

infrared analysis) and 2.5 g. (19%) of crude XX. This material was chromatographed on alumina, then recrystallized from acetonitrile to give colorless plates, m.p. 136–139°. Infrared absorption gave the following (CHCl_3): 6.23 (s), 7.5 (s), and 9.0 (s) μ .

Anal. Calcd. for $\text{C}_{20}\text{H}_{16}\text{Cl}_2\text{NOP}$: C, 61.87; H, 4.15; Cl, 18.26; N, 3.61. Found: C, 61.97; H, 4.33; Cl, 18.05; N, 3.65.

Salt XXI was dehydrohalogenated as follows. A solution of 500 mg. of XXI in water was treated with excess sodium carbonate. There was collected 350 mg. of phosphorane XXII, m.p. 192–195° (from ethyl acetate), undepressed upon admixture of authentic material.³⁴

Ketenimine XXIV. A solution of 3.7 g. (0.022 mole) of triethyl phosphite in 10 ml. of benzene was added to 5 g. of chlorodiphenylacetonitrile in 20 ml. of benzene. The mixture was refluxed until gas evolution stopped. (The gas was collected by passing it through deuteriochloroform; n.m.r. analysis showed it to be ethyl chloride.³⁵) The solution was evaporated and the residue was suspended in ether and filtered. There was collected 300 mg. of tetraphenylsuccinonitrile (XXV), m.p. 210–213°. Recrystallization raised

(34) Prepared by Dr. K. W. Ratts.

(35) The spectrum obtained was identical with that reported for ethyl chloride in the NMR Spectra Catalog, Vol. 1, Varian Associates, Inc., Palo Alto, Calif, 1962.

the melting point to 210–215°, undepressed (213–216°) upon admixture of authentic material, m.p. 211–216°, prepared by the method of Auwers.³⁶

The ethereal filtrate was evaporated; 6.6 g. of yellow oil (crude XXIV) remained; infrared absorption showed (capillary film): extremely intense absorption at 4.95 μ . N.m.r. absorption showed (CDCl_3): singlet at τ 2.76, multiplet at 6.03, and multiplet at 8.85 peak areas in the ratio 10:3.8:5.8 (theory 10:4:6).

Hydrolysis of XXIV. To a solution of 2.0 g. (6.1 mmoles) of XXIV in 15 ml. of acetone was added 1 ml. of water and 3 drops of concentrated hydrochloric acid. The solution was refluxed for 1 hr. and stirred overnight at room temperature. It was then diluted with water and extracted with chloroform. The extracts were washed, dried, and evaporated to 1.6 g. of viscous oil. Chromatography on silica gel followed by recrystallization from methylcyclohexane yielded a white solid, m.p. 114–115°; infrared absorption spectrum (CHCl_3) revealed a carbonyl band at 5.85 μ .

Anal. Calcd. for $\text{C}_{18}\text{H}_{22}\text{NO}_4\text{P}$: C, 62.24; H, 6.39; N, 4.03; P, 8.92. Found: C, 62.06; H, 6.30; N, 3.97; P, 8.75.

Acknowledgment. R. D. P. wishes to acknowledge many fruitful discussions with Dr. K. Wayne Ratts.

(36) K. Auwers and V. Meyer, *Ber.*, 22, 1227 (1889).

The Preparation and Reactions of a Homologous Series of Aliphatic Polyenylic Cations

T. S. Sorensen

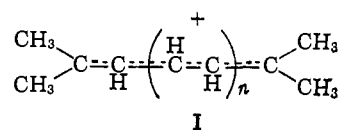
Contribution from the Department of Chemistry, University of Alberta, Calgary, Alberta, Canada, Received May 7, 1965

Solutions of a number of stable, aliphatic polyenylic cations have been obtained in concentrated sulfuric acid and other strong acids. The structure of the ions has been proven using n.m.r. and ultraviolet spectroscopy. The cyclization reaction of these ions was investigated, the structure of the resulting carbonium ions was deduced, and a comparison of the $T_{1/2}$ values for this reaction was made. Free-radical formation was shown for one of the higher members during its oxidative decomposition by the sulfuric acid. An attempt has been made to relate the n.m.r. proton shifts with the excess positive charge density on the carbon atoms to which the protons are bonded. The value of this proportionality constant was found to be about 13–15 p.p.m. per electron charge. A linear relationship between λ_{max} and n is found for the electronic spectra of the ions. A number of new polyenes have been synthesized in this work and characterized by all of the usual physical tools.

Introduction

The preparation of the carbonium ions I ($n = 0$ and 1) have been recently reported.^{1–3} Ion I ($n =$

1) is particularly interesting because of the subsequent slow cyclization reaction which it undergoes and which



now appears to be a general reaction for dienylic cations. It thus became of interest to attempt to extend the number of double bonds in I, to study the effects of this presumed further delocalization of the positive charge by n.m.r. and ultraviolet spectroscopy, and particularly to examine any cyclization reactions in view of the multiple sites now available for this process.

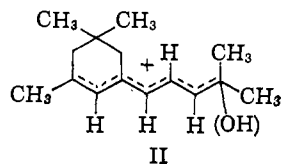
Only one previous example of a stable aliphatic polyenylic cation of established structure has been reported.² The ion II has been prepared by dissolving the corresponding alcohol in concentrated sulfuric acid. This ion however has a rather complex n.m.r. spec-

(1) N. C. Deno, H. G. Richey, Jr., N. Friedman, J. D. Hodge, J. J. Houser, and C. U. Pittman, Jr., *J. Am. Chem. Soc.*, **85**, 2991 (1963).

(2) N. C. Deno, C. U. Pittman, Jr., and J. O. Turner, *ibid.*, **87**, 2153 (1965).

(3) T. S. Sorensen, *Can. J. Chem.*, **42**, 2768 (1964).

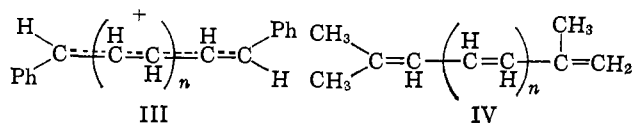
trum and significantly, appears to be stable toward cyclization. The corresponding tetraene can be re-



covered from the sulfuric acid solution by the usual high-dispersion technique.

The interaction of polyenes with concentrated sulfuric acid has long been known to produce brightly colored solutions. Kuhn and Grundmann report⁴ that tetradeca-1,3,5,7,9,11-hexaene produces a blue color in this solvent. The Carr-Price test is another diagnostic tool, involving a color reaction between polyenes and antimony trichloride. Like many diagnostic color tests however, the actual structure of the colored species in these solutions is not known. Wassermann has studied the interaction between several carotenoid polyenes and trichloroacetic acid in nonpolar solvents and has shown⁵ the existence of carbonium ion-trichloroacetate ion pairs. Recently, De Vries has presented ultraviolet evidence for the existence of a tetraenylic cation, in which cyclopentenyl rings occupy the end positions.⁶

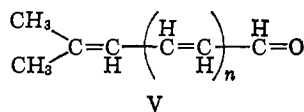
The above discussion has been limited to aliphatic carbonium ions. Hafner and Pelster⁷ have, for example, reported the actual isolation of phenyl-substituted polyenylic cation salts of structure III ($n = 0-3$); however, the ultraviolet data presented are only qualitative in nature.



Results

The ion represented by structure I ($n = 1$) was originally chosen for study because of the anticipated simplicity of its n.m.r. spectrum. This ion was formed by protonation of 2,6-dimethyl-1,3,5-heptatriene (IV, $n = 1$). In order to keep this simplicity, polyenes of structure IV, $n = 2-5$, have been synthesized in anticipation that the most basic site would again be the $>C=CH_2$ group and that protonation would therefore lead to the symmetrical ions I ($n = 2-5$).

