*J. Org. Chem.* 1982, *47*, 287-292

(M$^+$; calcd for $C_{12}H_{20}O$, 180.1515). For **19b**: white solid; mp 36.0–37.5 °C; IR 2937 (s), 2860 (m), 1738 (s), 1475 (w), 1455 (w), 1389 (w), 1363 (m), 1230 (w), 1158 (w), 1142 (m), 1132 (w), 1108 (w), 1054 (w), 855 (w) cm$^{-1}$; NMR $\delta$ 2.65–2.28 (br d, $J \approx 6$ Hz, 2 H), 2.23–1.15 (m, 9 H), 0.90 (s, 9 H); mass spectrum, $m/z$ 180.1514 (M$^+$; calcd for $C_{12}H_{20}O$, 180.1515). Various pyrolyses at 190 and 310 °C (Wood's metal bath; complete pyrolysis in ca. 15 min.) gave a 70–80% yield of the two major products. **19b** was usually 35–50% of the mixture, with a range of 9–83% under nominally identical conditions.

**2-Oxabicyclo[3.3.1]nonane-3-thione (14).** Jones oxidation of 3-cyclohexene-1-ethanol (Aldrich) gave the carboxylic acid **11**, which was iodolactonized according to Klein.[11] The product (**12**) was converted to lactone **10**[10] with tributylstannane and azobis(isobutyronitrile) catalyst.[12]

A solution of **10** (795 mg, 5.68 mmol) and reagent **13** (1.44 g, 3.58 mol)[13,14] in toluene (8.5 mL) was heated for 3 h at reflux and stirred overnight at room temperature. The white precipitate was filtered, washed with warm $CH_2Cl_2$, and discarded. The solution and washings were concentrated, and the mixture was purified by column chromatography (16 × 2.2 cm Woelm active silica gel; 70–150 mesh) with benzene/ether as the eluant [300 (benzene), 40 (3:1), 20 (1:1), 20 (1:3), and 100 mL (ether)]. Fractions containing the desired product (followed by TLC) were combined, and the solvent was removed to yield a solid (75–80% pure). Sublimation [40–65 °C (0.1 torr)] gave a pale yellow solid identified as **14**: mp 68.5–70.0 °C; IR 2950 (s), 2875 (w), 1449 (w), 1380 (m), 1361 (w), 1350 (w), 1328 (w), 1297 (m), 1233 (s), 1214 (s), 1169 (w), 1150 (s), 1097 (s), 1069 (m), 1031 (w), 1014 (w), 950 (m), 905 (w) cm$^{-1}$; NMR $\delta$ 4.93 (br s, 1 H), 3.15 (d, fine structure, $J \approx$ Hz, 2 H), 2.40–1.35 (m, 9 H).

Anal. Calcd for $C_8H_{12}OS$: C, 61.52; H, 7.75. Found: C, 61.50; H, 7.65.

**2-Oxabicyclo[3.3.1]nonan-3-one Tosylhydrazone (1a).** Thiolactone **14** (203 mg, 1.30 mmol) was placed in a 25-mL two-necked flask fitted with a dry ice condenser and a septum. The system was flushed with argon and cooled (–70 °C) while anhydrous ammonia was introduced through the septum with constant magnetic stirring. After 12–13 mL of ammonia had condensed in the flask (ca. 45 min), the gas inlet was removed and the cold bath warmed to –20 °C (15 min) and maintained at that temperature for 3.5 h. Finally the dry ice condenser and cold bath were removed to allow the ammonia to evaporate under a gentle stream of argon. When most of the solvent was gone, $CH_2Cl_2$ (3–4 mL) was added through the septum and all the remaining solvent removed at room temperature (45 min to 1 h). This gave a viscous oil containing **15** as the major product: 78–80% (by NMR); IR ($CDCl_3$) 3700–3100 (w), 2950 (s), 2890 (w), 2870 (w), 1638 (s), 1450 (w), 1388 (m), 1337 (m), 1313 (w), 1275 (w), 1245 (w), 1235 (m), 1210 (m), 1114 (w), 1100 (m), 1068 (m), 1039 (w) cm$^{-1}$; NMR ($CDCl_3$) $\delta$ 7.30 (br s, ~1 H, variable), 4.47 (br s, 1 H), 3.03–2.23 (m, 2 H), 2.30–0.90 (m, 9 H plus excess due to minor product). The minor product appeared (TLC, NMR) to be the hydroxy thio amide from ring opening of **14**. The mixture was used without further handling.

