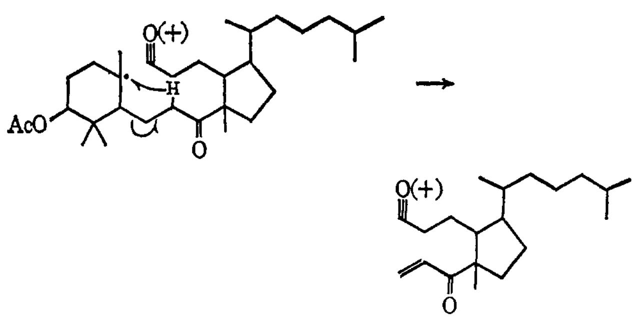
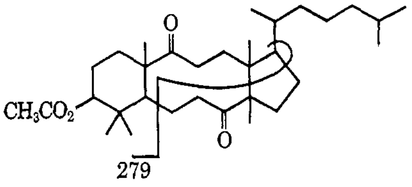
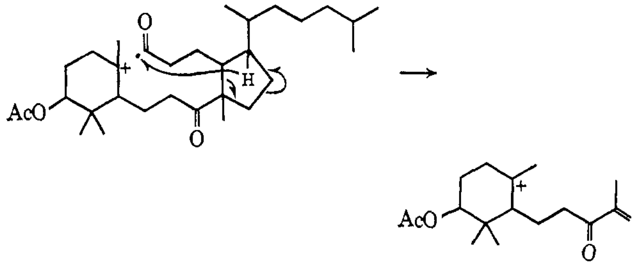


m/e 305 ($C_{20}H_{33}O_2$)

Corresponding fragments occur at m/e 319 and 207 in the spectrum of the higher homolog, XI. Another prominent fragment of the composition $C_{18}H_{32}O_2$ at m/e 280 (m/e 294 in seco-diketolanosterol-Ac) confines the possible carbonyl locations to a sufficiently small area of the B–C ring moiety to permit exclusion of alternative positions based on possible chemical structures of the olefinic precursor. Finally, an abundant fragment recorded at m/e 279 ($C_{17}H_{27}O_3$) obviously comprises such a portion of the molecule as to include C_{14} and C_{15}, since it appears unshifted at the same mass in the spectrum of the lanosterol derivative XI. An alternative formation of this fragment ion would have to include C_{17} in the latter case and thus require the highly unlikely rupture of two bonds attached to the same carbon atom (XI). Genesis of this important ion may be initiated by cleavage α to the carbonyl group with reverse charge distribution, followed by radical-induced fragmentation of the 15,16 and 13,14 bonds.



XI



m/e 279

From the abundant fragment at m/e 279 and associated high-resolution data it is also apparent that C_{14} bears the methyl group which migrated during biosynthesis of IV.

That the cyclization of III is mechanistically analogous to that of the normal substrate I follows from the nonincorporation of ^3H into IV on cyclization of unlabeled III in a medium containing ^3H_2O (0.235 Ci ml).

Acknowledgments. The authors are indebted to Dr. D. H. Smith for the determination of real-time high-resolution mass spectra (Model AEI MS-902 on line to SDS Sigma 7), to Miss P. C. Wszolek for the low-resolution spectra of the TMSE double bond isomers (AEI MS-12) (University of California at Berkeley), and to Dr. T. Nishida (Stanford University) for the time-averaged nmr spectra. Financial support was provided by the National Aeronautics and Space Administration (Grants NsG 101 and NGR 05-0030134 to A. L. B.), National Institutes of Health (GM 10421 to E. E. v. T. and GM 12493 to R. B. C.), and the American Heart Association (to R. B. C.).

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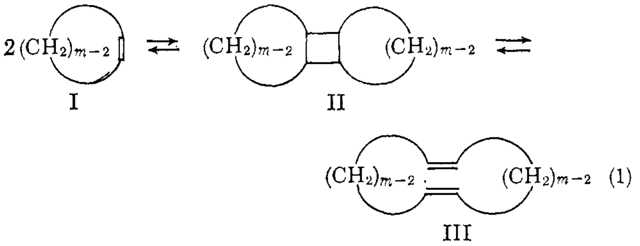
Received February 26, 1968

The Synthesis of Carbon Macrocycles to C_{120}

Sir:

