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OLIGOMERS OF ALLENE. I. ON LEBEDEV'S β-TETRAMER

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Almost fifty years ago the thermal polymerization of allene was reported to afford a variety of unsaturated liquid hydrocarbons.[1] These compounds were described as the dimer, trimer, α- and β-tetramers, pentamer and hexamer oligomers of allene. The dimer was postulated to be 1,2-dimethylenecyclobutane; this conclusion was subsequently verified by other workers.[2,3,4] Although this substance is actually obtained only in low yield (ca. 5%), the impression has arisen that it is the sole or major product of the self-condensation of allene. Homologues of allene containing alkyl, aryl or halo substituents routinely produce a wide assortment of four-membered ring compounds.[5] The mechanism for these conversions has been discussed in terms of a dimeric cycloaddition intermediate (I).[6]

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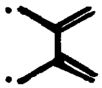
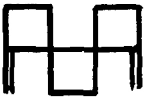
[1] S. V. Lebedev, Zhur. Russ. Fiz.-Khim. Obshch., 45, 1357 (1913).
[2] R. N. Meinert and C. D. Hurd, J. Am. Chem. Soc., 52, 4540 (1930).
[3] K. Alder and O. Ackermann, Chem. Ber., 87, 1567 (1954).
[4] A. T. Blomquist and J. A. Verdol, J. Am. Chem. Soc., 78, 109 (1956).
[5] Y. A. Titov, Russ. Chemical Reviews, 30, 327 (1961).
[6] J. D. Roberts and C. M. Sharts, Organic Reactions, 12, 23 (1962).

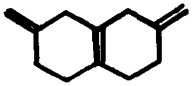
In view of current interest in the cycloaddition reaction as well as Lebedev's observations on higher allene oligomers, it was decided to reinvestigate the thermal polymerization of allene. The reaction conditions employed were similar to those originally reported; specifically, liquid allene in a sealed glass tube under nitrogen was heated at 140° for 1.5 days. A pale yellow liquid was obtained which proved to be a mixture of unreacted allene (ca. 50%) and a residual oil. The latter material on distillation gave three main fractions: the first (10%), b.p. 70-100°/atm. pressure, was tentatively identified as the dimer (75%) plus other minor products; the second (55%), b.p. 96-97°/8.6 mm., was found to be mostly the tetramer (93%); and the third (35%), b.p. 73-76°/ 0.3 mm., was mainly an unseparable mixture of two pentamers (95%). The second cut was purified further by gas chromatography on a PDEAS column to yield a clear liquid whose physical constants were in agreement with those previously reported for the β-tetramer (b.p. 107-108°/13 mm.; n_D^{25} 1.5248). Lebedev stated that the β-tetramer absorbed two molar equivalents of hydrogen in ethanol (PtO_2) and was oxidized by aqueous permanganate to both succinic and oxalic acids. On the basis of this data, the β-tetramer was originally formulated as a dispiro-compound (II).



I



II



III

The ultraviolet spectrum of the substance exhibited no specific high intensity bands, and the infrared data revealed only an intense C=C stretch (1645 cm.$^{-1}$) and a strong $=C{<}^{H}_{H}$ out-of-plane bending (875 cm.$^{-1}$). The material analyzed correctly for $C_{12}H_{16}$ and the mass spectrum confirmed the molecular weight of 160. The n.m.r. patterns showed three types of absorption in the ratio of 1:1:2——four vinylidene methylene protons (4.65 δ); 4 doubly allylic ring protons (2.59 δ); and 8 singly allylic ring protons (2.33, 2.17, 2.08 δ).[7] Most significantly, hydrogen was smoothly taken-up to the extent of *two* moles in neutral media (ethanol, PtO_2), but *three* moles were consumed in an acidic solvent (glacial acetic acid, PtO_2). Tetrahydro-β-tetramer, $C_{12}H_{20}$, (b.p. 132-134°/55 mm.; n_D^{30} 1.4795) possessed an ultraviolet maximum at 194 mμ (log ε 3.97) and added one equivalent of *m*-chloroperbenzoic acid. This last data confirmed the presence of an inert, tetrasubstituted double bond in the original material.

If one assumes the β-tetramer is formed without isomerization of allene units (*i.e.*, allene → propyne or carbon-carbon migration), seven new, alternative structures may be suggested which will satisfy all the above spectral and chemical information. They are 2,6-dimethylene-$\Delta^{9,10}$-octalin; 2,7-dimethylene-$\Delta^{9,10}$-octalin; 2,6-dimethylene-$\Delta^{9,10}$-octahydroazulene; 4,6-dimethylene-bicyclo-[4:2:0]-$\Delta^{1,8}$-octene;

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[7] Assignments were analogous to those made for the protons in β-terpinene; see, B.M. Mitzner and E.T. Theimer, *J.Org.Chem.* **27**, 3359 (1962).

4,7-dimethylenebicyclo-[4:2:0]-$\Delta^{1,8}$-octene; 3,3^1-dimethylenedicyclo-cyclopent-1-enyl; and 3,4^1-dimethylenedicyclo-cyclopent-1-enyl.

In order to identify the β-tetramer with one of the above formulations, the substance was dehydrogenated with chloranil to form 2,7-dimethylnaphthalene (by m.p., mixed m.p., u.v., i.r., and picrate). Further, the tetramer was observed to readily adsorb two equivalents of hydrogen bromide[8] and, on pyrolysis, the dibromide rearranged to yield 2,7-dimethyltetralin[9] [n.m.r. data: 3 aromatic protons (6.77 δ); methyl on an aromatic ring, (2.23 δ); methyl on a saturated ring (doublet at 1.08 and 0.99 δ)]. It is concluded that the major product formed by the thermal polymerization of allene is 2,7-dimethylene-$\Delta^{9,10}$-octalin (III). Additional work on this material as well as the other oligomers isolable from this reaction will be reported at a later date.[10]

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[8] J. G. Traynham and W. C. Baird, Jr., ibid., 27, 3189 (1962).

[9] E. A. Coulson, J. Chem. Soc. 77 (1935).

[10] All compounds reported here gave correct elemental analyses.