A solution of the crude oil (~1.01 mmol of **15**) from above and $TsNHNH_2$ (210 mg, 1.13 mmol) in anhydrous EtOH (2 mL) was sealed under argon and stored for 6 days at room temperature (see preparation of **1b**). Chromatography as before (two plates, eluted with 1:1 ether/toluene; $R_f$ 0.47–0.58) followed by recrystallization (benzene/pentane) gave a white solid (31 mg, 10%) identified as **1a**: mp 137.5–139.5 °C; IR ($CHCl_3$) 3300 (br, m), 3030 (w), 2955 (s), 2890 (w), 2875 (w), 1639 (s), 1598 (w), 1488 (w), 1450 (w), 1377 (s), 1330 (s), 1312 (w), 1301 (w), 1287 (w), 1247 (s), 1160 (vs), 1100 (m), 1087 (m), 1072 (w), 1012 (s, br), 960 (m), 897 (w), 862 (w), 803 (w) cm$^{-1}$; NMR ($CDCl_3$) $\delta$ 7.79 and 7.28 (2 d, $J \approx 8$ Hz, overlapping with one variable proton, 5 H), 4.53 (br s, 1 H), 3.00–2.20 (m, with s at 2.42, 5 H), 2.30–0.90 (m, ~9 H).

Anal. Calcd for $C_{15}H_{20}N_2O_3S$: C, 58.43; H, 6.54; N, 9.09. Found: C, 58.56; H, 6.52; N, 9.06.

**Preparation and Pyrolysis of Lactone Tosylhydrazone Sodium Salt 17a.** A solution of **1a** (18.5 mg, 0.060 mmol) was treated with $NaOCH_3$ (0.065 mmol) to give **17a** (see **1b** → **17b**) which was used directly for pyrolysis. Spectra were obtained on a separate sample: IR ($CDCl_3$) 2950 (s), 1637 (m), 1488 (w), 1420 (w), 1385 (w), 1345 (w), 1285 (w), 1211 (w), 1162 (s), 1120 (m), 1082 (s, with sh), 1026 (m), 1005 (m), 803 (w) cm$^{-1}$; NMR ($CDCl_3$) $\delta$ 7.67 (d, $J \approx 8$ Hz, 2 H), 7.10 (d, $J \approx 8$ Hz, 2 H), 4.40 (br s, 1 H), 3.00–2.10 (m, 5 H), 2.10–0.90 (m, ~9 H).

Pyrolysis at 190 °C (as for **17b**) gave an ~70% total yield of 2-oxabicyclo[3.3.1]non-3-ene (**18a**) and bicyclo[3.2.1]octan-6-one (**19a**) (ratio of ~14:1). Ether **18a** was collected by VPC (110 °C, $t_R = 3.5$ min) as a waxy white solid and characterized from the following data: IR 3085 (w), 2960 (s), 2872 (w), 1633 (s), 1439 (w), 1250 (w), 1225 (s), 1207 (w), 1100 (w), 1044 (m), 1012 (w), 880 (w) cm$^{-1}$; NMR (Varian HR-220) $\delta$ 6.44 (d, $J = 6.0$ Hz, 1 H), 4.57 (ddd, $J \approx 6, 6, 1.5$ Hz, 1 H), 4.25 (s, 1 H), 2.29 (br s, 1 H), 2.00–0.70 (m, ~8 H); mass spectrum, $m/z$ 124.0883 (M$^+$; calcd for $C_8H_{12}O$, 128.0888).

Ketone **19a** was the minor product (6–7%) in several runs of the pyrolysis. However, it was ≥30% of the mixture in two runs (310 and 190 °C) and ≥50% in another (190 °C). This product was also collected (110 °C, $t_R = 15$ min) and identified by its spectral properties (IR, NMR) that were identical with those of an authentic sample.[3,18]

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**Registry No. 1a**, 79855-46-2; **1b**, 79855-47-3; **5**, 79822-44-9; **6**, 79855-48-4; **7**, 79855-49-5; **10**, 6051-04-3; **11**, 10468-32-3; **12**, 79855-50-8; **13**, 19172-47-5; **14**, 79855-51-9; **15**, 79855-52-0; **17a**, 79855-53-1; **17b**, 79855-54-2; **18a**, 79855-55-3; **18b**, 79855-56-4; **19a**, 5019-82-9; **19b**, 79872-80-3; 3-cyclohexene-1-ethanol, 18240-10-3.

