

A more detailed account of the analysis will be submitted to *Acta Crystallographica*.

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## Macrocyclic Polydimethylsiloxanes

Sir:

The possibility that macromolecular polycondensates may consist partially or wholly of large cyclic molecules has been raised repeatedly<sup>1-3</sup> and analyzed theoretically<sup>4</sup> but never tested by observation. We have now obtained evidence for macrocyclic populations in dimethylsilicone (D) polymers and characterized their distribution.

Equilibrated polydimethylsiloxane mixtures were prepared by heating octamethylcyclotetrasiloxane (with or without added diluent) with traces of KOH. The reaction mixtures were decatalyzed and chain-stopped with trimethylchlorosilane-pyridine and fractionated by molecular distillation, solvent extraction, vapor phase chromatography (v.p.c.), and gel permeation chromatography (g.p.c.).<sup>5</sup> Milligram quantities of the individual cyclics up to D<sub>25</sub> were collected by v.p.c. for spectroscopic characterization. The distribution curves, obtained either from the fractionation data or from high resolution g.p.c. tracings on the unfractionated equilibrates, showed that the isolated macrocyclics formed part of a continuous population that extended to at least D<sub>400</sub>. This macrocyclic population, arbitrarily defined as the cyclics above D<sub>12</sub>, was found to constitute 2-3% of the total polymer in commercial methylsilicone oils, gums, and rubbers; 8-10% of the total in systems equilibrated at 200-250 g./l. concentration; and probably 50-80% of the precipitated "polymer" fractions recovered<sup>6</sup> in low yields from such equilibrates.

The molar cyclization constants,  $K_n$ , characterizing the stabilities of the  $n$ -unit rings, D <sub>$n$</sub> , were calculated from the relation<sup>4</sup>

$$K_n = [D_n]_{\text{equil}} x^{-n} \\ = [D_n]_{\text{equil}} \left( \frac{\bar{P}_w - 1}{\bar{P}_w + 1} \right)^{-n}$$

where  $x$  and  $\bar{P}_w$  are, respectively, the degree of condensation and the weight-average degree of polymerization in the acyclic portion of the equilibrate. A plot of  $\log K_n$  vs.  $\log n$  (Figure 1) showed a stability maximum at D<sub>4</sub>, a minimum at D<sub>12</sub>, a second maximum at D<sub>15</sub>,<sup>7</sup> a region of steepening slope above the second maximum, and finally a straight line with a slope of  $-2.86 (\pm 5\%)$  over the range D<sub>40</sub>-D<sub>200</sub> and probably beyond.

The linear relationship observed for the largest

(1) P. J. Flory, "Principles of Polymer Chemistry," Cornell University Press, Ithaca, N. Y., 1953, Chapter I.

(2) H. F. Mark, *Monatsh.*, **83**, 545 (1952).

(3) H. J. Krause, *Z. Elektrochem.*, **59**, 1004 (1955).

(4) H. Jacobson and W. H. Stockmayer, *J. Chem. Phys.*, **18**, 1600 (1950).

(5) J. C. Moore, *J. Polymer Sci.*, **2A**, 835 (1964).

(6) M. Morton and E. E. Bostick, *ibid.*, **2A**, 523 (1964).

(7) On a weight rather than molar basis, this maximum comes at D<sub>18</sub>, the 32-atom ring.

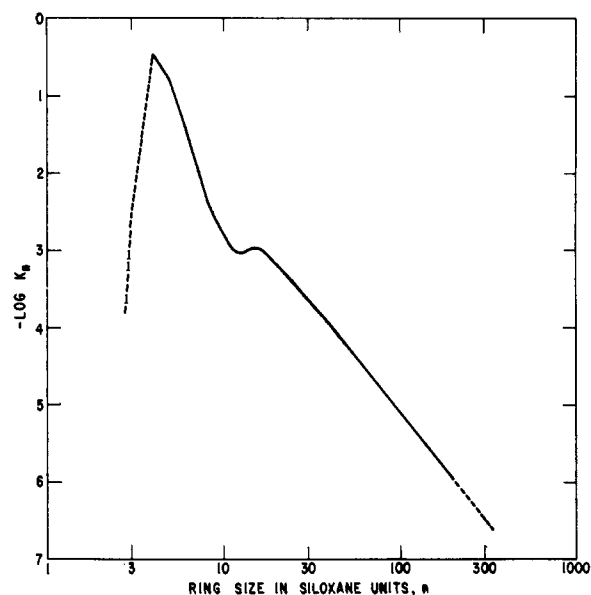


Figure 1. Dependence of molar cyclization constant,  $K_n$ , on number of siloxane units per ring,  $n$ , for polydimethylsiloxanes in toluene at 110°. The dotted portions of the curve are considered less reliable than the remainder.