The synthesis of the polyenes was straightforward. An aldehyde homologation reaction,⁸ involving the addition of 1-methoxybut-1-en-3-yn Grignard reagent to a carbonyl compound, reduction of the triple bond with lithium aluminum hydride and prototropic rearrangement of the resulting dienol, was used to synthesis the aldehydes V ($n = 1, 2, \text{ and } 4$). The reaction of



(4) R. Kuhn and C. Grundmann, *Chem. Ber.*, 71B, 442 (1938).

(5) A. Wassermann, *J. Chem. Soc.*, 4329 (1954); *Trans. Faraday Soc.*, 53, 1029 (1957).

(6) L. De Vries, *J. Am. Chem. Soc.*, 83, 2392 (1961).

(7) K. Hafner and H. Pelster, *Angew. Chem.*, 73, 342 (1961).

(8) (a) H. H. Inhoffen, F. Bohlmann, and G. Rummert, *Ann.*, 569, 226 (1950); (b) D. Marshall and M. C. Whiting, *J. Chem. Soc.*, 4082 (1956).

these aldehydes with the ylide of methallyltriphenylphosphonium chloride in the Wittig reaction then afforded good yields of the corresponding polyenes. The hexaene was synthesized by reaction of the aldehyde V ($n = 2$) with the triphenylphosphorus ylide from ethyl γ -bromocrotonate in the Wittig reaction, to yield a pentaunsaturated ester, which was treated with methyl magnesium bromide, and the resulting alcohol dehydrated to give the polyene. The polyenes where $n = 3-5$ were solids and were recrystallized and sublimed to yield in high per cent a single crystalline compound which we feel confident is the all *trans* isomer, the more soluble *cis* isomers, if any, remaining in the mother liquors. Certainly one would expect the aldehydes formed by the acid-catalyzed rearrangement to be mainly the more stable all *trans* compounds, as has been found^{8b} in other cases where this homologation reaction has been used. The infrared spectra of the aldehydes contain no strong bands in the $650-850\text{-cm}^{-1}$ region, characteristic of *cis* double bonds. The conditions used in the Wittig reaction are those reported^{9,10} to be favorable for *trans* bond formation (ether solvent, chloride phosphonium salt, and butyllithium in heptane as the base). Products formed by use of resonance-stabilized Wittig reagents, such as that from γ -bromocrotonic ester, are reported¹⁰ to give predominantly the

Table I. Ultraviolet Spectra of the Polyenes and Carbonium Ions

Compd.	n	λ_{max} , $\text{m}\mu$	$\epsilon_{\text{max}} \times 10^{-4}$	Solvent
IV	2	288.4	4.00	Isooctane
		301.2	5.86	
		315.5	5.10	
	3	301.5	2.87	Isooctane
		315.0	6.13	
		330.6	10.6	
		348.5	10.5	
		376.4	13.0	
	4	322	3.20	Isooctane
		337.7	7.18	
		356.4	12.43	
		376.4	13.0	
402.2		14.9		
5	343	3.62	Isooctane	
	360.8	7.68		
	378.8	13.5		
	402.2	14.9		
	464	...		
I	0	305 ^a	1.05	96% H ₂ SO ₄
	1	396	5.0	96% H ₂ SO ₄
	2	472.7	11	80% H ₂ SO ₄
		464	...	Heptafluorobutyric acid
	3	549.8	15	80% H ₂ SO ₄
		536.3	~8 ^b	Heptafluorobutyric acid
	4	625.5	>17	80% H ₂ SO ₄
		609	~22	Heptafluorobutyric acid
	5	702	>8 ^c	80% H ₂ SO ₄
		678	~17 ^c	Heptafluorobutyric acid
Cyclized ion VII		370.5	3.5	80% H ₂ SO ₄
Cyclized ion VIII		452.5	4.9	80% H ₂ SO ₄

^a From ref. 11. ^b ϵ_{max} values in heptafluorobutyric acid varied in an unexplicable manner in some cases. ^c One would expect a value of about 25.

(9) L. D. Bergelson and M. M. Shemyakin, *Tetrahedron*, 19, 149 (1963).

(10) S. Trippett, *Quart. Rev.* (London), 17, 406 (1963).

(11) N. C. Deno, J. Bollinger, N. Friedman, K. Hafer, J. C. Hodge, and J. J. Houser, *J. Am. Chem. Soc.*, 85, 2998 (1963).

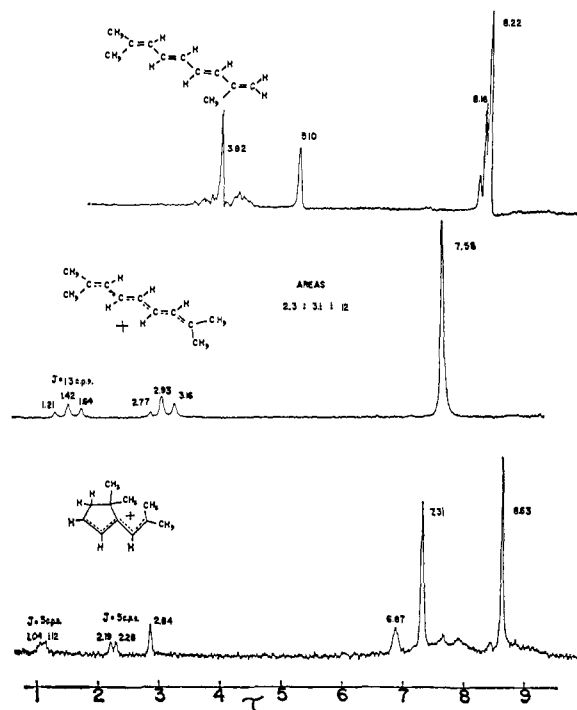


Figure 1. N.m.r. spectrum of the tetraene, trienylic cation, and the resulting cyclized ion.

trans coupling. The infrared spectra of the solid polyenes are very similar to one another with no strong bands in the 650–850-cm.⁻¹ region.

The tetraene is a liquid at room temperature but solidifies about 0°. This product is a mixture of at least two isomers since two peaks are observed on v.p.c. The peak areas indicate about 15% of a low-retention product and 85% of a high-retention product. There is a small peak at τ 8.06 in the n.m.r. spectrum of the tetraene (Figure 1) which is likely due to the presence of the minor isomer. These two isomers quite probably have the 3,4-*cis*,5,6-*trans* and 3,4-*trans*,5,6-*trans* structures with the latter representing the major peak. This assignment is made on the assumption that the *trans* aldehyde undergoes both *cis* and *trans* coupling with the Wittig reagent, the *trans* isomer predominating under the experimental conditions.

Over-all, the n.m.r. spectra of the polyenes completely substantiates their structures; indeed the spectra are virtually identical with each other, except for the changing intensity of the peak at τ 3.8 relative to the others. The actual curves for $n = 2-4$ are shown in Figures 1–3. The ultraviolet spectra of the polyenes are reported in Table I and are in general accord, taking appropriate account of methyl substituents, in both the position of the various maxima and in their relative intensities, when compared to the spectra of known polyenes¹² of similar structure.

The polyenes were not volatile enough to add from the gas phase to the sulfuric acid as has been done previously.³ In order to get as dilute an addition as possible, *ca.* 2 ml. of the sulfuric acid and 40 ml. of purified pentane were cooled to and maintained at *ca.* -30° while a solution of *ca.* 200 mg. of the polyene

(12) P. Nayler and M. C. Whiting, *J. Chem. Soc.*, 3037 (1955); F. Sondheimer, D. A. Ben-Efraim, and R. Wolovsky, *J. Am. Chem. Soc.*, 83, 1675 (1961).