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# On the Thermal Isomerization of *trans*-Cyclooctene to *cis*-Cyclooctene

Ursula Holle Andrews, John E. Baldwin,* and Michael W. Grayston

*Department of Chemistry, University of Oregon, Eugene, Oregon 97403*

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The thermal isomerization of *trans*-1,2-dideuteriocyclooctene in adequately conditioned Pyrex ampules gives *cis*-1,2-dideuteriocyclooctene, a result which excludes radical chain, [1,3] hydrogen shift, and [1,2] hydrogen shift mechanisms. When inadequately conditioned ampules are employed, deuterium scrambling is evident in the *cis*-cyclooctene formed but not in the *trans*-cyclooctene recovered.

The ground-state properties of *trans*-cyclooctene[1] have been well-defined. The lowest energy conformation of this dissymmetric strained olefin is the "twist" or "crown" form **1**, with a C(8)–C(1)–C(2)–C(3) dihedral angle of 136°.[2-5]

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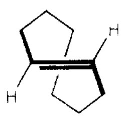

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Torsional strain about the olefinic carbons is associated with rehybridization, lending s character to the atomic orbitals which mix with an interorbital angle of about 20° to form the $\pi$ bond.[6–12] The absolute stereochemistry of *trans*-cyclooctene has been established, 1 being the (*R*)-(−) enantiomer.[3,13] The heats of hydrogenation of *trans*- and *cis*-cyclooctene in hexane differ by 11.4 kcal/mol,[14] a finding in accord with force-field calculations.[7,8,15–19]

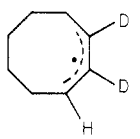
The thermal chemistry of *trans*-cyclooctene has not been so thoroughly surveyed. Cope and Pawson[20] studied the thermal racemization of chiral *trans*-cyclooctene at 132.7–183.9 °C and found an Arrhenius activation energy of 35.6 ± 0.9 kcal/mol for this process. They also observed isomerization to *cis*-cyclooctene and formation of polymer as competing side reactions, even though 2,6-di-*tert*-butylphenol was employed as a polymerization inhibitor.

Roth[21] found that *trans*-cyclooctene gave both *cis*-cyclooctene and 1,7-octadiene at 250 °C; higher temperatures were required to interconvert *cis*-cyclooctene and 1,7-octadiene. Greater ring strain in the trans isomer apparently led to ring opening by a retro-ene reaction under milder conditions.

The isomerization of *trans*-cyclooctene to *cis*-cyclooctene might occur by a variety of distinct paths. Among the most plausible would be direct rotation about the double bond, as in the cis–trans isomerization of 2-butene ($E_a = 62.8$ kcal/mol),[22] a radical chain process involving a comparatively low-energy *trans*-cyclooctene-3-yl to *cis*-cyclooctene-3-yl radical isomerization,[23] and a [1,3] shift of hydrogen.[24] Among the less plausible would be isomerization by way of a [1,2] hydrogen shift and a cyclooctylidene intermediate.

Concerted [1,3] shifts of hydrogen have not yet been observed in thermal hydrocarbon rearrangements. The reaction mode characterized as "allowed" by orbital symmetry theory, involving antarafacial migration of hydrogen with respect to an allylic unit,[24] might be expected to impose inordinantly high energetic demands on most olefins; an exceptional olefin possessing a ground-state geometry particularly favorable to such an antarafacial hydrogen transfer, however, might rearrange with this allowed stereochemistry.[25] The twisted double bond of *trans*-cyclooctene and its comparatively high ground-state energy might provide improved access to high-energy transition states, and thus it might exhibit the allowed but ordinarily awkward antarafacial hydrogen transfer.

Deuterium labeling at C(1) and C(2) could distinguish among all of these mechanistic alternatives. Direct rotation about C(1)–C(2) would convert *trans*- to *cis*-1,2-dideuteriocyclooctene. A radical chain process by way of radical 2 would lead to a mixture of *cis*-1,2- and -2,3-dideuteriocyclooctene. The [1,3] hydrogen shift possibility would afford 2,3-dideuterio product. Reaction by way of the cyclooctylidene intermediate 3 would give 1,2- and 3,3-dideuterio-*cis*-cyclooctene.



