Isolation and Identification of the Polyenes Formed During the Thermal Degradation of β,β-Carotene

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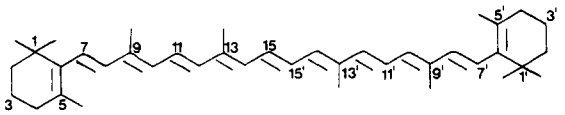
It has been proposed that carotenoid natural products are the source of part of the aromatic fraction of petroleum. In order to understand the mechanisms by which carotenoids are converted to aromatic products, an investigation of the polyene intermediates formed in the thermal degradation of β,β-carotene was initiated. As a result of this investigation, four polyene intermediates have been isolated and identified: 1,12-bis(2,6,6-trimethylcyclohex-1-enyl)-3,6,10-trimethyldodeca-1,3,5,7,9,11-hexaene, 1,12-bis(2,6,6-trimethylcyclohex-1-enyl)-3,7-dimethyldodeca-1,3,5,7,9,11-hexaene, 1,6-bis(2,6,6-trimethylcyclohex-1-enyl)-3-methylhexa-1,3,5-triene, and 1,6-bis(2,6,6-trimethylcyclohex-1-enyl)hexa-1,3,5-triene. Independent syntheses confirmed the structures of the polyene intermediates. ^{1}H NMR established the type and number of methyl substituents. Mass spectra of the saturated analogues confirmed the positions of the in-chain methyl substituents. The structures of the polyene intermediates are consistent with proposals that β,β-carotene thermally degrades by a series of symmetry-allowed electrocyclic processes followed by a thermal elimination. However, not all of the degradation products arise from electrocyclic-type processes. The presence of 1,1,3-trimethylcyclohexane and long-chain aromatics indicates that disproportionation reactions are occurring in the complex degradation reaction.

Carotenoid pigments are isoprenoid natural products characterized by a chain of conjugated double bonds with methyl branches spaced along the chain. Cyclohexenyl terminal groups with 1,1,5-trimethyl substitution are characteristic of many carotenoids, e.g., β,β-carotene (1).



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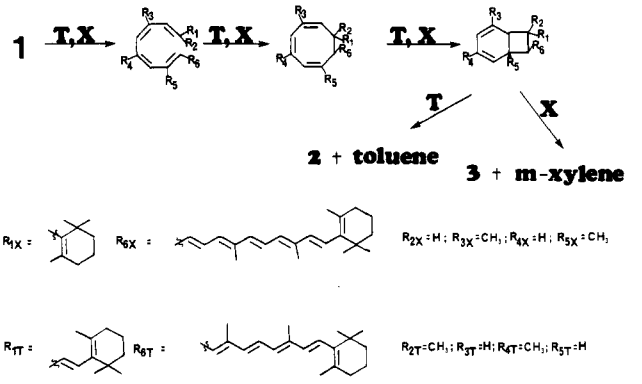
Large quantities of these pigments are generated each year in the biosphere.[1] Carotenoids in biomass and organic waste may become attractive sources of chemicals in the future. Biomass and organic waste will likely acquire an increasingly important role as a source of aromatic hydrocarbons for the chemical industry.[2]

Part of the aromatic fraction of petroleum may form from the carotenoids deposited in sedimentary environments.[3] β,β-Carotene (1) and other carotenoid natural products thermally degrade to give mainly toluene, *m*-xylene, 2,6-dimethylnaphthalene, and β-ionene.[4-7] Toluene, *m*-xylene, and 2,6-dimethylnaphthalene are common constituents of most petroleums.

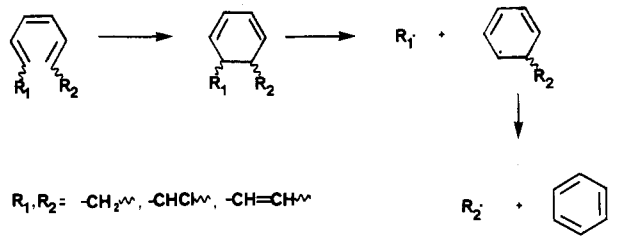
The 11 conjugated double bonds of 1 make it susceptible to thermolytic degradation. The predominance of a small number of thermal degradation products indicates that only a few of the many possible reaction pathways are energetically favorable. However, the observation of greater than 200 degradation products in the GC/MS indicates that many types of degradational reactions are occurring.

The complex nature and limited knowledge of the chemistry involved in the thermolytic degradation of

Scheme I. Proposed Mechanism for *m*-Xylene and Toluene Formation from β,β-Carotene



Scheme II. Proposed Triene Cyclization Mechanism for Polyene Degradation to Aromatics



polyenes has resulted in some seemingly contradictory mechanistic evidence in the areas of carotenoid and polyene polymer degradations.[8-14] Mass spectral investigations of the thermolysis mixtures of deuterium-labeled

(1) Schwendinger, R. B. "Organic Geochemistry, Methods and Results"; Eglinton, G., Murphy, M. T. J., Eds.; Springer-Verlag: New York, Heidelberg, Berlin, 1969; pp 425–437.
(2) Collin, G. *Chem. Int.* **1980**, *No. 6*, 16–22.
(3) Erdman, J. G. *Geochim. Cosmochim. Acta* **1961**, *22*, 16.
(4) Van-Hasselt, J. F. B. *Recl. Trav. Chim. Pays-Bas* **1911**, *30*, 1.
(5) Cholnoky, L. V.; Zechmeister, L. *Justus Liebigs Ann. Chem.* **1930**, *95*, 478.
(6) Kuhn, R.; Winterstein, A. *Ber. Dtsch. Chem. Ges.* **1932**, *65*, 1873; **1933**, *66*, 1733.
(7) Day, W. C.; Erdman, J. G. *Science* **1963**, *141*, 808.
(8) Ishiwatari, M.; J. *Anal. Appl. Pyrolysis* **1980**, *2*, 153–167.
(9) Enzell, C. R.; Wahlberg, I. "Biochemical Applications of Mass Spectrometry"; Waller, G. R., Ed.; Wiley: New York, 1980; Suppl. Vol. 1, Chapter 13B, pp 407–438.
(10) Johannes, B.; Brzezinka, H.; Budzikiewicz, H. *Org. Mass Spectrom.* **1974**, *9*, 1095.
(11) Johansen, J. E.; Eidem, A.; Liaeen-Jensen, S. *Acta Chem. Scand., Ser. B* **1974**, *B28*, 385.
(12) Starnes, W. H., Jr.; Edelson, D. *Macromolecules* **1979**, *12*, 797–802.
(13) O'Mara, M. M. *Pure Appl. Chem.* **1977**, *49*, 649.
(14) Chien, J. C. W.; Karasz, F. E.; Capistran, J.; Schen, M. "Preprints of Papers, Division of Polymer Chemistry", 183rd National Meeting, of the American Chemical Society, Las Vegas, NV, March 28–April 2, 1982; American Chemical Society: Washington, DC, 1982; p76.

