthalene was collected and reinjected, it was found to show two well-separated peaks (1:1) plus a trace of naphthalene. This new peak, longer retained than *trans*-9,10-dihydronaphthalene, was collected and identified as *cis*-1-phenylbuta-1,3-diene by comparison of its uv spectrum (λ_{max}^{MeOH} 259, 296 (s), and 223 mμ (optical density 0.98, 0.07 and 1.54)) with that recorded for authentic material. Further support for its identity was provided by comparison of its retention time with that of authentic material, as well as coinjection.

Room Temperature Photolysis of *trans*-9,10-Dihydronaphthalene (3). The photolysis of *trans*-9,10-dihydronaphthalene (**3**) was performed on material prepared as above and collected from glpc in one of two ways. In one method, the hydrocarbon was collected as previously described in a Dry Ice cooled glass capillary, washed quickly into a previously degassed quartz uv cell with degassed pentane, sealed by means of a hand-lapped glass stopper, and photolyzed for 3 min. In another method for slightly larger collections, the gas chromatograph outlet was slightly modified by attachment of a syringe needle. The collection was made through a rubber septum into an acetone–Dry Ice cooled U-tube vented at the other end by means of a fine syringe needle. After collection the sample was diluted with degassed pentane and irradiated for 3 min.

Analysis of reaction products as well as collection for uv analysis was performed by glpc on $^1/_4$ in × 8 ft columns. Two liquid phases found to have quite different and useful separation properties were the Dow Corning silicone oil, DC550 (employed 5% by weight on acid-washed Chromosorb G), and Steroid Analytical Phase (STAP, employed 5% by weight on Chromosorb P). The separation and analysis of 12 apparent products by glpc and a graphic representation of glpc traces (DC550 and STAP) are included in the Discussion.

Another means of separation which was found to be effective was column chromatography on silver nitrate impregnated silica gel. This separation technique, although having the disadvantage of removing by oxidation all hydroaromatics, had the advantage of being operable on a larger scale. This advantage permitted elimination of purification steps at the tetrabromide **11** stage and also eliminated the glpc isolation of *trans*-9,10-dihydronaphthalene. In one experiment, 1 g of tetrabromide was debrominated in the usual manner with lithium amalgam. The reaction mixture after debromination was distilled at room temperature and under high vacuum into an acetone–Dry Ice cooled quartz vessel, diluted with pentane, and irradiated for 3 min at room temperature. The photoproduct was concentrated to ~1 ml on a rotary evaporator and placed on a silica gel column (1.5 × 33 cm) prepared from 44 g of silica gel which was deactivated with 10% by weight of a 50% aqueous solution of silver nitrate. The hydrocarbons were eluted with spectral grade pentane (prepared by stirring with concentrated surfuric acid in portions until color was no longer generated in the acid layer, then distilling from calcium hydride) and pentane–ether (Malinckrodt Anhydrous) solutions. Forty-five fractions of ~15 ml were taken and analysis was performed directly using pentane or approximate pentane–ether solutions as references. There were 15 fractions of neat pentane, 5 each of 1, 3, 5, and 10% ether, and finally 10 fractions of 50% ether.

Detection and Trapping of Cyclodeca-1,3,5,7,9-pentaene from the Low-Temperature Photolysis of *trans*-9,10-Dihydronaphthalene (3) (TLB). The low-temperature photolysis of the hydrocarbon **3** was performed in a fashion similar to that described above for room temperature experiments. *trans*-9,10-Dihydronaphthalene (**3**) was collected from glpc in a Dry Ice cooled glass capillary and washed into a previously degassed quartz uv cuvette with a degassed solution of ether, isopentane, and absolute ethyl alcohol (EPA, 5:5:2). Experience in similar experiments made it possible to prepare such samples of correct concentration for uv analysis with minimal handling. It is noteworthy that the effect on the uv spectrum of cooling the sample to −190° (EPA is a glass at this temperature) is a hyperchromic one involving extreme sharpening of the absorption bands, and doubling of optical density. The quartz cuvette was suspended in a quartz Dewar[27] with both ends open by means of a glass rod having a suitable ground glass joint at one end for attachment to the cuvette, and one for attachment to a movable bracket for cell positioning at the other end. The adjustable bracket and the open-end Dewar were permanently connected by attachment to a plate perpendicular to the quartz Dewar; this plate served as a cover for the sample compartment of a Cary 14M uv spectrometer of the photolysis chamber of a Rayonet photochemical reactor. The sample was carefully positioned in the open-end quartz Dewar and cooled to −190° by the rapid distillation of liquid nitrogen (approximately 1 l. each 3 min) from a large Dewar up through the open-end Dewar and past the suspended quartz cuvette. The temperature of −190° was easily maintained as measured by means of a thermocouple. The nitrogen distillation was made possible while the above apparatus was positioned in the Cary uv spectrometer or the Rayonet photochemical reactor by slight modifications to these instruments; in particular, holes were opened in the floors of sample and photolysis chambers, respectively. Moreover, the apparatus could be transferred from the photochemical reactor to the uv spectrometer in less than 1 min. This transfer required momentary stopping of the liquid nitrogen distillation, but no significant warming of the sample. In several experiments the thermocouple indicated a warming from −190 to −160°, but since the thermocouple was directly outside of the cuvette and of considerably less mass it is certain that the sample never warmed that much.