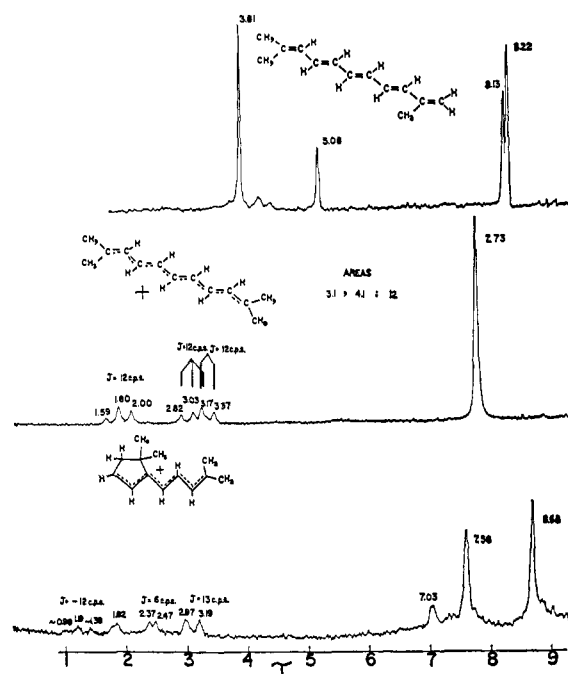


Figure 2. N.m.r. spectrum of the pentaene, tetraenylic cation, and the resulting cyclized ion.

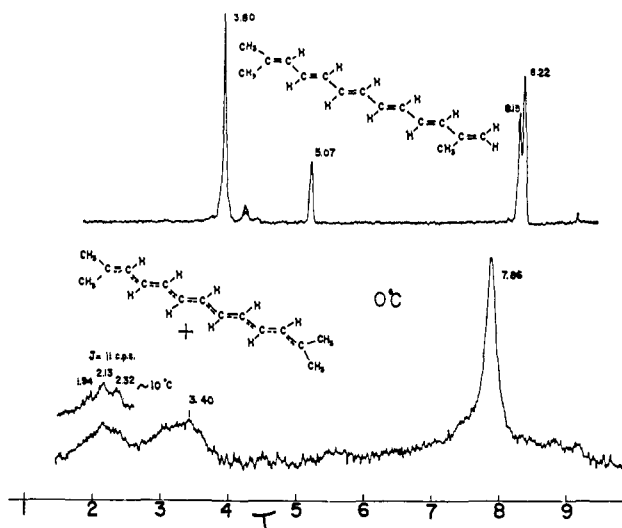


Figure 3. N.m.r. spectrum of the hexaene and pentaenylic cation.

in 40 ml. of pentane was added dropwise over a 30-min. period. The sulfuric acid–pentane mixture was stirred with a magnetic stirring bar such that the drops of polyene solution fell at the vortex edge of the stirred solution. After addition, most of the pentane was decanted from the sulfuric acid and the rest evaporated off at 0.1 mm.

The spectra of the original tetraene, the resulting trienylic cation, and the subsequent cyclization product are shown in Figure 1. A similar series is shown in Figure 2 for the pentaene and the tetraenylic ion. Only the hexaene and the pentaenylic ion are shown in Figure 3. The homologated ions become progressively less stable in concentrated sulfuric acid, not because of cyclization, but because they are increasingly more easily oxidized. In the case of the pentaenylic ion, the spectrum in Figure 3 could be obtained at around

0°; on standing only a few minutes at room temperature, the signals disappeared into a general background absorption. This is accompanied by a strong odor of sulfur dioxide from the solution.

The spectrum of the pentaenylic ion is very broad and poorly resolved even considering the temperature of the solution. At -30°, it is very much worse and we suspected that radicals were present. This has been confirmed by e.s.r. measurements at -30° which give a single broad line of half-width 13 gauss, corresponding approximately to the splitting expected for an odd electron interacting with the π -electron system.¹³ As yet, no fine structure has been resolved, probably because of exchange reactions. Radical formation could occur most simply by abstraction of an electron from the conjugated polyene, such as has been found for aromatic compounds like anthracene or perylene,¹⁴ or possibly by electron abstraction from the carbonium ions to give a dication radical. All of the polyene must be extracted into the sulfuric acid as either the normal ion or a paramagnetic one. The fact that one observes the normal ion in the n.m.r. spectrum and that on warming, this decomposes by an oxidation mechanism, means that the carbonium ion itself is unstable to oxidation. However, although this oxidation mechanism may require the initial formation of a dication radical, simple loss of a proton from this species would lead easily to the cation radical. The question of which species is involved in the e.s.r. spectrum may be cleared up if the hyperfine splittings can be obtained. On warming to 25°, the e.s.r. signals disappear.

On account of these complications, all the rearrangement reactions have been studied in the less oxidizing 90% sulfuric acid. With the pentaenylic ion, even this acid concentration causes general oxidation before any recognizable cyclization products are formed. In addition, solubility problems are encountered; the solutions are too dilute for satisfactory n.m.r. spectra and a good deal of polymerized material is present. Sufficient concentrations of the hexaenylic ion in either 90% sulfuric acid or trifluoroacetic acid, to measure n.m.r. spectra, could not be obtained, mainly polymer being formed. This ion has however been characterized by its visible spectrum in several solvents.

The half-life for cyclization of the trienylic ion in 90% sulfuric acid is about 40 min. at 25°, that of the tetraenylic ion, about 3 days at 25° and 6-7 min. at 76°. The cyclized ions are stable for extended periods and no further cyclizations have been observed. The cyclization reactions were observed to be very markedly accelerated by light. This was first suspected because there was no correspondence between $T_{1/2}$ values measured by means of electronic spectra and those measured by n.m.r. spectroscopy, the former being much shorter. Even the fluorescent light of the laboratory causes the color of the tetraenylic ion to disappear many times faster than an identical sample kept in the dark. The $T_{1/2}$ values reported above are from n.m.r. results where the tubes have been shielded from light and are moreover, concentrated enough that light catalysis should not be a signif-

(13) The half-width of the resolved hyperfine spectrum of the anthracene positive ion, which contains a similar number of carbon-hydrogen bonds, is about 13 gauss.¹⁴ There would of course be no similarity in the splitting pattern.

(14) A. Carrington, R. Dravnieks, and M. C. R. Symons, *J. Chem. Soc.*, 847 (1959), and references therein.

icant factor.¹⁵ The cyclization and oxidation reactions are also very temperature dependent. Both the tetraenylic and pentaenylic ions have been kept at -10° for 6 months in 80% acid with very little change in color.

The ultraviolet spectra of the ions I and the cyclized ions are reported in Table I. Where $n = 2$, the ion is yellow, $n = 3$, carmine, $n = 4$, royal blue, and $n = 5$, blue. The spectra were obtained by extracting very dilute pentane solutions with cold 80% sulfuric acid. This acid concentration gives quantitative ion formation where solubility permits and does not appear to cause appreciable oxidation of the ions. The cells were 0.1-cm. thickness in order that as concentrated a carbonium ion solution as possible (around $5 \times 10^{-5} M$) could be used¹⁶ and measurements were made as quickly as possible. Reproducible ϵ -values have been obtained for ions I ($n = 2$ and 3); for $n = 4$, the values are rather variable and it is generally noted that a polymer scum is formed at the interface of the two liquids after the extraction process is finished. Ion I ($n = 5$) has generally only about a third of the expected intensity with even more polymer formation apparent. The latter two ions could be observed in heptafluorobutyric acid using the same extraction procedure as above. There was no apparent polymer formation when this acid was used.

Qualitative experiments have been performed in an attempt to evaluate the pK_a of these polyenes. Dilute sulfuric acid however does not dissolve the higher polyenes even though other results would indicate that the ion should be formed. A coloration characteristic of the pentaenylic ion has been obtained in formic acid, concentrated hydrochloric acid, methanesulfonic acid, and trifluoroacetic and heptafluorobutyric acids. The pK_a values are, therefore, probably no higher than three on the $-H_0$ scale and probably even less.¹⁷

Recovery Experiments

The trienylic ion was chosen as representative of the series and appeared to offer the best chance for reisolating the rather unstable polyenes. Indeed, the tetraene, IV ($n = 2$), could be recovered from solutions of the trienylic ion, I ($n = 2$), by the usual rapid dispersal of the sulfuric acid solution into excess hydroxide solution. Separate experiments gave recoveries of 32 and 42%, based on quantitative ultraviolet spectra measurements. The recovered tetraene was also characterized by its v.p.c. retention time, which is identical with that of the high-retention isomer of the mixed tetraenes used to make the carbonium ion. The recovered material shows essentially only this one peak (>99% of the total v.p.c. absorption). The ca. 15% of the *cis*-tetraene in the original mixture has therefore isomerized or less likely, selectively polymerized. This

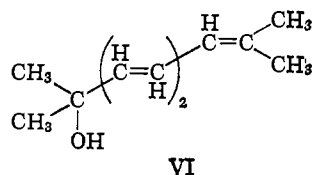
(15) Because of oxidation in the 90% acid, the ϵ_{max} of the cyclized ion formed for use in the n.m.r. experiments is only about one-half of the magnitude of that found by visible spectra using 80% acid.