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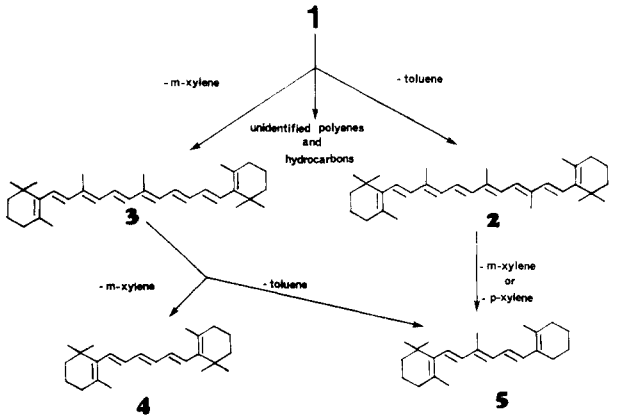
Scheme III. Polyene Hydrocarbons Formed During the Degradation of β,β-Carotene



carotenoids have shown that reaction takes place in well-defined regions of the polyene chain.[9-11] In-chain reactions occur without hydrogen shifts and formally involve scission of double bonds only.[9] In contrast, various chain-scission, hydrogen-hopping, and ring-closure-type mechanisms have been suggested in the thermal degradation of polyacetylene.[14] The octatetraene mechanism (Scheme I) has been proposed for the formation of *m*-xylene and toluene from β,β-carotene.[15] Starnes and Edelson[12] have proposed that the polyene polymer formed by the thermal elimination of HCl from polyvinyl chloride (PVC) largely decomposes via a triene-type mechanism (Scheme II) rather than the octatetraene mechanism. In contrast to the octatetraene mechanism, the triene-cyclization mechanism involves cleavage of the polymer backbone. This cleavage explains the large molecular weight reduction in the polymer associated with benzene formation in dilute solution.[16]

In an effort to better understand the mechanisms involved in the thermal decompositions of polyene hydrocarbons, an investigation of the types of intermediates formed in the thermolytic degradation of β,β-carotene (1) was initiated. As a result of this investigation, four previously unidentified polyene hydrocarbons, **2–5**, have been isolated and identified. Independent syntheses of the four polyenes confirmed their structures. The structures of **2** and **3** indicate that **2** is formed by the elimination of toluene from β,β-carotene and **3** by the elimination of *m*-xylene from β,β-carotene. Polyenes **2** and **3** undergo further degradation to form more aromatic hydrocarbons and the shorter chain polyenes **4** and **5** (Scheme III). Polyene **2** eliminates mainly *p*-xylene, **5**, some *m*-xylene, and a trace of toluene. Polyene **3** thermally degrades to give mainly toluene, some *m*-xylene, **4**, **5**, but no *p*-xylene.

Results and Discussion

Formation and Isolation. When a sample is heated at 170 °C in dodecane solvent, the absorption spectrum (300–600 nm) of *all-trans*-β,β-carotene undergoes the changes shown in Figure 1. After only a few minutes at 170 °C, the absorption maximum undergoes a small hypsochromic shift with a lowering of the extinction coefficient and the formation of a cis band.[17] All of these changes are due to the rapid formation of cis isomers from *all-trans*-β,β-carotene. After several hours at 170 °C, a large

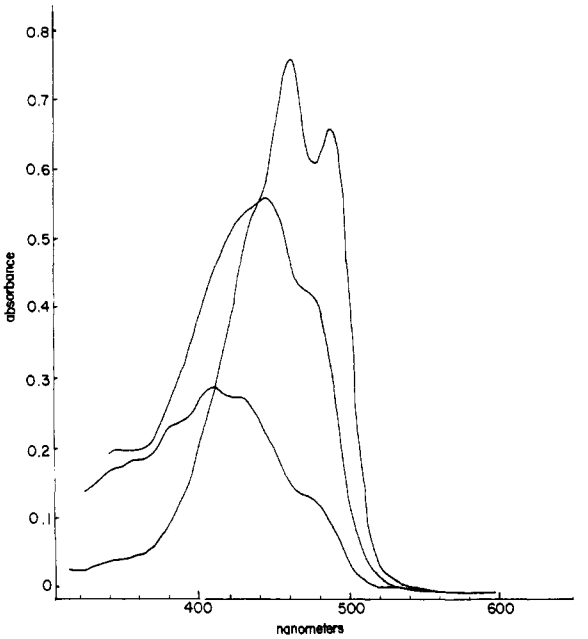


Figure 1. UV spectra of the thermal degradation mixture of β,β-carotene: (1) absorbance = 0.77, 30 min at 170 °C; (2) absorbance = 0.56, 180 min at 170 °C; (3) absorbance = 0.29, 371 min at 170 °C.

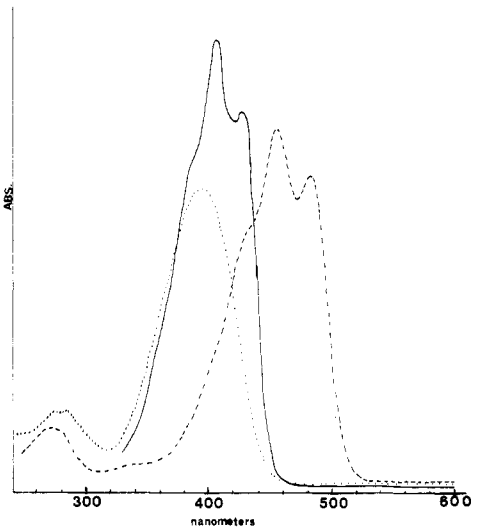


Figure 2. Absorption spectra of β,β-carotene (- - -), polyene 2 (···), and the rearrangement product of ββ-carotene (—).

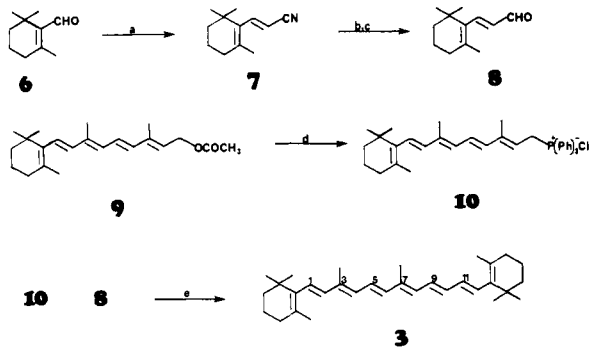
increase in absorbance values between 390 and 410 nm relative to the 440–450-nm range occurs. The increase in absorbance values is due to the formation of polyenes **2**, **3**, and a yet unidentified rearrangement product of β,β-carotene (Figure 2).

β,β-Carotene and polyene **2** thermally break down at 160 °C with first-order rate constants of 1.12×10^{-3} and 4.8×10^{-4} min^{-1}, respectively.[18,19] The slower rate of degradation results in a buildup of intermediates **2** and **3** relative to β,β-carotene. On termination of the reaction after 18 h, the concentrations of **2** and **3** were greater than the concentration of β,β-carotene.

Polyenes **2–5** were isolated from the complex degradation mixture by a series of chromatographic separations. Initial concentration of the polyene intermediates from unreacted β,β-carotene and other reaction products was

(15) Vetter, W.; Englert, G.; Rigassi, N.; and Schwieter, U. "Carotenoids"; Isler, O., Ed.; Birkhauser Verlag: Basel and Stuttgart, 1971; pp 249–250.
(16) Kelen, T. *J. Macromol. Sci., Chem.* **1978**, *12*, 349.
(17) Schwieter, U.; Englert, G.; Rigassi, N.; Vetter, W. *Pure Appl. Chem.* **1969**, *20*, 365–420.
(18) Byers, J. D.; Erdman, J. G. *Adv. Org. Geochem.*, in press.
(19) Byers, J. D., unreported results, 1981.