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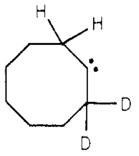

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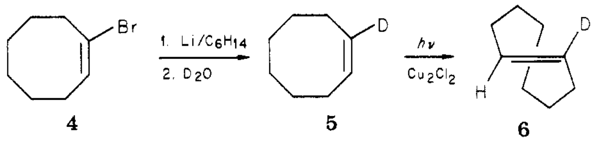
## Results and Discussion

Initial experiments toward making mechanistic distinctions for the thermal conversion of *trans*-cyclooctene to the cis isomer employed *trans*-1-deuteriocyclooctene. *cis*-1-Deuteriocyclooctene (5) was prepared from 1-bromocyclooctene[26] (4) through quenching of the corre-



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(1) (a) Willstätter, R.; Waser, E. *Ber.* **1910**, *43*, 1176–1183. (b) Kiegler, K.; Wilms, H. *Naturwissenschaften* **1948**, *35*, 157–158. (c) Ziegler, K.; Wilms, H. *Justus Liebigs Ann. Chem.* **1950**, *567*, 1–43. (d) Cope, A. C.; Pike, R. A.; Spencer, C. F. *J. Am. Chem. Soc.* **1953**, *75*, 3212–3215.

(2) (a) Traetteberg, M. *Acta Chem. Scand. B* **1975**, *29*, 29–36. (b) Gavin, R. M., personal communication quoted in: Bach, R. D.; Mazur, U.; Hamama, I.; Lauderback, S. K. *Tetrahedron* **1972**, *28*, 1955–1963. (c) Gavin, R. M., Jr.; Wang, Z. F. *J. Am. Chem. Soc.* **1973**, *95*, 1425–1429.

(3) Manor, P. C.; Shoemaker, D. P.; Parkes, A. S. *J. Am. Chem. Soc.* **1970**, *92*, 5260–5262.

(4) Ganis, O.; Lepore, U.; Paiado, G. *J. Chem. Soc., Chem. Commun.* **1969**, 1054–1955. Ganis, P.; Lepore, U.; Martuscelli, E. *J. Phys. Chem.* **1970**, *74*, 2439–2444.

(5) Ferguson, G.; Hawley, D., unpublished. Ermer, O. *Angew. Chem., Int. Ed. Engl.* **1974**, *13*, 604–606.

(6) Allinger, N. L. *J. Am. Chem. Soc.* **1958**, *80*, 1953–1955.

(7) Manor, P. C. Ph.D. Dissertation, Massachusetts Institute of Technology, 1968; quoted in ref 2c.

(8) Allinger, N. L.; Sprague, J. T. *J. Am. Chem. Soc.* **1972**, *94*, 5734–5747.

(9) Mock, W. L. *Tetrahedron Lett.* **1972**, 475–478.

(10) Beckenbaugh, W. M.; Wilson, S. R.; Loeffler, P. A. *Tetrahedron Lett.* **1972**, 4821–4822.

(11) Robin, M. B.; Taylor, G. N.; Kuebler, N. A.; Bach, R. D. *J. Org. Chem.* **1973**, *38*, 1049–1051. Batich, C.; Ermer, O.; Heilbronner, E.; Wiseman, J. *Angew. Chem., Int. Ed. Engl.* **1973**, *12*, 312–314.

(12) Burgoine, K. T.; Davies, S. G.; Peagram, M. J.; Whitham, G. H. *J. Chem. Soc., Perkin Trans 1* **1974**, 2629–2637. Sauers, I.; Grezzo, L. A.; Staley, S. W.; Moore, J. H., Jr. *J. Am. Chem. Soc.* **1976**, *98*, 4218–4222.

(13) Cope, A. C.; Mehta, A. S. *J. Am. Chem. Soc.* **1964**, *86*, 1268–1269, 5626–5630 and references therein.

(14) Rogers, D. W.; Von Voithenberg, H.; Allinger, N. L. *J. Org. Chem.* **1978**, *43*, 360–361. For earlier determinations of heats of hydrogenation for *cis*- and *trans*-cyclooctene in acetic acid, see: Turner, R. B.; Meador, W. R. *J. Am. Chem. Soc.* **1957**, *79*, 4133–4136.

(15) Ermer, O.; Lifson, S. *J. Am. Chem. Soc.* **1973**, *95*, 4121–4132. Ermer, O. *Tetrahedron* **1975**, *31*, 1849–1854.

(16) Anet, F. A. L.; Yavari, I. *Tetrahedron* **1978**, *34*, 2879–2886.