(16) The solutions were made as concentrated as possible to minimize the effects of any rapid decomposition of some of the carbonium ion, which might be caused by trace amounts of impurities in the sulfuric acid. There was some evidence for this in the case of the pentaenylic ion where the ϵ of the carbonium ion peak increased as the calculated concentration of the ion increased, i.e., Beer's law was not obeyed. For $n = 2$ and 3, no difficulty was encountered.

(17) N. C. Deno in "Progress in Physical Organic Chemistry," Vol. 2, S. G. Cohen, A. Streitwieser, Jr., and R. W. Taft, Ed., Interscience Publishers, Inc., New York, N. Y., 1964, p. 170.

latter possibility cannot be ruled out since the yields of recovered material are by no means quantitative.

Actually, the first product from the quenching procedure appears to be the alcohol VI. A colorless oil is collected, when the original cold hexane extract



(see the Experimental Section), without drying, is evaporated under a nitrogen stream and the residue distilled at 25° onto a cold finger. This oil has an ultraviolet spectrum in hexane, peaks at 264.5, 274, and 285.5 m μ , ϵ_{max} 37,400, 50,600, and 39,000, respectively, which is very typical of a conjugated triene (cf. with 2,6-dimethyl-1,3,5-heptatriene, a trialkylated triene with peaks at 262, 272, and 282.5 m μ in cyclohexane¹⁸). The infrared spectrum contains a peak at 3600 cm.⁻¹ (OH) and further, this material regenerates the trienyl ion in quantitative yield when added to sulfuric acid. In order to obtain the uncontaminated spectrum of this alcohol, the hexane solution used for the ultraviolet measurement, has to be made up and quickly measured because even at 25°, dehydration is occurring to give the tetraene. This process soon goes to completion in the direction of the tetraene formation.¹⁹

When the trienyl ion is prepared in 90% sulfuric acid and left at room temperature for several hours, it is transformed into a new cyclized ion; although not quantitatively (extraneous background absorption from τ 7-9 in Figure 1). There has been recovered from this solution, by the same quenching procedure as above, an 8% yield of a volatile oil having a camphor-like odor. Most of the pentane-soluble recovered product is a viscous tar, and attempts to improve the recovery yield of the volatile fraction have not been successful. The recovered oil shows two major peaks (90% of the total area) when subjected to v.p.c. Both peaks appear at shorter retention times than those found for either of the original tetraenes. When the recovered material is put back into sulfuric acid, the spectrum of the original cyclized carbonium ion is produced in 70% yield. Sufficient recovered material has not been obtained so that a separation of the two main products could be attempted. The n.m.r. spectrum of the mixture contains however a good deal of saturated C(CH₃)₂ absorption; indeed the strongest absorption is a single peak at τ 8.95. There is also strong methylene absorption at 7.5-8. The ultraviolet spectrum is non-descript and of very low intensity relative to the original tetraene.

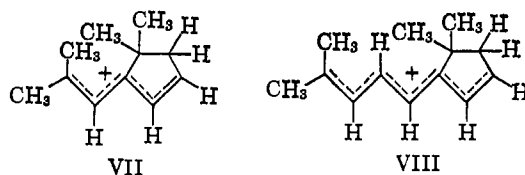
Discussion

The n.m.r. spectra of the carbonium ions (I) are in excellent accord with that expected. The cyclized ions are assigned the structures VII and VIII. Both

(18) T. S. Sorensen, *Can. J. Chem.*, **42**, 2781 (1964).

(19) The alcohol VI is stable at 25° in the original undried hexane extract of the basic solution. If this same solution is diluted several thousand times with the same solvent, the alcohol becomes unstable. It would appear that the glass surface of the ultraviolet cell may be acting as a catalyst however, since the dehydration process was desirable, no effort was made to make this surface basic.

these structures correspond to simple cyclization reactions followed by an allylic proton shift, and in contrast to simple dienyl ion cyclizations, no alkyl rear-



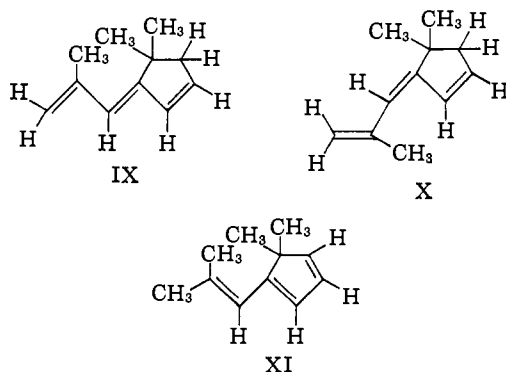
rangements are observed. This is presumably due to the increased delocalization of the positive charge and the resulting diminished energy requirement for having the terminal positions completely alkylated.

The structure of ion VII is based on the following reasoning: (1) the ultraviolet maximum is that of a dienyl ion modified by a cyclopentenyl ring system²⁰; (2) the τ -values and integrated peak areas of the methyl groups in the n.m.r. spectrum correspond to two methyl groups on a dienyl carbonium ion center and two on a center one carbon removed from the charge; (3) a single, unsplit proton peak, indicative of a proton on a carbon atom which is between carbonium ion centers; and (4) two peaks, each one a doublet of $J = 5$ c.p.s., one corresponding to a proton on a carbonium ion center and one as in (3). Ion VII is rather similar to an ion produced from cyclization of a trivinyl carbonium ion.²¹ These facts seem to be uniquely satisfied by structure VII and cannot be reconciled with any product formed by 1,7 cyclization.

The structure of ion VIII is based on very similar reasoning, the ultraviolet spectrum is now that of a trienyl ion modified by a cyclopentenyl system, the δ^+ C(CH₃)₂ protons are likewise those of a trienyl ion. The highest field alkene protons are now a doublet with a triplet observed for the proton between these ($J = 13$ c.p.s.); the pair of doublets for the cyclopentenyl protons corresponding to those in VII are similarly present.

Molecular model studies indicate that 1,7 or 1,9 cyclizations are not very likely to occur because in order to bring the necessary end carbon atoms together one has to distort the planarity of the whole π -electron system. There is also a good deal of evidence available to show that cyclopentenyl rings may be particularly stable.²²

When the ion VII is quenched in base, one might expect three possible products, viz., IX, X, and XI.



(20) The argument used here is really an extension of the fact that simple cyclopentenyl ring systems absorb in the ultraviolet at considerably shorter wave lengths than their open-chain analogs.¹²

(21) T. S. Sorensen, *Can. J. Chem.*, in press.

(22) N. C. Deno and J. J. Houser, *J. Am. Chem. Soc.*, **86**, 1741 (1964).

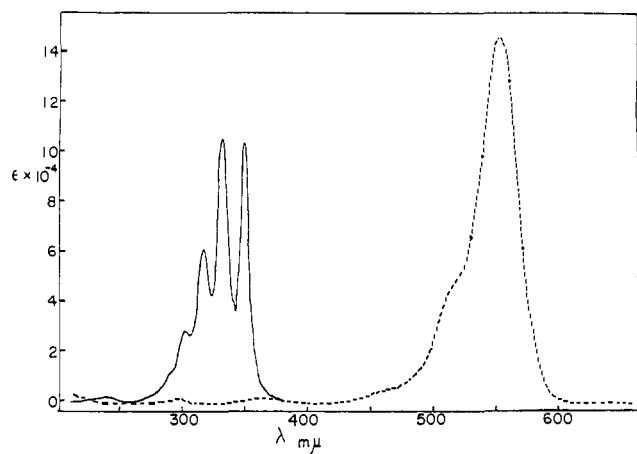
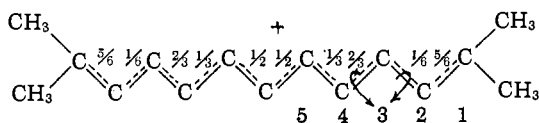


Figure 4. Ultraviolet spectra: —, polyene (IV, $n = 3$); -----, the resulting ion (I, $n = 3$).