Scheme IV.[a] Synthesis of Polyene Intermediate 3



[a] (a) Diethyl (cyanomethyl)phosphonate, NaH, 77% yield; (b) diisobutylaluminum hydride; (c) NH_4Cl, 2 N H_2SO_4, 80% yield; (d) methanolic HCl, triphenylphosphine; (e) NaOH, 74% yield.

accomplished by chromatography on magnesium hydroxide with hexane as the eluant. The first clear fractions contained mainly polyenes **4** and **5**. The next slightly yellow fractions contained **2** and **3** along with the previously mentioned rearrangement product. High-performance liquid chromatography (HPLC) using cyano-bonded-phase silica separated polyenes **4** and **5** from polyenes **2** and **3**. The rearrangement product was obtained free of the polyenes **2**–**5**. Nonaqueous reverse-phase HPLC on C18-bonded-phase silica separated polyene **4** from **5** and polyene **2** from **3**.

Characterization. The ^1H NMR spectra of polyenes **2**–**5** are similar to that of β,β-carotene.[20] Three distinctly different types of methyl substituents are present on the polyene molecule. The in-chain methyl protons, e.g., C9, C9′, C13, C13′, on β,β-carotene **1** absorb furthest downfield at 1.95 ppm. The *gem*-dimethyl protons absorb furthest upfield at 1.05 ppm. The allylic methyl protons, e.g., C5 and C5′ on β,β-carotene, absorb at 1.70 ppm.

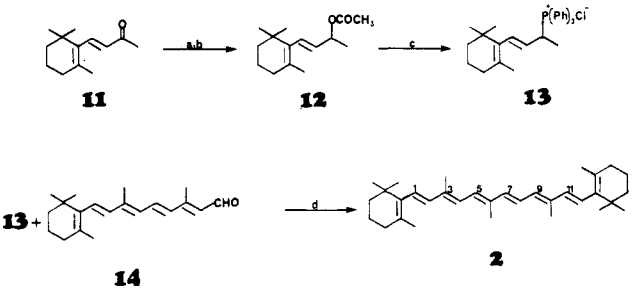
The ^1H NMR spectra of **2**–**5** allow not only the determination of the types of methyl substituents but also the number of in-chain methyl groups on the polyene chain. Polyene **2** has three in-chain methyl groups and nine olefinic protons. Polyene **3** has two in-chain methyl substituents and ten olefinic protons. Polyene **4** has no in-chain methyl groups and six olefinic protons. Polyene **5** has five olefinic protons and one in-chain methyl substituent.

The mass spectra of **2** and **3** exhibit molecular ions at *m/e* 444 and 430, respectively. Following hydrogenation, molecular ions at *m/e* 460 and 446 were noted. The data are consistent with the presence of eight double bonds in each polyene molecule. The mass spectra of **4** and **5** exhibit molecular ions at *m/e* 324 and 338, respectively. The fully hydrogenated analogues have molecular ions at *m/e* 334 and 348, respectively. Polyenes **4** and **5** each contain five double bonds per molecule.

The mass spectral fragmentation patterns of the saturated analogues of **2**–**5** are diagnostic of the in-chain methyl substitution patterns. Ions resulting from fragmentation α to in-chain methyl branches have masses 2 units less than predicted. The saturated analogue of **2** has fragment ions at *m/e* 179, 235, 249, and 305. The expected fragments were *m/e* 181, 237, 251, and 307. The saturated analogue of **3** has fragment ions at *m/e* 179, 221, 249, and 291. The expected ions were *m/e* 181, 223, 251 and 293. The saturated analogue of **5** showed ions at *m/e* 179 and

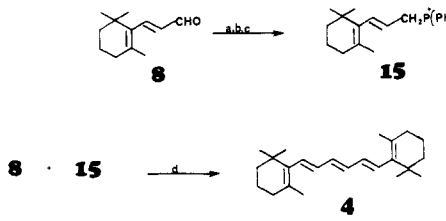
(20) Vetter, W.; Englert G.; Rigassi, N.; Schwieter, U. "Carotenoids"; Isler, O., Ed.; Birkhauser Verlag: Basel and Stuttgart, 1971; p 239.

Scheme V.[a] Synthesis of Polyene Intermediate 2



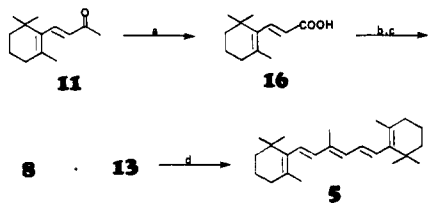
[a] (a) $LiAlH_4$, quantitative; (b) Ac_2O, pyridine, 90% yield; (c) methanolic HCl, PPh_3; (d) NaOH, 55% yield.

Scheme VI.[a] Synthesis of Polyene Intermediate 4



[a] (a) $LiAlH_4$, quantitative; (b) AC_2O, pyridine, 88% yield; (c) methanolic HCl, PPh_3; (d) NaOH, 35% yield.

Scheme VII.[a] Synthesis of Polyene Intermediate 5



[a] (a) NaOH, Cl_2; (b) $LiAlH_4$; (c) pyridinium dichromate, 85% yield; (d) NaOH, 75% yield.

193. Work is underway to establish the mechanism of this type fragmentation. The fragmentation patterns are consistent with the in-chain methyl substitution patterns shown in Scheme III.

Syntheses of 2–5. Independent syntheses of **2**–**5** were carried out in order to establish the structures of the four intermediates (Schemes IV–VII).

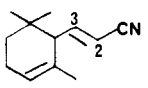
Polyene **3** was synthesized in a 74% yield by the Wittig condensation of aldehyde **8** with retinyltriphenylphosphonium chloride (**10**). Retinyl acetate (**9**) was converted to **10** by the procedure of Stern.[21] Formation of the phosphonium salt from the acetate gives a reaction product relatively free of side products such as (dehydroretinyl)triphenylphosphonium salt.

Aldehyde **8** was prepared from β-cyclocitral[22] in the following manner. β-Cyclocitral (**6**) was condensed with diethyl (cyanomethyl)phosphonate[23,24] to give the cyano product **7** in a 77% yield. The cyano product **7** was approximately 90:10 trans/cis as estimated by ^1H NMR. The cyano compound **7** was then reduced with diisobutylaluminum hydride[25] followed by mild acid hydrolysis to

(21) Stern, M. H. U.S. Patent 3517067, 1970 (assigned to Eastman Kodak Co.).
(22) Gedye, R. N.; Parkash, C. A.; Deck, K. *Can. J. Chem.* **1971**, *49*, 1764–1766.
(23) Haeck, H. H.; Kralt, T.; Van Leeuwen, P. H. *Recl. Trav. Chem. Pays-Bas* **1966**, *85*, 334–338.
(24) Ramamurthy, V.; Tustin, G.; Yau, C. C.; Liu, R. S. H. *Tetrahedron* **1975**, *31*, 193–199.

give 8 in an 80% yield. The aldehyde product 8 has a broadened doublet at 7.25 ppm for the C3 olefinic proton and a doublet of doublets at 6.2 ppm for the C2 olefinic proton. A doublet at 9.4 ppm for the aldehydic proton was observed. An alternate synthesis of 8 gave the aldehyde free of isomeric impurities (Scheme VII).[26,27]

Temperatures above 20 °C and excess sodium hydride resulted in the formation of considerable quantities of the α-cyano compound **25**. The ^{1}H NMR of **25** has a pair of



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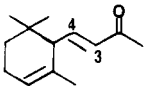

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singlets (3 H each) at 0.85 and 0.90 ppm compared to a singlet at 1.02 ppm (6 H) for the *gem*-dimethyl protons in the β isomer **7**. The C2 olefinic proton changes from a broadened doublet at 7.25 ppm in the β isomer **7** to a doublet of doublets ($J_{2,3}$ = 17 Hz, $J_{1',3}$ = 8 Hz) in the α isomer **25**. These changes are analogous to differences between the ^{1}H NMR of α- and β-ionone (**26** and **11**, respectively).[28]

Formation of the α isomer was minimized by keeping the reaction temperature lower than 0 °C and avoiding use of excess sodium hydride. Any α isomer formed was carried along as an impurity. In the final reaction step, involving sodium hydroxide, the double bond isomerized into conjugation with the other double bonds of polyene **3**. No evidence of the unconjugated isomer of **3** was obtained.

