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 $\rightarrow$ 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 $[-(CH_2)_3CH{=}CH(CH_2)_3-]_n$ 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.

[7] Bell Telephone Laboratories, Inc., and Rutgers, The State University.

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

[9] On leave from The Weizmann Institute of Science, Rehovoth, Israel, 1966–1967.

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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).

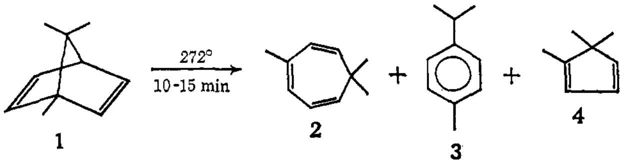
[2] R. J. Crawford and A. Mishra, *J. Am. Chem. Soc.*, **88**, 3963 (1966).

[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).

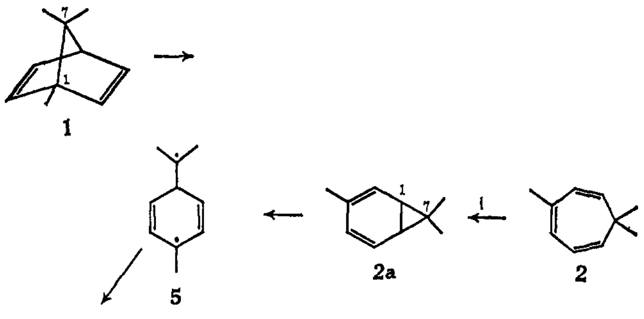
[5] (a) J. A. Berson and M. R. Willcott, III, *J. Am. Chem. Soc.*, **88**, 2494 (1966); (b) *Record Chem. Progr.*, **27**, 139 (1966).

The relatively unknown compound bornadiene (**1**) was prepared by distilling 2,6-dichlorobornane from a solution of potassium octyl oxide in 1-octanol maintained at 230°.[6] An early fraction (bp 190–210°) assayed rich in bornadiene by vapor phase chromatography (vpc).[7] A simple bulb-to-bulb vacuum distillation followed by preparative-scale vpc provided bornadiene in acceptable (greater than 50%) yield. The exceedingly volatile purified bornadiene was dissolved in about ten times its own weight of 2-methylpentane (Phillips, 99 mole %); the resulting mixture was vaporized in a nitrogen stream and passed through a 200-ml stirred-flow reactor maintained at 272.2 ± 0.25°.[8] The flow rate was varied between 20 and 6 cc/min and the exit gas was trapped in a vessel maintained at Dry Ice temperature. Vpc analysis indicated that between 60 and 90% of the bornadiene had reacted. At 60% conversion the vpc record was dominated by 3,7,7-trimethyltropilidene (**2**) and *p*-cymene (**3**), both products being identified by isolation and comparison of nuclear magnetic resonance and infrared spectra with those of authentic samples. Small but significant amounts of 1,5,5-trimethylcyclopentadiene (**4**) were also found. At the lowest flow rate (6 cc/min, 90% conversion) secondary products began to appear and to complicate the vpc analysis. Vpc analysis of the mixture resulting from the exposure of pure 3,7,7-trimethyltropilidene to the same conditions made it clear that we were observing the onset of the tropilidene skeletal rearrangements.[5] Our present experience with the bornadiene isomerization can best be summarized by noting that the ratio of *p*-cymene to 3,7,7,-trimethyltropilidene is 0.304 ± 0.008, at conversions ranging from 60 to 90%.

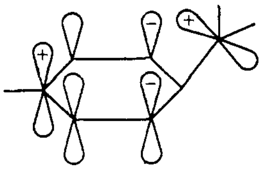


relative amounts 1.0 0.304 trace

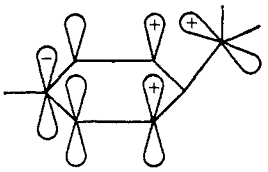
This ratio is informative only when considered simultaneously with the results of pyrolysis of 3,7,7-trimethyltropilidene. In a naive but not totally unsatisfactory approximation, both bornadiene and trimethyltropilidene would be expected to generate diradical **5**, or its operational equivalent. The bonds to be broken (C_{-1}–C_{-7}, in both bornadiene and caradiene) are the weakest bonds in the respective molecules. Each can be estimated to rupture with an activation energy of 45–50 kcal/mole. Clearly a common intermediate can be anticipated from these two different pyrolytic reactions. This hypothesis is in direct opposition to the experimental facts. The *x*,7,7-trimethyltropilidenes, and thereby the corresponding caradienes, can undergo a large number of rearrangements, some of which formally pass through diradical **5** without aromatization becoming a significant factor.[5] On the other hand, if the same diradical **5** is formed from bornadiene it must disproportionate to one molecule of aromatic material (*p*-cymene) for every three molecules of trimethyltropilidene.



One explanation for this dichotomy is that the two diradicals possess different enthalpies of formation and should reasonably be expected to behave differently.[9] This may indeed be the correct interpretation. However, we can also invoke the following argument using the principles of orbital symmetry in sigmatropic reactions.[10] Consider the diradical **5**. If it is considered at the point of no return on the reaction diagram, then it can be envisioned as an sp^2 radical at C_7 and a pentadienyl radical extending over five of the six carbon atoms of the unsaturated cyclohexane ring. The diradical should possess a geometrical description which is independent of its genesis. The electronic description, however, can differ by exhibiting the vestiges of the C_1 and C_7 bonding orbitals of either bornadiene or caradiene. The difference in electronic description is exceedingly subtle, but it might account for the divergence of the bornadiene and caradiene reactions. In the cycloheptatriene series the rearrangement of an optically active trideuteriomethyldimethyltropilidene has been proposed as the most satisfactory test of this particular mechanistic question.[5,10b] A corresponding investigation of optically active 7-trideuteriomethyl-1,7-dimethyl-2,5-norbornadiene to examine the steric consequence of the reorganization in order to correlate it with the tropilidene work is being undertaken in these laboratories.



5, from bornadiene



5, from the caradiene **2a**

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(6) This is an adaptation of the original synthesis of bornadiene reported by M. Hanack, H. Eggensperger, and R. Hahnle, *Ann. Chem.*, **652**, 96 (1962).

(7) All vpc analyses were carried out on an Aerograph 90-P3 chromatograph fitted with a 15 ft × 0.25 in. column of 15% Carbowax 20M on Chromosorb W, HMDS treated, operated at 135° with 20–60 cc of helium/min as a carrier gas.

(8) The flow reactor is modeled after the one described by E. S. Lewis and W. C. Herndon, *J. Am. Chem. Soc.*, **83**, 1955 (1961).

(9) This point is easy to discuss but is difficult to verify by experiment. We are currently conducting investigations of the kinetics of both bornadiene and the *x*,7,7-trimethyltropilidene rearrangements in an attempt to establish the difference in enthalpy of the two diradicals.

(10) (a) Most recently summarized in R. Hoffmann and R. B. Woodward, *Accounts Chem. Res.*, **1**, 17 (1968); (b) see also J. A. Berson, *ibid.*, **1**, 152 (1968).