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ELECTROCYCLIC REACTIONS OF TETRAENES

INFLUENCE OF TERMINAL SUBSTITUENTS

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Abstract—Conjugated tetraenes with both central double bonds of *cis* configuration undergo a series of thermal reactions, the observable products being markedly dependent on the nature of the terminal substituents. Dimethyl 2E,4Z,6Z,8E-decatetraene-1,10-dioate (16) was prepared and found to cyclize readily at 50° to *trans* dimethyl 2,4-bicyclo[4.2.0]octadiene-6,7-dicarboxylate (18). This reaction proceeds to equilibrium, and the rates and equilibrium constants at the indicated temperatures are: 3.0×10^{-5} sec^{-1} −40°; 8.2×10^{-5} sec^{-1}, 16.0, 50°; −10.0, 75°; −7.47, 100°, with the equilibrium favoring (18). A sample of 1,8-diphenyl-1E,3Z,5Z,7E-octatetraene (1) showed no reaction below 120°, and at 175° all *trans* 1,8-diphenyl-octatetraene, *cis* and *trans* stilbenes, *trans*-5-phenyl-6-(*cis*-styryl)-1,3-cyclohexadiene, *cis*-5-phenyl-6-(*trans*-styryl)-1,3-cyclohexadiene, and *cis* and *trans* 6,8-diphenyltricyclo[3.2.1.0^{2,7}]oct-3-enes were formed. At 100° in the presence of excess dimethyl acetylenedicarboxylate 1 gave dimethyl *trans*-3,4-diphenyltricyclo[4.2.2.0^{2,5}]deca-6,9-dien-6,7-dicarboxylate. Finally 1,4-di(1-cyclohexen-1-yl)-1,3-butadiyne, hydrogenated over a Lindlar catalyst, gave only tricyclo[10.4.0.0^{4,11}]hexadeca-1,3,5-triene.

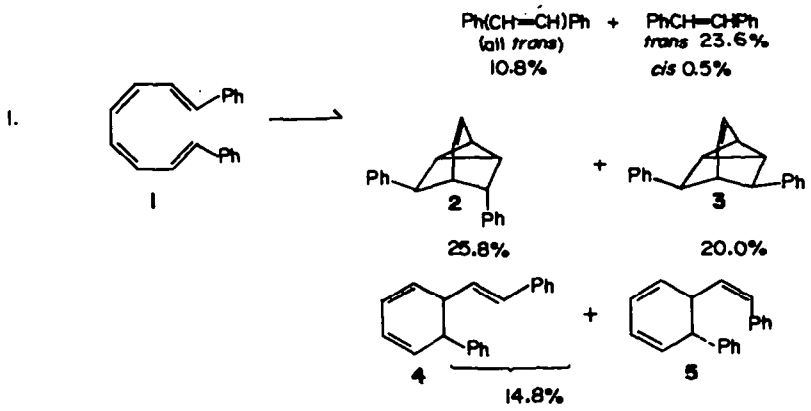
Perhaps the first clear-cut example of an electrocyclic reaction was the observation that 1,3,5-cyclooctatriene is in equilibrium with bicyclo[4.2.0]octa-2,4-diene at 80°.[2] Shortly thereafter Cope and Marshall[3] reported that benzoylcyclo-octatetraene reacted with phenylmagnesium bromide to give 1,9-diphenyl-2,4,6,8-nonatetraen-1-one. After a brief hiatus further cleavages of cyclootatrienes with anionic substituents began to appear. Anet[4] showed that treatment of 7,8-diacetoxybicyclo[4.2.0]octa-2,4-diene with LAH gave 2,4,6-octatrienedial, and Cantrell and Schechter[5] found that cyclooctatetraene dianion reacts with acid chlorides to give 1,8-diacycloctatetraenes in low yield. At about the same time Hoever[6] found that treatment of 7,8 - dibromobicyclo[4.2.0]octa - 2,4 - diene with cyanide gave 1,8-dicyano-1,3,5,7-octatetraene, while a 1-cyano derivative of the bicyclic diene, produced photochemically, unravelled slowly at 138° to a open chain tetraene.[7] That ring openings of cyclotatrienes are not inevitable was illustrated by Meister,[8] who found that all *cis* 1,8-dimethoxy-1,3,5,7-octatetraene gave 7,8-dimethoxybicyclo[4.2.0]octa - 2,4 - diene. Finally Ziegenbein[9] showed that partial hydrogenation of 1,7-octadien-3,5-diyne gave 1,3,5-cyclooctatriene, while Roth and Pelzer[10] obtained a series of products derived from ring cleavage of 1,3,5-cyclooctatriene at 450°.

Just as this burst of activity was coming to an end Woodward and Hoffman[11] published their classic series of papers on the conservation of orbital symmetry. The electrocyclic reaction between octatetraene and cyclooctatriene was shown to follow the W-H protocol,[12,13] and the elegant study of Huisgen *et al.*[14] established both the very rapid rate of this electrocyclization process and the precarious free energy balance between the two valence isomers. Along with our initial study on the stereochemistry of this electrocyclic process,[12] we had begun a broader study of the influence of substituents on the reaction. Our hope had been to develop a more accurate picture of the transition state for the 8π electrocyclic reaction, but we have succeeded only in showing that the combination of rates and equilibrium constants make direct observation of the 8π electrocyclization generally difficult and often impossible. Here we report on three different tetraenes each of which produces a different observable reaction.

RESULTS

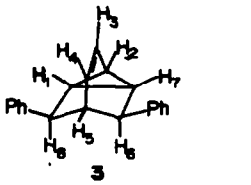
Of the three molecules which we have studied, 1,8 - diphenyl - 1E,3Z,5Z,7E - octatetraene (1) was the first to be looked at. This compound was reported[15] to isomerize above its melting point (191–193°) to the all *trans* isomer. It seemed surprising that the facile 8π electrocyclization would not occur under these conditions, so we reinvestigated the thermal behavior of 1, and a preliminary report of that work has been published.[16] Compound 1 was prepared as described previously,[15] and its physical properties were in complete accord with those reported. To avoid competition with bimolecular processes 1 was not heated neat, but was examined in dilute solution in ethyl acetate. To our surprise the solution showed no change whatsoever when heated under nitrogen at temperatures up to 120°! At higher temperatures in solution 1 undergoes a series of thermal reactions leading to at least seven products (eqn 1). The mixture of products was separated by preparative layer chromatography and 95.3% of the material was recovered.[17] Three of the seven were known products, all *trans* - 1,8 - diphenyl - 1,3,5,7 - octatetraene, *cis*-, and *trans*-stilbenes, and were readily identified by their physical properties or by comparison with authentic samples. The remaining four are new compounds and their identification will be considered next.

