Reaction of N-Bromosuccinimide with [2.2]Metacyclophane.— In a 100 ml, round-bottomed flask was placed 1 g of I, 2.5 g of N-bromosuccinimide, 0.5 g benzoyl peroxide, and 60 ml of reagent carbon tetrachloride. The mixture was allowed to reflux for 24 hr and then allowed to cool. The mixture was then freed of succinimide by suction filtration and the solvent was concentrated to about one-half of its original volume. This solution was chromatographed on 120 g of neutral, activity 1 Woelm alumina. In the first fractions a white solid was obtained which had mp 105–125° unrecrystallized, and which was mainly recovered I. Gradual elution with ether gave yellow solids, mp 140–180°. These compounds gave a very positive green Beilstein flame test; however, the nmr spectrum revealed that they no longer possessed the metacyclophane structure as evidenced by the lack of the high-field aromatic protons.

# Oligomers of Allene. III.[1] Tetramers Formed in the Thermal Polymerization of Liquid Allene[2,3]

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Polymerization of allene gives two tetramers, 2,6- and 2,7-dimethylenebicyclo[4.4.0]dec-9,10-ene. Hydrogenation afforded 2,6- and 2,7-dimethylbicyclo[4.4.0]dec-9,10-ene or 2,6- and 2,7-dimethylbicyclo[4.4.0]dec-9,10-ane, depending upon the exact conditions. Isomerization of the tetramer mixture by hydrogen bromide–acetic acid yielded 2,6- and 2,7-dimethyltetralin, confirmed by reduction of 2,6- and 2,7-dimethylnaphthalene. Aromatization of the tetramers by chloranil led to 2,6- and 2,7-dimethylnaphthalene. A second set of tetramers, 2-methylene-6- and -7-methylbicyclo[4.4.0]dec-9,10-ene, may have resulted either by use of propene-contaminated allene or by an internal hydrogen-transfer step.

Thermal polymerization of allene was originally reported to afford a variety of higher oligomers.[4,5] The liquid product boiling above 150° was separated by fractional distillation into four distinct components—an α-tetramer (I), a β-tetramer (II), a pentamer (III), and a hexamer (IV). The structural assignments were based on a combination of microanalytical, oxidative, and hydrogenation data. Treatment of each olefin with dilute potassium permanganate solution yielded oxalic and succinic acids, while catalytic hydrogenation in ethanol established the degree of unsaturation. For example, the β-tetramer II absorbed 2 equiv of hydrogen to give the tetrahydro-β-tetramer (V), whose saturated nature was established by a failure to react with bromine water. These
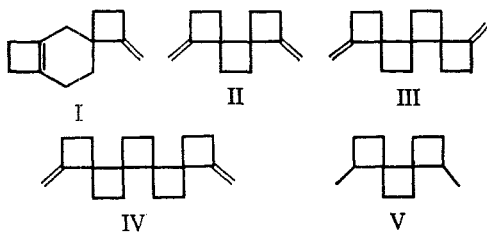
specific compounds have not been mentioned or isolated again, although the gaseous and liquid phase polymerization of allene has been extensively restudied in the last half-century.[6–14]

Recently, a new investigation on the allene oligomers provided for examination a quantity of liquid olefins. To recapitulate briefly, it can be stated that the dimer fraction is a mixture of 1,2-dimethylenecyclobutane (VI) and 1,3-dimethylenecyclobutane (VII); the trimer fraction is composed of 3-methylenebicyclo[4.2.0]-octa-1,6-ene (VIII), 1,2,3-trimethylenecyclohexane (IX), and 1,5- (or 1,6-) dimethylenespiro[3.3]heptane (X).[1] A report is now made on the exact nature of the tetrameric mixture.
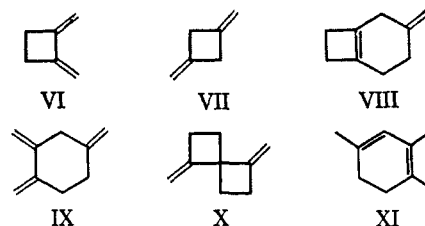
The crude, semiviscous reaction oil was distilled under reduced pressure; the high-boiling fraction was preparatively gas chromatographed and separated into two principal products as determined by parallel analysis on a variety of substrates. The major, homogeneous component (43%) was tentatively identified as the β-tetramer II on three points: similar boiling point, similar refractive index, and similar odor ("kerosene-like"). A molecular weight determination (mass

(1) Part II: B. Weinstein and A. H. Fenselau, *J. Chem. Soc., Sect C,* 368 (1967).

(2) A portion of these results was communicated earlier; see B. Weinstein and A. H. Fenselau, *Tetrahedron Letters,* 1463 (1963).

(3) Presented in part before the Division of Organic Chemistry, 148th National Meeting of the American Chemical Society, Chicago, Ill., Aug 1964, Abstracts, p 72S.

(4) S. V. Lebedev and B. K. Merezhkovsky, *Zh. Russ. Fiz.-Khim. Obshch,* **45,** 1249 (1913).

(5) S. V. Lebedev, *ibid.,* **45,** 1357 (1913).

(6) R. N. Meinert and C. D. Hurd, *J. Am. Chem. Soc.,* **52,** 4540 (1930).

(7) K. Alder and O. Ackermann, *Chem. Ber.,* **87,** 1567 (1954).

(8) A. T. Blomquist and J. A. Verdol, *J. Am. Chem. Soc.,* **78,** 109 (1956).

(9) J. K. Williams and W. H. Sharkey, *ibid.,* **81,** 4269 (1959), footnote 7.

(10) B. C. Anderson, "Gas Chromatography," H. J. Noebek, R. F. Wall, and N. Brenner, Ed., Academic Press Inc., New York, N. Y., 1961, p 327.

