

ues for complete scrambling thus indicating that prior to the loss of acetylene in the first field-free region of the double focusing MS9 mass spectrometer, the six carbon atoms are completely randomized.

Experiments to determine if hydrogen scrambling also occurs, independent of and concurrent with the carbon scrambling, are now underway.

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Interlocked Ring Systems Obtained by the Metathesis Reaction of Cyclododecene. Mass Spectral Evidence

Sir:

In this communication¹ we wish to report that a mixture of interlocked ring systems (catenanes) could be identified in the metathesis product of cyclododecene, as evidenced by mass spectroscopic analysis. Cycloolefins, when subjected to a transition metal catalyzed metathesis reaction, undergo a ring-enlargement process to yield a mixture of various oligomeric cyclopolylefins.² Ring enlargement results from an intermolecular metathetic process. However, when cycloolefins beyond a certain minimum ring size are already present in the equilibrium mixture, they can in addition undergo a further intramolecular metathetic process. The latter process can in principle give rise to the formation of catenanes, e.g., 7 and nectinodanes³

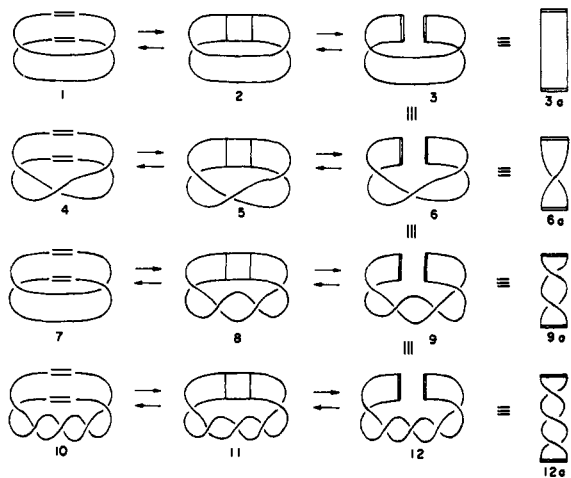


Figure 1.

(1) This communication and the accompanying one (D. A. Ben-Efraim, C. Batich, and E. Wasserman, *J. Amer. Chem. Soc.*, **92**, 2133 (1970)) represent work carried out independently at both the Weizmann Institute of Science, Rehovoth, Israel, and the Bell Telephone Laboratories, Murray Hill, N. J.

(2) (a) E. Wasserman, D. A. Ben-Efraim, and R. Wolovsky, *ibid.*, **90**, 3286 (1968); (b) K. W. Scott, N. Calderon, E. A. Ofstead, W. A. Judy, and J. P. Ward, 155th National Meeting of the American Chemical Society, San Francisco, Calif., March 1968, Abstract L. 54; (c) "Addition and Condensation Polymerization Processes," *Advances in Chemistry Series*, No. 91, American Chemical Society Publications, Washington, D. C., 1969.

(3) Catenane (Latin *catena* = chain), nectinodane (Latin *necto* = to tie), and plectane (Latin *plecto* = to twist) are the generic names used for interlocked ring, knot, and twisted strip systems, respectively; cf. (a) E. Wasserman, *J. Amer. Chem. Soc.*, **82**, 4433 (1960); (b) H. L. Frisch and E. Wasserman, *ibid.*, **83**, 3789 (1961).

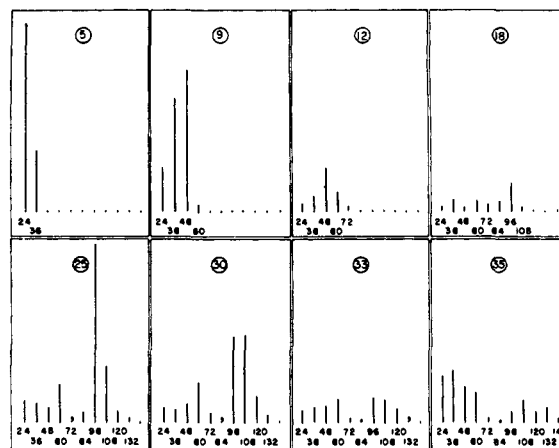


Figure 2. Mass spectra of the xylene-extractable portion of the metathesis product of cyclododecene at various stages of "distillation" in the mass spectrometer. Circled numbers denote the number of the spectrum recorded. The numbers on the bottom denote the number of carbon atoms in the ring. Only relative intensities of molecular ion peaks are given. Other fragments are very small and therefore omitted.

