Oligomers of Allene. IV.[1] Pentamers Formed in the Thermal Polymerization of Liquid Allene[2]

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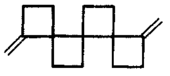
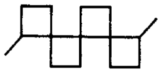
Polymerization of allene gives four pentamers—6′-methylene-3′,4′,7′,8′-tetrahydrospiro[2- and 3-methylene]cyclobutane-1,2′(1′H,5′H)-naphthalene and 7′-methylene-3′,4′,5′,6′-tetrahydrospiro[2- and 3-methylene]cyclobutane-1,2′(1′H,8H′)-naphthalene. Hydrogenation afforded 6′-methyl-3′,4′,7′,8′-tetrahydrospiro[2- and 3-methyl]cyclobutane-1,2′(1′H,5′H)-naphthalene and 7′-methyl-3′,4′,5′,6′-tetrahydro[2- and 3-methyl]cyclobutane-1,2′(1′H,8H′)-naphthalene or 6′-methyl-3′,4′,7′,8′,9′,10′-hexahydrospiro[2- and 3-methyl]cyclobutane-1,2′(1′H,5′H)-naphthalene and 7′-methyl-3′,4′,5′,6′,7′,8′-hexahydro[2- and 3-methyl]cyclobutane-1,2′(1′H,8H′)-naphthalene, depending upon the exact conditions. Attempted aromatization of the pentamer mixture by chloranil led to the dehydro pentamers 6′-methyl-3′,4 -dihydrospiro[2- and 3-methylene]cyclobutane-1,2′(1′H)-naphthalene and 7′-methyl-3′,4′-dihydrospiro[2- and 3-methylene]cyclobutane-1,2′(1′H)-naphthalene. Ozonolysis of the dehydro pentamers yielded 6′-methyl-3′,4′-dihydrospiro[2- and 3-]cyclobutanone-1,2′(1′H)-naphthalene and 7′-methyl-3′,4′-dihydrospiro[2- and 3-]cyclobutanone-1,2′(1′H)-naphthalene.

The thermal polymerization of allene gives a series of higher oligomers whose structures were originally assigned on the basis of a combination of microanalytical, oxidation, and hydrogenation data.[3,4] For example, allene pentamer (I), a major product, absorbed 2 equiv of hydrogen to form the tetrahydro pentamer (II); the saturated nature of the latter was ascertained by a failure to react with bromine water. No further work has been devoted to this material, although the gaseous and liquid phase polymerization of allene has been extensively restudied in the last half-century.[5–13]



I



II

Recently, a new investigation furnished a large quantity of mixed allene oligomers. The dimer fraction was shown to be a mixture of 1,2-dimethylenecyclobutane and 1,3-dimethylenecyclobutane, while the trimer fraction was composed of 3-methylenebicyclo-[4.2.0]octa-1,6-ene, 1,2,4-trimethylenecyclohexane, and 1,5- or 1,6-dimethylenespiro[3.3]heptane.[14] The tetramer fraction consisted of 2,6-dimethylenebicyclo-[4.4.0]dec-9,10-ene, 2,7-dimethylenebicyclo[4.4.0]dec-9,10-ene, 2-methylene-6-methylbicyclo[4.4.0]dec-9,10-ene, and 2-methylene-7-methylbicyclo[4.4.0] dec-9,10-ene.[1] A report is now made on the exact nature of the pentameric oligomer.

A typical allene polymerization yielded a high-boiling mixture, which was separated by gas chromatography into pentameric and four higher oligomeric fractions, as determined by parallel analysis on a variety of substrates. The principal component was tentatively identified as the pentamer I by comparison with the original constants for the boiling point and refractive index. An analytical chromatogram revealed that the pentamer actually consisted of two components. Every effort to separate on a preparative scale the shoulder of the major peak was frustrated; however, for quantitative purposes a capillary column resolved this mixture into a 3:1 ratio of two constituents.[15] A molecular weight determination (mass spectroscopy, 200) and a microanalysis ($C_{15}H_{20}$) on the liquid supported the pentameric formulation.