(11) Y. M. Slobodin and A. P. Khitrov, *Zh. Obshch. Khim.,* **33,** 153 (1963).

(12) Y. M. Slobodin and A. P. Khitrov, *ibid.,* **33,** 2822 (1963).

(13) Y. M. Slobodin and A. P. Khitrov, *ibid.,* **34,** 1727 (1964).

(14) Y. M. Slobodin and A. P. Khitrov, *Zh. Organ. Khim.,* **1,** 1531 (1965).

spectroscopy, 160) and a microanalysis ($C_{12}H_{16}$) supported the tetrameric nature of this compound. The remaining product is a mixture of both a pentamer and a hexamer of allene, whose structures will be discussed at a later date.

Hydrogenation of the tetramer II under *neutral* conditions (platinum oxide in ethanol) terminated with the consumption of 2 molar equiv of hydrogen. The resulting tetrahydro-β-tetramer ($C_{12}H_{20}$) possessed physical constants in agreement with the earlier values for the tetrahydro-β-tetramer V. However, in *acid* solution (platinum oxide in acetic acid), the β-tetramer II absorbed 3 molar equiv of hydrogen to form a hexahydro-β-tetramer ($C_{12}H_{22}$), which was partially separated into a mixture of three isomers on gas chromatographic analysis. Further reduction of tetrahydro-β-tetramer V in acetic acid provided the same mixture of hexahydro-β-tetramers. Thus, the β-tetramer II contains two easily reduced double bonds and a third, more highly substituted double bond. The originally proposed structure for the β-tetramer II has only two reducible double bonds and must therefore be considered incompatible with the present evidence.

At this point it would be advantageous to state the spectra collected on these various hydrocarbons. The β-tetramer II has in the infrared an intense exocyclic methylene band (816 cm^{-1}) that is not seen in the almost identical spectra of the tetrahydro and hexahydro-β-tetramers. The ultraviolet spectrum of the β-tetramer II in cyclohexane exhibited a maximum around 250 mμ, whose molar extinction coefficient suggested the presence of a chromophore comparable with partial structure XI in trace quantities. An ultraviolet absorption for the tetrahydro-β-tetramer V could be detected using two techniques. First, under dry nitrogen, a maximum at 194 mμ (log ϵ 3.97) was observed in cyclohexane[15,16] and, second, a maximum at 352 mμ was seen in a *n*-hexane solution of iodine.[17] Chemically, the tetrahydro-β-tetramer V reacted smoothly with *m*-chloroperbenzoic acid to yield an unstable monoepoxide. These results permit the conclusion that the tetrahydro-β-tetramer V possesses one tetrasubstituted double bond. No ultraviolet absorption for the hexahydro-β-tetramer was observed by use of these techniques, nor did the compound combine with *m*-chloroperbenzoic acid.

Incisive information on the structure of these tetrameric substances was available from the nmr spectra. The β-tetramer II produced signals at δ 4.65 (4 H), 2.59 (4 H), and a multiplet at 2.33, 2.17, and 2.08 (8 H). The unsplit character of the first resonance and the location suggest the presence of two pairs of methylenecyclohexane hydrogens (or an equivalent nonconjugated 4-methylenecyclohexene system). The second absorption corresponds to two sets of doubly allylic hydrogens, while the last group is characteristic for hydrogens in a singly allylic arrangement. These assignments are very similar to the signals seen for the protons in β-terpinene (XII), in which the doubly allylic hydrogens (H$_y$) absorb at δ 2.72, and the four singly allylic hydrogens (H$_x$) at 2.24, 2.13, and 2.05.[18]

(15) R. A. Micheli and T. H. Applewhite, *J. Org. Chem.*, **27**, 345 (1962).
(16) This measurement was made by Dr. T. H. Applewhite, Western Regional Laboratory, U. S. Department of Agriculture, Albany, Calif., to whom we express our thanks.
(17) W. Hückel and O. Fechtig, *Chem. Ber.*, **92**, 693 (1959).


XII   XIII   XIV
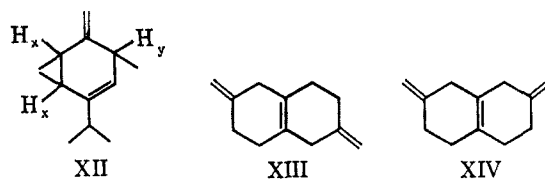
With due consideration for this interpretation of the spectral data, the chemical evidence, and for the fact that any arrangement of carbon atoms must follow a series of allene units (the "allene rule"), then either structure XIII or XIV can represent the β-tetramer.[19] Since it is impossible at this juncture to differentiate between these two, the formula XIII will be used at this time to symbolize the β-tetramer.


XV, 6-methyl   XVII, 6-methyl
XVI, 7-methyl   XVIII, 7-methyl
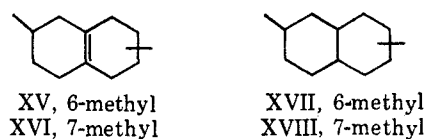
The hydrogenation products would correspond to XV or XVI for the tetrahydro-β-tetramer and XVII or XVIII for the hexahydro-β-tetramer. The observed doublet at δ 1.03 (J = 6 cps) shown by the tetrahydro-β-tetramer(s) does provide supporting evidence for the proposed structures XV and XVI; unfortunately, the difference in the chemical shifts of the allylic and nonallylic hydrogens in the tetrahydro-β-tetramer(s), was not sufficiently great to provide any diagnostic information. To simplify future discussion, the structure XV will symbolize the tetrahydro-β-tetramer, while the hexahydro-β-tetramer is similarly represented by XVII. The chemistry of the hexahydro-β-tetramer XVII may be concluded by stating that both 2,6- and 2,7-dimethylnaphthalenes (XIX and XX) on reduction with hydrogen under pressure using ruthenium catalyst afforded a mixture of three completely saturated decahydronaphthalenes. This composite product is identical with the earlier hexahydro-β-tetramer XVII formed from both compounds XIII and XV.