The n.m.r. data and the v.p.c. retention times (compared to the isomeric tetraenes), shown by the crude recovered product, are not inconsistent with these structures however; an independent synthesis of the carbonium ion VII will likely be required for its final structure proof.

In attempting to rationalize the effect of light on the cyclization reactions one can note that the double-bond character of the bonds in the simple valence bond concept varies along the chain as represented below, using as an example, the pentaenylic ion. This approach is certainly an oversimplification, in quantitative terms (see later discussion), but this does not affect the conclusions drawn here. The ion may not be entirely in this all *trans* conformation; however, one has to assume that this will be the most stable. The ion will have every



opportunity to exist in this conformation since this geometry is the direct result of the protonation of the all *trans* polyene. For the cyclization of C-1 to C-5 to occur, it is necessary to rotate a $1/6$ bond and a $2/3$ bond in order to get the *s-cis*, *s-cis* conformation necessary to bring these two reacting ends together. Light catalyzed *cis-trans* interconversions are of course very common and this quite likely explains the accelerating effect of light in these reactions.

The relative rates ($T_{1/2}$) of these cyclizations²³ are dienyl \approx tetraenyl \gg trienyl. This order is not easily rationalized although the transition state in the cyclization of the dienyl ion suffers from much greater steric repulsions than are present in the higher homologs.

Ultraviolet Spectra

The data for ions I ($n = 1-5$) in 80% sulfuric acid fit the empirical relationship, $\lambda_{\max} = 330.5 + 65.5n$ m μ . This result is typical of polymethine dyes and is predictable on the basis of the free-electron theory

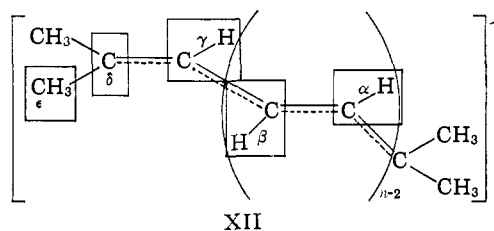
(23) The dienyl cyclization is not strictly comparable to the others since a somewhat different acidity of sulfuric acid was used. This will affect a numerical comparison but the rough comparison is not appreciably changed since these rates do not appear to be very acid dependent.

which gives $\lambda \propto n$ for large values of n . When the above data are fitted to the free-electron expression however, the calculated value of a , the length of the box, is much too small to be realistic. One could also use a periodic sine potential for the electron as proposed by Kuhn,²⁴ particularly since in these ions, the carbon atoms alternate in electron density in a regular manner. The amplitude of the sine potential (V_0) which will ordinarily be calculated from one set of experimental data, should in this case differ for each ion and one cannot test the validity of this equation. The λ_{\max} of the first member of the series ($n = 0$) cannot be included in the empirical equation. The λ_{\max} is too low; however, this anomaly can be rationalized in terms of considerable 1-3 orbital overlap, which has the effect of increasing the transition energy.²⁵ This argument assumes that there is no appreciable 1-3 orbital overlap in the higher analogs; however, this is a questionable hypothesis (see preceding discussion).

The ultraviolet curves of the carbonium ions have a characteristic shoulder on the short wave length side of the peak in all cases. Figure 4 shows the spectrum of the pentaenyl ion and the resulting tetraenylic ion. The λ_{\max} of the trienyl ion prepared by Deno and Pittman agrees very well with that of ours, 470 vs. 473 m μ . The ion prepared by De Vries had λ_{\max} 552 compared to 549 m μ for our tetraenylic ion. This correspondence is excellent but probably rather fortuitous.²⁶ The value of 960 m μ reported by Wassermann for protonated β -carotene is quite reasonable; the calculated value for a linear polyenylic ion with ten double bonds, using the above empirical equation, is 1008 m μ . A comparison of the spectra of the carbonium ions in 80% sulfuric acid and in the less polar solvent, heptafluorobutyric acid, shows that a hypsochromic shift of the λ_{\max} is general in the latter solvent. This would make the comparison of the λ_{\max} of protonated carotene even better.

N.m.r.—Charge Density Correlation^{26a}

In Figure 5, we have plotted the τ values for the methyl protons of the ions (I) against $1/n$ where n is defined according to XII. The rationale behind this particular



choice of numbers was the expectation that the n.m.r. methyl proton resonances would be a function of the excess charge density on the carbon atoms to which the methyl groups were bonded.^{25,27} This particular choice of n equates $1/n$ with excess positive charge density if

(24) H. Kuhn, *J. Chem. Phys.*, 17, 1198 (1949).

(25) T. J. Katz and E. H. Gold, *J. Am. Chem. Soc.*, 86, 1600 (1964).

(26) Cyclopentenyl rings generally appear to lower the λ_{\max} of carbonium ions compared to open-chain analogs, but alkyl groups on the chromophore will increase the λ_{\max} . A combination of both effects could result in little over-all change.

(26a) NOTE ADDED IN PROOF. We wish to acknowledge the valuable comments of Dr. D. G. Farnum who, in his capacity as referee, suggested to us a quantitative approach to this correlation similar to that which follows.

(27) C. MacLean and E. L. Mackor, *Mol. Phys.*, 4, 241 (1961).

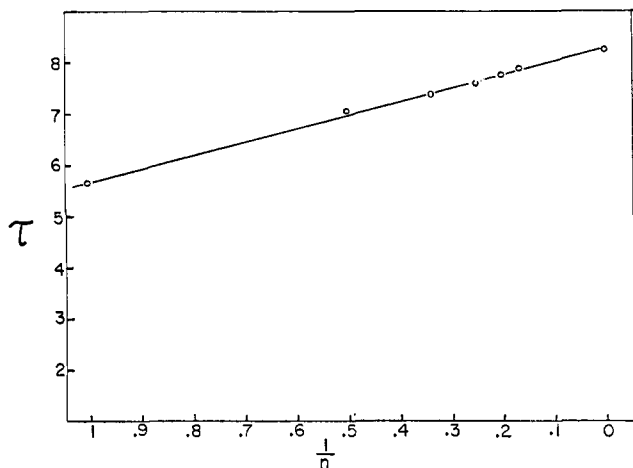
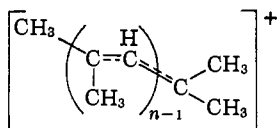


Figure 5. Relationship between chemical shifts (τ) of methyl-group protons vs. $1/n$ where n is defined as in XII.

one uses simple resonance structures to distribute the charge equally. Thus, where $n = 3$, $1/n = 1/3$ and from XII, there are seen to be three resonance structures placing one-third of a positive charge on carbon atoms δ , β , and δ . However, it is expected that the charge will be delocalized to some extent on all the carbon atoms of XII and this point is developed later.

The first point on the graph is for the *t*-butyl cation.²⁸ Strictly speaking, this cation does not belong with the above series but with the series



which differs only in that the resonance contributing structures are, in this case, tertiary carbonium ions.²⁹ The last point is for the $(\text{CH}_3)_2\text{C}=\text{methyl}$ protons of the polyenes, the τ -values of which are quite constant in position throughout the polyene series at 8.21 ± 0.02 in dilute carbon tetrachloride solution. Thus, for $n = \infty$ in a neutral polyene, we would still expect to find this same τ -value. When this infinitely long polyene is protonated, the charge density at individual carbon atoms will be negligibly affected and one would expect τ -values to remain the same as before protonation. One might still have a solvent shift between carbon tetrachloride and the protonating acid solvent however, and in order to check this point, the methyl resonances of *n*-valeric, *n*-butyric, and 4,4-dimethyl-2-pentenoic acids have been measured in both solvents. The methyl group is quite insulated from the carboxylic acid group, which becomes protonated in the sulfuric acid solvent. Ex-

(28) G. A. Olah, E. B. Baker, J. C. Evans, W. S. Tolgyesi, J. S. McIntyre, and I. J. Bastien, *J. Am. Chem. Soc.*, **86**, 1360 (1964).