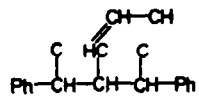
Initially we will consider compound 3, isolated in 20% yield and readily obtained pure by recrystallization, because its symmetry rendered its NMR spectrum more amenable to analysis. A very strong molecular ion peak in its mass spectrum at *m/e* 258 (rel. intens. = 90%) showed that 3 was isomeric with 1. Catalytic hydrogenation, as well as the NMR spectrum, showed the presence of a single double bond. Thus the basic eight carbon skeleton now contained three new rings, the

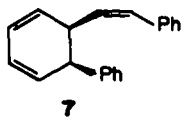


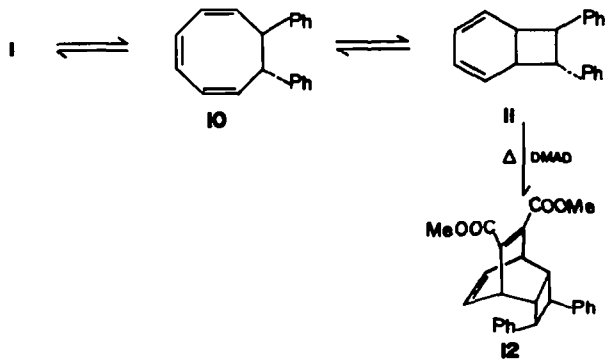
phenyl groups remaining intact. For convenience we will discuss the NMR spectrum of 3 using the numbering for the protons as shown. The spectrum has peaks which may be divided up into four groups; 1.6–2.1(3H), 3.0–3.5(3H), 4.8–6.1(2H) and 7.1(10H). The narrow band at 7.1 shows that both phenyl groups are intact and are apparently symmetrically situated in the molecule. The very complex multiplet between 1.6 and 2.1 was not immediately informative, but was eventually assigned to the three cyclopropyl protons, H_1, H_2 and H_7. In the region between 3.0 and 3.5 there are two simple patterns, a doublet (relative area = 2) at 3.4 and a triplet (rel. area = 1) at 3.15, both clearly broadened by additional coupling. The triplet at 3.5 has an apparent coupling of approximately 4–5 Hz. Irradiation of the olefinic region at 4.8 ppm cleaned up both doublet and triplet patterns and showed $J_{5,6} = J_{5,8} = 4.5$ Hz. The olefinic region has two single proton multiplets at 4.83 and 6.03. Decoupling experiments established that the proton responsible for the 4.83 pattern is coupled to the proton giving the triplet at 3.15, while that proton giving rise to the 6.03 multiplet is coupled to one related to the 1.6–2.1 multiplet. Consideration of both chemical shifts and the interrelations established by decoupling shows that 3 must contain a grouping 6.

All of the carbon atoms of 3 are accounted for in the partial structure 6, and these must be fitted into a tricyclic system. In view of the formation of tricyclo[3.2.1.$0^{2,7}$]oct-3-ene, reported by Roth and Pelzer,[10] during pyrolysis of cyclooctatriene, assignment of the structure 3 is almost automatic. However it is not immediately obvious whether the *exo, exo*-isomer 3 or its *endo endo* counterpart is the correct assignment. A more complete analysis of the NMR spectrum[18] showed $J_{2,3} = 5.5$ Hz, $J_{3,4} = 8.0$ Hz, $J_{2,4} = J_{3,5} = 2.0$ Hz, $J_{4,5} = 6.5$ Hz and $J_{5,6} = J_{5,8} = 4.5$ Hz, while the coupling between H_1 and H_8 (or H_6 and H_7) was too small to be resolved. Unfortunately the $J_{5,6}$ doesn't seem to provide decisive information since Gurudata and Stothers[19] found that for the bicyclo[2.2.2]oct-2-ene system couplings between the bridgehead and the *exo*, or *endo* protons were quite variable and of similar magnitude. Of greater value was their observation that $J_{5,6}$ (*endo, endo*) is large (8–10 Hz) while $J_{5,6}$ (*endo, exo*) is small (*ca.* 2.0 Hz). Three pieces









of evidence support the assignment of 3 as the correct one. First the very small coupling between H_1 and H_8 indicates the dihedral angle between these two should be near 90°. Second it has been found that for *exo, exo* - 5, 8 - dibromotricyclo[3.2.1.0^{2,7}]oct - 3 - ene the chemical shift between H_3 and H_4 is large and is reduced where one bromine is in an endo position,[20] a pattern followed exactly in the present case. Third the *endo, endo* isomer would have to be derived from 7 via an internal Diels–Alder reaction, an unlikely reaction on steric grounds.

Compound 2 has a molecular weight of 258, and an NMR spectrum with a very strong resemblance to that of 3. Catalytic hydrogenation showed the presence of a single double bond, confirming the tricyclic nature of the non-aromatic skeleton. In the NMR spectrum of 2 there are three significant changes from that of 3. The aromatic region has a ten proton broad multiplet extending from 6.9 to 7.4, indicating the two phenyl groups are no longer symmetrically situated. The resonance at 4.83 in 3 appears at 5.48 in 2, and the 2.0–3.5 region is notably altered, having two broad doublets at *ca.* 2.4 and 3.22 and a singlet at 2.47. This quite unexpected lack of coupling between the bridgehead and an *exo* proton was also observed with *exo,endo*-5,8-dibromotricyclo-[3.2.1.0^{2,7}]oct-3-ene.[20] All of the spectral changes are in accord then with those expected for a shift of a phenyl group from an *exo*- to an *endo*-position. Hence the assignment of structure 2 to this low melting relatively abundant product.

The final product was obtained as an oil constituting 14.8% of the reaction product. The oil had a UV max at 256 nm with an extinction coefficient of 20,000, based on a molecular weight of 258. Catalytic hydrogenation required three moles of hydrogen, and the saturated product had a molecular ion peak at $m/e = 264$, confirming the molecular weight assigned to the oil. The NMR spectrum of the oil had only three broad multiplets at 7.0–7.4, 5.4–6.5 and 3.0–3.7 with relative areas 11:5:2 respectively. These results showed that the product must be monocyclic (exclusive of the phenyls) and that it could not be 7,8-diphenyl-1,3,5-cyclooctatriene. The reduced material was found to be separable on glc giving two compounds in the ratio of 5:1. The NMR spectra of these two reduced materials were virtually superimposable and contained a triplet at 2.35 ppm (J = 7.5 Hz) assignable to benzylic protons. Mechanistic considerations and the need to fit three double bonds into a monocyclic system with a chromophore having a maximum at 256 suggested the thermal products were isomeric forms of 5 - phenyl - 6 - styryl - 1,3 - cyclohexadiene. Both propenylbenzene[21] and cyclohexadiene[22] have maxima near to 256 nm.

When the thermal product was heated at 175° a portion was transformed to 2, but no 3 was observed. Further heating of the residual oil at 175° produced no change. This result excludes *trans* - 5 - phenyl - 6 - (*trans* - styryl) - 1,3 - cyclohexadiene as a constituent of the oil since it would form 3 readily when heated. Of the remaining three possible isomers *trans* - 5 - phenyl - 6 - (*cis* - styryl) - 1,3 - cyclohexadiene (**5**) would be expected to be converted into 2 quite readily, while *cis* - 5 - phenyl - 6 - *trans* - styryl) - 1,3 - cyclohexadiene (4) could conceivably give 2, but would be expected to react very slowly as a result of steric hindrance. The final isomer, 7, would give the unobserved *endo, endo*-tricyclic product, if indeed it could undergo an intramolecular Diels–Alder reaction at all. On the basis of the experimental evidence alone, the presence of 7 as a constituent of the thermally stable oil cannot be excluded.