Hydrogenation of the pentamer I under neutral conditions (platinum oxide in ethanol) terminated with the consumption of 2 molar equiv of hydrogen. The resulting tetrahydro pentamer ($C_{15}H_{24}$), seen as a mixture of three compounds by gas chromatography, possessed physical constants in agreement with the literature values attributed to the tetrahydro pentamer II. However, in acid solution (platinum oxide in glacial acetic acid), the pentamer I absorbed 3 molar equiv of hydrogen to form a hexahydro pentamer ($C_{15}H_{26}$), consisting of four components. Further reduction of the tetrahydro pentamer in acetic acid led to the same mixture of hexahydro pentamers. This information permits the pentamer to be formulated with three cyclic rings, two easily reduced centers of unsaturation, and a third, highly substituted double bond. The older structures for the pentamer I and the dihydro pentamer II must be considered incompatible with the present evidence.

The infrared spectrum of the pentamer disclosed an intense exocyclic methylene (872 cm^{-1}). In contrast, the spectra of the tetrahydro pentamers and hexahydro pentamers were almost identical and did not contain the methylene band. The ultraviolet spectrum of the pentamer had no selective absorption peak; thus, the various unsaturated centers cannot exist in a conjugated pattern. The existence of a residual tetrasubstituted double bond in the tetrahydro pentamer was confirmed however by a maximum (350 $m\mu$) as observed in an *n*-hexane solution of iodine.[16] The 60-MHz nuclear magnetic resonance (nmr) spectrum of

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[1] Part III: B. Weinstein and A. H. Fenselau, *J. Org. Chem.*, **32**, 2278 (1967).

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

[3] S. V. Lebedev and B. K. Merezhkousky, *Zh. Russ. Fiz-Khim. Obshch.*, **45**, 1249 (1913).

[4] S. V. Lebedev, *ibid.*, **45**, 1357 (1913).

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

[6] K. Alder and O. Ackmermann, *Chem. Ber.*, **87**, 1567 (1954).

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

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

[9] 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.

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

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

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

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

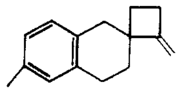
[14] B. Weinstein and A. H. Fenselau, *J. Chem. Soc., Sect. C*, 368 (1967).

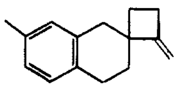
[15] This measurement was made by Dr. R. Teranishi, Western Regional Laboratory, U. S. Department of Agriculture, Albany, Calif., to whom we express our thanks. The column was 30.5 m long and was coated with SF-96.

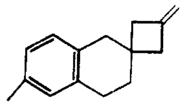
[16] W. Hückel and O. Fechtig, *Chem. Ber.*, **92**, 693 (1959).

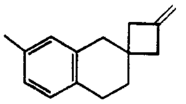
the pentamer held signals at δ 4.70 (singlet, vinylic methylene, 4 H), 2.61 (singlet, doubly allylic, 2 H), 2.39 and 2.19 (triplet, singly allylic), and 2.0–1.6 (complex, saturated). At 100 MHz the methylenic region resolved sufficiently to imply, but not establish, the presence of a methylenecyclobutane ring system.