rings apparently represents the first experimental verification of the Jacobson-Stockmayer cyclization theory.<sup>4</sup> This predicts a dependence of  $K_n$  on  $n^{-2.5}$  in a  $\Theta$  solvent, but the treatment is easily extended to show a dependence on  $n^{-(2+a)}$ , where  $a$  is the exponent in the intrinsic viscosity-molecular weight relationship, in other solvents. Reported values of  $a$  for polydimethylsiloxane in toluene, admittedly at 25 rather than 110°, range from 0.59<sup>8</sup> to 0.84.<sup>9</sup> The deviations of the smaller-ring  $K_n$  values from the limiting line suggest, however, that the random distribution of end-to-end segment distances presumed by the theory is not attained until the chain segments are 70-80 atoms long.

The distribution of stabilities in the lower cyclic siloxanes shows a remarkable parallel to that in alicyclic rings containing *one-half* as many ring atoms. Thus, if one compares the  $K_n$  values for  $n$ -unit ( $2n$ -atom) siloxane rings with the reported tendencies of  $\alpha,\omega$ -disubstituted aliphatics to yield  $n$ -atom ring esters,<sup>10</sup> anhydrides,<sup>10</sup> lactones,<sup>11</sup> or cycloalkanones,<sup>12</sup> one finds in each series a sharp maximum at an  $n$  of 4-6, corresponding to the smallest strainless ring; a minimum at 9-13; a second maximum, broader and weaker than the first, at 15-18; and a gradual decline beyond. This parallelism probably arises because the  $-\text{CH}_2-$  and  $-\text{O}_{1/2}\text{Si}(\text{CH}_3)_2\text{O}_{1/2}-$  repeating units, although quite different in size, are rather similar in shape, in steric requirements relative to interunit distances, and in preferences as to interunit angles. We suggest it is these geometrical characteristics of the repeating unit as a whole, rather than simply the numbers of

(8) V. S. Tsvetkov and P. K. Chandler, *Vysokomolekul. Soedin.*, **1**, 609 (1959).

(9) H. H. Takimoto, C. T. Forbes, and R. K. Laudenschlager, *J. Appl. Polymer Sci.*, **5**, 153 (1961).

(10) E. W. Spanagel and W. H. Carothers, *J. Am. Chem. Soc.*, **57**, 929 (1935).

(11) M. Stoll and A. Rouvé, *Helv. Chim. Acta*, **18**, 1087 (1935).

(12) Whether *via* the Ruzica, Ziegler, Hunsdecker, diketene, or acyloin syntheses.

atoms or the local bond conformations, that determine the stability relations in a series of cyclics.

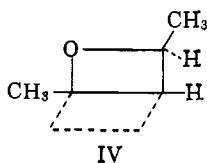
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### *cis-trans* Isomerization of Olefins by Intramolecular Energy Transfer

Sir:

Recently, we reported<sup>1</sup> upon the photochemistry of *trans*-4-hexen-2-one (I). Among the plethora of isolable products was the isomeric *cis*-4-hexen-2-one (II), possibly a chemical consequence of intramolecular energy transfer<sup>2</sup> (irradiation by light absorbed only by the carbonyl group, resulting in reaction at the non-conjugated double bond). However, one can write plausible alternative mechanisms for this isomerization<sup>3</sup>; an unambiguous demonstration of intramolecular photosensitization required that substrates be devised for which internal energy transfer would be unequivocal. Two such systems have now been explored, with the carbonyl group acting as the donor moiety in one and phenyl filling this role in the other. Both exhibit the same phenomenon: *absorption of light at one site in the molecule results in a chemical reaction at a second, nonconjugated site.*

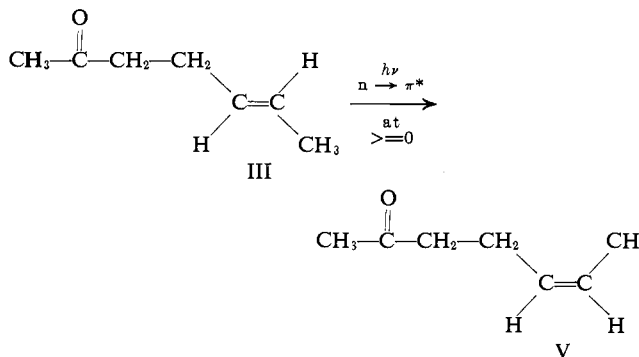
(a) *trans*-5-Hepten-2-one (III)<sup>4</sup> was irradiated, using a Hanovia 450-watt high-pressure mercury arc with a Corex filter, so as to limit incident light to that which would effect only the carbonyl  $n \rightarrow \pi^*$  transition. The reaction was followed by the withdrawal of aliquots and examination of these by vapor phase chromatography (v.p.c.). Two new peaks were observed to form,<sup>5</sup> and these products were isolated by preparative v.p.c.; their mass spectra and elemental analyses indicated that they were isomers of the starting material. The infrared and nuclear magnetic resonance (n.m.r.) spectra of the first photoproduct allowed its assignment as the oxide IV, analogous to the trimethylene oxide obtained by Srinivasan<sup>6</sup> from the photolysis of 5-hexen-2-one. Pyrolysis of IV gave exclusively the *trans*-unsaturated ketone, III.