At first glance it appears that the entire series of products is formed without the intervention of an 8π electrocyclic reaction. However the presence of 11, and presumably 10, in equilibrium with 1 was demonstrated by trapping experiments with dimethyl acetylenedicarboxylate (DMAD) (eqn 2). At 80° no reaction between 1 and DMAD was observed in 68 hr, but at 100° a slow reaction occurs which was not complete after 6 days. An adduct (12) was obtained as a viscous oil which was separated from the reaction mixture with great difficulty by preparative tlc. A molecular ion peak appears in the mass spectrum at $m/e = 400$, and above 200° the adduct decomposed with the formation of dimethyl-phthalate. The IR spectrum shows the presence of conjugated ester (1710, 1260 cm^{-1}), mono-substituted phenyl (1595, 722, 695 cm^{-1}) and olefinic (1620 cm^{-1}) functions. The NMR spectrum shows resonances for the phenyl groups (partially resolved doublet at 7.15, 7.17, area 10), the methyl esters (singlet at 3.67, area 6), and eight additional protons. The latter can be divided into four sets of bands, each set having two very similar one proton multiplets. The spectrum is sufficiently complex that no coupling constants can be derived from first order analysis, hence the positions and spacings of the multiplets are listed here. Furthest downfield are two triplets of doublets at 6.30 and 5.58 with 6.5 and 1.5 Hz spacing. A second pair of multiplets show up at 4.18 and 4.02, the low field group being reasonably interpreted as an overlapping triplet of triplets with 4.5 and 2.0 Hz spacings. The higher field multiplet is not fully resolved and appears to be a septet with 2.0 Hz intervals. A complex set of peaks between 3.2 and 3.8, partially obscured by the methyl ester singlet, could not be disentangled. Finally at the up field end are two more multiplets at 2.94 and 2.68, both triplets of doublets with 9.1, 4.0 and 10.0, 3.2 Hz spacings respectively. Decoupling experiments showed coupling between the 4.02 and the 6.30 and 2.94 bands, while the 4.18 proton is coupled to the 5.58 and 2.68 protons. These results are in accord with the assigned structure 12, although the position of the cyclobutane ring was assigned on steric grounds only.

As a second example for study we chose dimethyl *trans, cis, cis, trans* - 2,4,6,8 - decatetraene - 1,10 - dioate (16) because the strong electron attracting substituents would provide a valuable contrast to the phenyl substituents, and because the desired starting material for its synthesis was a known compound.[24] Shortly after our work was initiated Cantrell[25] discussed with us his work on the carboxylation of cyclooctatetraene dianion which eclipsed a part of our study. Since the work by Cantrell is published, only the results which extend his findings will be reported here. The tetraene 16 was prepared from *trans*-2-penten-4-ynoic acid in three steps (eqn 3). The properties of our sample were in essential agreement with those reported by Cantrell except that our sample exhibited a distinct three fingered peak in the UV spectrum accompanied by a weak *cis* peak. Through the fine structure could be attributible to contamination by some all *trans*-isomer, we have found no other evidence of the presence of that isomer.

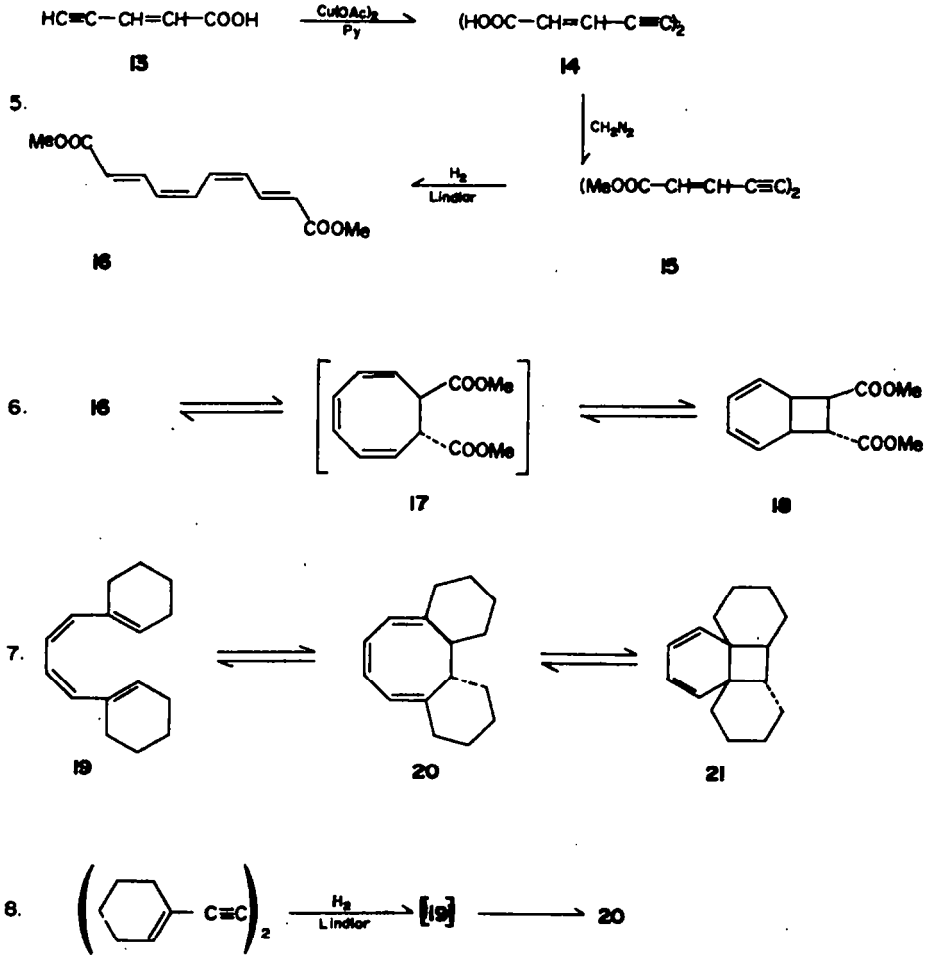
A dilute solution of 16 in benzene undergoes a slow conversion to a new compound with a UV max at 272 nm when heated to 40°. This new compound has been shown by Cantrell to be *trans* - 7,8 - dicarbomethoxy - 2,4 -

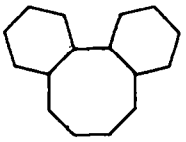
bicyclo[4.2.0]octadiene (18). Though we assume that the reaction proceeds via *trans* - 7,8 - dicarbomethoxy - 1,3, 5 - cyclooctatriene (17), we have not been able to obtain any evidence of its presence (eqn 4). The rate of formation of 18 is readily followed by the disappearance of the strong band at 328 nm in the spectrum of 16, and the reaction follows clean first order kinetics. At 40° the rate constant is 3.01×10^{-5} sec^{-1}, but the reaction does not proceed to completion. After 94 hr (*ca.* 15 half lives) the ration of 18/16 was 14.4, though it appears that equilibrium may not have been reached. At 50° the rate of reaction was 8.16×10^{-5} sec^{-1}, and at the following temperatures the ratio of 18/16 after 100 hr in each case was 50° 16.0, 75° 10.0, 100° 7.47 and 150° 4.16. No attempt was made to approach equilibrium from 18, but assuming equilibrium was reached the data give $\Delta H^\circ = -860$ cal. and $\Delta S^\circ = -6$ eu.