The pentameric fraction could be dehydrogenated by chloranil in a facile manner to a dehydro pentamer ($C_{15}H_{18}$). On monitoring the reaction by gas chromatography, the initially formed product peak gradually increased in concentration until the reaction was considered complete (24 hr). By contrast, the allene β-tetramer reacted stepwise in the presence of this dehydrogenating agent to first give an isomeric β-tetramer, which in turn was converted into a dialkylnapthalene. The existence of a tetralin ring system in the dehydro pentamer was substantiated by analytical, molecular weight, and spectral information. The aromatic nucleus was seen in both the infrared (1610 and 1500 cm^{-1}) and the ultraviolet (a cluster of maxima at 264, 269, 273, and 279 mμ); the latter system resembled those absorptions in the corresponding spectra for both 2,6- and 2,7-dimethyltetralin.[1] Most importantly, in the infrared spectrum there was an absorption (869 cm^{-1}) that could only be interpreted as signifying the presence of an exocyclic methylene group in the molecule. The validity of this assignment was confirmed in the 60-MHz nmr spectrum by a methylene multiplet at δ 4.72. As noted earlier, the splitting of this methylene absorption may be associated with the methylenecyclobutane system. In addition to this resonance there were detected three aromatic protons at δ 6.90, one singlet methyl on an aromatic ring at δ 2.27, and two groups corresponding to both benzilic–allylic and saturated hydrogens. Although the integration for the first three types of hydrogen was accurate, the values for the number of benzilic–allylic and saturated protons were definitely nonintegers. The former group integrated for 6.30 H, and the latter for 3.65 H. On the basis of all the evidence presented here, either of the two sets of structures represented by formulas IIIa–b and IIIc–d may be considered valid for the structure of the dehydro pentamers. The former pair (IIIa–b) would contain six benzilic–allylic hydrogens and four saturated hydrogens; the corresponding quantities for the latter pair (IIIc–d) are eight and two. From the numbers found by integration, the dehydro pentamer mixture is calculated to be composed of IIIa–b and IIIc–d in the ratio 84:16. Additional evidence on this point was accessible *via* the 100-MHz spectrometer, where the two methylene groups in IIIa–b and IIIc–d have separable chemical shifts at δ 4.80 and 4.69. The integrated areas of the two different methylene groups approximated the ratio 82:18, in excellent agreement with the original argument.

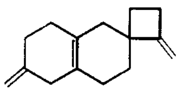

IIIa

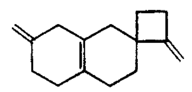

IIIb

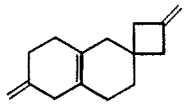

IIIc

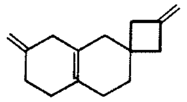

IIId

The assumption that the dehydro pentamers are a mixture of IIIa–d leads to the conclusion that the pentamers must be a mixture of four compounds having the general structures IVa–d which are shown below.

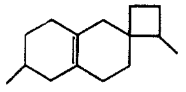

IVa

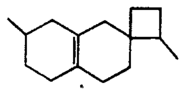

IVb

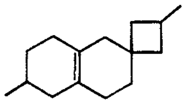

IVc

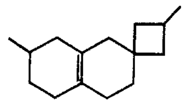

IVd

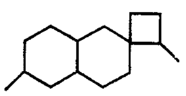
This seems most reasonable, as the pentamers readily undergo dehydrogenation to IIIa–d, but do not completely aromatize because of the presence of the blocking spiro atom. The gas chromatographic analysis of the barely separable pentamers, which coincidentally indicated a composition ratio of 3:1, is explainable on the basis of the similarity of all four structures. Molecular models of IVa–b suggest that the hindered methylene group will undergo a slightly reduced interaction with the column substrate, in contrast to the exposed methylene groups of IVc–d. This suggestion explains the longer retention time observed for the less preponderant pentamer and again agrees with the integration data on the dehydro pentamer. The tetrahydro pentamer is therefore represented as a mixture of Va–d, while the hexahydro pentamer is described by structures VIa–d.

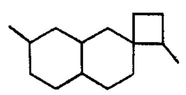

Va


Vb


Vc


Vd


VIa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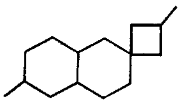
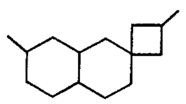

VIc


VId

The proof for the presence of the methylenecyclobutane has rested so far entirely upon spectral evidence. Chemical evidence was obtained by careful ozonization of the dehydro pentamers IIIa–d at −78° in a methylene chloride solution containing an ozone deactivator, pyridine.[17] The resulting dehydroketo pentamer ($C_{14}H_{16}O$) possessed an ultraviolet spectrum almost identical with the spectrum of the dehydro pentamer. The nmr spectrum revealed that the aromatic ring was