(17) While some early force-field calculations (Buemi, G.; Favini, G.; Zuccarello, F. *J. Mol. Struct.* **1970**, *5*, 101–110. Zuccarello, F.; Buemi, G.; Favini, G. *Ibid.* **1973**, 295–302) favored a chair conformation for ground-state *trans*-cyclooctene, this conclusion has not been supported by subsequent work[8,15–16] (Favini, G.; Rubino, C.; Todeschini, R. *Ibid.* **1977**, *41*, 305–313).

(18) For calculations on bridged *trans*-cyclooctenes (Bredt's rule-violating bridgehead olefins), see: Burkert, U. *Chem. Ber.* **1977**, *110*, 773–777.

(19) For an early theoretical approach to conformational analysis of medium and large cycloalkenes, see: Pauncz, R.; Ginsburg, D. *Tetrahedron* **1960**, *9*, 40–52.

(20) Cope, A. C.; Pawson, B. A. *J. Am. Chem. Soc.* **1965**, 3649–3651.

(21) Roth, W. R. *Chimia* **1966**, *20*, 229–236.

(22) Rabinovitch, B. S.; Michel, K. W. *J. Am. Chem. Soc.* **1959**, *81*, 5065–5071.

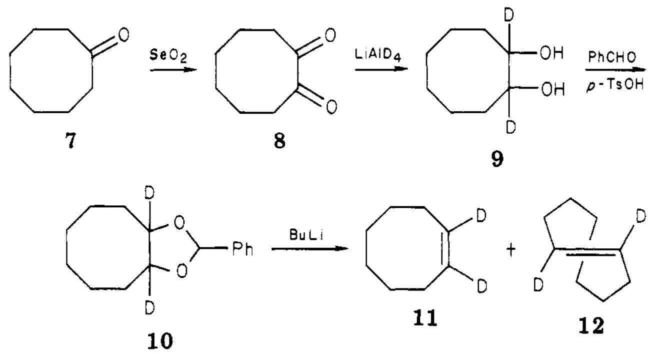
(23) The [1-$^2$H]allyl radical has a rotational barrier of 15.7 ± 1.0 kcal/mol: Korth, H.-G.; Trill, H.; Sustmann, R. *J. Am. Chem. Soc.* **1981**, *103*, 4483–4489.

(24) Woodward, R. B.; Hoffmann, R. "The Conservation of Orbital Symmetry"; Verlag Chemie-Academic Press: Weinheim/Bergstr., Germany, 1970; p 114 ff.

(25) Bingham, R. C.; Dewar, M. J. S. *J. Am. Chem. Soc.* **1972**, *94*, 9107–9112. The [1,3] allylic hydrogen shift in propene is predicted to have $E_a = 49.2$ kcal/mol.

(26) Wittig, G.; Dorsch, H.-L. *Justus Liebigs Ann. Chem.* **1968**, *711*, 46–54.

Scheme I



sponding lithium reagent with deuterium oxide. The $^2$H NMR spectrum[27] of the cis olefin demonstrated that all of the deuterium label was at C(1). The $^1$H NMR spectral data for unlabeled and labeled samples of *cis*-cyclooctene indicated the latter was monodeuterated to the extent of 62%. Photolysis of the cuprous chloride complex[28,29] of *cis*-1-deuteriocyclooctene gave the trans isomer, which could be readily purified by preparative GLC on 1,2,3-tris(2-cyanoethoxy)propane (TCEP) or Apiezon L columns.

Pyrolysis of *trans*-1-deuteriocyclooctene (62% monodeuterated) at approximately 270 °C in the gas phase was followed by GLC separation and $^1$H NMR spectroscopic analysis of the products. The ratio of vinyl ($\delta$ 5.64) to allylic ($\delta$ 2.15) proton absorption intensities in the *cis*-cyclooctene had increased by 19%, while the 1,7-octadiene-*d* from **6**, when compared with unlabeled diene through $^1$H NMR spectroscopy,[30] was seen to have the deuterium label evenly divided between allylic ($\delta$ 2.04) and C(2,7) vinylic ($\delta$ 5.91) absorptions, a result in complete harmony with a retro-ene mechanistic formulation for this isomerization.[21,31] The increase in vinyl to allylic proton absorption intensities in the *cis*-cyclooctene product, relative to this ratio in substrate **6**, was consistent with formation of *cis*-1-deuteriocyclooctene and *cis*-3-deuteriocyclooctene in a 7:3 proportion.

A sample of *cis*-1-deuteriocyclooctene (**5**) similarly heated at about 270 °C was recovered unchanged: all deuterium remained at C(1) (=C(2)). Only traces of 1,7-octadiene were produced. Repetition of the isomerization and of the control experiment with a less completely labeled sample of *trans*-1-deuteriocyclooctene prepared through the 1-cyclooctenyl Grignard reagent in THF gave similar results.