Treatment of the β-tetramer XIII with hydrogen bromide in glacial acetic acid[20] produced a brominated liquid, which after heating, gave an isomeric hydrocarbon ($C_{12}H_{16}$), described by the trivial name pseudo-β-tetramer, whose constitution is represented by structure XXI or XXII. Again, only the structural formula XXI is employed for the pseudo-β-tetramer. Previously, hydrogenation of XIX and XX, with rhodium-on-alumina catalyst, yielded both authentic XXI and XXII, but the products had not been fully characterized.[21] A repetition of this work afforded both XXI

XIX, 6-methyl   XXI, 6-methyl   XXIII, 6-methyl
XX, 7-methyl   XXII, 7-methyl   XXIV, 7-methyl
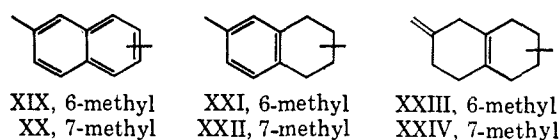
(18) B. M. Mitzner and E. T. Theimer, *J. Org. Chem.*, **27**, 3359 (1962).
(19) Three more interesting isomeric representations are conceivable, but are inadmissible on the basis of subsequent information.

i   ii   iii
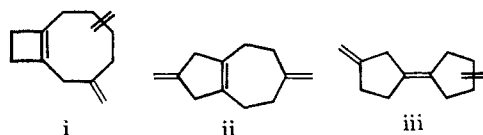
(20) J. G. Traynham and W. C. Baird, Jr., *ibid.*, **27**, 3189 (1962).
(21) E. A. Coulson, *J. Chem. Soc.*, 77 (1935).

and XXII, whose ultraviolet spectra are identical with those of the pseudo-β-tetramer XXI. The nmr spectrum of the isomerized XXI corroborated the suspected tetralin ring system by providing signals at δ 6.77 (3 H, aromatic), 2.9–2.5 (4 H, benzylic), 2.23 (3 H, aromatic methyl), 2.2–1.2 (3 H, aliphatic), and 1.04 (3 H, secondary methyl, J = 6 cps) Thus, the β-tetramer XIII is confirmed as a bicyclic [4.4.0]dec-9,10-ene derivative; however, no insight is furnished into the orientation of the two methylene groups.

The complete aromatization of the β-tetramer XIII was achieved by subjecting it to the action of chloranil in refluxing benzene.[22] The progress of the reaction was monitored by gas chromatography. Initially, the formation of the pseudo-β-tetramer XXI was detected, but after 36 hr the concentration of a third component reached a maximum, with a retention time identical with either of the naphthalenes XIX and XX. After chromatography over alumina, the impure product yielded a colorless, crystalline compound (35–40%), whose infrared and ultraviolet spectra suggested that the material was composed of XIX and XX in almost equal amounts. This assumption was completely verified by spectral measurements on artificial mixtures. The melting points of both the naphthalenic hydrocarbon and the picrate derivative showed a depression from the sums expected for the pure 2,6- or 2,7-dimethylnaphthalenes. Unequivoval proof that the two naphthalenes XIX and XX were present in equal quantities was achieved by gas chromatography of a sample on a substrate known to be specific for mixtures of various alkylnaphthalenes (Bentone-34 combined with SE-30).[23–25] Two peaks were seen with retention times identical with those of pure XIX and XX. This result was extremely gratifying, as these particular isomeric dialkylnaphthalenes appear as a single peak on many gas chromatographic substrates.[26]

In one instance the crude, dehydrogenated β-tetramer reaction liquid was directly treated with picric acid to produce 2,7-dimethylnaphthalene picrate (15%), identical with an authentic sample; yet, no preferential separation of a similar picrate from a solution containing equal amounts of pure XIX and XX was observed, and attempts to repeat the original result met with failure. The evidence so far presented clearly establishes that the β-tetramer must be a mixture of equal amounts of both XIII and XIV, while the tetrahydro-β-tetramer consists of XV and XVI, the hexahydro-β-tetramer is composed of XVII and XVIII, and the pseudo-β-tetramer is comprised of XXI and XXII.

Lebedev described an α-tetramer I, but such a substance was not seen in the work here. However, a very small amount of a different product (1.9%) was isolated and characterized as dihydro-β-tetramer (XXIII or XXIV). The formula $C_{12}H_{18}$ followed from

both a microanalysis and a mass spectral molecular weight determination. The compound did not possess any significant absorption in the ultraviolet; in the infrared, the most prominent feature was an exocyclic methylene peak. The nmr spectrum contained signals at δ 4.69 (2 H, exocyclic methylene) and 0.95 (3 H, secondary methyl, J = 5 cps). Hydrogenation of the β-tetramer in ethanol using just 1 equiv of hydrogen gave a mixture, which was separated by preparative gas chromatography into starting material, tetrahydro-β-tetramer, and a dihydro-β-tetramer. This latter substance was shown to be identical with the original dihydro-β-tetramer on the basis of physical, infrared, and mass spectral comparisons The dihydro-β-tetramer found in the allene polymerization liquid is therefore a mixture of XXIII and XXIV

To rationalize the existence of the dihydro-β-tetramer, two explanations were entertained: first, a hydrogen-transfer reaction between the β-tetramer and some other species was occurring in the sealed-tube reaction vessel; or, secondly, an impurity, specifically propene, was present in the allene. The crude oligomer mixture was subjected to both gas chromatographic and ultraviolet spectroscopic analysis in order to seek evidence for the presence of any possible aromatic derivatives of the tetramer, formed as the result of an internal aromatization process. None of these substances was observed to be present in detectable amounts (>0.5%). Unfortunately, the allene from the first commercial source was now exhausted and a sample was no longer available for mass spectral and gas chromatographic analyses. The allene from a second supplier did not produce the dihydro-β-tetramer in a parallel polymerization, which suggested that the original allene was contaminated with propene. It is conceivable that Lebedev's α-tetramer I could have resulted from the presence of a similar impurity.