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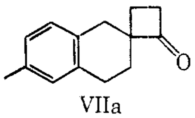
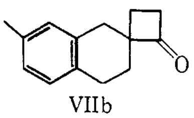
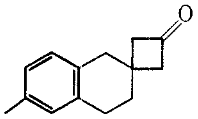
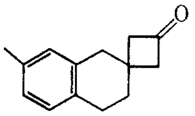
[17] G. Slomp and T. L. Johnson, *J. Am. Chem. Soc.*, **80**, 915 (1958).

still intact, but the methylene group apparently disappeared during the ozonolysis reaction. Dramatically, the infrared spectrum exhibited an intense carbonyl maximum (1770 cm^{-1}), which, in the case of the allene trimers,[1] confirmed the presence of a cyclobutanone ring system. The location of such a principal carbonyl stretching band (in terms of frequency) is inversely related to the C–CO–C angle, *i.e.*, the smaller the angle, the greater the frequency of the absorption.[18,19] In addition to ring size, ring strain may affect this angle and, thus, the position of the observed absorption band. One illustration of this relationship exists in strained cyclopentanones (7-norbornanones), where the ketone appears in the region 1760–1780 cm^{-1}.[20] However, in order to incorporate a cyclopentanone system into the structure of the dehydroketo pentamer, secondary processes involving skeletal rearrangements must occur following the primary bond-forming process that produce the pentamers from allene. Since no evidence supporting this hypothesis exists in the case of the other oligomers, the formulation of the dehydroketo pentamer as a cyclobutanone appears very reasonable. With the starting dehydro pentamers depicted as IIIa–d, then the dehydroketo pentamers must be represented by VIIa–d.

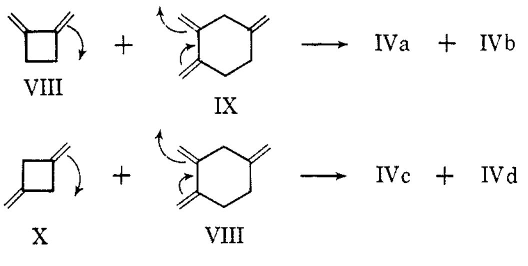

VIIa


VIIb

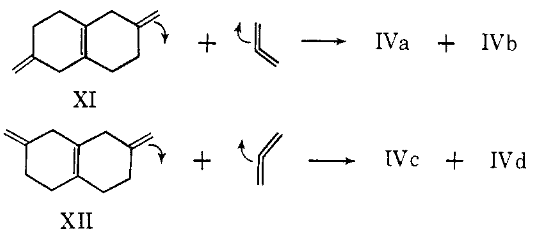

VIIc


VIId

A proposed mechanism for the formation of the four pentamers IVa–d follows.



The diene 1,2-dimethylenecyclobutane (VIII) reacts with the triene 1,2,4-trimethylenecyclohexane (IX) to form IVa and b by either a Diels–Alder mechansim or by formal radical intermediates.[1,14] Simultaneously, the diene 1,3-dimethylenecyclobutane (X) combines with the triene IX to give IVc and d. It will be recalled that in the early stages of the allene polymerization reaction, the reactive compounds VIII, IX, and X are present in appreciable quantities, but as the reaction proceeds these compounds decrease and a corresponding increase is seen in the pentamer concentration. The 84:16 distribution between the sets IVa–b and IVc–d would parallel the initially observed 75:25 ratio between IX and X, which is found for much shorter reaction periods. Alternatively, excess allene may react by either central or terminal addition with the two β-tetramers (XI and XII) to produce the pentamers.