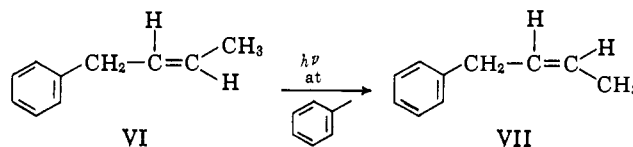
The second photoproduct, V, had n.m.r. and mass spectra essentially identical with those of the original

- (1) H. Morrison, *Tetrahedron Letters*, 3653 (1964).
- (2) Intermolecular transfer of electronic excitation has been known for some time; cf. T. Förster, *Discussions Faraday Soc.*, 27, 7 (1959). Examples of intramolecular transfer are relatively few and limited to spectroscopic observations; cf. G. Weber, *Nature*, 180, 1409 (1957); O. Schnepf and M. Levy, *J. Am. Chem. Soc.*, 84, 172 (1962); P. Leermakers, G. Byers, A. Lamola, and G. Hammond, *ibid.*, 85, 2670 (1963).
- (3) Intermolecular energy transfer does not appear to be a factor in our systems since *trans*-2-hexene is not isomerized when included in the reaction mixtures.
- (4) W. Kimel and A. Cope, *J. Am. Chem. Soc.*, 65, 1992 (1943).
- (5) Irradiation of 4 g. of III for 12 hr. produced IV and V in yields of ca. 30% each (by v.p.c.).
- (6) R. Srinivasan, *J. Am. Chem. Soc.*, 82, 775 (1960).

ketone. However, its infrared spectrum showed a band at 14.4  $\mu$  (*cis*-disubstituted olefin), but lacked the 10.4  $\mu$  band (*trans*-disubstituted olefin) characteristic of III. An analogous change in infrared spectra was observed in the conversion of I to II. These data allow the assignment of *cis*-5-hepten-2-one as compound V and establish that internal photosensitization had occurred.



(b) *trans*-1-Phenyl-2-butene (VI) (Aldrich; 96% *trans* by v.p.c.) was irradiated through a filter solution so that the light admitted (248–282  $m\mu$ ) was absorbed only by the aromatic ring.<sup>7</sup> After 2 hr., distillation followed by preparative v.p.c. provided, in addition to starting material, a single isomeric photoproduct, VII. The infrared, n.m.r., and mass spectra are consistent with its assignment as *cis*-1-phenyl-2-butene, again a product of internal energy transfer.<sup>9</sup>



These and other donor-acceptor systems are presently under investigation as possible probes for the geometric requirements of energy transfer; their potential utility in organic synthesis is also being explored.

**Acknowledgment.** Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and to the Purdue Research Foundation, for support of this research.

(7) Benzene, despite its high triplet energy ( $E_t = 84$  kcal.), seems to have been neglected in the literature as a solution phase sensitizer, although its use in the gas phase has been reported; cf. R. Cundall and T. Palmer, *Trans. Faraday Soc.*, 56, 1211 (1960). Thus, whereas common ketone sensitizers ( $E_t \sim 74$  kcal.) are inefficient in isomerizing simple olefins<sup>8</sup> ( $E_t \sim 80$  kcal.), we find that irradiation of a benzene solution of *trans*-2-hexene produces a photostationary mixture of *cis-trans* isomers within ca. 10 hr. Its ability to function as solvent as well as sensitizer promises to make benzene the agent of choice for effecting such isomerization.

(8) G. Hammond, N. Turro, and P. Leermakers, *J. Phys. Chem.*, 66, 1144 (1962).

(9) The observation of a common photostationary mixture of VI and VII (1.0:1.0) for the intra- and intermolecular systems (benzene serving as donor in the latter case<sup>7</sup>) suggests that vibrational energy transfer, via internal conversion of the initial benzenoid excited state to a high vibrational level of its ground state, is not operable here. (Specific intermolecular energy transfer from benzene solvent to the aromatic ring of the olefin would also accommodate the data, however, and this question is still under study.)

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