Synthetic and thermally derived **3** have identical HPLC, MS, UV, IR, and ^{1}H NMR properties. Hydrogenation of synthetic **3** gave a molecule with a mass spectral fragmentation pattern identical with that of hydrogenated material from the degradation mixture of β,β-carotene.

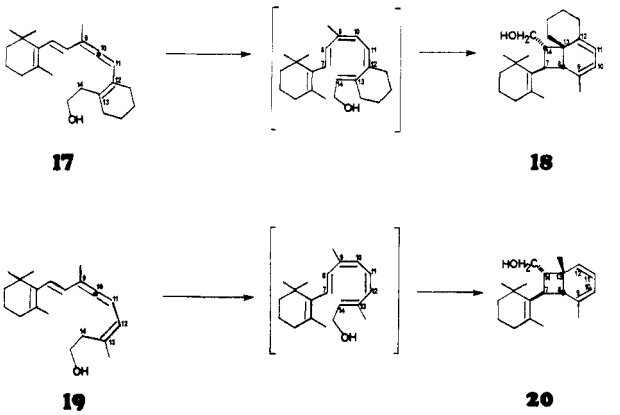
Polyene **2** was prepared in a 52% yield by the Wittig condensation of β-ionyltriphenylphosphonium chloride (**13**) with retinal (**14**) according to the procedure of Stern.[21] β-Ionyltriphenylphosphonium chloride (**13**) was prepared from β-ionone (**11**) by the procedure outlined in Scheme V. Synthetic and thermally derived **2** were identical in every respect. Hydrogenation of synthetic and thermally derived **2** gave products with identical mass spectral fragmentation patterns.

Polyene **4** was synthesized in a 35% yield by the condensation of the phosphonium salt **15** with the aldehyde **8** (Scheme VI). The synthetic product was identical with products obtained from the thermal degradation of **1** and **2**.

Polyene **5** was prepared in a 75% yield by condensation of aldehyde **8** with β-ionyltriphenylphosphonium chloride **13** (Scheme VII). The synthetic material was identical with material obtained by the thermal degradation of **1**–**3**.

Octatetraene Mechanism. The octatetraene cyclization mechanism has ample literature precedent.[29,30] The *trans,cis,cis,trans*-tetraene moiety undergoes a facile eight-electron conrotatory cyclization to give a cycloocta-1,3,5-triene which further cyclizes by a six-electron disrotatory ring closure to give a bicyclo[4.2.0]octa-2,4-diene.

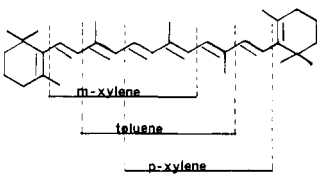
Scheme VIII. Carotenoid-Type Polyenes That Undergo the Octatetraene Cyclization



17 **18**

19 **20**

Chart I. Possible Ways to Eliminate Aromatics from Polyene 2



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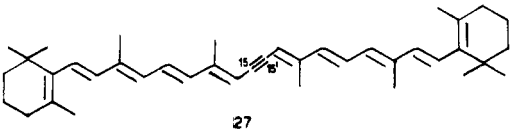
Okamura and co-workers[31,32] have reported the electrocyclization of tetraenes **17** and **19** to give the bicyclo[4.2.0]octa-2,4-dienes **18** and **20** (Chart I, Scheme VIII). Their data provide convincing evidence that carotenoid-type polyenes thermally rearrange by the octatetraene mechanism.

The importance of the cyclooctatetraene intermediate in the thermal rearrangements of carotenoid polyenes can be seen from data on the thermal decomposition of acetylenic analogues of β,β-carotene. When the C15,C15′ double bond of β,β-carotene is replaced by a triple bond as in **27**, the thermal loss of toluene and *m*-xylene is totally



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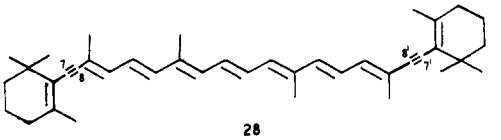
inhibited.[33] Since the C15,C15′ bond is always involved in the octatetraene cyclization, it is reasonable that substitution of a triple bond at that key position would inhibit decomposition pathways to toluene and *m*-xylene. Substitution of the C7, C8 double bond with an acetylenic bond does not inhibit the loss of toluene and *m*-xylene. The C7,C8 double bond is not always involved in the in-chain cyclizations. However, substitution of the C7,C8 and C7′,C8′ double bonds with acetylenic bonds, as in heteroxanthin (**28**), prevents the formation of $(M - 106)^{+\cdot}$ ions[9].



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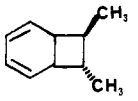
(25) Marshall, J. A.; Andersen, N. H.; Schlicher, J. W. *J. Org. Chem.* **1970**, *35*, 858–861.
(26) Lee, K. H. U.S. Patent 3966967, 1975 (assigned to Regents of the University of California at Berkeley).
(27) Corey, E. J.; Schmidt, G. *Tetrahedron Lett.* **1979**, 399–402.
(28) "Sadtler Standard Spectra"; Sadtler Research Laboratories, Inc.: Philadelphia, PA, 1980; spectra 19839M and 23059M.
(29) Marvell, E. N.; Seubert, J. *J. Am. Chem. Soc.* **1967**, *89*, 337.
(30) Huisgen, R.; Dahmen, A.; Huber, H. *J. Am. Chem. Soc.* **1967**, *89*, 7130.
(31) Okamura, W. H.; Knudsen, C. G.; Chandraratna, R. A. S.; Walkeapaa, L. P.; Chauhan, Y. S.; Carey, S. C.; Cooper, T. M.; Birge, R. R., accepted for publication in *J. Am. Chem. Soc.*
(32) Okamura, W. H.; Chandraratna, R. A. S., submitted for publication in *J. Am. Chem. Soc.*
(33) Vetter, W.; Englert, G.; Rigassi, N.; Schwieter, U. "Carotenoids"; Isler, O., Ed.; Birkhauser Verlag: Basel, Stuttgart, 1971; p 251.

m-Xylene is formed by an octatetraene cyclization mechanism utilizing the C7,C8 or C7′,C8′ double bonds. If both are substituted with acetylenic double bonds, then the pathways for xylene formation have been eliminated.

Steric interactions of the substituents on the cyclobutyl ring of the bicyclic intermediate play a large role in its formation and decomposition. Intermediate **29** is formed



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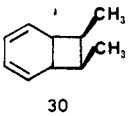

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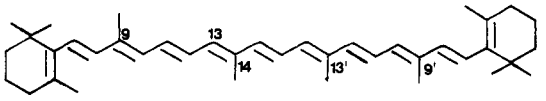
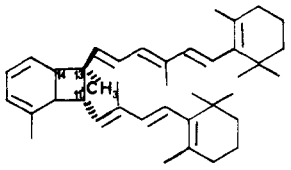


31

at a lower temperature (20 vs. 40 °C) and more irreversibly than intermediate **30**.[30] The two cis methyl groups in **30** add additional strain to the bicyclic intermediate.