As a third example we chose *cis, cis*-dicyclohex-1-enyl-1,3-butadiene (19), since it seemed reasonable to expect that direct observation of the 8π electrocyclization could be made in this case. The expectation was based on the presumption that the extremely strained bicyclo[4.2.0] form 21 would not appear in any perceptible amount at equilibrium. Once again the tetraene 19 was approached by acetylenic coupling and Lindlar reduction, this time starting with 1-ethynyl-cyclohexene.[26] However the reduction step gave only two products aside from the reactant, 21% of a polyene presumed to be either a mono or di-*trans* isomer of 19, and tricyclo[10,4,0,$0^{6,11}$]hexadeca-1,3,5-triene (20). The product 20 was identified by its molecular weight (*m/e* 214), an UV spectrum with max at 244, 252 and 269 nm, and the presence of two singlets at 5.59 and 5.65 comprising only four protons in the olefinic region of the NMR spectrum. Hydrogenation of 20 required three moles of hydrogen and gave tricyclo[10,4,0,$0^{6,11}$]hexadecane (22), familiarly known as mousane in our laboratory. Some attempts to examine the Lindlar reduction mixture directly to see whether ring closure of 19 might be occurring during workup proved abortive. We had hoped to reduce the Lindlar product over platinum oxide to produce stable saturated compounds, hence to identify the presence of 19 through the thermally stable 1,4-dicyclohexylbutane. Unfortunately hydrogenation over platinum proceeded so slowly that if 19 had been present, it cyclized faster than it reduced and only 22 was obtained.

DISCUSSION

Conjugated tetraenes with both central double bonds of Z configuration can potentially undergo a broad series of electrocyclic reactions (Scheme 1). Prior to the present work acyclic tetraenes of proper configuration had been observed to undergo only an 8π electrocyclization to a cyclooctatriene followed in most cases by a 6π electrocyclization to a bicyclo[4.2.0]octadiene. That this was an artificial restriction imposed by the choice of reaction temperatures was shown by the study of





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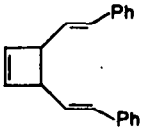
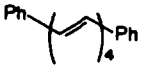
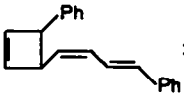
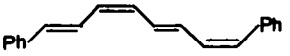
9. I ⇌  ⇌ 

10. I ⇌  ⇌ 

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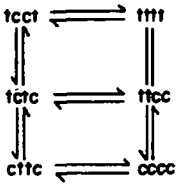
11. 

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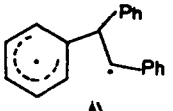
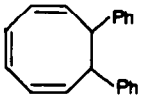
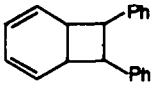
I ⇌ 10 ⇌ 11 ⇌ 

tccc ⇌  ⇌ 

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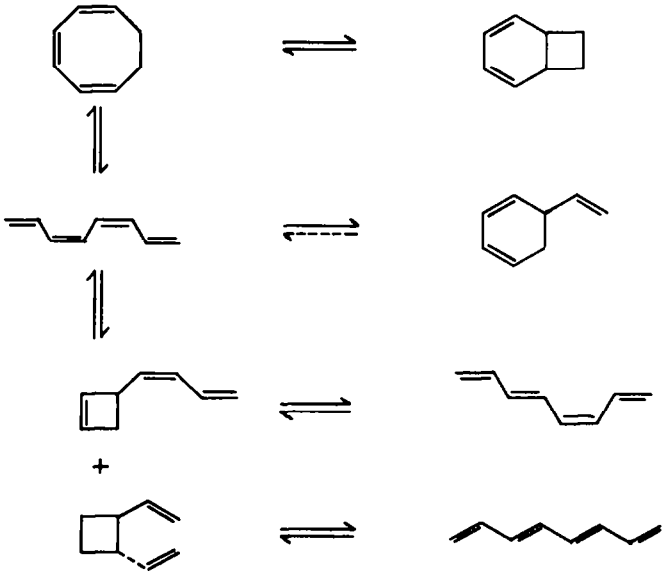


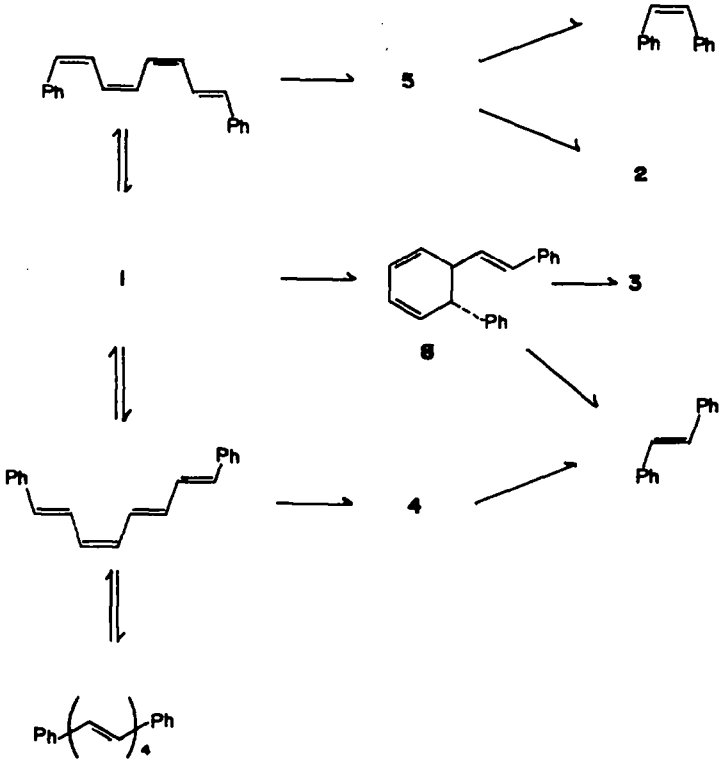
Scheme 1.

the retroelectrocyclization of cyclooctatriene.[10] Consequently with the reversibility of the octatetraene-cyclooctatriene-bicyclo[4.2.0]octadiene series it is possible for a triene-cyclohexadiene rearrangement to occur if the temperature is high enough. Finally *cis-trans* isomerization of dienes has been shown to take place via a cyclobutene,[27] but the process has not been shown to occur with tetraenes. The present studies show that many, if not all, of these electrocyclic processes can occur with tetraenes, but the directly observable reactions are sharply dependent on the substitution patterns and the reaction conditions.