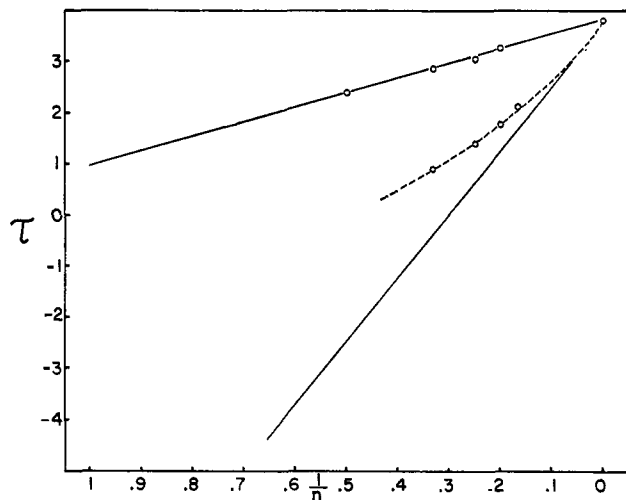
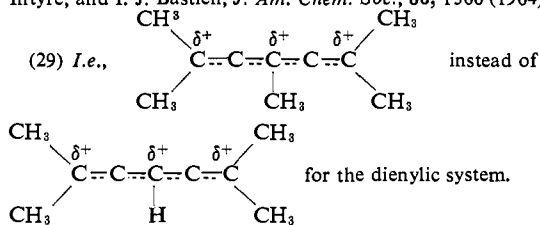


Figure 6. Relationship between chemical shifts (τ) of protons vs. $1/n$ where n is defined as in XII: -----, β -protons; ———, γ -protons.

perimentally, the resonance position of the methyl protons in the two solvents is within 0.1 τ -unit in each case. Therefore, no solvent corrections will be made.

In Figure 6, we have plotted the τ -values of the alkenyl protons of the ions also against $1/n$ where n is defined in the same sense as above. The top line is for the γ -hydrogens of XII while the bottom line is for the β -hydrogens. The point for $n = \infty$ is taken as the τ -value of the alkene hydrogens of the polyenes which are quite constant throughout the series at $\tau 3.81 \pm 0.02$ in carbon tetrachloride solution. The absorption at $\tau 4.1$ – 4.3 probably corresponds to one of the protons; however, we do not know which one. In using this τ -value, we apply the same reasoning as above. Any calculations of $\Delta\tau$, where $\Delta\tau = \tau_{n=\infty} - \tau_n$, are very dependent on the value chosen for $\tau_{n=\infty}$. In the following calculations therefore, the uncertainty in the figure of $\tau 3.81$ for $n = \infty$ (sulfuric acid solvent), must be borne in mind.

Both the plot of τ_{CH_3} vs. $1/n$ and $\tau_{\text{H}\gamma}$ vs. $1/n$ appear to be reasonably linear; that of $\tau_{\text{H}\beta}$ vs. $1/n$ definitely appears to be curved. In the first two cases, the relationship might not be a strictly linear one since the slope of the lines are probably not great enough to show any particular divergence. In any case, we shall treat these as essentially linear relationships when compared to the behavior found in the $\tau_{\text{H}\beta}$ vs. $1/n$ plot.

It has been shown,³⁰ that in the n.m.r. spectra of aromatic cations and anions, the linear relationship

$$\Delta\tau_{\text{H}} = k\Delta\rho \quad (1)$$

holds fairly well, where $\Delta\tau_{\text{H}}$ is the difference between the chemical shift of the protons in the ions and in a related neutral species, $\Delta\rho$ is the excess charge localized at the carbon atom to which these protons are bonded, and k is about 10.7 p.p.m. per electron charge. This same type of relationship

$$\Delta\tau_{\text{CH}_3} = k_1\Delta\rho \quad (2)$$

has been postulated^{25, 27} for methyl groups attached to

(30) G. Fraenkel, R. E. Carter, A. McLachlan, and J. H. Richards, *J. Am. Chem. Soc.*, **82**, 5846 (1960); T. Schaefer and W. G. Schneider, *Can. J. Chem.*, **41**, 966 (1963).

carbon atoms, where k_1 is 3.27 or 4.25 p.p.m. per electron charge. If one accepts these $\Delta\tau$ - $\Delta\rho$ relationships, then the carbonium ion series prepared in this work make a good system for studying charge delocalization. In comparing the n.m.r. spectra of the homologous ions, most extraneous effects (other than $\Delta\rho$) which could affect the τ -values are absent, since the solvent is the same, the counterion is the same, there are no gross changes in molecular shape, and no heteroatoms are present. There is however the solvent problem involved in obtaining a point for $n = \infty$ (see above).

We will attempt to break down the excess positive charge, which is delocalized throughout the molecule into the fragments designated in the boxes in XII. From the direction of the n.m.r. shifts, the absolute sign of the partial charge on each fragment is positive. Designating the local, excess, positive charge densities as $\alpha, \beta, \gamma, \delta$ as in XII, and excepting ϵ for the present, we get

$$(n-2)\alpha + (n-2)\beta + \gamma + 2\delta = 1 \quad (3)$$

Further, the charge density at alternate carbon atoms along the chain will be assumed to be equal. This is the same as giving equal weight to the simple resonance structures. Therefore, $\delta = \beta$ and $\gamma = \alpha$ (this is exact for $n = 3$) and eq. 3 becomes

$$n\beta + (n-1)\gamma = 1 \quad (4)$$

From eq. 1, $\Delta\tau_{H\beta} = k\beta$ and $\Delta\tau_{H\gamma} = k\gamma$ giving

$$\frac{n\Delta\tau_{H\beta}}{k} + (n-1)\frac{\Delta\tau_{H\gamma}}{k} = 1 \quad (5)$$

The solution of eq. 5 using the values of $\Delta\tau_{H\beta}$ and $\Delta\tau_{H\gamma}$ for $n = 3, 4,$ and 5 gives values of k which increase as n increases. In order to attempt to correct for this increase, there has been added a charge density term (ϵ) covering each methyl group. From the observed linearity of $\Delta\tau_{CH_3}$ and $1/n$ and the reasonable assumption that $\Delta\tau_{CH_3}$ is proportional to ϵ , we get $\epsilon = k_2/n$, an inverse term in n . For four methyl groups, eq. 5 becomes eq. 6. The solutions of

$$\frac{n\Delta\tau_{H\beta}}{k} + \frac{(n-1)\Delta\tau_{H\gamma}}{k} + \frac{4k_2}{n} = 1 \quad (6)$$

this equation containing the two unknowns, using the data for $n = 3, 4,$ and 5 , are not very self-consistent; k varies from 13.8 to 15.5 depending upon which two sets of data³¹ are used in the solution. The value of k_2 from this solution also varies but averages to about 0.2. The exact meaning of ϵ is not entirely clear; however, it should be noted that the addition of this term has not been dictated by the observed change of τ_{CH_3} with n nor is any quantitative figure from this plot used in the calculations. The above result is consistent in suggesting that in the ions under considerations, k should be higher than the value of 10.7 p.p.m. per electron charge, which has been found for the aromatic cations and anions. Varying the values of $\Delta\tau_{H\beta}$ and $\Delta\tau_{H\gamma}$ by 0.2 p.p.m. in either direction (because of possible uncertainties in $\tau_{n=\infty}$) results in k values which are higher and lower than the above

(31) The τ -values for $n = 3$ have been redetermined as 0.92 for the average of the low-field protons and 2.86 as the average for the high-field protons.

figures but even the lower k values are higher than 10.7. In Table II, using $k = 14.7$ and $k_2 = 0.2$, we have recorded the values of $\beta, \gamma,$ and ϵ for $n = 2, 3, 4, 5,$ and 6 .