Steric constraints are also important in the thermal rearrangements of polyene hydrocarbons. Schwieter et al.[17] reported results that demonstrate the importance of steric factors in the thermal elimination reactions of β,β-carotene (**1**) and unsymmetrical β,β-carotene **31**. By shifting the C13 methyl group to C14, the mass spectral intensity ratio of the $(M - 92)^{+\cdot}$ and $(M - 106)^{+\cdot}$ peaks (I_{M-92}/I_{M-106}) is reduced from 12.9 for β,β-carotene to 0.56 for **31**. The number of structurally possible ways to eliminate toluene and *m*-xylene remains the same in the two cases. In β,β-carotene, the cyclobutyl group of intermediate **32** has a



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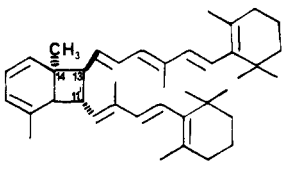


33

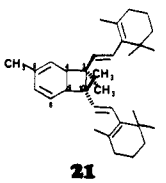
quaternary carbon at C13 while in **33** only two tertiary carbons are at the C13 and C11′ positions. The less sterically hindered intermediate **33** results in an enhancement in the formation of *m*-xylene. By movement of the methyl group from C13 to C14, one of the pathways for toluene formation has also been sterically inhibited.

If the cyclic end groups are replaced by acyclic substituents, a large decrease in the intensity ratio I_{M-92}/I_{M-106} is observed.[9] This decrease is due to the replacement of a bulky cyclohexene substituent with a less space-demanding acyclic substituent, resulting in an increase in the formation of *m*-xylene.

Steric factors also explain why toluene is formed in much greater yields than *m*-xylene. The intensity ratio of the $(M - 92)^{+\cdot}$ to the $(M - 106)^{+\cdot}$ peaks in the mass spectrum of the thermal degradation mixture of β,β-carotene is 12.9. An intensity ratio of 2 would be expected on the basis of the number of ways to eliminate toluene (4) and *m*-xylene (2). Steric restraints from the bulky cyclohexene ring cause *m*-xylene not to be formed in the amount predicted.

The importance of steric factors to the thermal degradation of polyene hydrocarbons can be seen in the thermal decomposition of polyene **2**. There are three different ways polyene **2** can undergo the octatetraene cyclization to give aromatic hydrocarbons. Each region of the polyene chain undergoing cyclization gives a different aromatic hydrocarbon (Chart II). An examination of molecular models of the three bicyclic intermediates **21–23** leads to the prediction that *p*-xylene should be preferentially formed

Chart II. Proposed Intermediates in the Thermal Decomposition of 2



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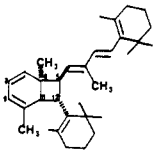

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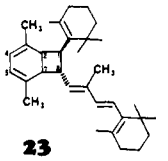

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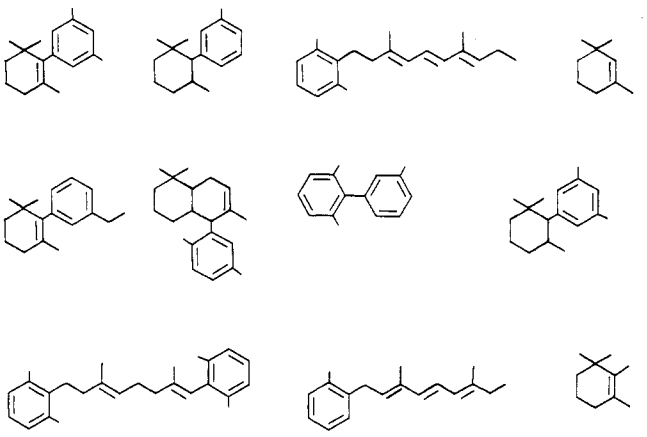
Chart III. Tentative Structures of Products Identified by GC/MS in the Degradation of β,β-Carotene



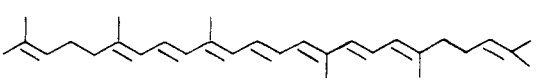
in comparison to *m*-xylene and that toluene should be formed in very small amounts (Chart III). The bicyclic intermediate **21** leading to the formation of toluene has two contiguous quaternary carbons (C3 and C10) on the cyclobutyl ring. As a result, it should be the least favored of the three bicyclic intermediates. The intermediate leading to *m*-xylene, **22**, has an extra methyl–cyclohexenyl steric interaction not found in the intermediate **23** for *p*-xylene formation. As predicted, the ratio of *p*-xylene to *m*-xylene to toluene was 42:14:1. The *p*-xylene formed in the thermal degradation of β,β-carotene probably forms from the polyene intermediate **2**.

Polyene **3** undergoes thermal degradation to give toluene and *m*-xylene (7.5:1, respectively) with no formation of *p*-xylene. The same steric factors leading to the preferential formation of toluene in β,β-carotene apply to **3**.

The slower rates of degradation of **2** and **3** relative to β,β-carotene are probably due to the increased steric constraints associated with the cyclization of shorter chain polyenes.

Earlier work has indicated that carotenoids possessing fewer than nine double bonds do not usually give rise to losses of xylene but do frequently eliminate toluene.[9] In light of these observations, it is interesting that polyene **2** (eight double bonds) preferentially loses xylene.

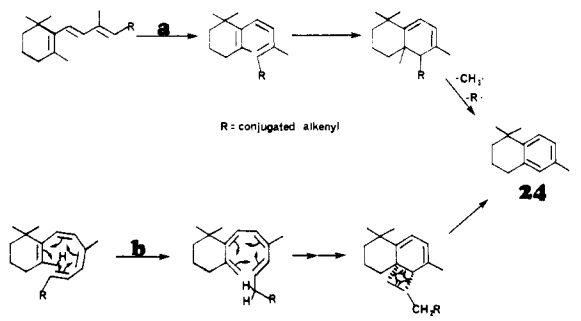
The triterpenoid **34** should theoretically give rise only to losses of toluene. However, the intensity ratio of **34** was



34

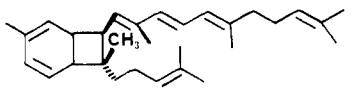
1.3.[9] This deviation may be explained by isomerizations and the steric interactions in the bicyclic intermediates. The four possible ways of forming toluene from **34** have

Scheme IX.[a] Proposed Mechanisms for β-Ionene Formation from β,β-Carotene



[a] (a) reference 12; (b) reference 18.

bicyclic intermediates with quaternary carbons in the cyclobutyl rings, e.g., **35**. The steric strain of such inter-



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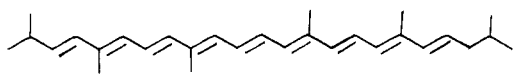


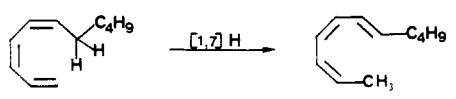
36

mediates should slow down or inhibit the toluene-producing reaction. Under thermal stress, the isolated double bonds of **34** can migrate into conjugation resulting in the polyene **36**. The low intensity ratio of **36** (1.3) compared to that of β,β-carotene (12.9) results from fewer steric constraints from the acyclic end groups of **36**.