A proposed mechanism for the formation of the two β-tetramers XIII and XIV follows.

VI   VIII   IX

IX   XIII   XIV
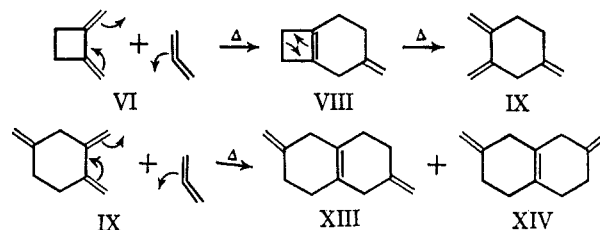
The conjugated diene 1,2-dimethylenecyclobutane (VI) reacts with excess allene to form 3-methylenebicyclo[4.2.0]octa-1,6-ene (VIII) either by a Diels–Alder mechanism or by formal radical intermediates. Literature support for a Diels–Alder sequence involving allene is somewhat sparse, but several examples have been reported in recent years.[27–30] Trimer VIII then undergoes a thermally induced rearrangement to yield 1,2,4-trimethylenecyclohexane (IX) by means of a valence isomerization sequence.[31] Trimer IX is the thermodynamically favored structure, since it possesses some conformational freedom, in addition to several less

(22) E. A. Brande, L. M. Jackman, R. P. Linstead, and G. Lowe, J. Chem. Soc., 3123 (1960).

(23) J. V. Mortimer and P. L. Gent, Nature, 197, 789 (1963).

(24) "Aerograph Research Notes," Summer Issue, Wilkens Instrument and Research, Walnut Creek, Calif., 1963, p 2.

(25) An inferior separation of 2,6- and 2,7-dimethylnaphthalene is obtained with Bentone 34 and Apiezon L as the substrate; see M. Van Der Stricht and J. Van Rysselberge, J. Gas Chromatog., 1, 29 (1963).

(26) A capillary column, 200 ft × 0.01 in., and coated with poly-m-phenyl ether, failed to resolve a mixture of 2,6- and 2,7-dimethylnaphthalene; see "Previews and Reviews," Varian Aerograph, Walnut Creek, Calif., May 1966, p 5.

(27) H. Pledger, Jr., J. Org. Chem., 25, 278 (1960).

(28) D. S. Matteson, J. J. Drysdale, and W. H. Sharkey, J. Am. Chem. Soc., 82, 2853 (1960), footnote 3.

(29) E. V. Elam and R. H. Hasek, U. S. Patent 2,906,541 (Nov 15, 1960); Chem. Abstr., 55, 7321b (1961).

(30) W. C. Agosta, J. Am. Chem. Soc., 86, 2638 (1964).

(31) E. Vogel, Angew. Chem. Intern. Ed. Engl., 2, 1 (1963).

Table I
Gas Chromatographic Data for β-Tetramers and Related Derivatives

Compd	Instrumental detection[a]	Column substrate[b]	Column temp, °C[c]	Flow rate[d]	Retention time[e]
β-Tetramer	T	EGS	150	75	10.5
	H	DEGS	86	15	14.8
	H	DEGS	130	15	3.6
Dihydro-β-tetramer	T	EGS	150	75	6.4
	H	DEGS	110	15	6.1
Tetrahydro-β-tetramer	H	DEGS	86	15	7.2
Hexahydro-β-tetramer	H	DEGS	86	15	5.7, 6.3, 6.6
	T	DEGS	110	50	7.1, 9.1, 11.0
2,6-Dimethyldecalin	T	DEGS	110	50	7.1, 9.2, 11.6
2,7-Dimethyldecalin	T	DEGS	110	50	7.1, 9.1, 10.9
Pseudo-β-tetramer	H	DEGS	130	15	6.3
2,6- and 2,7-dimethyltetralin	H	DEGS	130	15	6.3
Dehydrogenated β-tetramer	H	DEGS	130	15	10.9
2,6- and 2,7-dimethylnaphthalene	H	DEGS	130	15	10.8

[a] Thermal conductivity (T) or hydrogen flame (H).   [b] Diethylene glycol succinate (DEGS), ethylene glycol succinate (EGS).   [c] Regulated.   [d] Helium and hydrogen carrier gases (in milliliters per minute).   [e] Given in minutes.

eclipsed hydrogens, which are denied to the more rigid bicyclo[4.2.0]octane system (VIII). The unsymmetrical conjugated diene system in compound IX is very reactive and combines with excess allene by a second Diels–Alder or radical route to give two adducts, 2,6-dimethylenebicyclo[4.4.0]dec-9,10-ene (XIII) and 2,7-dimethylene bicyclo[4.4.0]dec-9,10-ene (XIV).

The synthesis of the dihydro-β-tetramer follows an analogous sequence, in which the trimer IX adds to propene to give 2-methylene-7-methylbicyclo[4.4.0]-dec-9,10-ene (XXIII) and 2-methylene-6-methyl-bicyclo[4.4.0]dec-9,10-ene (XXIV).