(knots) e.g., 10, depending on the appropriately twisted conformations (cf. Figure 1). The key intermediate in all these topological transformations is the twisted strip molecule with n half-twists where $n = 0, 1, 2, 3 \dots$ (e.g., 2, 5, 8, 11). The degree of twisting or coiling of the molecule depends, to a large extent, on the absolute and relative length of the chains joining the reacting olefinic functions, as well as their flexibility. In addition, mutual hydrophobic interactions of the two chains *vs.* those with the environmental solvating agent will play an important role.

Cyclododecene was subjected to the metathesis reaction in *n*-octane at room temperature using a WCl_6 - EtAlCl_2 - EtOH catalyst in *n*-pentane in a similar manner to that which has already been described.^{2a,4a,c}

The product most of which was insoluble in common organic solvents contained also some lower oligomers.⁵ Examination of the xylene-soluble part, by vapor phase chromatography, indicated the presence of C_{24} , C_{36} , C_{48} , C_{60} , C_{72} , and higher oligomers. The presence of oligomers in the soluble fraction as high as C_{144} was evident from mass spectral analysis. The total product was thus thoroughly Soxhlet extracted with xylene to obtain the soluble oligomer fraction, which in turn after removal of solvent was examined in a mass spectrometer⁶ (Atlas CH4) in the following way. The sample was introduced into the source and "distilled" in the mass spectrometer (at $ca. 5 \times 10^{-6}$ mm) over a period of 2 hr. The temperature reading range of the source was 90–230°. During this fractional distillation, the spectra were continuously displayed on an oscilloscope and occasionally recorded,

(4) The metathesis reaction for pentene-2 was first reported by (a) N. Calderon, H. Y. Chen, and K. W. Scott, *Tetrahedron Lett.*, **34**, 3327 (1967); also cf. (b) N. Calderon, E. A. Ofstead, and W. A. Judy, *J. Polymer Sci., A-1*, **5**, 2209 (1967); (c) N. Calderon, E. A. Ofstead, J. P. Ward, W. A. Judy, and K. W. Scott, *J. Amer. Chem. Soc.*, **90**, 4133 (1968).

(5) Yields for the lower oligomers were approximately 5, 4, 3, and 1%, respectively, for dimer, trimer, tetramer, and pentamer.

(6) A multistep-directed synthesis approach by a German group has been pursued for the last 10 years. Recently, mass spectrometric evidence for a heteroatom containing catenane was brought up by W. Vetter and G. Schill, *Tetrahedron* **23**, 3079 (1967), and previous publications in the series.

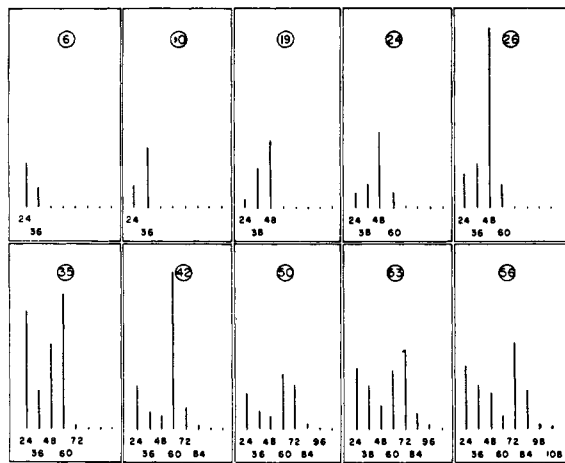
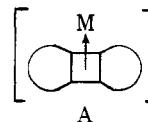


Figure 3. Mass spectra of the xylene-extractable portion of the metathesis product of cyclododecene after catalytic hydrogenation, at various stages of "distillation" in the mass spectrometer. Circled numbers denote the number of the spectrum recorded. The numbers on the bottom denote the number of carbon atoms in the ring. Only relative intensities of molecular ion peaks are given. Other fragments are very small and therefore omitted.

whenever pronounced changes in the spectrum were observed. Representative spectra at various stages of the fractionation are given in Figure 2. Upon following the continuous change of spectra, one could observe that at the beginning of the distillation only lower oligomers are distilled, followed by a gradual appearance of higher ones and a simultaneous disappearance of the lower ones. However, upon further distillation when still higher oligomers start to appear, the relative intensity of the molecular ion peaks of the lower oligomer region starts to reintensify markedly. We interpret this significant reintensification to be a result of fragmentation formed from cleavage of interlocked ring systems of various sizes present in the mixture.