Experimental Section

All boiling points are uncorrected. The infrared spectra were obtained as neat films on a Perkin-Elmer Model 421 double-grating instrument, and the ultraviolet spectra were taken in cyclohexane with a Cary Model 14 spectrophotometer, unless otherwise stated. Molecular weights were determined with a Consolidated Electrodynamics Corp. Model 21-103C mass spectrometer. The nmr spectra were measured either by a Varian Associates Model A-60 or HR-100 spectrometer with the compounds dissolved in deuteriochloroform containing tetramethylsilane as an internal reference. Gas–liquid 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. The separation data is summarized in Table I. Ethylene glycol succinate polyester, phenyldiethanolamine succinate polyester, 1,2,3-triscyanoethoxypropane, and Carbowax 20 M and SF-96 were generally the most useful analytical substrates. These materials 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. All hydrogenations were corrected to standard temperature and pressure. The elemental analyses were performed by Messrs. E. H. Meier and J. Consul, Microanalytical Laboratory, Department of Chemistry, Stanford University.

Isolation of the Pentameric Oligomers of Allene.—The crude reaction mixture, obtained by heating liquid allene in a sealed glass tube for 36 hr, was distilled to yield a pentameric–hexameric fraction [bp 72–75° (0.02 mm)]. Further separation into the individual oligomers was effected by preparative gas chromatography employing a 2.0-m 1,2,3-triscyanoethoxypropane column.

6′-Methylene-3′,4′,7′,8′-tetrahydrospiro[2- and 3-methylene]-cyclobutane-1,2′(1′H,5′H)-naphthalene and 7′-Methylene-3′,-4′,5′,6′-tetrahydrospiro(2- and 3-methylene]cyclobutane-1,2′-(1′H,8′H)-naphthalene (Pentamers).—The mixture of pentamers was a colorless liquid: bp 73° (0.02 mm); n^{20}D 1.5307 [lit.[4] bp 131–132° (10.5 mm); n^{20}D 1.5281]; M (mass spectrometer) 200; infrared spectrum, 3065 m-w (C=C—H), 2905 s (C—H), 1665 m-w and 1650 m-w (C=C), and 872 s (=CH$_2$) cm^{-1}; ultraviolet spectrum, end absorption; nmr spectrum, δ 4.70 (singlet, vinylic methylene, 4 H), 2.61 (singlet, doubly allylic, 2 H), 2.39 and 2.19 (triplet, singly allylic), and 2.0–1.6 (complex, saturated).

Anal. Calcd for $C_{15}H_{20}$: C, 89.94; H, 10.06. Found: C, 90.24; H, 9.99.

6′-Methyl-3′,4′,7′,8′-tetrahydro[2- and 3-methyl]cyclobutane-1,2′(1′H,5′H)-naphthalene and 7′-Methyl-3′,4′,5′,6′-tetrahydro[2- and 3-methyl]cyclobutane-1,2′(1′H,8H′)-naphthalene (Tetrahydro Pentamers).—An alcoholic solution of the pentamers (2.00 g, 0.010 mole) was added to a stirred, previously reduced suspension of platinum oxide (0.205 g) in absolute ethanol (5.0 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 flask to 60° with a lamp failed to increase the consumption of hydrogen beyond 2.05 molar equiv. The filtered solution was evaporated under reduced pressure to afford a colorless oil (2.00 g), which consisted of three components (1:3:2) by gas chromatographic examination: bp 72° (0.15 mm); n^{20}D 1.4956 [lit.[4] bp 123.5–124.5° (8 mm); n^{20}D 1.4962]; M (mass spectrometer) 204; infrared spectrum, 2900 s (CH), 1449, and 1432 and 1369 w (CH$_3$) cm^{-1}; ultraviolet spectrum, end absorption. A sample of tetrahydro pentamer was

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[18] P. von R. Schleyer and R. D. Nicholas, *J. Am. Chem. Soc.*, **83**, 182 (1961).

[19] J. I. Brauman and V. W. Laurie, *ibid.*, in press.

[20] W. G. Dauben and R. M. Coates, *ibid.*, **86**, 2490 (1964).