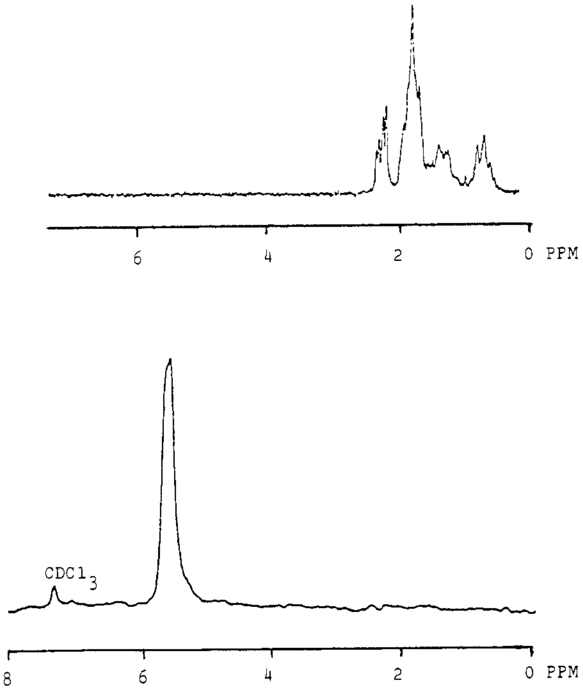


**Figure 1.** $^1$H NMR (top, 1000-Hz sweep width) and $^2$H NMR (bottom, 154-Hz sweep width) spectra of *trans*-1,2-dideuteriocyclooctene.

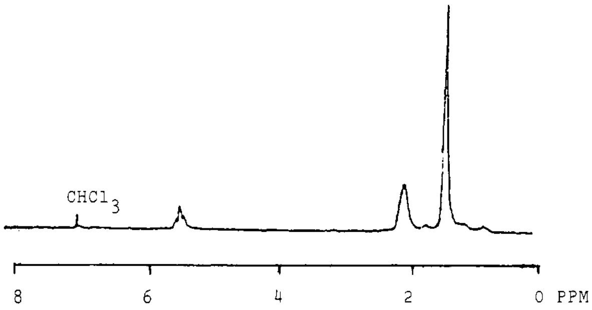


**Figure 2.** $^1$H NMR spectrum of deuterium-labeled *cis*-cyclooctene formed through thermal rearrangement of *trans*-1,2-dideuteriocyclooctene in washed but unconditioned ampules.

The proton spectra alone were consistent with the proposition that about 60% of the isomerization of *trans*- to *cis*-cyclooctene proceeds by way of a [1,3] hydrogen shift, with the remaining 40% occurring through rotation about the C(1)–C(2) bond. Other interpretations of the experimental observations could not be excluded, though, and we took these preliminary results only as justification for more thorough study and additional control experiments, using more extensively labeled substrates and $^2$H NMR spectroscopy.

To avoid possible complications from secondary deuterium isotope effects and to use labeled materials more favorable to $^2$H NMR spectroscopy, we desired *cis*- and *trans*-1,2-dideuteriocyclooctene. The route outlined in Scheme I provided these labeled olefins.

Oxidation of cyclooctanone (**7**) with selenium dioxide gave the 1,2-dione **8**,[32] which was reduced with $LiAlD_4$ to a mixture of dideuterio diols **9**. Condensation with benzaldehyde gave the expected three acetals (**10**), which were converted with *n*-butyllithium into a mixture of the 1,2-dideuteriocyclooctenes (**11** and **12**). All steps in the sequence except the reduction with $LiAlD_4$ had precedent in the literature; final separation and purification of the cycloolefins was accomplished by GLC.

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(27) For summaries of applications of deuterium NMR spectroscopy, see: Mantsch, H. H.; Saitô, H.; Smith, I. C. P. *Prog. Nucl. Magn. Reson. Spectrosc.* **1977**, *11*, 211–271. Smith, I. C. P. *Aldrichimica Acta* **1977**, *10*, 35–39.

(28) Deyrup, J. A.; Betkouski, M. *J. Org. Chem.* **1972**, *37*, 3561–3562.