In practice, a sample of *trans*-9,10-dihydronaphthalene as an EPA solution in the carefully positioned quartz cuvette was placed in the photochemical reactor, cooled to −190°, irradiated for 1 min at that temperature, transferred quickly to the uv spectrometer, and allowed to reequilibrate at −190°, and a uv spectrum was recorded. Spectra at this stage exhibited quite complex, broad absorption between 240 and 280 mμ. The sample was warmed to room temperature momentarily and then recooled to −190°, and another spectrum was recorded. An obvious visual result of the warming was the generation of a maximum at 247 mμ, corresponding to *cis*-9,10-dihydronaphthalene, in the spectrum of warmed material. To detect more subtle changes, the two uv traces were reduced to a numerical representation by listing an optical density for each millimicron wavelength division. The two listings were subtracted, and the resulting data plotted as a difference spectrum with unit (millimicron) wavelength resolution. The results of several such experiments were consistent with respect to position of maxima and minima, but varied by exhibiting changes in baseline slope—a phenomenon very likely caused by inaccuracies in cell positioning.

Because the generation of *cis*-9,10-dihydronaphthalene upon warming was indicative of thermal decomposition of a cyclodecapentaene (see Discussion), the low-temperature photolysis of *trans*-9,10-dihydronaphthalene was repeated, and diimide reduction

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[27] The authors are grateful to Professor Harry S. Mosher, Stanford University, for loan of the equipment for low-temperature uv determination.

at the lowest possible temperature was performed on the product. A mixture of 1 ml of distilled water, 2 ml of absolute methyl alcohol, and 500 mg (3.07 mmol) of sodium diazodicarboxylate in a 5-ml round-bottomed flask equipped with magnetic stirrer was degassed by bubbling argon through it, then cooled to a barely stirrable paste by means of an acetone–Dry Ice bath. A solution of 370 mg (6.15 mmol) of acetic acid in 1 ml of absolute methyl alcohol was similarly degassed and cooled. While several milligrams of *trans*-9,10-dihydronaphthalene was irradiated for 2 min at −190° a small portion of the methanolic acetic acid (~$^1/_5$th) was added to the stirring diimide reduction paste. After photolysis the EPA solution of photoproduct was poured into the stirring diimide reduction mixture by melting the frozen EPA glass with the warmth of the fingers; this addition was followed by rapid addition of the remaining methanolic acetic acid. The reaction mixture was allowed to warm up to room temperature over 15–20 min, and then extracted with three 3-ml portions of pentane. The combined pentane extracts were washed with two 3-ml portions of distilled water, dried briefly over magnesium sulfate, filtered, and concentrated to ~50 ml on a rotary evaporator. Analysis by glpc on both STAP and DC550 columns (see below) showed the presence of cyclodecane as an approximately 40% component of the hydrocarbon products. This compound was identified by comparison of retention time and coinjection with authentic material prepared by Wolf-Kishner reduction of commercial cyclodecanone. The product of four such photolyses and low-temperature diimide reductions, when combined and purified by glpc, afforded sufficient material for substantiation of the identity of cyclodecane by comparison of its mass spectral fragmentation pattern with that of authentic material.