We have obtained large unbranched carbocyclic systems by the direct combination of increasing numbers of cyclooctene molecules. The available evidence indicates the formation of rings up to C_{120}, over twice the size of the largest carbocycles previously identified.[1] Such formation of larger from smaller rings is an exception to the usual procedure for the synthesis of macrocycles by cyclization of a linear system. Another exception is the recent report of Story, *et al.*, who found that di- or trimeric cyclic peroxides of cyclic ketones eliminate CO_2 to form carbocycles up to C_{22}.[2]

The procedure we have been investigating may be formally described by eq 1. The intermediate cyclobutane (II) could revert to the C_m cyclic olefin I or form the C_{2m} cyclic diene III. Repetition of (1) with two molecules of III or one of I and one of III could lead to higher cyclic polyolefins. Our initial attempts to carry out transformation 1 photochemically were put aside with the report of the remarkable olefin metathesis reaction observed with linear olefins. Using a WCl_6–$EtAlCl_2$–EtOH catalyst, Calderon, *et al.*, converted 2-pentene into a mixture with 2-butene and 3-hexene,[3] a conversion which may be viewed as going through a transient cyclobutane intermediate. Since a cyclic olefin undergoing a similar transformation



(1)

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[1] F. Sondheimer, Y. Amiel, and R. Wolovsky, *J. Am. Chem. Soc.*, **81**, 4600 (1959), report $C_{54}H_{108}$.

[2] P. R. Story, D. D. Denson, C. E. Bishop, B. C. Clark, Jr., and J.-C. Farine, *ibid.*, **90**, 817 (1968).

[3] N. Calderon, H. Y. Chen, and K. W. Scott, *Tetrahedron Letters*, **34**, 3327 (1967).

would correspond to (1), we examined a cycloolefin under the metathesis conditions.[4]

Cyclooctene (IV) was chosen because ring strain might drive the reaction preferentially to the relatively strainless C_{16} or higher cyclic polyolefins. To a solution of 5.5 g of IV in 160 ml of benzene at 5–20° was added 1.2 ml of 0.05 M 1:1 WCl_6–EtOH in benzene, followed by 0.6 ml of 0.2 M $EtAlCl_2$ in benzene, taking care to exclude moisture.[3] While the reaction seemed to be complete within 15 min, it was normally left for 2 hr. After removal of the aromatic solvent the nmr of the viscous mixture resembled that of IV but with poorer resolution. The ratios of vinyl, allyl, and methylene protons (δ 5.3, 2.0, and 1.3) were similar to that of IV, consistent with the formation of cyclic polyolefins. Mass spectrometry (using an AEI MS-9 spectrometer[5]) of the reaction mixture indicated the presence of multiples of cyclooctene, $(C_8H_{14})_n$, with intense parent peaks at m/e 110n. In a typical run the yield of the lower members, as indicated by vpc, were: for $n = 1$, 13%; 2, 9%; 3, 5%; and 4, 5%. Hydrogenation of the reaction mixture at 3 kg/cm^2 over platinum in octane at 85° for 48 hr yielded a mixture from which the fully hydrogenated C_{16}, C_{24}, and C_{32} fractions ($n = 2$–4) were separated by preparative vpc. Their melting points corresponded to those in the literature for monocyclic $(CH_2)_{8n}$ within 1–2°;[1] their mass spectra had the parent peak at m/e 112n and gave no evidence for the presence of tertiary carbon atoms. The nmr spectrum consisted of a single peak at δ 1.33 for $n = 2$. This $C_{16}H_{32}$ resulted from hydrogenation of a $C_{16}H_{28}$ fraction which was partially resolved by gas chromatography into two peaks. Its infrared spectrum indicated a mixture of *cis–trans* isomers.

Evidence for the larger rings was obtained by comparison of the mass spectra of hydrogenated and unhydrogenated original reaction mixtures. For $n \leqq 6$ the m/e 110n peak is replaced by one at m/e 112n. For $n = 7$ the hydrogenated sample contained both m/e 110n and 112n peaks. Peaks indicating partial hydrogenation were very weak or nonexistent. For $n = 8$–15 both hydrogenated and unhydrogenated samples had only m/e 110n parent ion peaks. Clearly, the larger molecules were not hydrogenated under our conditions.