Furthermore, a similar experiment was conducted as before, but now the xylene extractable mixture was catalytically fully hydrogenated under drastic conditions to yield a mixture of cycloparaffinic oligomers. Mass spectral examination of the product using the same technique as above indicated a similar behavior as was observed in the cyclopolyolefinic series. Representative spectra of the cycloparaffinic series are given in Figure 3. Here, in the saturated case, the molecular ion peaks of the C_{24} oligomer (m/e 336) and the C_{36} oligomer (m/e 504) were particularly rechecked (slower scanning and exact counting) toward the end of the distillation when the pronounced enhancement of the peaks occurred. The molecular ion peaks were still of the same m/e , *i.e.*, 336 and 504, corresponding to the saturated ring fragments of C_{24} and C_{36} . Similar reintensified fragments corresponding to monomers $C_{12}H_{24}$ in the saturated series or $C_{12}H_{22}$ in the cycloolefinic series were not observed. The obtention of saturated fragments of the lower oligomers and also the absence of monomeric fragments, since monomers of this size can by no means form catenanes, provide additional evidence for presence in the mixture of catenanes composed from rings of various sizes.

Intermediates containing a cyclobutane ring have so far not been identified in our present experiments or in the published^{2a,4} work. A quasicyclobutane



complexed with a transition metal catalyst represented by A might be assumed as a transition state in the metathesis reaction. Finally, no evidence has been found for doubly charged ions when examined on the isolated cycloparaffinic or cyclopolyolefinic rings.

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Mass Spectral Evidence for Catenanes Formed via a "Möbius-Strip" Approach¹

Sir:

We have interpreted the mass spectra of large carbocyclics as indicating the presence of interlocking rings (catenanes). The macrocyclics were obtained by the enlargement of cyclododecene using the olefin metathesis reaction^{3a,b} as reported previously.^{2,4} We

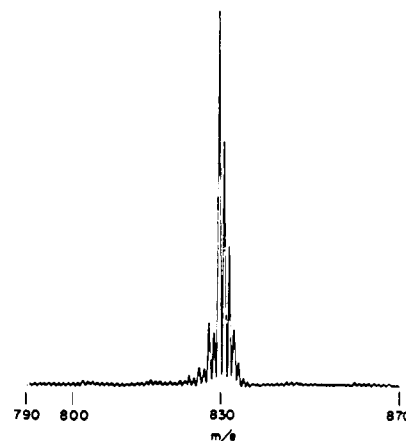


Figure 1. Part of a mass spectrum of a mixture of *cis-trans* isomers of cyclohexaconta-1,13,25,37,49-pentaene.

had noted that the simple cyclic polyolefins thus obtained (I, in which only two of the many double bonds are shown) could undergo an additional metathesis which is intramolecular.² If, as shown in eq 1, a 360° twist had occurred in I prior to the metathesis

(1) The work reported in this and the accompanying communication by R. Wolovsky (*J. Amer. Chem. Soc.*, **92**, 2132 (1970)) are similar but independent verifications of the suggestion that cyclic olefins should yield catenated systems under the metathesis conditions.²

(2) E. Wasserman, D. A. Ben-Efraim, and R. Wolovsky, *ibid.*, **90**, 3286 (1968).

(3) (a) N. Calderon, H. Y. Chen, and K. W. Scott, *Tetrahedron Lett.*, **34**, 3327 (1967); (b) N. Calderon, E. A. Ofstead, J. P. Ward, W. A. Judy, and K. W. Scott, *J. Amer. Chem. Soc.*, **90**, 4133 (1968).

(4) K. W. Scott, N. Calderon, E. A. Ofstead, W. A. Judy, and J. P. Ward, 155th National Meeting of the American Chemical Society, San Francisco, Calif., April 1968, Abstract L54, published in "Addition and Condensation Polymerization Processes," *Advances in Chemistry Series*, No. 91, American Chemical Society Publications, Washington, D. C., 1969; N. Calderon, E. A. Ofstead, and W. A. Judy, *J. Polymer Sci., A-1*, **5**, 2209 (1967).