In approximate repetitions of the above procedures (RHG), similar results were observed. Irradiations were carried out on appropriate amounts of **3** in 6 ml of EPA, contained in a quartz reaction vessel thoroughly degassed with nitrogen. The sample, cooled to −190° in liquid nitrogen, was irradiated for 45-sec periods each of seven times, with 2537-Å light from a Rayonet reactor fitted out with a new lamp.

A slurry of 1.0 g of potassium diazodicarboxylate in 4 ml of methanol and 2 ml of water which had been thoroughly degassed with argon was treated with a few drops of a solution of 0.7 ml of acetic acid in 2 ml of methanol, and was then cooled to −78° with a Dry Ice–isopropyl alcohol bath. The photoproduct was raised to this temperature with a similar bath and transferred by syringe to the diimide reduction flask. The remainder of the acetic acid solution was then added, and the reduction system was allowed to come to room temperature over 30 min and then stirred an additional 30 min. The crude product was then isolated by pentane–water extraction and carefully concentrated under low vacuum. The crude product was then reduced again with hydrogen over 5% palladium on charcoal.[14] After isolation and analysis, the results in Table IV were obtained. In two of the above irradiation experiments, the cyclodecane was isolated by glpc and identified by its characteristic nmr peak (singlet at τ 1.50).

Table IV. Per Cent Yields of Products in Diimide Reduction of [10]Annulene

Concn	*trans*-Decalin	*cis*-Decalin[b]	Cyclodecane[b]
2.5×10^{-2}	97		
$1.5\text{–}4.0 \times 10^{-3}$ [a]	92	88	12
$1.5\text{–}4.0 \times 10^{-3}$ [a]	85	67	33
6×10^{-4}	78	86	14

[a] Estimated. [b] Based on starting material consumed.

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Valence Tautomers of Heterocyclic Aromatic Species[1a]

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Abstract: The photorearrangement of 2,5-di-*tert*-butylfuran (**1**) to 2,4-di-*tert*-butylfuran (**17**) and 2,2,7,7-tetramethylocta-4,5-dien-3-one (**18**) has been shown to proceed *via* the di-*tert*-butyl cyclopropenyl ketone (**16**). Independent photolysis of the furan **17** gave no cyclopropenyl ketone **16**. These results and the formation of 1,5-di-*tert*-butyl-3,3-dimethylbicyclo[3.1.0]hexan-2-one (**3**) and the cyclopropenyl ketone (**4**) from 2,3,5-tri-*tert*-butylfuran (**2**) are rationalized in terms of a proposed general mechanism for the photochemical rearrangement of five-membered aromatic heterocyclic compounds.

The photochemistry of five-membered aromatic heterocycles has been the object of a considerable amount of study since the first irradiation-induced conversion of a benzenoid to a valence bond isomer (Dewar benzene) was reported in 1962.[2a] However, there has so far been no attempt to arrive at a systematic view of the reactions and rearrangements which these molecules undergo on irradiation. As part of a broader study of valence tautomers of aromatic systems,[2b] we have examined the photochemistry of some derivatives of furan.[3] These results, together with related work carried out in these laboratories and the rearrangements reported in the literature, have allowed us to arrive at a general mechanistic description of the photochemical behavior of these compounds.

The furan derivatives chosen for study were 2,5-di-*tert*-butylfuran[4] (**1**) and 2,3,4-tri-*tert*-butylfuran[5] (**2**). The tri-*tert*-butyl derivative in particular seemed a likely candidate for conversion to valence tautomers, especially the Dewar isomer, because the nonplanarity of the latter structure would offer relief of the considerable strain involved in the presence of two (cis) *tert*-butyl

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(1) (a) Abstracted from the Ph.D. Thesis of T. H. Whitesides (Stanford University, 1969); (b) National Science Foundation Graduate Fellow, 1964–1968.

(2) (a) E. E. van Tamelen and S. P. Pappas, *J. Amer. Chem. Soc.*, **84**, 3789 (1962); (b) E. E. van Tamelen, *Angew. Chem., Int. Ed. Engl.*, **4**, 738 (1965).

(3) A portion of these results has been communicated previously: E. E. van Tamelen and T. H. Whitesides, *J. Amer. Chem. Soc.*, **90**, 3894 (1968).

(4) R. Ramasseul and A. Rassat, *Bull. Soc. Chim. Fr.*, **30**, 2214 (1963).

(5) H. Wynberg and U. E. Wiersum, *Chem. Commun.*, 1 (1965).