   IX   XXIII   XXIV
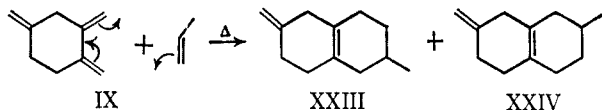
In closing, it should be noted that all of these reactions have been represented as irreversible processes. This hypothesis was tested in only one case and shown to be a valid conclusion. The β-tetramer was heated at 140° in a sealed tube in the absence of allene, and after 36 hr only unchanged β-tetramer was observed on gas chromatographic examination. This choice of material represents a reasonable model in that bond breaking with the formation of at least two fragments is required if an equilibrium is involved in the formation of these adducts.

Experimental Section

All boiling points are uncorrected. The infrared spectra were obtained as neat films for liquids or in potassium bromide disks for solids on a Perkin-Elmer Model 421 double-grating instrument, and the ultraviolet spectra were taken in cyclohexane with a Cary Model 14 or a Beckman Model DK-2 spectrophotometer, unless otherwise stated. Molecular weights were determined with a Consolidated Electrodynamics Corp. Model 21-103C mass spectrometer. The nmr spectra were measured by a Varian Associates Model A-60 spectrometer with the compounds dissolved in deuteriochloroform containing tetramethylsilane as an internal reference. Gas–liquid partition chromatography was accomplished by use of Wilkens Aerograph A-600B (hydrogen flame) and A-90-P2 (thermal conductivity) instruments. Consistent and corroborative results were obtained from both detector devices, but the data were not specifically corrected for varying molar detector response. Diethylene glycol succinate polyester, ethylene glycol succinate polyester, phenyldiethanolamine succinate polyester, 1,2,3-triscyanoethoxypropane, and Carbowax 20 M were generally the most useful analytical sub-

strates. These liquids were used in a concentration of 20% by weight on hexamethyldisilazane-treated Chromosorb W (60–80 mesh). The columns were made of stainless steel tubing with a length of 2.0 m and an outside diameter of 0.63 cm. Gas chromatographic data is given in Table I. Glass plates coated with Brinkmann Instruments silica gel G were routinely employed for thin layer chromatography with a solution of 2% ceric sulfate–sulfuric acid (2 N) as the developer. The elemental analyses were performed by Messrs. E. H. Meier and J. Consul of the Microanalytical Laboratory, Department of Chemistry, Stanford University.

Isolation of the Tetrameric Oligomers of Allene.—The crude reaction mixture, obtained by heating liquid allene in a sealed glass tube at 140° for 36 hr, provided only a small amount of condensate with a boiling range under 150° at atmospheric pressure. A spinning-band column distillation at reduced pressure gave two main fractions, bp 95–100° (9.0 mm) and 72–75° (0.02 mm). Further separation was effected by preparative gas chromatography with a Beckman Instruments Megachrom equipped with 1.83-m Ucon Polar columns (170°, 9-psi pressure difference), followed by a second separation using a 2.0-m 1,2,3-triscyanoethoxypropane column in the aerograph A-90-P2. The presence of compounds with retention times equal to 2,6- and 2,7-dimethyltetralin or 2,6- and 2,7-dimethyldecalin was not observed in the crude oligomer mixture.

2,6- and 2,7-Dimethylenebicyclo[4.4.0]dec-9,10-ene (β-Tetramer).—These were isolated as a colorless liquid: bp 107–108° (13 mm); n^{25}D 1.5248 [lit. bp 101° (10 mm), n^{20}D 1.5262[4,5]]; M (mass spectrometer) 160; infrared spectrum, 3065 m (C=CH), 2890 s (CH), 1645 m (C=C), and 876 s (=CH₂) cm⁻¹; ultraviolet spectrum showed end absorption; nmr spectrum, δ 4.65 singlet (area 4, exocyclic methylene), 2.59 singlet (area 4, doubly allylic), 2.17 triplet (area 8, singly allylic, J = 4 cps).

The β-tetramer (1.0 g) was sealed under nitrogen in a Carius tube and was heated to 140° for 36 hr. At the end of this period the tube was opened and the slightly yellow product was examined by gas chromatography with the use of both EGS and DEGS columns. The chromatograms were identical with those obtained from the tetramer before heating.

Anal. Calcd for C₁₂H₁₆: C, 89.94; H, 10.06. Found: C, 89.91; H, 10.14.

2,6- and 2,7-Dimethyl[4.4.0]dec-9,10-ene (Tetrahydro-β-tetramer).—An alcoholic solution (25.0 ml) of β-tetramer (2.00 g, 0.0125 mole) was added to a stirred, previously reduced suspension of platinum oxide (0.204 g) in absolute ethanol (20.0 ml). Hydrogen gas was readily absorbed for about 1 hr, at which point the reaction ceased. A longer reaction time of 10 hr or heating the contents of the hydrogenation flask to 60° with a lamp failed to increase the consumption of hydrogen beyond 2.03 molar equiv. The filtered solution was evaporated under reduced pressure to afford a colorless oil (2.01 g), which consisted only of a single component by routine screening on a variety of gas chromatographic substrates: bp 132–134° (55 mm); n^{30}D 1.4795 [lit. bp 95° (13.5 mm); n^{20}D 1.4829[4,5]]; M (mass spectrometer) 164; infrared spectrum, 2910 s (CH), 1450 and 1435 s (CCH₃); ultraviolet spectrum, 194 mμ (log ε 3.97); nmr spectrum, δ

2.0–1.0 multiplets and 0.91 doublet ($J = 5$ cps). A sample of tetrahydro-β-tetramer was dissolved in n-hexane (10.0 ml) and then diluted with an equal volume of a solution prepared by addition of iodine (0.100 g) to n-hexane (100.0 ml). The mixed solution was spectrophotometrically compared with a second solution composed of equal volumes of n-hexane and the stock iodine solution. There was observed a maximum at 352 mμ (ε' 8.5). The compound was titrated in chloroform with standardized m-chloroperbenzoic and was found to contain one double bond. The isolated, but unstable monepoxide was not characterized.