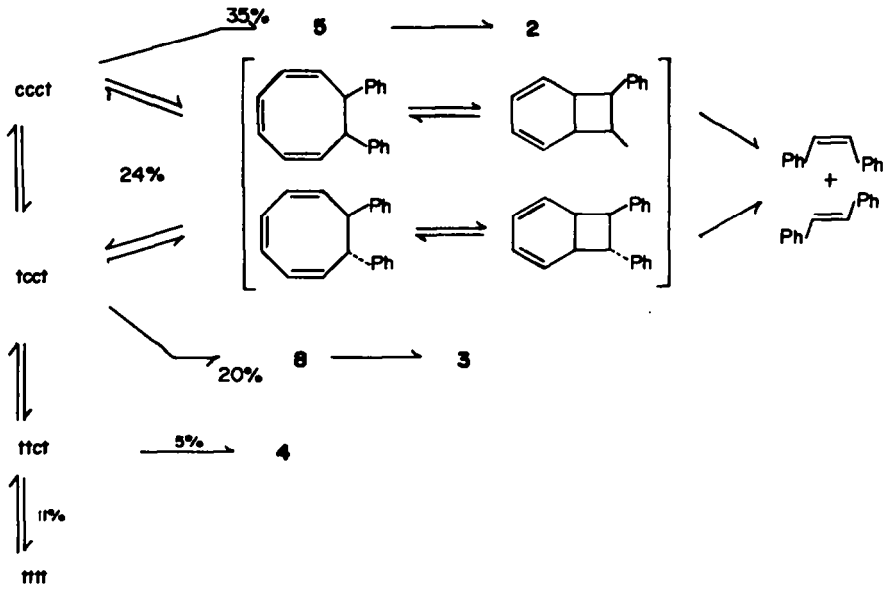
The most complex behavior of the tetraenes investigated by us was exhibited by **1**, the complexity obviously resulting from the necessarily high reaction temperature. The temperature required to bring about an observable reaction of **1** (>120°) is typical for triene electrocyclizations,[23] but most atypical for tetraenes.[12-14] At first glance it appears that all reactions of **1** occur without the intervention of an 8π electrocyclic reaction, a totally unanticipated and indeed almost incomprehensible result. It is in fact possible to devise a scheme which will account for all of the products without recourse to an 8π electrocyclization (Scheme 2). The unusual step in this sequence involves the loss of benzene from **4**, **5** and **8** to form stilbene, and though we have observed the loss of methane from 5,6 - dimethyl - 1,3 - cyclohexadiene at 300°,[28] we do not know of a precedent for the loss of benzene under the conditions used here. An alternate route to the stilbenes via **10** and **11** (eqn 4) requires cleavage of the cyclobutane ring of a bicyclo[4.2.0]octadiene. This cleavage does have precedents,[29] and a rough calculation based on the stabilization energy of a cyclohexadienyl radical of 24 kcal/mol[30] indicates an enthalpy of activation in the present case of *ca.* 24 kcal/mol. To distinguish between the two routes we prepared 1-3,4,5,6-D_4, and found that reaction of the labelled sample gave *trans*-stilbene containing no deuterium. Thus the process via **4**, **5** and **8** can be eliminated. Further evidence favoring the route through **10** and **11** was obtained by trapping **11** with DMAD. That evidence does not prove that **10** and **11** are the source of the stilbene since both could be present as the result of an unproductive equilibrium.

Whatever the source of the stilbenes it is clear that the 8π electrocyclization does proceed faster than the 6π reaction. At 80° the use of DMAD as a trapping reagent failed to provide evidence for the presence of **11** in the reaction mixture. At 100° however trapping of **11** does occur, albeit very slowly. The reaction under these conditions did not appear to be a clean process, and the adduct was difficult to isolate and purify. Thus no kinetic study was attempted even though the rate of conversion of **1** to **10** would be of considerable interest,[31] since two phenyl groups have been found to accelerate a 4π electrocyclization quite markedly,[32] while they have very little influence on the rate of a 6π electrocyclization.[23]

Whether the 4π electrocyclization participates in the sequence of reactions cannot be given a completely unequivocal answer here, but arguments for its intervention will be given. Because of its symmetry **1** can undergo *cis-trans* isomerization via two cyclobutenes only (eqns 7 and 8), and the conrotatory process must interconvert isomers at two bonds simultaneously. If all double bond isomerizations occur via such a route, the sequence of eqn (9) must result. That is, no isomer with three like configurations can be formed. Assume for a moment that only normal single rotation geometric



Scheme 2.



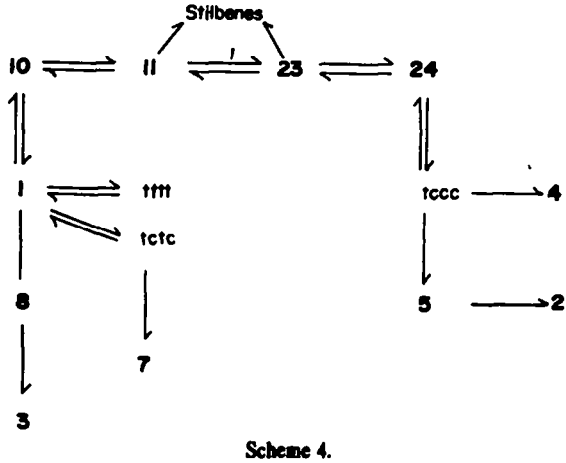
Scheme 3.

isomerization occurs, leading then the sequence of Scheme 3 to explain the observed results. Note first that the presence of **5** and **2** require the presence of the tr, *cis, cis, cis* (or *cis, trans, cis, cis*) isomer in the mixture. Consequently we can conclude that some isomerization route other than via a cyclobutene is required.

If we now assume that the double bond isomerization is fast enough to establish equilibrium, then tccc reacts fast enough to give 35% of **5**, tcct gives 20% of **8**, but tctt gives only 5% of **4**. If **7** is present tctt might produce less than 5% of **4**. *But* it has been well established[23,33] that trienes of the tct type cyclize about 100× faster than those of the tcc type! Hence equilibrium amongst the tetraene isomers could not have been reached. Now if we make the reasonable assumption that via the normal isomerization tcct should convert to tctt at least as fast as to tccc, then **4** should become the major product. We conclude therefore that since tctt cannot be present to any major extent in the reaction mixture, it cannot be an intermediate in the formation of the all *trans* tetraene.

We propose therefore that the special route leading from **1** → tccc is that shown in eqn (10). This process can interconvert only these two stereoisomers, and these are the source of over 80% of the observed products. The all *trans* tetraene then can be formed directly from **1** via the route of eqn (9), and the incompletely identified minor product previously considered to be mainly **4** could be either **4** formed from tccc or **7** formed from the tctc obtained from **1** via eqn (8). This sequence is shown in Scheme 4.

Two objections might be raised to this sequence. First the amount of products derived from tccc compared with the amount of stilbenes indicates that the diradical of eqn (10) must reclose much faster than it cleaves to give the stilbenes. However Berson[34] has found that *trans*-1,2-dipropenylcyclobutanes undergo conversion to the *cis* isomer about four times faster than cleavage to pentadienes. While this does not counter this objection completely it does show that a stabilized diradical can reclose faster than it fragments. Second one may question whether the geometric isomerizations can occur via the cyclobutene route fast enough to qualify for a role in



Scheme 4.

