while complete scrambling of all eight carbon atoms requires 100:7.0, scrambling of the six carbons bearing hydrogens requires 100:9.5, and no scrambling requires 100:108.2.

Our results clearly establish that carbon scrambling occurs in benzothiophene prior to formation of many mass spectral decomposition products and while scrambling processes involving C–H bond cleavage cannot be excluded, they are not necessary to explain the present results. The extent to which H/D scrambling in other systems is founded on ring atom scrambling is being investigated. It was of much interest to note that carbon scrambling also accompanies fragmentation of the *doubly charged* benzothiophene molecular ion, the $M^{2+} - C_2H_2$ daughter ions being formed in abundance ratios (Table I) very similar to those of the corresponding singly charged ions.

[14] National Science Foundation undergraduate summer research participant, 1969.

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Received October 24, 1969

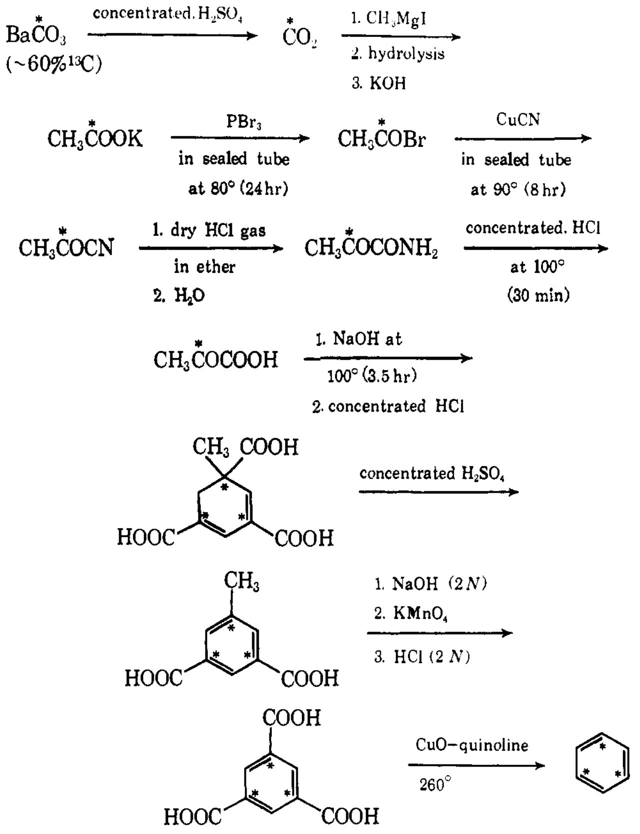
Carbon Scrambling in Benzene upon Electron Impact

Sir:

The scrambling of aromatic hydrogens upon electron impact has been shown to occur in benzene,[1] pyridine,[2] and thiophene.[3] Similar scrambling in bicyclo aromatics and heterocycles has also been observed.[4] In benzene, the observed scrambling has been rationalized[1] by postulating carbon randomization, proceeding *via* valence isomerization involving structures such as benzvalene, prismane, and "dewar" benzene, in analogy to known photochemical transformations.[5] We now present evidence for carbon scrambling in benzene in the mass spectrometer.

1,3,5-$^{13}C_3$-Benzene required for mass spectral analysis was prepared by the sequence of reactions outlined in Scheme I. Experimental details have been described by Anker[6] and Hughes and Reid.[7,8]

Scheme I



The mass spectrum of unlabeled benzene shows peaks at *m/e* 52, 51, and 50, arising from the loss of C_2H_2 from the M^+, $M^+ - 1$, and $M^+ - 2$ ions, with corresponding "metastable peaks" at *m/e* 34.7, 33.8, and 32.9, respectively. Other than the metastable transition for loss of acetylene from the molecular ion, there are no metastable transitions from the molecular ion to daughter ions in the *m/e* 50–54 region. 1,3,5-$^{13}C_3$-Benzene prepared by the above sequence of reactions is not isotopically pure but is contaminated by $^{13}C_0$-, $^{13}C_1$-, and $^{13}C_2$-benzenes.[9] The loss of acetylene and ^{13}C-containing acetylenes from the M^+, $M^+ - 1$, and $M^+ - 2$ ions of $^{13}C_0$-, $^{13}C_1$-, $^{13}C_2$-, and $^{13}C_3$-benzenes gives rise to overlapping peaks in the *m/e* 50–55 region. Similar overlapping is encountered when "metastable peaks" arising from decomposition in the second field-free region are considered. This complication does not arise if "metastable peaks" arising from the loss of acetylene and ^{13}C-containing acetylenes from the molecular ion of 1,3,5-$^{13}C_3$-benzene in the first field-free region of a double focusing AEI MS9 mass spectrometer are considered.[10] These "metastable peaks" for the processes 81 → 55, 81 → 54, and 81 → 53 were examined. The ion with *m/e* 81 could only be 1,3,5-$^{13}C_3$-benzene[12] and the loss of 26, 27, and 28 mass units corresponds to the loss of C_2H_2, $^{13}CCH_2$, and $^{13}C_2H_2$, respectively.