Anal. Calcd for $C_{12}H_{20}$: C, 87.73; H, 12.27. Found: C, 87.59; H, 12.04.

2,6- and 2,7-Dimethyl[4.4.0]decane (Hexahydro-β-tetramer). A. From β-Tetramer.—A glacial acetic acid solution (5.0 ml) of β-tetramer (0.080 g, 0.00050 mole) was added to a stirred, previously reduced suspension of platinum oxide (0.010 g) in glacial acetic acid (2.0 ml). The reaction proceeded rapidly for 20 min with the absorption of hydrogen corresponding to 2.0 molar equiv followed by the slow uptake of another 0.98 mole of hydrogen gas in the next 30 min. No additional absorption of hydrogen was noted in an additional 9-hr period. The filtered solution was poured onto ice (70 g) and the aqueous phase was extracted with ether (three 150-ml portions). The combined ethereal extracts were dried over anhydrous magnesium sulfate and the solvent was removed *in vacuo* to yield a colorless oil (0.080 g), which consisted of three components by routine screening on a variety of gas chromatographic substrates: bp 215–216° (750 mm); $n^{27.5}$D 1.4665; M (mass spectrometer) 166; infrared spectrum, 2910 s (CH), 1450 and 1440 m (CH₃), and 1370 mw cm⁻¹; ultraviolet spectrum showed end absorption.

Anal. Calcd for $C_{12}H_{22}$: C, 86.66; H, 13.34. Found: C, 86.81; H, 13.18.

B. From Tetrahydro-β-tetramer.—Tetrahydro-β-tetramer (0.081 g, 0.00050 mole) was hydrogenated with the aid of pre-reduced platinum oxide catalyst (0.030 g) in glacial acetic acid (5.0 ml). Within 1 hr the gas uptake terminated with an absorption of 0.98 molar equiv of hydrogen. Employment of the isolation technique described in part A furnished a hydrocarbon whose gas chromatographic and physical properties were identical with those of the authentic hexahydro-β-tetramer mixture.

C. From 2,6-Dimethylnaphthalene.—High-pressure (1000 psi of hydrogen gas) reduction of 2,6-dimethylnaphthalene (26.0 g, 0.166 mole) was readily accomplished at 80° within 30 min using absolute ethanol as a solvent and ruthenium oxide (2.5 g) as a catalyst. The filtered solution was evaporated *in vacuo* and the colorless, residual liquid was distilled at 216–218° (755 mm) to yield 2,6-dimethyl-1,2,3,4,5,6,7,8,9,10-decahydronaphthalene (24.5 g). On gas chromatography the liquid appeared to be a mixture of three substances (1:7:1) whose retention times were identical with those observed for the hexahydro-β-tetramer mixture. The neat infrared spectrum showed only minor differences with an authentic sample; the index of refraction (n^{25}D 1.4706) was slightly greater ($n^{27.5}$D 1.4665).

Anal. Calcd for $C_{12}H_{22}$: C, 86.66; H, 13.34. Found: C, 86.72; H, 13.38.

D. From 2,7-Dimethylnaphthalene.—High-pressure (1000 psi of hydrogen gas) reduction of 2,7-dimethylnaphthalene, followed by the isolation procedure described in part C, gave 2,7-dimethyl-1,2,3,4,5,6,7,8,9,10-decahydronaphthalene, purified by distillation at 213° (750 mm). Gas chromatography revealed that the product consisted of three components (1:4:4) with retention times virtually the same as those of the authentic hexahydro-β-tetramer mixture. The neat infrared spectrum was almost superimposable with the products obtained in both parts A, B, and C; the index of refraction (n^{25}D 1.4714) was slightly greater (n^{25}D 1.4706).

Anal. Calcd for $C_{12}H_{22}$: C, 86.66; H, 13.34. Found: C, 86.38; H, 13.21.

2-Methylene-6- and -7-methyl[4.4.0]dec-9,10-ene (Dihydro-β-tetramer). A. From Oligomer Mixture.—Dihydro-β-tetramers were obtained as a colorless liquid: M (mass spectrometer) 162; infrared spectrum, 3070 w (C=CH), 2910 s (CH), 1660 m (C=C), 1450 m (CH₃), 1353 m and 880 s (C=CH₂) cm⁻¹; ultraviolet spectrum showed end absorption; nmr spectrum, δ 4.68 singlet (area 2, exocyclic methylene), 2.61 singlet (area 2, doubly allylic), 2.5–1.1 (area 11, singly allylic and saturated), 0.94 doublet (area 3, methyl group located on a tertiary carbon, $J = 5$ cps).

Anal. Calcd for $C_{12}H_{18}$: C, 88.82; H, 11.18. Found: C, 88.44; H, 11.07.

B. From β-Tetramer.—A solution of β-tetramer (0.320 g, 0.0010 mole) in absolute ethanol (5.0 ml) was added to a stirred suspension of previously reduced platinum oxide (0.010 g) in ethanol (5.0 ml). After 1 equiv of hydrogen gas had been absorbed, the reaction was terminated and the mixture was processed in the usual manner. Gas chromatography on an EGS column demonstrated the presence of unreduced β-tetramer (35%), tetrahydro-β-tetramer (31%), and a third substance (34%). This latter material was collected on a preparative scale to give a product whose retention times on both EGS and DEGS substrates were identical with those of the material described in part A. The mass spectral fragmentation pattern and the infrared spectrum were superposable with authentic dihydro-β-tetramer.