Scheme 4. Generally $\Delta H^{\neq}$ for electrocyclization of tcc trienes is about 33 kcal/mol.[23] Frey[27] found $\Delta H^{\neq}$ for the *cis-trans* isomerization of 4-methyl-1,3-pentadienes to be 45 kcal/mol. However phenyl groups reduce the $\Delta H^{\neq}$ for cyclobutene ring opening by 5 kcal/mol each on *cis*-3,4-diphenylcyclobutane.[32] Also *trans* disubstituted cyclobutenes usually have a $\Delta H^{\neq}$ some 4 kcal/mol less than cis isomers.[35] Thus even if the styryl groups are no more effective than phenyls, the $\Delta H^{\neq}$ for the present geometric isomerizations could be *ca.* 30 kcal/mol. Thus on energetic grounds the cyclobutene route is a viable candidate for the role attributed to it in Scheme 4.

The thermal behavior of **16** is much simpler than that of **1**, a result partly of the stability of **18** and partly of the temperatures used in our studies. During the studies at 150° two new products began to appear in very small amounts after prolonged heating. These had very much smaller R_f values on silica gel than **16** or **18** and only UV spectra were obtained. It is clear that these do not correspond to such possible products as maleic or fumaric esters, other geometric isomers of **16** or the tricyclic analogs of **2** or **3**. Since no trienes other than the tcc type are present unless gometric isomerizations were

occurring, no ring closure of the 6π type was expected at this temperature. It is unfortunate that the rate studies cannot provide any information about the rates of the individuals steps 16→17 or 17→18. Huisgen and his students[13,14] showed that the tcct isomer of decatetraene forms dimethylcyclooctatriene faster than the monocyclic goes to the bicyclic valence isomer. If that is also the case with 16, then our failure to observe any 17 even as a transient requires that 17 revert to 16 much faster than it forms 18. That this rate differential is correct is shown by the finding of Antkowiak and Schechter[35] that cyclooctatetraene dianion reacts with methyl chloroformate to give some 16 but no 18. In view of our equilibrium data that result is compatible only with formation of 17 and rapid reversion to 16. The unpredictable nature of these rates and equilibria, which has been clearly noted by Huisgen *et al.*[37] is nicely illustrated by the reaction of cyclooctatetraene dianion with ketones.[38] Thus benzophenone leads to 1,1,10,10 - tetraphenyl - 2,4,6,8 - decatetraen - 1,10 - diol while acetone gives 2,4 - bicyclo[4.2.0]octadien - 7,8 - bis - dimethylcarbinol.

EXPERIMENTAL

1-Phenyl-1-buten-3-yne. This enyne was prepared from 4 - chloro - 4 - phenyl - 1 - butyne by a modification of a procedure given by Akhtar *et al.*[15] To a soln containing 39.0 g (0.67 mol) KOH in 320 ml i-PrOH was added 55.9 g (0.34 mol) of 4 - chloro - 4 - phenyl - 1 - butyne and the mixture was heated under reflux for 8 hr. About 200 ml of pentane was added to the cooled mixture and enough water was then added to produce separate layers. The pentane layer was separated, dried ($MgSO_4$) and the pentane was removed by distillation. The product was distilled, b.p. 49–50° (0.5 mm), [lit.[15] b.p. 56° (1 mm)] giving 24.7 g; IR (neat) 3300, 3050, 2120, 950, 725, 695 cm^{-1}; NMR (CCl_4) δ 2.91 (d, 1H, J = 3 Hz), 6.00 (d of d, 1H, J = 3, 18 Hz), 6.90 (d, 1H, J = 18 Hz), 7.2 (m, 5H).

1,8 - Diphenyl - trans - 1, trans - 7 - octadien - 3,5 - diyne. Preparation was carried out by the procedure of Akhtar *et al.*[15] A soln containing 48.6 g ammonium chloride and 30.9 g cuprous chloride in 600 ml water was acidified to pH 4–5 with HCl, and 6.0 g (0.047 mol) of 1-phenyl-1-buten-3-yne was added. The mixture was shaken in an atmosphere of O_2 for 7 hr. The light green ppt was dissolved with dil. HCl, and the remaining yellow solid was isolated by filtration. The solid was extracted with ether in a Soxhlet extractor, and the ether was evaporated. The residue was crystallized from $CHCl_3$/i-PrOH m.p. 135–135.5 [lit.[15] m.p. 133°], 3.3 g (54%); NMR (CCl_4)δ, 7.3 (s, 10H), 7.05 (d, 2H, J = 16 Hz), 6.2 (d, 2H, J = 16 Hz).

1,8-Diphenyl-trans-1, cis-3, cis-5, trans-7-octatetraene (1). The above dienediyne, 3.5 g (13.8 mmol), was dissolved in EtOAc and hydrogenated over 500 mg of Lindlar catalyst until two equivs of H_2 were taken up. The catalyst was removed and was washed with $CHCl_3$. The organic solns were combined and the solvents removed under reduced pressure. The residual solid was washed with 8 ml of ether giving light yellow crystals, 2.6 g (73%), m.p. 193–194° [lit.[15] m.p. 191–193°]; UV max (cyclohexane) 390 nm (4.75), 369 nm (4.88), 350 nm (4.83), 240 nm (4.55).

Thermal reaction of 1. A soln containing 5.2 g (20 mmol) of 1 in 10 ml EtOAc was degassed under N_2 and sealed. The soln was heated at 175° for 7.5 hr. The cold soln deposited some yellow crystals. The solvent was removed under reduced pressure and the residue was washed thoroughly with a total of 20 ml of pentane. The insoluble material was isolated by filtration, giving 560 mg (11%) of all *trans*-1,8-diphenyloctatetraene, m.p. 235–236° [lit.[15] m.p. 234–235°], UV max ($CHCl_3$) 360 nm (4.82), 378 nm (4.98) 400 nm (4.88). The pentane soln was concentrated under reduced pressure, and the concentrate was separated by preparative layer chromatography on Merck PF/254 silica gel using three developments with hexane. Five products were obtained from the chromatography and are listed here in order of decreasing R_f values.

(a) *cis*-stilbene, 18 mg (0.5%), UV max (EtOH) 221 nm (4.22), 279 nm (3.99) [lit.[39] 222 (4.36), 280 (4.13)]; NMR (CCl_4) δ, 6.55 (s, 2H), 7.15 (s, 10H).

(b) *trans*-stilbene, 856 mg (24%), m.p. 124–125° mixed m.p. with authentic sample 125°, UV max (EtOH) 228 nm (4.26), 295 nm (4.98), 308 nm (4.46), 320 nm (Sh) (4.26); NMR (CCl_4) δ 7.05 (s, 2H), 7.1–7.6 (m, 10H).

(c) 4 + 5, 770 mg of oil (15%); UV max (EtOH) 256 nm (ε ~ 20,000, based on MW = 258); NMR (CCl_4) δ 7.0–7.4 (m, 11H), 5.4–6.5 (m, 5H), 3.7–3.0 (m, 2H).