(29) For other routes to *trans*-cyclooctene, see ref 1 and: (a) Corey, E. J.; Carey, F. A.; Winter, R. A. E. *J. Am. Chem. Soc.* **1965**, *87*, 934–335. (b) Cope, A. C.; Bach, R. D. "Organic Syntheses", Wiley: New York, 1973; Collect. Vol. V, pp 315–320. (c) Wittig, G.; Polster, R. *Justus Liebigs Ann. Chem.* **1957**, *612*, 102–108. (d) Swenton, J. S. *J. Org. Chem.* **1969**, *34*, 3217–3218. (e) Turro, N. J. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 331. (f) Vedejs, E.; Snoble, K. A. J.; Fuchs, P. L. *J. Org. Chem.* **1973**, *38*, 1178–1183. (g) Hines, J. N.; Peagram, M. J.; Thomas, E. J.; Whitham, G. H. *J. Chem. Soc., Perkin Trans. 1* **1973**, 2332–2337. (h) Hiyama, T.; Nozaki, H. *Bull. Chem. Soc. Jpn.* **1973**, *46*, 2248–2249. (i) Bridges, A. J.; Whitham, G. H. *J. Chem. Soc., Chem. Commun.* **1974**, 142–143. (j) Inoue, Y.; Moritsugu, K.; Takamuku, S.; Sakurai, H. *J. Chem. Soc., Perkin Trans. 2* **1976**, 569–574. (k) Inoue, Y.; Takamuku, S.; Sakurai, H. *J. Chem. Soc., Chem. Commun.* **1976**, 423–24; *J. Phys. Chem.* **1977**, *81*, 7–11; *J. Chem. Soc., Perkin Trans. 2* **1977**, 1635–1642; *Synthesis* **1977**, 111. (l) Corbally, R. P.; Perkins, M. J.; Elnitzki, A. P. *J. Chem. Soc., Perkin Trans. 1* **1979**, 793–798.

(30) McGehee, C. L., Summers, C. H. *Dev. Appl. Spectrosc.* **1964**, *4*, 405–416.

(31) Hoffmann, H. M. R. *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 556–577.

(32) Wittig, G.; Krebs, A. *Chem. Ber.* **1961**, *94*, 3250–3275.

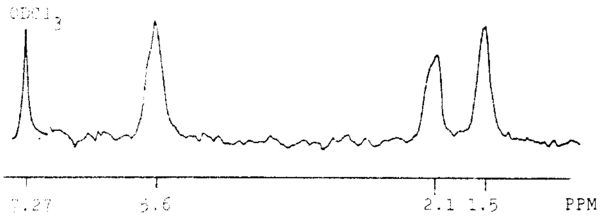

**Figure 3.** $^2$H NMR spectrum of deuterium-labeled *cis*-cyclooctene formed through thermal rearrangement of *trans*-1,2-dideuteriocyclooctene in washed but unconditioned ampules.

A 100% and positionally clean deuterium incorporation in cis and trans isomers was determined by $^1$H and $^2$H NMR. The spectra for the trans isomer **12** (Figure 1) demonstrated the efficacy of the synthetic route; spectra for the cis isomer **11** were just as unambiguous.

Thermolysis at 291.6 °C for 24 h of *trans*-1,2-dideuteriocyclooctene (**12**) in Pyrex ampules that had been soaked in hydrochloric acid, rinsed with water, soaked in concentrated aqueous ammonia/EDTA solution, rinsed copiously with water, and thoroughly dried gave rise to totally unscrambled recovered starting material, the expected 2,3-dideuterio-1,7-octadiene,[21,31] some minor products, and *cis*-cyclooctene: the latter showed a vinyl proton NMR resonance, in qualitative confirmation of the experimental observation made earlier with monodeuterated compounds. *cis*-1,2-Deuteriocyclooctene (**11**) after being heated to 291.6 °C for 24 h was recovered unchanged: all deuterium label remained at the olefinic carbons.

That the $^1$H NMR spectrum of Figure 2, and the earlier observations on the thermal rearrangement of **6**, could not be taken as confirmation of a [1,3] hydrogen shift component in the isomerization was immediately apparent in the deuterium NMR spectrum of the *cis*-cyclooctene product derived from **12**, for deuterium label was present at vinyl, allylic, and nonallylic carbons (Figure 3) in 0.79:0.56:0.65 proportions.

The *cis*-cyclooctene recovered from this pyrolysis of **12** was subjected to mass spectroscopic analysis, which indicated that intermolecular deuterium exchange must have taken place; intermolecular exchange was by no means complete, however, for 62% of the material remained dideuterated.