2,6- and 2,7-Dimethyl-1,2,3,4-tetrahydronaphthalene (Pseudo-β-tetramer). A. From β-Tetramer.—To a chilled (10°), stirred, and nitrogen-blanketed solution of β-tetramer (2.02 g, 0.0126 mole) in glacial acetic acid (16.0 ml) was added at once a mixture of 30–32% hydrogen bromide in acetic acid (7.0 g, 0.0259 mole of HBr) and glacial acetic acid (9.0 ml). After 30 min, gas chromatographic analysis indicated the complete conversion of the β-tetramer into several products; therefore, at the end of 1 hr, the purple solution was poured onto ice (100.0 g) and the organic material was extracted with n-pentane (two 150-ml portions). The combined extracts were washed to neutrality with both 5% sodium bicarbonate solution and water and dried with magnesium sulfate, and the solvent was removed *in vacuo*. The cloudy, green residual oil (3.00 g) was chromatographed on an alumina column (17.0 g, neutral, activity I) using n-hexane (100.0 ml) as the eluent. On evaporation of the solvent, the remaining oil (2.38 g) proved to be unstable even at −20° in the absence of air. The infrared spectrum revealed the total absence of the band at 875 cm⁻¹ (C=CH₂). The ultraviolet spectrum exhibited only end absorption with a shoulder at 245 mμ (ε ca. 2800). Two drops of the oil added to a saturated solution of silver nitrate in ethanol gave a thick, white precipitate of silver bromide. This bromo-substituted product could not be further purified for elemental analysis.

Preparative gas chromatography on a DPEAS column gave only a new compound: M (mass spectrometer) 160; infrared spectrum 3040 w (C=CH), 2910 s (CH), 1610 and 1570 w (C=C), 1450 m, 805 m and 795 (ortho-disubstituted benzene) cm⁻¹; ultraviolet spectrum, 215 mμ (log ε 3.94), 264 (2.78), 269 (2.93), 272 (2.90), and 278 (3.03); nmr spectrum, δ 6.77 (area 3, aromatic), 2.90–2.33 (area 4, benzilic), 2.23 singlet (area 3, methyl group attached to an aromatic ring), 2.2–1.2 (area 3, alicyclic), and 1.03 doublet (area 3, aliphatic methyl attached to a tertiary carbon, $J = 5$ cps).

Anal. Calcd for $C_{12}H_{16}$: C, 89.94; H, 10.06. Found: C, 89.91; H, 10.14.

B. From 2,6-Dimethylnaphthalene.—A high-pressure autoclave was charged with a small amount of rhodium-on-alumina catalyst (1.0 g) and a solution of 2,6-dimethylnaphthalene (7.8 g, 0.050 mole) in methylcyclohexane (200.0 ml) and pressurized with hydrogen gas to 1000 psi at room temperature. The rocked reaction vessel was heated (50°) overnight and cooled, and the filtered contents were distilled to yield 2,6-dimethyl-1,2,3,4-tetrahydronaphthalene (or 2,6-dimethyltetralin) (7.0 g). The product was repurified by preparative gas chromatography with a DEGS column to give a colorless liquid: bp 117° (14–16 mm); n^{25}D 1.5227; mp −5° (lit.[21] bp 237–239°; mp 14–17°); infrared spectrum, 3040 w (C=CH), 2910 s (CH), 1610 and 1570 w (C=C), 1450 m, 805 and 795 m (ortho-disubstituted benzene) cm⁻¹; ultraviolet spectrum, 215 mμ (log ε 3.96), 263 (2.72), 268 (2.90), 272 (2.68), and 277.5 (3.01).

Anal. Calcd for $C_{12}H_{16}$: C, 89.94; H, 10.06. Found: C, 89.60; H, 10.00.

C. From 2,7-Dimethylnaphthalene.—High-pressure (1000 psi of hydrogen gas) reduction of 2,7-dimethylnaphthalene (10.0 g, 0.064 mole) as described in part B, followed by the same isolation procedure, afforded 2,7-dimethyl-1,2,3,4-tetrahydronaphthalene (or 2,7-dimethyltetralin) (9.0 g). Additional purification by gas chromatography yielded a colorless liquid: bp 119° (15 mm); $n^{26.5}$D 1.5218; mp −15° (lit.[21] bp 237–238°; mp <0°); infrared spectrum, 3040 w (C=CH), 2910 s (CH), 1610 and 1570 w (C=C), 1450 m, 810 and 790 m (ortho-disubstituted benzene) cm⁻¹; ultraviolet spectrum, 215 mμ (log ε 3.97), 264.5 (2.71), 269.5 (2.90), 272.5 (2.87), and 278 (3.02).

Anal. Calcd for $C_{12}H_{16}$: C, 89.94; H, 10.06. Found: C, 89.83; H, 9.97.