(d) 2, 1340 mg of thick oil (26%), NMR (CCl_4) δ, 6.9–7.4 (m, 10H), 6.05 (d of d of d, 1H, J ~ 8, 5, 1.5 Hz), 5.48 (d of d of d, 1H, J ~ 8, 6, 1.8 Hz), 3.22 (broad d, 1H, J ~ 5 Hz), 2.47 (s, 1H), 2.4 (broad d, 1H, J ~ 5 Hz), 1.5–2.0 (m, 3H). A purified sample of 2 kept in the refrigerator crystallized after several months, m.p. 53–54°. (Found: C, 92.85; H, 6.94. Calc. for $C_{20}H_{18}$: C, 92.98; H, 7.02).

(e) 3, 1037 mg of crystals, m.p. 80–83° (20%). The compound was sublimed *in vacuo* and recrystallized from EtOH, m.p. 84.5–85°; NMR (CCl_4) δ 7.1 (m, 10H), 6.03 (d of d of d, 1H, J = 8, 5, 2 Hz), 4.83 (d of d of d, 1H, J = 8, 6, 1.8 Hz), 3.4 (broad d, 2H, J ~ 4 Hz), 3.15 (broad t, 1H, J ~ 5 Hz), 1.6–2.1 (m, 3H); mass spec. *m/e* = 258 (90%). (Found: C, 92.89; H, 6.88. Calc. for $C_{20}H_{18}$: C, 92.98; H, 7.02).

Trans - 3,5 - *Diphenyltricyclo*[2.2.2.$0^{2,6}$]*octane.* A soln containing 120 mg (0.46 mmol) of 2 in 5 ml EtOAc was hydrogenated at atmospheric pressure with 25 mg platinum oxide. After the catalyst had been removed, the solvent was evaporated and the residue was purified by glc (10% SE-30 on 60/80 Chromosorb G at 240°). The main product (72%) was a colorless solid, m.p. 67–68°, after recrystallization from EtOH. NMR (CCl_4) δ, 0.9–1.6 (m, 3H), 1.6–2.1 (m, 5H), 3.3 (s, 1H), 3.4 (broad d, 1H), 7.0–7.4 (m, 10H); mass spec. *m/e* 260 (52%). (Found: C, 92.17; H, 7.58. Calc. for $C_{20}H_{20}$: C, 92.26; H, 7.74.)

exo - cis - 3,5 - *Diphenyltricyclo*[2.2.2.$0^{2,6}$]*octane.* A sample (150 mg, 0.58 mmole) of 3 was hydrogenated, and the product was purified as described for the above molecule. The product was a crystalline solid, m.p. 94.5–95°, NMR (CCl_4) δ, 0.5–1.4 (m, 3H), 1.4–2.0 (m, 4H), 2.0–2.4 (m, 1H), 3.6 (d, 2H, J = 5 Hz), 7.1–7.6 (m, 10H); mass spec. *m/e* 260 (61%). (Found: C, 92.13; H, 7.57. Calc. for $C_{20}H_{20}$: C, 92.26; H, 7.74%).

Cis and trans - 1 - *Phenyl* - 2 - β - *phenylethylcyclohexane.* A sample (104 mg, 0.4 mmol) of the mixture of 4 + 5 was hydrogenated over platinum oxide as described above. The product was purified on the SE-30 column at 245° and a single major peak was collected (65%). This material was separated on a 20% FFAP column at 220° giving 70% of an oil, NMR (CCl_4 δ, 6.8–7.2 (m, 10H), 0.8–2.9 (m with superposed t at 2.35, J = 7.5 Hz, 14H); mass spec. *m/e* (rel. intens) 264(33%), 131(28%), 117(36%), 104(53%), 91(100%). (Found: C, 90.57; H, 9.31. Calc. for $C_{20}H_{24}$: C, 90.85; H, 9.15%). A second fraction (30%) recovered from the FFAP column was an oil, NMR (CCl_4) δ 6.8–7.2 (m, 10H), 1.0–2.9 (m with superposed t at 2.35, J = 7.5 Hz, 14 H); mass spec. *m/e* 264.

Pyrolysis of mixture of 4 + 5. A small sample of the impure mixture of 4 + 5 was heated at 175° in EtOAc in a sealed tube for 18 hr. Tlc of the mixture on silica gel three times eluted with hexane gave two spots, the major one corresponding to the R_f of unreacted starting material and the second to that of 2.

Pyrolysis of 1-3,4,5,6-D_4. A sample of 1-3,4,5,6-D_4 obtained by reduction of 1,8 - diphenyl - 1,7 - octadien - 3,5 - diyne with Lindlar catalyst (reduced over deuterium) with deuterium was heated as described for thermal reaction of 1. The products were separated as described above and the following NMR spectra were observed (CCl_4) δ:

(a) *cis*-stilbene 6.55 (s, 2H), 7.15 (s, 10H).

(b) *trans*-stilbene 7.05 (s, 2H), 7.1–7.6 (m, 10H).

(c) 4 + 5 7.0–7.4 (m, 11H), 5.4–6.5 (m, 2H), 3.0–3.7 (m, 1H).

(d) 2 6.9–7.4 (m, 10H), 3.22 (d, 2H), 2.47 (s, 1H), 1.9 (s, 1H).

(e) 3 7.1 (m, 10H), 3.4 (d, 2H, J ~ 4 Hz), 3.15 (t, 1H, J ~ 4 Hz), 1.8 (s, 1H).

Dimethyl 3,4 - *diphenyl* - 7,9 - *tricyclo*[4.2.2.$0^{2,5}$]*decadien* - 7,8 - *dioate* (12). A soln containing 300 mg (1.16 mmol) of 1 and 360 mg (2.54 mmol) dimethyl acetylenedicarboxylate in 19 ml toluene

was heated at 100° for 6 days. The solvent and excess DMAD were removed by distillation under vacuum, and the residue was separated by tlc (silica gel-methylene chloride eluant-twice developed). The main product was a brown oil, 163 mg, R_f = 0.66. This product was rechromatographed as above giving 104 mg (26%) of a yellow oil. IR (CCl_4) 3100, 1710, 1620, 1595, 1372, 1260, 722, 695 cm^{-1}; NMR (CCl_4) 7.16 (apparent d, 10H), 6.30 (m, 1H), 5.58 (m, 1H), 4.18 (m, 1H), 4.02 (m, 1H), 3.67 (s, 6H), 3.2–3.8 (m, 2H), 2.94 (m, 1H), 2.68 (m, 1H).

2,8 - Decadien - 4,6 - diyn - 1,10 - diol. Trans - 2 - Penten - 4 - yn - 1 - ol[40] (70.6 g, 0.86 mol) was added over 25 min to a well-stirred soln containing 500 g ammonium chloride and 312 g cuprous chloride in 1250 ml water. The soln was maintained at 55° and O_2 was bubbled through the mixture for 2.5 hr. The organic products were removed by ether extraction and after evaporation of the ether diol was crystallized from water, m.p. 155–157 [lit.[41] m.p. 155–156], IR (KBr pellet), 3450, 1620, 1070, 955 cm^{-1}; NMR (CCl_4) δ, 3.12 (s, OH), 4.16 (d of d, 4H, J ~ 5, 1 Hz), 5.83 ($\frac{1}{2}$ AB, resplit, 2H, J = 18, ~1 Hz), 6.42 ($\frac{1}{2}$ AB resplit, 2H, J = 18, 5 Hz).