Conclusion

Substantial evidence has been presented in support of the proposal that polyene hydrocarbons thermally degrade by the octatetraene mechanism. However, experimental evidence suggests that other mechanisms are occurring in the degradation process. A simple electrocyclic mechanism cannot explain the formation of products such as 1,1,3-trimethylcyclohexane, *o*-xylene, and 1-methyl-3-ethylbenzene. 1,1,3-Trimethylcyclohexane and 1-methyl-3-ethylbenzene are formed in quantities equal to that of the xylenes and toluene. Preliminary GC/MS data indicate the presence of the products shown in Chart III. From the tentative structural data, it appears that disproportionation reactions giving aromatic and saturate hydrocarbons are occurring in the degradation reaction.

The major hydrocarbon formed in the thermal degradation of β,β-carotene is β-ionene (**24**). At higher temperatures, β-ionene yields can approach 50%.[34] Two mechanisms have been proposed for the formation of β-ionene (Scheme IX).[12,18] One of the mechanisms proposes an unusual [1,9] hydrogen shift. Molecular models indicate that the [1,9] sigmatropic rearrangement would be favored by the positioning of the orbitals. In the triene **37** a [1,7]



37

shift takes place upon heating. The helical geometry of the triene favors such an unusual rearrangement.[35] Either of the two mechanistic proposals or other mechanisms for β-ionene formation cannot be unequivocally proven until the thermal decompositions of appropriately labeled products are investigated.

Other polyene hydrocarbon intermediates have been isolated from the thermal degradation mixture of β,β-carotene. The unidentified rearrangement product, mentioned previously, has the same molecular weight as β,β-carotene but a significantly shorter conjugated polyene chain (as evidenced by its absorption spectrum). Further heating of the rearrangement product did not produce the polyenes **2** or **3**. The rearrangement product has a greater thermal stability than **2**, **3**, or β,β-carotene. Further work will establish the structure of the rearranged β,β-carotene. An isomerized lycopene[17] has been reported which is thermally more stable and no longer capable of losing toluene and *m*-xylene. The isomerized lycopene and rearranged β,β-carotene may have similar structural characteristics.

Experimental Section

β,β-Carotene was purchased from Aldrich Chemical Co. and recrystallized from benzene–methanol before use in the degradation experiments. Retinal and retinyl acetate were used as received from Sigma Chemical Co.

High-performance liquid chromatography (HPLC) was carried out by using a Waters Model 203 liquid chromatograph equipped with a Model 440 fixed-wavelength absorbance detector. Wavelengths commonly monitored were 436, 405, and 313 nm.

Mass spectra of the polyene products were obtained by solid probe injection into a Finnigan Model 4000 mass spectrometer. Very rapid heating of the probe to 300 °C resulted in minor thermal degradation prior to introduction of the molecules into the 70-eV electron beam. The mass spectra showed intense molecular ions.

GC/MS of the hydrogenated polyenes was obtained by gas chromatography on a SE-54 0.24-mm glass capillary column (2 m). The gas chromatograph was interfaced with a Finnigan Model 4000 mass spectrometer.

Individual components of the thermal degradation mixtures were identified by GC/MS (Perkin-Elmer Sigma II chromatograph and a Kratos MS 24 mass spectrometer). Separations were made with a SE-54 glass capillary column (60 m × 0.24 mm). A temperature program of 4 °C/min from 44 to 300 °C was used. Hexane was used as the solvent. The mass spectrometer was operated in the EI mode at 70 eV. Standard compounds were used as references by coinjection.

m-Xylene was separated from *p*-xylene by GC on 5% SP-1200, 1.75% Benton 34, and 100/120 Supelcort (6 ft × $^1/_8$ in.) at an isothermal temperature of 80 °C.

NMR data were obtained on a Varian EM-390 spectrometer operating at 90 MHz. $CDCl_3$ was used as a solvent with tetramethylsilane (Me_4Si) as a standard.

Absorbance spectra of the products were obtained on a Perkin-Elmer Model 320 spectrophotometer. Quartz cells with a 20-mm path length were commonly used.

IR spectra were obtained on a Perkin-Elmer 283B infrared spectrophotometer in the neat form on sodium chloride plates.

Thermal Degradations of Polyenes 1–3. The thermal degradations of the polyenes were carried out by dissolving the polyenes in deoxygenated *n*-dodecane or hexane (concentrations of approximately 170 mg/mL) and flame sealing the cold solutions under vacuum in thick-walled glass tubes. Thermolyses of the *n*-dodecane solutions were carried out at 170–200 °C for 15–18 h by using an oil bath controlled to ±0.02 °C. Care was taken not to expose the heated solutions to light. The hexane solutions were heated at 170 °C for 1–5 days. The thick-walled tubes were placed in hexane in an autoclave and heated to a temperature

(34) Edmunds, F. S.; Johnstone, R. A. W. *J. Chem. Soc.* **1965**, 2892–2897.

(35) Fleming, I. "Frontier Orbitals and Organic Chemical Reactions"; Wiley: Chichester, New York, Brisbane, Toronto, 1976; pp 99–100.

of 170 °C. This prevented excessive pressure on the glass tubes.

Thermolysis mixtures from heating β,β-carotene at 170 °C in hexane or dodecane were almost identical by GC/MS with thermolysis mixtures from heating neat β,β-carotene (no solvent) at 275 °C for 1 h.

Thermal degradation of β,β-carotene at 145 °C for 13 days gave a 19.0% yield of toluene and a 3.39% yield of the xylenes. At the end of 13 days, β,β-carotene and polyenes **2** and **3** were still present in substantial amounts.

After cooling the degradation mixture to room temperature, the solution was loaded onto magnesium hydroxide packed with hexane as the solvent. The column was developed with hexane. Care was taken not to expose the adsorbed polyene products to light.

Separation of the rearranged β,β-carotene from the polyenes **2–5** was achieved by HPLC on 5-μm Spherisorb cyano packing (60 cm × 4.1 mm) with hexane as the eluant. The flow rate was 0.6 mL/min. Absorbances at 436 and 313 nm were monitored. The first-eluting peak contained mainly **4** and **5** while the second peak contained **2** and **3**.

Polyene **2** was separated from **3** by HPLC on 5-μm C18 packing (Waters Radial Compression column, 8 mm × 10 cm) with methanol as the eluant. The flow rate was 2 mL/min. Absorbance was monitored at 436 nm. The retention volumes of **2** and **3** were 39.2 and 35.2 mL, respectively.

Polyene **4** was separated from **5** by HPLC on the C18 packing with methanol as the eluant. Absorbance was monitored at 313 nm. The flow rate was 2 mL/min. The retention volumes of **4** and **5** were 16.24 and 18.24 mL, respectively.

^{1}H NMR, MS, IR, and UV for all isolated polyenes (**2–5**) were identical with those described for the synthetic products.