Table II. Delocalization of the Excess Positive Charge

Position in XII	n				
	2	3	4	5	6
$\beta = \delta$...	0.20	0.163	0.137	0.114
$\gamma = \alpha$	0.11	0.065	0.051	0.037	...
ϵ	0.1	0.067	0.05	0.04	0.033

Since $\Delta\tau_{H\gamma}$ vs. $1/n$ also appears to be reasonably linear, another approach can be used, $\Delta\tau_{H\gamma} = k_3/n$.

$$\frac{n\Delta\tau_{H\beta}}{k} + \frac{(n-1)k_3}{nk} + \frac{4k_2}{n} = 1 \quad (7)$$

Regrouping, $\Delta\tau_{H\beta} = (k/n) - (4k_2k/n^2) - [(n-1)k_3/n^2]$. As $n \rightarrow \infty$, the second term becomes unimportant and $(n-1/n^2) \rightarrow 1/n$. Thus, eq. 7 becomes

$$\Delta\tau_{H\beta} = \frac{k - k_3}{n} \quad (8)$$

The limiting slope of $\Delta\tau_{H\beta}$ vs. $1/n$ should be equal to $k - k_3$. Experimentally, k_3 is about 3 p.p.m. and the slope is about 10 to 12 p.p.m., giving a value for k of 13-15 p.p.m. per electron charge.

The above treatment differs from those commonly made in n.m.r. and e.s.r. spectroscopy in that a series of related ions has been available for study. More work is needed, perhaps on related series, to find out whether the ϵ term is necessary, since there are other explanations for the discrepancies in the solution of eq. 5.

Experimental Section

Ultraviolet spectra were measured using a Beckman DK-1. Infrared spectra have been obtained on all compounds using a Perkin-Elmer Model 337 spectrophotometer. The n.m.r. spectra were recorded using a Varian Associates A-60 spectrometer equipped with a variable temperature probe using internal tetramethylsilane as a reference for the neutral molecules and tetramethylammonium cation¹ for the carbonium ions. V.p.c. analyses were carried out on an Aerograph Hy-Fi Model 600, employing a 6 ft. \times $1/8$ in. column of 5% SE-30 on Chromosorb W. All boiling points and melting points are uncorrected. Practically all of the compounds synthesized and used in this work are sensitive to oxygen; consequently they must be stored under nitrogen in the freezing compartment of a refrigerator.

7-Methyl-2,4,6-octatrienal. A solution of 1-methoxybut-1-en-3-yn (24.6 g., 0.3 mole) in 100 ml. of purified tetrahydrofuran was added dropwise to 0.33 mole of ethylmagnesium bromide in 200 ml. of tetrahydrofuran. This mixture was then cooled in an ice bath while 24.2 g. (0.29 mole) of β, β -dimethylacrolein in 100 ml. of tetrahydrofuran was added dropwise over a 1-hr. period. After 1 hr. at room temperature, 13.8 g. (0.30 mole) of ethanol was added and then 11.4 g. (0.30 mole) of solid lithium aluminum hydride was added cautiously through a powder funnel over a 15-min. period. The solution became warm and was

stirred for 1 hr. after the addition while it gradually cooled. The excess hydride was cautiously decomposed with water followed by 250 ml. of saturated tartaric acid solution. The aqueous layer was extracted with several portions of ether and the ether layers were dried over magnesium sulfate. The residue after removal of the solvents was distilled at *ca.* 0.05 mm. to yield a fraction b.p. 56–62°, n_D^{25} 1.6536 (Abbé refractometer with sodium light source), as a fragrant, yellow oil, yield 27 g. (66%) (lit.,³² from a different synthesis, b.p. 63–64° (0.02 mm.)). The n.m.r. spectrum was consistent with the proposed structure, a single peak at τ 8.12, a complex alkene region, and a doublet at 0.57 and 0.44. The infrared spectrum contained strong bands near 1000 cm^{-1} , characteristic of *trans* double bonds. In isooctane, the aldehyde had absorption maxima at 324.2 $\text{m}\mu$ (ϵ 44,000) and 311.3 $\text{m}\mu$ (ϵ 43,800). A pale yellow semicarbazone derivative had m.p. 217–217.5° (from ethanol).

5-Methyl-2,4-hexadienal. This was prepared in 60% yield in a similar manner to the above aldehyde, starting with acetone instead of β,β -dimethylacrolein, b.p. 70–72° (10 mm.), n_D^{25} 1.5560. The reported constants,³³ using a similar method of preparation, are b.p. 72–73° (8 mm.), n_D^{25} 1.5550. This aldehyde solidified in the refrigerator.

11-Methyl-2,4,6,8,10-dodecapentaenal. This was prepared in 27% yield in a similar manner to the above aldehyde, starting with 7-methyl-2,4,6-octatrienal instead of β,β -dimethylacrolein. Several recrystallizations of the crude solid from benzene yielded yellow-orange plates, m.p. 135–136° (lit.,³² from a different synthesis, m.p. 136–137°). The infrared spectrum contained strong bands at 990 and 1005 cm^{-1} , characteristic of *trans* double bonds. The n.m.r. spectrum was consistent with the proposed structure; a single peak at τ 8.18, a complex alkene region, and a doublet at 0.53 and 0.66. In isooctane, the aldehyde had a λ_{max} at 395.2 $\text{m}\mu$ (ϵ 57,600) and 373.5 $\text{m}\mu$ (ϵ 63,400).

Ethyl 11-Methyl-2,4,6,8,10-dodecapentaenoate. Ethyl γ -bromocrotonate and triphenylphosphine in benzene gave the corresponding phosphonium salt. The ylide³⁴ was prepared by adding the salt to an equivalent amount of sodium ethoxide in absolute ethanol. A solution of 7-methyl-2,4,6-octatrienal (6.8 g., 0.05 mole) in 50 ml. of absolute ethanol was added under nitrogen over a 15-min. period to a stirred solution (100 ml.) of the above phosphorane. The reaction mixture was stirred for 4 hr. and then 100 ml. of water and 1 ml. of acetic acid were added and the solution was heated to the boiling point. After standing overnight, the crude crystals were filtered off and recrystallized from ethanol. Yield of the first two crops was 3.9 g. (34%), m.p. 95–97°. An analytical sample had m.p. 99.5–101.5° (from ethanol).

Anal. Calcd. for $\text{C}_{15}\text{H}_{20}\text{O}_2$: C, 77.55; H, 8.68. Found: C, 77.14; H, 8.66.

The n.m.r. spectrum was consistent with the proposed structure: a single peak at τ 8.19, a complex alkene region as well as the ethyl peaks. In isooctane,

(32) I. N. Nazarov and Zh. A. Krasnaya, *Zh. Obshch. Khim.*, **28**, 2440 (1958); *Chem. Abstr.*, **53**, 3043i (1959).

(33) E. M. Kosower and T. S. Sorensen, *J. Org. Chem.*, **28**, 692 (1963).

(34) F. Bohlmann, *Chem. Ber.*, **90**, 1519 (1957).

the ester had λ_{max} at 383.8 $\text{m}\mu$ (ϵ 70,200), 363.2 (82,900), and 346.6 (57,500).