TABLE I

GAS CHROMATOGRAPHIC DATA FOR PENTAMERS AND RELATED DERIVATIVES

Compound	Instrumental detection[a]	Column substrate[b]	Column temp,[c] °C	Flow rate,[d] ml/min	Retention time, min
Pentamers	T	EGS	150	75	18.5, 20.0
	H	PDEAS	130	15	18.0, 19.2
Tetrahydro pentamers	T	C	178	50	10.4, 11.6, 13.0
Hexahydro pentamers	T	C	178	50	8.5, 9.5, 10.7, 11.6
	T	EGS	174	75	4.0, 4.9
Dehydro pentamers	T	EGS	179	100	9.6
Dehydroketo pentamers	T	SF-96	235	80	7.0
	H	PDEAS	178	15	14.0

[a] Thermal conductivity (T) or hydrogen flame (H). [b] Carbowax (C), ethylene glycol succinate (EGS), phenyldiethanolamine succinate (PDEAS), fluoromethylsilicone (SF-96). [c] Regulated. [d] Helium and hydrogen carrier gases.

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 350 mμ (ϵ' 10.9).

Anal. Calcd for $C_{15}H_{24}$: C, 88.16; H, 11.84. Found: C, 87.93; H, 11.77.

6′-Methyl-3′,4′,7′,8′,9′,10′-hexahydrospiro[2- and 3-methyl]-cyclobutane-1,2′(1′H,5′H)-naphthalene and 7′-Methyl-3′,4′,-5′,6′,7′,8′-hexahydro[2- and 3-methyl]cyclobutane-1,2′(1′H,-8H′)-naphthalene (Hexahydro Pentamers). A. From Pentamers.—A glacial acetic acid solution (5.0 ml) of pentamers (2.00 g, 0.010 mole) was added to a stirred, previously reduced suspension of platinum oxide (0.200 g) in glacial acetic acid (5.0 ml). Within 1 hr over 2 molar equiv of hydrogen had reacted, and by the end of 8 hr the reaction stopped with the absorption of exactly 3 molar equiv of hydrogen gas. The filtered solution was poured onto ice (50 g) and the aqueous phase was extracted with ether (three 100-ml portions). The combined ethereal extracts were dried over anhydrous magnesium sulfate and the solvent was removed *in vacuo* to yield a colorless oil (1.79 g), which consisted of two partially separable components on an EGS column and at least four components on a Carbowax column: bp 72° (0.2 mm); $n^{20}{}_{D}$ 1.4877; M (mass spectrometer) 206; infrared spectrum, 2945 and 2910 s (CH), 1449 m (CH_3), and 1370 m–w cm^{-1}; ultraviolet spectrum, end absorption.

Anal. Calcd for $C_{15}H_{26}$: C, 87.30; H, 12.70. Found: C, 87.00; H, 12.75.

B. From Tetrahydro Pentamers.—Tetrahydro pentamers (0.854 g, 0.00419 mole) were hydrogenated with the aid of reduced platinum oxide catalyst (0.100 g) in glacial acetic acid (5.0 ml). The uptake of gas was completed after 3 hr and was equal to 1.01 molar equiv of hydrogen. The undistilled product (0.805 g) behaved in the same manner as the hexahydro pentamers obtained in A on both EGS and Carbowax columns. The distilled liquid possessed the same physical constants as tabulated in A for the hexahydro pentamers.

6′-Methyl-3′,4′-dihydrospiro[2- and 3-methylene]cyclobutane-1,2′(1′H)-naphthalene and 7′-Methyl-3′,4′-dihydrosipro[2- and 3-methylene]cyclobutane-1,2′(1′H)-naphthalene (Dehydro Pentamers).—Chloranil (9.37 g, 0.033 mole) was added to a stirred, nitrogen-blanketed benzene solution (250.0 ml) containing pentamers (2.01 g, 0.010 mole). An exothermic reaction commenced, which continued for approximately 0.5 hr at 50–60°. External heating was begun at 60–65° and was continued for 16 hr. Gas chromatographic analysis on a PDEAS column showed the gradual conversion of the pentamers into a new product during this interval. The reaction solution was filtered, evaporated to dryness, and then chromatographed on an alumina column (grade I, neutral, 100 g) with *n*-hexane as the eluent. The product was purified by preparative gas chromatography to give a colorless liquid (0.940 g): M (mass spectrometer) 198; infrared spectrum, 3040 w, 2915 s (CH), 1666 and 1610 s (C=CH), 1497 and 1430 s (CH_3), and 869 and 800 s (aromatic) cm^{-1}; ultraviolet spectrum, 222 mμ sh (log ϵ 4.03), 264.5 (3.07), 269 (3.18), 273 (3.15), and 279 (3.22); nmr spectrum (60 MHz), δ 6.90 (singlet, aromatic, 2.94 H), 4.60–4.85 (multiplet, vinyl group exocyclic to a four-membered ring, 2.14 H), 2.81 (multiplet, benzilic and allylic, 6.35 H), 2.27 (singlet, methyl group on an aromatic ring, 2.99 H), and 2.0–1.5 (multiplet, saturated, 3.59 H); nmr spectrum (100 MHz), δ 4.80 (vinyl, 0.38 H) and 4.69 (vinyl, 1.75 H).