Preparation of 3-(2,6,6-Trimethylcyclohex-1-enyl)prop-2-enenitrile (7). The experiment was carried out in a dry apparatus with an argon atmosphere. Sodium hydride (50% dispersion in mineral oil, 1.92 g, 0.04 mol) was added to dry tetrahydrofuran (30 mL), and the mixture was cooled to 0 °C. A solution of diethyl (cyanomethyl)phosphonate (7.08 g, 0.04 mol) in dry tetrahydrofuran (10 mL) was added dropwise to the sodium hydride suspension. After the addition was complete, the reaction mixture was stirred 1 h at room temperature. A solution of β-cyclocitral (**6**; 6 g, 0.04 mol) in THF (40 mL) was added dropwise with ice bath cooling. The reaction mixture was stirred 5 h at 0 °C, and the mixture poured into 0.5 L of water. After saturation of the aqueous layer with sodium chloride, the product was extracted with diethyl ether. The combined extracts were dried over magnesium sulfate, and following filtration, the solvent was removed by distillation at atmospheric pressure. The residue was distilled at 0.08 mmHg: bp 110–115 °C; yield 77%; MS, calcd for $C_{12}H_{17}N$ *m/e* 175.1361, found *m/e* 175.1368; ^{1}H NMR ($CDCl_3$) 1.05 (s, 6 H, *gem*-dimethyl), 1.50 (m, 4 H, CH_2), 1.52–1.75 (CH_2), 1.82 (allylic CH_3), 2.05 (2 H, CH_2—C=C), 5.25 (1 H, d, J = 17 Hz, =CHCN), 7.02 ppm (1 H, br d, J = 17 Hz, CH=C); UV (hexane) 272 nm; IR (neat) 2219 (nitrile), 1364, 1385 (*gem*-dimethyl), 1378 (methyl), 970 cm^{-1} (*trans*-alkene).

Preparation of 3-(2,6,6-Trimethylcyclohex-1-enyl)prop-2-enal (8). The nitrile **7** (5.23 g, 0.03 mol) was dissolved in dry hexane (250 mL) and placed in a dry apparatus under an argon atmosphere. The solution was cooled to −60 °C and diisobutylaluminum hydride (1 M in hexane, 60 mL, 0.06 mol) added in one portion. The mixture was stirred at −60 °C for 30 min and at 0 °C for 5 h. Ethyl formate (6 mL) was added dropwise, and stirring was continued for 1 h at 0 °C. Saturated ammonium chloride solution (100 mL) was added, and stirring was continued for 1 h at ambient temperature. Aqueous sulfuric acid (2 N) was added and the product extracted with diethyl ether. The extracts were washed one time with saturated sodium chloride solution and then dried over magnesium sulfate. After removal of the solvent, the product was distilled at 0.08 mmHg (75–80 °C): yield 80%; MS, calcd for $C_{12}H_{18}O$ *m/e* 178.1358, found *m/e* 178.1350; ^{1}H NMR ($CDCl_3$) 1.10 (s, 6 H, *gem*-dimethyl), 1.50–1.75 (CH_2) 1.80 (s, 3 H, CH_3), 2.10 (2 H, CH_2—C=), 5.9–6.3 (1 H, =CHCHO), 7.25 (1 H, d, J = 17 Hz, CH=C) 9.4 ppm (1 H, d, CHO); UV (hexane) 281 nm; IR (neat) 1690 (carbonyl), 973 (*trans*-alkene), 1368, 1388 (*gem*-dimethyl), 1380 (methyl), 2720 cm^{-1} (CHO).

Preparation of Retinyltriphenylphosphonium Chloride (10). Retinyl acetate (**9**; 1 g, 0.0032 mol), triphenylphosphine (0.9593 g, 0.0037 mol), and methanol (1.8 mL) were mixed and heated to 30 °C under an argon atmosphere. A solution of hydrogen chloride in methanol (0.135 g, concentration 0.197 g/mL, 0.69 mL) and methanol (2 mL) were added dropwise to the solution of retinyl acetate. The addition took approximately 15 min. The resulting clear solution was stirred at 30–35 °C for 2 h. The reaction product was used without isolation or purification.

Preparation of 1,12-Bis(2,6,6-trimethylcyclohex-1-enyl)-3,7-dimethyldodeca-1,3,5,7,9,11-hexaene (3). The retinyltriphenylphosphonium chloride prepared above was added at the same time as a solution of potassium hydroxide (0.404 g, 0.007 mol) in methanol (4 mL) to a solution of aldehyde **8** (0.5705 g, 0.0032 mol) precooled to 0 °C. The reaction mixture was stirred for 30 min at 0 °C and 2 h at room temperature. The reaction mixture was then poured into water and extracted several times with diethyl ether. The combined ethereal extracts were washed once with water and then dried over magnesium sulfate. Following filtration, the solvent was removed under reduced pressure. The residue was mixed with hexane and loaded onto a basic alumina (Brockman activity grade I) column (150 g). The column was developed with hexane. The orange band eluting with hexane contained pure **3**: yield 74%; ^{1}H NMR ($CDCl_3$) 1.05 (s, 12 H, *gem*-dimethyl), 1.40–1.70 (8 H, CH_2), 1.70 (6 H, C2′ and C2″ CH_3), 1.95 (10 H, in-chain methyls and CH_2C=C), 6.0–6.8 ppm (10 H, olefinic protons); UV (hexane) 389 nm; MS, *m/e* 430 (base peak M^+), 428, 415, 378, 361, 346, 320, 265, 240, 225, 201, 175, 157, 133, 109; calcd for $C_{32}H_{46}$ *m/e* 430.3600, found *m/e* 430.3584.

Preparation of β-Ionyl Acetate (12). β-Ionone (**11**) was reduced with $LiAlH_4$ to give β-ionol. β-Ionol (10.30 g, 0.053 mol) was dissolved in acetic anhydride (10.81 g, 0.106 mol) and pyridine (9.12 g, 0.115 mol). The reaction was carried out under an argon blanket. The reaction mixture was stirred 6 h at room temperature. Ice–water (100 mL) was added, and stirring was continued for 15 min. The aqueous layer was then extracted with diethyl ether. The combined ethereal extracts were washed successively with 2 N HCl, saturated sodium bicarbonate solution, and water. The extracts were then dried over magnesium sulfate and filtered, and the solvent was removed under reduced pressure: yield 90%; ^{1}H NMR ($CDCl_3$) 1.00 (s, 6 H, *gem*-dimethyl), 1.98–2.02 (5 H, $OC(O)CH_3$ + CH_2—C=C), 1.65 (3 H, C=CCH_3), 1.2–1.6 (7 H, CH_2, $C(OAc)CH_3$), 6.10 (br d, 1 H, C^3H=C—COAc, J = 15 Hz), 5.22–5.6 (1 H, C=C^4HCOAc), 3.5 ppm (1 H, CHOAc); IR (neat) 1735 (acetate carbonyl), 1235 cm^{-1} O—C=O).

Preparation of (β-Ionyl)triphenylphosphonium Chloride. β-Ionyl acetate (2.56 g, 0.01 mol), triphenylphosphine (2.86 g, 0.011 mol), and methanol (4 mL) were heated to 35 °C under an argon atmosphere. Methanolic hydrogen chloride (1.86 mL, concentration 0.197 g/mL, 0.366 g, 0.01 mol) was added dropwise and the reaction mixture stirred at 35 °C for 2 h. The resulting product was used without purification or isolation.