If carbon atoms in benzene do not scramble prior to loss of acetylene, then 1,3,5-$^{13}C_3$-benzene can only lose $^{13}CCH_2$. However if the carbon atoms scramble prior to loss of acetylene, and if the scrambling is complete, C_2H_2, $^{13}CCH_2$, and $^{13}C_2H_2$ would be lost in the ratio of 20:60:20, respectively.[13] The experimental results[14] (the average of three sets of readings) show the loss of $21.4 \pm 3.8\%$ C_2H_2, $60.8 \pm 3.8\%$ $^{13}CCH_2$, and $17.8 \pm 1.8\%$ $^{13}C_2H_2$. This agrees closely with calculated val-

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[1] K. R. Jennings, *Z. Naturforsch.*, **22a**, 454 (1967).

[2] D. H. Williams and J. Ronayne, *Chem. Commun.*, 1129 (1967).

[3] D. H. Williams, R. G. Cooks, J. Ronayne, and S. W. Tam, *Tetrahedron Lett.*, 1777 (1968).

[4] R. G. Cooks, I. Howe, S. W. Tam, and D. H. Williams, *J. Amer. Chem. Soc.*, **90**, 4065 (1968); W. G. Cole, D. H. Williams, and A. N. H. Yeo, *J. Chem. Soc., B*, 1284 (1968).

[5] D. Bryce-Smith and H. C. Longuet-Higgins, *Chem. Commun.*, 593 (1966), and references therein.

[6] H. S. Anker, *J. Biol. Chem.*, **176**, 1333 (1949).

[7] D. M. Hughes and J. C. Reid, *J. Org. Chem.*, **14**, 516 (1949).

[8] Modifications have been made in some of the experimental procedures in order to render them more suitable to the smaller quantity of materials involved.

[9] The mass spectral analysis of trimesic acid (1) shows an isotopic purity of 7.8% $^{13}C_0$, 27.0% $^{13}C_1$, 45.3% $^{13}C_2$, and 19.9% $^{13}C_3$. It is expected that the isotopic purity of the benzene derived from this acid should be the same.

[10] The intensities of these metastables can be determined with the aid of a "metastable defocuser."[11] The electrostatic analyzer was set initially at 4 kV.

[11] M. Barber and R. M. Elliot, paper presented at the 12th ASTM E-14 Meeting on Mass Spectrometry, Montreal, 1964; K. R. Jennings in "Some Newer Physical Methods in Structural Chemistry," R. Bonnet and J. G. Davis, Ed., United Trade Press, London, 1967, pp 105–109.

[12] No correction has been made for the natural ^{13}C isotope of 1,3-$^{13}C_2$-benzene.

[13] The derivation of these ratios is from $(3!/2!1!):(3 \times 3):(3!/2!1!)$.

[14] Partial overlap of the 80 → 54 and 80 → 53 "metastable peaks" with the 81 → 54 and 81 → 53 peaks, respectively, has been corrected for by assuming that the individual "metastable peaks" are gaussian.

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.

Acknowledgment. We wish to thank Shell Research Ltd. for a grant for the purchase of ^{13}C-enriched chemicals.

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Received October 22, 1969

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

Sir:

In this communication[1] 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 spectoscopic analysis. Cycloolefins, when subjected to a transition metal catalyzed metathesis reaction, undergo a ring-enlargement process to yield a mixture of various oligomeric cyclopolyolefins.[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 nectinodanes[3] (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 $n = 0, 1, 2, 3 \ldots$ (*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.

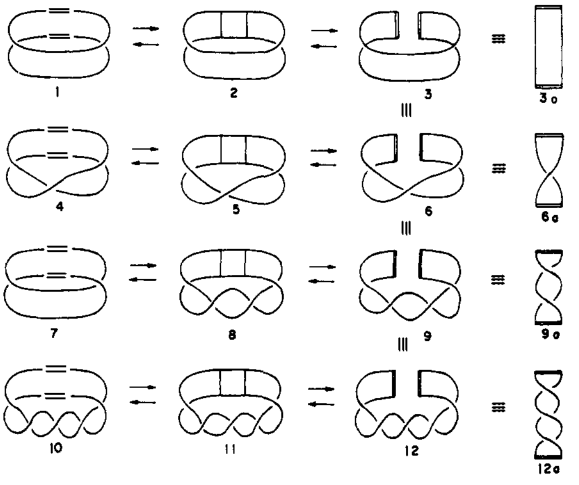

Figure 1.

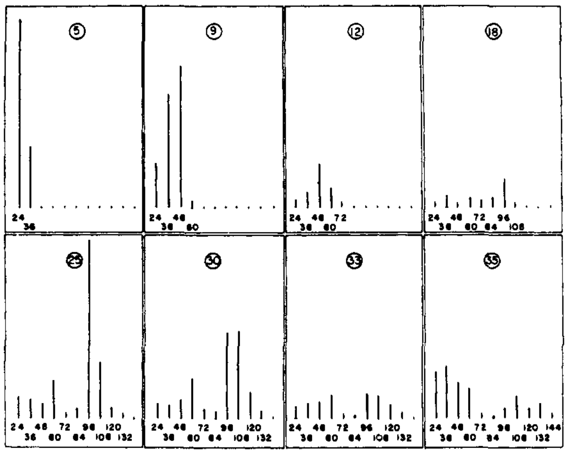

Figure 2. Mass spectra of the xylene-extractable portion of the metathesis product of cyclododecene at various stages of "distillation" in the mass spectrometer. Circled numbers denote the number of the spectrum recorded. The numbers on the bottom denote the number of carbon atoms in the ring. Only relative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

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 spectrometer[6] (Atlas CH4) in the following way. The sample was introduced into the source and "distilled" in the mass spectrometer (at *ca.* 5×10^{-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,

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[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).

[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.