Anal. Calcd for $C_{15}H_{18}$: C, 90.85; H, 9.15. Found: C, 90.62; H, 9.15.

6′-Methyl-3′,4′-dihydrospiro[2- and 3-] cyclobutanone-1,2′-(1′H)-naphthalene and 7′-Methyl-3′,4′-dihydrospiro[2- and 3-]-cyclobutanone-1,2′(1H′)-naphthalene (Dehydroketo Pentamers).—Dehydro pentamers (0.965 g, 0.00487 mole) in a mixture of dichloromethane (15.0 ml) and pyridine (2.0 ml) were deoxygenated by bubbling nitrogen gas through the solution. The liquid was chilled to −78° and a stream of oxygen containing ozone (40–41 mg/l.) was passed into the solution for 8 min (at the rate of 1.5 l./min). Oxygen was blown through the reaction vessel to remove excess ozone, the contents were allowed to warm to 0°, and then a mixture of trimethylamine (20.0 ml) and dichloromethane (10.0 ml) was added all at once. Stirring at 0° was continued for another 2 hr, after which the solution was washed with hydrochloric acid (2 *N*, two 100-ml portions) and water (until neutral) and dried with magnesium sulfate. The solvent was removed by distillation to leave a yellow oil (1.0 g), which was chromatographed on alumina (activity I, neutral, 50 g) with hexane (200 ml), followed by hexane–benzene, benzene, benzene–ether, ether, and ethyl acetate. The hexane fractions produced a colorless oil (0.132 g), identified as dehydro pentamer, while the ether fractions afforded a ketonic product (0.305 g). Preparative gas chromatography on an SF-96 column gave a liquid: M (mass spectrometer) 200; infrared spectrum, 3040 m–w, 2915 m (CH), 1770 s (C=O), 1610 w, 1570 w, 1431 m–w (CH_3), 1095 m, and 805 m (aromatic) cm^{-1}; ultraviolet spectrum (ethanol), 216 mμ (log ϵ 4.04), 264 (2.73), 269 (2.90), 273 (2.87), and 278.5 (3.02); nmr spectrum, δ 6.92 (area 3, aromatic), 3.21–2.5 (multiplet, area 6, benzilic and ketonic methylene protons), 2.27 (singlet, area 3, aromatic methyl group), and 2.1–1.6 (multiplet, area 4, saturated protons).

Anal. Calcd for $C_{14}H_{16}O$: C, 83.96; H, 8.05. Found: C, 83.66; H, 8.06.

Registry No.—IIIa, 13639-82-2; IIIb, 13619-44-8; IIIc, 13619-45-9; IIId, 13619-46-0; IVa, 13639-83-3; IVb, 13619-47-1; IVc, 13619-48-2; IVe, 13619-49-3; Va, 13619-50-6; Vb, 13619-51-7; Vc, 13619-52-8; Vd, 13619-53-9; VIa, 13639-84-4; VIb, 13619-54-0; VIc, 13619-55-1; VId, 13619-56-2; VIIa, 13619-57-3; VIIb, 13619-58-4; VIIc, 13619-59-5; VIId, 13619-60-8; allene, 463-49-0.

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