Of particular significance, and the initial impetus for our interest in eq 1, is the distinct possibility of the formation of catenanes and knots in these reactions. For simple rings above C_{40} or C_{50}, multiple twisting of III before a III → I transformation could result in such topological isomers through a "Mobius strip" intermediate.[6] It is likely that the higher molecular weight materials contain substantial amounts of interlocked simple and knotted rings.

In conclusion, formation from IV of simple rings with n double bonds is unequivocal for $n = 2$–4. In addition, the analogous mass spectra for these low molecular weight rings and for the higher components, $n = 5$–15, indicate that the crude reaction mixture is largely composed of cyclic $[\text{-}(CH_2)_3CH{=}CH(CH_2)_3\text{-}]_n$ or isomers with the same monocyclic carbon skeleton at least to $n = 15$. Isolation of the higher constituents should allow study of the structural features of these and perhaps of larger cyclic systems. The cutoff at C_{120} has been determined by the present limitations of the mass spectrometer, and it is likely that even larger rings are present.

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[4] A referee has called our attention to some references which we had overlooked: G. Natta, G. Dall'Asta, I. W. Bassi, and G. Carella, *Makromol. Chem.*, **91**, 87 (1966), reported the treatment of various cycloolefins, including cyclooctene, with tungsten–aluminum catalysts to yield linear, crystalline polyalkenamers; N. Calderon, E. A. Ofstead, and W. A. Judy, *J. Polymer Sci., Part A-1*, **5**, 2209 (1967), treated several cycloolefins, including cyclooctene, with tungsten–aluminum catalysts and reported the formation of appreciable low molecular weight "extractables." These "extractables" are discussed in detail in a paper presented by 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, Abstracts, L54 (to be published in the Advances in Chemistry Series). This paper explicitly reports the formation of monocyclic compounds possessing molecular weights up to 1200 from various cycloolefins. A full paper on the metathesis of linear olefins will appear: N. Calderon, E. A. Ofstead, J. P. Ward, W. A. Judy, and K. W. Scott, *J. Am. Chem. Soc.*, in press.

[5] The mass spectrometric analyses were kindly performed by Dr. J. Wright.

[6] H. L. Frisch and E. Wasserman, *J. Am. Chem. Soc.*, **83**, 3789 (1961). These intermediates would actually be more highly twisted forms of the Mobius strip.

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[8] On leave from The Weizmann Institute of Science, Rehovoth, Israel, 1967–1968.

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Received March 14, 1968

Bornadiene Thermolysis. A New Entry into the Trimethyltropilidene Labyrinth

Sir:

Direct observation of reactive intermediates in thermal unimolecular rearrangements is unusual, and even a careful indirect demonstration of a short-lived intermediate is seldom without ambiguity. The lines of evidence implicating the trimethylene diradical as an intermediate in cyclopropane pyrolysis are securely based on kinetic data[1] and are reinforced by examination of the corresponding diradical formed by thermal decomposition of pyrazoline.[2] However, it is possible to construct from these data an energy surface in which all of the important reactions are concerted and thereby avoid any mention of a diradical. A similar situation is found in the formation of cyclopentene from vinylcyclopropane[3] and from 3-vinylpyrazoline.[4] Employing these two very different substrates to generate a common intermediate is not totally satisfactory since the chemistry of the short-lived diradical might depend to some extent on its progenitor. This specific objection can be overcome, and new insight gained into the behavior of thermally labile compounds, by attempting to create a common intermediate from reorganization of two isomeric substrates. We report here as an example of this method the skeletal rearrangement of bornadiene and compare it with the corresponding behavior of 3,7,7-trimethyltropilidene.[5]

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[1] (a) This subject is reviewed by H. M. Frey, *Advan. Phys. Org. Chem.*, 4, 147 (1966); (b) B. S. Rabinovitch, E. W. Schlag, and K. B. Wiberg, *J. Chem. Phys.*, **28**, 504 (1958).

[2] R. J. Crawford and A. Mishra, *J. Am. Chem. Soc.*, **88**, 3963 (1966).

[3] M. R. Willcott, III, and V. H. Cargle, *ibid.*, **89**, 723 (1967).

[4] R. J. Crawford and D. M. Cameron, *Can. J. Chem.*, **45**, 691 (1967).

[5] (a) J. A. Berson and M. R. Willcott, III, *J. Am. Chem. Soc.*, **88**, 2494 (1966); (b) *Record Chem. Progr.*, **27**, 139 (1966).