Preparation of 1,12-Bis(2,6,6-trimethylcyclohex-1-enyl)-3,6,10-trimethyldodeca-1,3,5,7,9,11-hexaene (2). The solution of β-ionyltriphenylphosphonium chloride prepared above was added at the same time as a solution of potassium hydroxide (0.80 g, 0.0143 mol) and methanol (5 mL) to a methanol (4 mL) solution of retinal (1.0 g, 0.035 mol) at 0 °C. The reaction mixture was warmed to room temperature and stirred overnight. The reaction mixture was diluted with water and the aqueous mixture extracted several times with diethyl ether. The combined extracts were washed once with water and then dried over magnesium sulfate. Following filtration, the solvent was removed under reduced pressure. The residue was mixed with hexane and loaded onto a basic alumina column (Brockman grade I, 150 g). The chromatography column was developed with hexane. The orange band eluting with hexane contained pure **2**: 55% yield; ^{1}H NMR ($CDCl_3$) 1.05 (s, 12 H, *gem*-dimethyl), 1.40–1.70 (8 H, CH_2), 1.70 6 H, C2′ and C2″ CH_3), 1.95 (13 H, in-chain methyls and CH_2—C=C), 6.0–6.8 ppm (9 H, olefinic protons); UV (hexane) 386 nm; IR (neat) 2840–3150 (CH), 970 (*trans*-alkene), 1363, 1387 (*gem*-dimethyls), 1380 cm^{-1} (methyl); MS, *m/e* 444 (molecular ion, base peak), 442, 429, 399, 359, 333, 307, 267, 239, 211, 159, 133, 119, 105.

Preparation of 1,6-Bis(2,6,6-trimethylcyclohex-1-enyl)-hexa-1,3,5-triene (4). The triphenylphosphonium salt **15** was prepared from the aldehyde **8** in a manner identical with the conversion of β-ionone (**11**) to β-ionyltriphenylphosphonium

chloride (13). The methanol solution of the phosphonium salt 15 was added at the same time as a solution of potassium hydroxide (0.80 g, 0.0143 mol) and methanol (5 mL) to a methanol-ether (4 mL) solution of aldehyde 8 (6.23 g, 0.035 mol) at 0 °C under an argon atmosphere. The reaction mixture was allowed to warm to room temperature and was stirred overnight. The reaction mixture was diluted with water and the aqueous mixture extracted several times with diethyl ether. The combined extracts were washed once with water and then dried over magnesium sulfate. Following filtration, the solvent was removed under reduced pressure. The residue was mixed with hexane and loaded onto a basic alumina column (Brockman grade I, 150g). The product was eluted with hexane. The first few fractions of 4 contained a retro-type polyene. These fractions were discarded without any further purification. A 35% yield of pure 4 was obtained. HPLC showed two major isomers at 14.48- and 16.24-mL retention volumes: ^{1}H NMR ($CDCl_3$) 1.04 (s, 12 H, *gem*-dimethyls), 1.4-1.70 (8 H, CH_2), 1.71 (6 H, C2′ and C2″ CH_3), 1.9-2.1 (br m, CH_2—C=C, 4 H), 6.05-6.80 ppm (6 H, alkene protons); IR (neat) 2840-3150 (CH), 970 (*trans*-alkene), 1363, 1387 (*gem*-dimethyls), 1380 (methyl); UV (methanol) 312 nm (16.24-mL HPLC peak) 308 (14.48-mL HPLC peak). The shorter wavelength of the 14.48-mL peak indicates cis stereochemistry. A cis peak was also noted fo the 14.48-mL peak. Each collected HPLC peak gave identical mass spectra for the saturated and unsaturated analogues: MS, *m/e* 324 (molecular ion, base peak), 322, 309, 105; calcd for $C_{24}H_{36}$ *m/e* 324.2817, found *m/e* 324.2810.

Preparation of 1,6-Bis(2,6,6-trimethylcyclohex-1-enyl)-3-methylhexa-1,3,5-triene. β-Ionyltriphenylphosphonium salt 13 (20.784 g, 0.044 mol) in methanol (7 mL) was added at the same time as a solution of potassium hydroxide (0.80 g, 0.014 mol) and methanol (5 mL) to a methanol (4 mL) solution of 8 (6.23 g, 0.035 mol) at 0 °C under an argon atmosphere. The reaction mixture was worked up as previously described. A 75% yield of pure 5 was obtained. Some retro product was removed by chromatography. HPLC showed two peaks (isomers) at 17.36- and 18.24-mL retention volumes: ^{1}H NMR ($CDCl_3$) 1.06 (s, 12 H, *gem*-dimethyls), 1.4-1.70 (8 H, CH_2), 1.71 (6 H, C2′ and C2″ CH_3), 1.9-2.1 (7 H, in-chain methyl and CH_2—C=C), 6.08-6.82 ppm (5 H, alkenyl protons); UV (methanol) 314 nm (18.24-mL peak) 309 (17.36-mL peak); MS, *m/e* 338, 336, 323, 105; calcd for $C_{25}H_{38}$ *m/e* 338.2974, found *m/e* 338.2964.

Hydrogenation of Polyene Intermediates 2-5. Each polyene intermediate (1 mg) was dissolved in ethyl acetate (5 mL) at room temperature. Palladium on activated carbon (100 mg) was added, and the hydrogenation carried out for 8 h at room temperature with stirring under a hydrogen gas pressure of 50 psi. The catalyst was removed by filtration and the sample concentrated in vacuo. No UV maxima in hexane were noted after hydrogenation: IR (neat) 2830-2950 (CH), 1458 (CH_2), 1362, 1380 (*gem*-dimethyl), 1370 (methyl); MS (saturated analogue of 3 - *m/e* 446) *m/e* 431, 390, 291, 249, 221, 179, 138, 125 (base peak), 111. MS (saturated analogue of 2 - *m/e* 460) *m/e* 445, 404, 305, 249, 235, 179, 138, 125 (base peak), 111. MS (saturated analogue of 4 - *m/e* 334) 319, 278, 125 (base peak), 111. MS of (saturated analogue of 5 - *m/e* 348) *m/e* 333, 292, 179, 193, 125 (base peak), 111.

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Gas-Phase Diels-Alder Reaction of the *o*-Quinodimethane Radical Cation and Neutral Styrene

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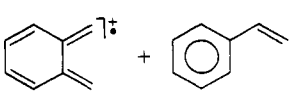
The collision complex formed in the ion-molecule reaction of *o*-quinodimethane radical cation and neutral styrene was investigated by using mass spectrometry/mass spectrometry (MS/MS) techniques. The reaction was conducted in a high-presure chemical-ionization source, where the reagents were ionized by low-energy charge exchange and the reaction products were collisionally stabilized. The collision complex was shown to have the structure of 2-phenyltetralin through the use of deuterium labeling and direct comparison with the properties of reference radical cations. These results establish the structural integrity of low-energy *o*-quinodimethane radical ions and are evidence for a Diels-Alder reaction mechanism.

Cycloaddition reactions, particularly the Diels-Alder reaction, are of considerable interest in both theoretical and experimental organic chemistry. However, there have been few reports of cycloadditions which involve radical cations reacting in either the gas phase[1] or in solution.[2] Furthermore, in the studies conducted of gas-phase reactions, no cycloadduct has been isolated and directly examined usually because the exothermicity of the reaction drives the adduct to dissociate to other products. Thus, indirect methods such as isotope labeling and product analysis have been employed to infer the structure of the intermediate.[1]

This is a report of the structure determination of the intermediate formed in the gas-phase reaction involving the *o*-quinodimethane radical cation (I) and styrene neutral (II) as depicted in eq 1. The approach makes use of the



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(1) See: Russell, D. H.; Gross, M. L. *J. Am. Chem. Soc.* **1980**, *102*, 6279 and references cited therein.
(2) Bellville, D. J.; Bauld, N. L. *J. Am. Chem. Soc.* **1982**, *104*, 2665. Bellville, D. J.; Wirth, D. D.; Bauld N. L. *Ibid.* **1981**, *103*, 718.

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