2,8 - Decadien - 4,6 - diyn - 1,10 - dioic acid (14). This compound was prepared via two routes, oxidation of the above diol[41] and coupling of *trans*-2-penten-4-ynoic acid.[24]

A. *Oxidation of 2,8 - decadien - 4,6 - diyn - 1,10 - diol.* A soln containing 99.6 g (1.0 mol) CrO_3 and 159.8 g H_2SO_4 acid and enough water to bring the soln to 500 ml was added slowly to a cold well-stirred soln containing 30.6 g (0.19 mol) of the diol in 575 ml acetone. Addition was made at a rate which kept the temp. below 25°, and the mixture was stirred for 2 hr after addition had been completed. The soln was poured into a large excess cold water, and the soln was extracted exhaustively with ether. The ether extracts were washed with $NaHCO_3$ aq, and the aqueous soln was acidified with 6N H_2SO_4. The organic acid was extracted with ether and the solvent was evaporated giving 13.0 g (36%) of the desired acid.

B. *Coupling of 2-penten-4-ynoic acid.* The reaction was carried out according to the literature[24] in 93% yield, UV max (EtOH) 255, 265, 294, 313 nm [lit.[41] 258, 265, 295, 315, 337 nm]; IR (KBr pellet) 1700, 1680, 1655, 955 cm^{-1}; NMR (DMSO-d_6) δ 6.31, 6.72 (AB, J = 16 Hz).

Dimethyl 2,8 - decadien - 4,6 - diyn - 1,10 - dioate (15). The diacid above, 13 g (0.07 mol), was dissolved in about 1.5 l ether and an ethereal soln of diazomethane was added until the yellow color just persisted. A few drops AcOH was added and the solvent was distilled. The residual solid was recrystallized from MeOH giving 8.3 g (55%) of yellow crystals, m.p. 106–107 [lit.[41] m.p. 103–104]; UV max (MeOH). 338(24,800), 315(26,600), 296(17,400), 268(25,800); IR (KBr pellet) 1705, 1605, 1270, 1165, 960 cm^{-1}; NMR (CCl_4) δ, 3.72(s, 6H), 6.33, 6.75 (AB, 4H, J = 16 Hz).

Dimethyl 2,4,6,8 - decatetraen - 1,10 - dioate (16). A sample of 15, 1.475 g (6.8 mmol), in 25 ml ether was hydrogenated over 0.79 g of Lindlar catalyst. The soln was cooled in an ice bath during the reduction. Removal of catalyst and evaporation of the solvent gave a yellow solid which was recrystallized from MeOH, 1.14 g (75%) of yellow prisms, m.p. 111.0–111.9 [lit.[25] 113–114°], UV max (MeOH 328(37,000), 344(31,000), 317sh, 245 nm; NMR ($CDCl_3$) 3.74 (s, 6H), 5.96 (d, J = 18 Hz), 6.0–7.0(m), 7.76 (d of d, J = 13, 18 Hz).

Dimethyl 2,4 - bicyclo[4.2.0]octadien - 7,8 - dicarboxylate (18). A dilute soln of 16 in CCl_4 was heated under reflux for 2.5 h under N_2. The solvent was removed and the residue was sublimed *in vacuo* and recrystallized from chloroform-hexane, m.p. 34–36° [lit.[25] m.p. 34–35°], UV max (MeOH) 272(3000), NMR (CCl_4) δ, 3.0–3.0 (m, 4H), 3.62, 3.66 (2s, 6H), 5.2–6.1 (m, 4H).

Rate and equilibrium studies. Rates of the rearrangement of 16 to 18 and the concentrations at equilibrium were determined by UV spectroscopy. Rates were conveniently followed in a Cary 15 spectrophotometer equipped with a thermostatted cell compartment using the decrease in absorption at 328 nm. Good first order plots through at least one half life were obtained in all cases. At 150° the equilibrium studies gave rise to slow formation of two new products with low R_f values on silica gel tlc separation with hexane/methanol 9:1 development. The slowest moving R_f = 0.13 had UV max (MeOH) 270sh, 280, 290sh, and the second (R_f = 0.17) showed UV max (MeOH) 282, 292.

1,4 - Di(1 - cyclohexenyl) - 1,3 - butadiyne. A soln containing 30 g (0.30 mol) cuprous chloride, 48 g ammonium chloride, and 1 ml conc. HCl in 200 ml water was heated to 55°, and a soln containing 10.6 g (0.10 mol) ethynylcyclohexene in 50 ml MeOH was added slowly. Air was bubbled through the solution for 2 hr, and a green ppt accumulated during the aeration. The ppt was removed by filtration and was washed with 1N HCl and then with hexane. The aqueous filtrate and washes were extracted with hexane and the combined hexane extracts were dried ($MgSO_4$). The hexane was evaporated and the solid residue was sublimed, m.p. 63.5–64.5 [lit.[42] m.p. 62.5–63]; 9.90 g (95%); UV max (hexane) 310(18,200), 291(23,000), 274(15,500), 246(26,000), 236(31,000); IR (CCl_4) 3150, 2135, 1638 cm^{-1}; NMR (CCl_4) δ 1.71 (m, 8H), 2.19 (m, 8H), 6.20 (m, 2H).

Tricyclo(10,4,0,0^{6,11})hexadeca - 1,3,5 - triene (20). The above diendiyne, 0.387 g (1.84 mmol), was reduced over 40 mg Lindlar catalyst in hexane containing 0.01 ml synthetic quinoline. When approximately 2 equivs of H_2 had been absorbed, the reaction was terminated and the product was separated by glc, 4% SE-30 on chromosorb G. Three compounds were obtained, 14% of starting material, 18% of what appeared to be *trans, trans - 1,4 -* dicyclo - hexenyl - 1,3 - butadiene and 68% of 20. A pure sample of 20 was collected by preparative glc from a 5% OV-17 on 45/60 Chromosorb G (6 ft × $\frac{1}{4}$") column, UV (max) 208(13,400), 244(4870), 252(4590), 269(4530); IR (neat) 3050, 1645, 1620 cm^{-1}; NMR (CCl_4) δ 1.56 (m, 12H), 2.15 (m, 4H), 2.67 (m, 2H), 5.59 (s, 2H), 5.65 (s, 2H); mass spec. *m/e* (rel. intens), 214(70%), 91(100%). (Found: C, 89.81; H, 10.16. Calc. for $C_{16}H_{22}$: C, 89.65; H, 10.35%).

Tricyclo[10,4,0,0^{6,11}]hexadecane (22). Hydrogenation of 20 (0.396 g, 18.5 mmol) over 100 mg platinum oxide catalyst in hexane at room temp. required 18 hr to proceed to completion. The product, 95% pure by glc, showed the following properties, IR (CCl_4) 2920, 2852, 1448 cm^{-1}; NMR (CCl_4) δ 0.9–2.1 (broad m); mass spec. *m/e* (rel. intens) 220(44%), 122(100%).

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