2,12-Dimethyl-1,3,5,7,9,11-tridecahexaene. Ethyl 11-methyl-2,4,6,8,10-dodecapentaenoate (3 g., 0.013 mole) in 20 ml. of tetrahydrofuran was added dropwise to a threefold excess of ice-cold methylmagnesium bromide solution. After 2 hr. at 25°, the mixture was poured into 200 ml. of cold, saturated ammonium chloride solution. The layers were separated, the aqueous layer was extracted with a further portion of ether, and 10 mg. of *p*-toluenesulfonic acid was added to the combined ether layers. The ether solution was refluxed for 30 min., cooled, washed with sodium bicarbonate solution and water, and then dried over potassium carbonate. The ether was removed and the residue was extracted with 500 ml. of warm pentane. The pentane solution was then put onto an alumina column (70 g. Woelm, neutral, activity 1) and eluted successively with petroleum ether (b.p. 30–75°), 10% benzene-petroleum ether, 50% benzene-petroleum ether, benzene and 10% ether-benzene. Most of the product comes off with benzene although smaller amounts are eluted by the less polar solvent mixtures. All of the material coming off the column up to and including that in the benzene eluent appeared to be a single product, 0.75 g. (29%) of bright yellow, fluffy needles. The product was always stored *in solution* in a freezing compartment. The hexaene was purified further by recrystallization from pentane or by sublimation at 50–60° (0.005 mm.), the latter method being more successful as the crystals are bigger and not so susceptible to polymerization or oxidation. On sublimation, long, lemon-yellow needles were formed, m.p. 96–100° dec., the polyene being put on the hot stage just below the melting temperature.

Anal. Calcd. for $\text{C}_{15}\text{H}_{20}$: C, 89.94; H, 10.06. Found: C, 89.83; H, 10.03.

The n.m.r. spectrum (10% in carbon tetrachloride) is shown in Figure 3, the area ratio of the protons being 8.8:1.9:9 (calcd. 9:2:9). The ultraviolet spectrum is given in Table I. The strongest absorption in the infrared occurred at 1000 cm^{-1} .

2-Methyl-2-propenyliidenetriphenylphosphonium Chloride. A solution of triphenylphosphine (131 g., 0.5 mole) and methallyl chloride (64 g., 0.71 mole) in 150 ml. of benzene was refluxed for 56 hr. The mixture was cooled and the salt was filtered off, washed with fresh benzene, and then dried at 100° (100 mm.) for several hours, m.p. 215–218°.

2,8-Dimethyl-1,3,5,7-nonatetraene. The above phosphonium salt (24.9 g., 0.071 mole) suspended in 100 ml. of dry ether was treated under a nitrogen atmosphere with 25 ml. of butyllithium in heptane solution (0.071 moles). Heat was produced and the mixture immediately turned red. This mixture was stirred for 35 min. and then 6.66 g. (0.06 mole) of 5-methyl-2,4-hexadienal in 50 ml. of ether was added over a 15-min. period. This solution was stirred for 3 hr. at 25° and then 200 ml. of water was added. The aqueous layer was extracted with an additional 200 ml. of ether and the combined ether layers were washed twice with saturated sodium bisulfite solution and once with water. After drying (K_2CO_3), the ether was removed and the residue was distilled to yield a fraction b.p. 38–43° (0.3 mm.), 5.70 g. (64%). The triphenylphos-

phine oxide remains in the distillation flask. This material was redistilled to yield a middle cut, n_D^{25} 1.6040 (Abbé refractometer with a sodium light source).

Anal. Calcd. for $C_{11}H_{16}$: C, 89.12; H, 10.88. Found: C, 88.88; H, 10.92.

The tetraene solidified in the refrigerator but attempts to crystallize the material from pentane were not very successful. The n.m.r. spectrum (10% in CCl_4) is shown in Figure 1, the area ratio of the protons being 5.1:2:8.8 (calcd. 5:2:9). The ultraviolet spectrum is given in Table I. The strongest infrared absorption was a band at 985 cm^{-1} ($=CH_2$). From v.p.c. analysis, the product was a mixture of two isomers, 15% of the total with a retention time at 110° of 5 min. and 85% of the total with a retention time of 6.5 min.

2,10-Dimethyl-1,3,5,7,9-undecapentaene. The same procedure (as above) was followed using 7-methyl-2,4,6-octatrienal (5.58 g., 0.041 mole), up to the point where the tetraene was distilled. The gummy residue at this point was extracted with 100 ml. of pentane which left most of the triphenylphosphine oxide behind. The pentane solution was then concentrated to about 10 ml. and cooled in a Dry Ice bath. The pentaene crystallized out and was quickly filtered and washed with fresh pentane (at -78°). The solid was quickly transferred to a sublimation apparatus and sublimed at 50° (0.005 mm.) to yield straw-colored needles, m.p. $56-57^\circ$, 2.99 g. (42%). The actual total yield was surely higher than this but the instability of these compounds made a quantitative isolation difficult.

Anal. Calcd. for $C_{13}H_{18}$: C, 89.59; H, 10.41. Found: C, 89.98; H, 10.45.

The n.m.r. spectrum is shown in Figure 2, the area ratio of the protons being 7.0:2.1:8.9 (calcd. 7:2:9). The ultraviolet spectrum is given in Table I. The strongest absorption in the infrared occurred at 993 cm^{-1} .

2,14-Dimethyl-1,3,5,7,9,11,13-pentadecaheptaene. The same procedure (as above) was followed using 11-methyl-2,4,6,8,10-dodecapentaenal (1.0 g., 0.0053 mole), except that this aldehyde was added as a slurry to the phosphorane solution and the extraction of the triphenylphosphine oxide-polyene residue was made with 250 ml. of hot petroleum ether. This petrol solution was chromatographed as in the hexaene preparation; the first few petrol eluent fractions were discarded as were all the eluent fractions after pure benzene. The rest of the fractions yielded 0.77 g. (64%) of orange-yellow crystals. These could be sublimed at 95° (0.005 mm.) or recrystallized from carbon tetrachloride to yield beautiful, long, very thin needles, m.p. $140-142^\circ$ (material put on the heating block just before this temperature is reached). A satisfactory analysis was not obtained. The crude material and the sublimed

material were only ca. 85% pure based on an n.m.r. integration. The recrystallized material was used for the ultraviolet and infrared work but we had poor analytical results in general when recrystallized materials were used. This material polymerized in a few days even in solution under nitrogen and in the cold. For structure proof, the n.m.r. spectrum of this material was very definitive. The peak positions, 8.21 and 8.14, 5.06, and 3.79, were virtually identical with those of the pentaene and hexaene. The area ratios were 8.8:2.0:11.1 (calcd., 9:2:11). There were also small impurity peaks from τ 8.3-9.3. The electronic spectrum is given in Table I. The strongest absorption in the infrared occurred at 1000 cm^{-1} .

Quenching of the Carbonium Ions. A solution of the carbonium ion, I ($n = 2$), was prepared from 0.10 g. of the tetraene, IV ($n = 2$), in 2 ml. of concentrated sulfuric acid in the usual manner. One milliliter of this solution was then added through a 0.25-ml. hypodermic syringe to the vortex of a vigorously stirred mixture of potassium hydroxide (14.6 g.), ice-water (90 g.), and purified hexane (5 ml.). The hexane layer was separated and kept cold. The alcohol VI could be isolated by transferring the undried hexane solution to a sublimation tube, blowing off the hexane with nitrogen, and carrying out a molecular distillation of the residue at 25° (0.01 mm.) into the cold finger.

Aliquots of the original hexane solution were also used for quantitative ultraviolet analysis for the amount of recovered tetraene. In some cases, when the freshly prepared ultraviolet solution was measured, a spectrum showing a mixture of the alcohol and the tetraene was obtained. Letting the solution stand for a few hours resulted in the complete disappearance of the alcohol peaks and the resulting increase in the absorption due to the tetraene. From two separate experiments, recovery yields of 32 and 42% were recorded.

The recovery of the product from the cyclized ion VII (from 2.0 g. of the tetraene and 20 ml. of 90% sulfuric acid) was accomplished in the same way. The hexane extract was dried over potassium carbonate, the hexane was distilled off carefully, and the residue was distilled under vacuum (0.01 mm.), collecting the volatile material in a Dry Ice cooled trap. The yield of volatile material was 160 mg. (8%). From v.p.c. analysis, there were two major components, with retention times at 110° of 1.25 and 1.6 min., respectively.

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