Chloranil Dehydrogenation of β-Tetramer.—An anhydrous benzene solution (250 ml) of β-tetramer (3.00 g, 0.0187 mole) and sublimed chloranil (15.0 g, 0.0525 mole) was gently refluxed under dry nitrogen for 36 hr. Periodically, samples were removed and analyzed by gas chromatography on a DEGS column. Only the tetramer was detected initially, but within 1 hr several substances had formed with longer retention times. The most abundant of these new materials had a retention time identical with that of either of the dimethyltetralins. At the end of 4 hr a third product with a retention time equal to that of either of the dimethylnaphthalenes was present to the same extent as the tetralin; the amount of unreacted tetramer still exceeded their combined amounts. After 10 hr the ratio of tetramer to tetralin to naphthalene was about 2:1:1. By the end of 36 hr the naphthalene peak was the only one present, although the chromatogram suggested the presence of trace amounts of both tetramer and tetralin. The cooled, brown reaction solution was filtered, the solvent was removed *in vacuo*, and the residual solid was triturated with hot *n*-pentane. The combined extracts were taken to dryness and the tan, semisolid (3.2 g) was placed directly on an alumina column (activity I, neutral, 125 g, packed in hexane). Elution with *n*-hexane (500 ml) gave an off-white, naphthalenic material (1.12 g), which was sublimed twice: mp 70–85°; infrared spectrum, 3040 and 3010 w, 2900 m, 1630 and 1600 mw, 1505 mw, 960 and 905 mw, 882 m, 830 and 815 s, and 632 mw cm^{-1}; ultraviolet spectrum, 228 mμ (log ε 5.03), 273 (3.69), 302 (2.64), 309 (2.69), 317 (2.56), and 323.5 (2.75). Gas chromatography at 179° on a 12-ft column packed with 15% Bentone-34 combined with 5% SE-30 methyl silicone gum using a hydrogen flame detector resolved the product into two components (44:56) with retention times of 53.7 and 57.1 min, respectively.

A 52:48 mixture of 2,6-dimethylnaphthalene and 2,7-dimethylnaphthalene possessed an infrared spectrum almost identical with that exhibited by the naphthalenic material isolated from the dehydrogenation of the β-tetramer. A 1:1 mixture of both dimethylnaphthalenes closely approximated the ultraviolet spectrum of the dehydro-β-tetramer. Both 2,6- and 2,7-di-

methylnaphthalene individually have similar, but different infrared and ultraviolet spectral patterns. On the Bentone-34 column, the retention times for 2,6- and 2,7-dimethylnaphthalene are 53.4 and 57.1 min, respectively.[24] A 1:1 mixture gave a resolution pattern and retention times identical with that of the dehydro-β-tetramer sample.

Another portion (0.080 g) of the dehydro-β-tetramer was dissolved in ethanol (5.0 ml) containing picric acid (0.150 g) and on standing gave yellow needles (0.180 g), mp 124–130°. The naphthalene mixture (0.075 g) recovered from decomposition of the picrate on an alumina column (activity I, basic, 5 g) with ether elution gave a product, which, on sublimation, possessed properties identical with those described previously for dehydro-β-tetramer. An equal mixture of 2,6- and 2,7-dimethylnaphthalenes (0.050 g) was used to prepare a picrate analogous to the above procedure (yellow needles), mp 120–130°. In one experiment, repeated recrystallization, rechromatography, and resublimation of the picrate (0.785 g) derived from dehydro-β-tetramer gave a small amount of 2,7-dimethylnaphthalene, mp 93–94°; the picrate had mp 131–133° and depressed melting points with 2,6-dimethylnaphthalene and the corresponding picrate.

Registry No.—Allene, 463-49-0; 2,6-dimethylenebicyclo[4.4.0]dec-9,10-ene, 13064-99-8; 2,7-dimethylenebicyclo[4.4.0]dec-9,10-ene, 13065-00-4; 2,6-dimethyl-[4.4.0]dec-9,10-ene, 13065-01-5; 2,7-dimethyl[4.4.0]dec-9,10-ene, 13065-02-6; 2,6-dimethyl[4.4.0]decane, 1618-22-0; 2,7-dimethyl[4.4.0]decane, 3868-66-4; 2-methylene-6-methyl[4.4.0]dec-9,10-ene, 13065-04-8; 2-methylene-7-methyl[4.4.0]dec-9,10-ene, 13065-05-9; 2,6-dimethyl-1,2,3,4-tetrahydronaphthalene, 7524-63-2; 2,7-dimethyl-1,2,3,4-tetrahydronaphthalene, 13065-07-1.

Aryl-Substituted Propargyl Alcohols and Related Compounds. II. 1-Mesityl-1,3-diphenyl-2-propyn-1-ol and 1-(α-Naphthyl)-1,3-diphenyl-2-propyn-1-ol[1,2]

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An acetylene–allene rearrangement occurs during conversion of 1-mesityl- and 1-(α-naphthyl)-1,3-diphenyl-2-propyn-1-ol to chlorides; the latter have allenyl structures. The relative ease of attack at the propargyl and allenyl positions of the carbonium ions (IV) formed from these and related alcohols and chlorides appears to depend on the hindrance around the unsaturated system. The mesityl chloro compound yields allenyl ethers with sodium alkoxides but in the α-naphthyl series only propargyl ethers were isolated although with sodium ethoxide some of the allene was probably formed. All of the compounds are readily converted to α,β-unsaturated ketones. Infrared spectra in the region 1000–1300 cm^{-1} are not very useful to distinguish propargyl from allenyl ethers and are worthless to show that a given reaction mixture has both such ethers present.

It was suggested earlier[1] that reactions of aryl-substituted propargyl alcohols such as I are best understood on the basis of carbonium ion intermediates such as IV. Reversible reactions were generally found to yield allenic products such as II or products expected from further reactions of the allenes (*e.g.*, VII). Attack on IV appeared to occur more rapidly at the propargyl

position unless that position was hindered. The present work was undertaken to show the generality of these suggestions and to explore more carefully the effect of hindrance around the carbon adjacent to the acetylenic group.

Most of the halides described in the first paper[1] had been reported earlier to have propargyl structures (IIIa, b, and b') but all in fact were allenyl halides (IIa, b, and b') and infrared spectral studies failed to show that the propargyl halides were present in the crude reaction mixtures. Repeated attempts to obtain halides of propargyl structures were unsuccessful; it was suggested that, with a leaving group as good as

(1) For part I, see T. L. Jacobs and D. M. Fenton, *J. Org. Chem.*, **30**, 1808 (1965), where references are given to earlier work on compounds of the type discussed in the present paper.

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