Conditioning the ampules by heating unlabeled reagent grade *cis*-cyclooctene in them at 310 °C for 48 h or longer reduced dramatically the extent of deuterium scrambling during subsequent isomerizations. In such conditioned tubes, *trans*-1,2-dideuteriocyclooctene (**3**) at 291.6 °C for 155 min gave nearly unscrambled *cis*-1,2-dideuteriocyclooctene (Figure 4) and only 1.5% minor products.

In the presence of undeuterated *trans*-cyclooctene, deuterium scrambling was observed in the thermolysis of *cis*-1,2-dideuteriocyclooctene (**11**) in unconditioned ampules. The recovered cis isomer had $^2$H NMR signal intensities at vinyl/allylic/methylene positions in the proportions 1.50:0.24:0.26. This information is consistent with a mechanism in which *cis*-cyclooctene may lose a hydrogen and enter into a chain process causing inter- and intramolecular scrambling of deuterium labels, a process initiated by interaction of *trans*-cyclooctene with active sites on the glass surface. Analogous control experiments were carried out to show that 1,7-octadiene is stable in unconditioned ampules, even in the presence of **1**. The cis olefin **11** by itself is stable with respect to deuterium scrambling and minor product formation under time and temperature conditions which cause catalyzed rearrangements of the *cis*-cyclooctene when *trans*-cyclooctene is present; yet, remarkably, preheating the ampules in the presence of *cis*-cyclooctene serves to condition them and thus avoid the secondary rearrangements.

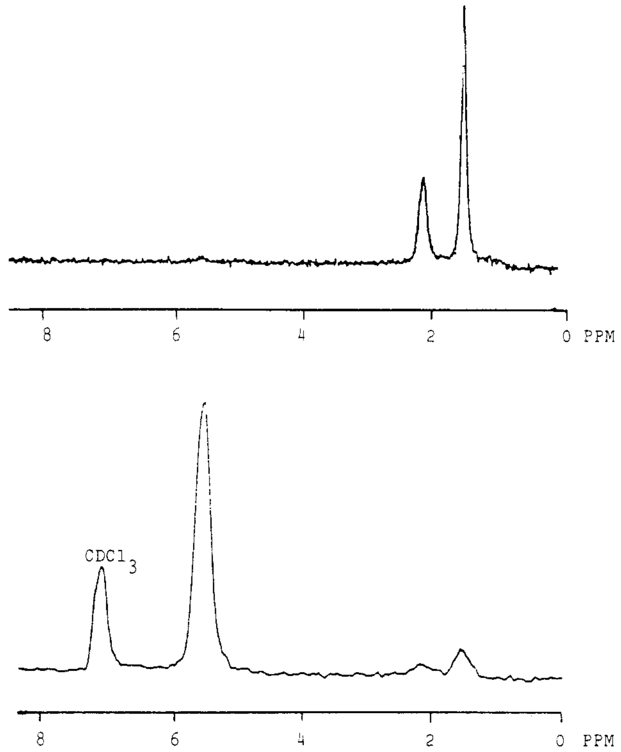

**Figure 4.** $^1$H (top, 1000-Hz sweep width) and $^2$H NMR (bottom, 154-Hz sweep width) NMR spectra of *cis*-1,2-dideuteriocyclooctene formed through thermal rearrangement of *trans*-1,2-dideuteriocyclooctene in conditioned Pyrex ampules.

In the course of this labeling study, analytical-scale pyrolyses were run to gain further understanding of the formation of both *cis*-cyclooctene and 1,7-octadiene from *trans*-cyclooctene and to demonstrate reliable first-order kinetic behavior. In one set of runs at 291.6 °C in exhaustively conditioned ampules, the rate constant for unimolecular disappearance of *trans*-cyclooctene was found to be $(2.11 \pm 0.05) \times 10^{-5}$ s$^{-1}$; the observed rate constants for formation of products were $(1.53 \pm 0.01) \times 10^{-5}$ s$^{-1}$ for 1,7-octadiene and $(0.58 \pm 0.05) \times 10^{-5}$ s$^{-1}$ for *cis*-cyclooctene. The two reactions were treated as competitive first-order processes for purposes of kinetic data reduction; there may, however, be reason to consider an alternative formulation postulating trans-to-cis isomerization and retro-ene isomerization of the initially formed and vibrationally excited *cis*-cyclooctene in competition with collisional deactivation. While rate data for the disappearance of *trans*-cyclooctene were reproducible and varied sensibly with temperature, partitioning ratios depended very sensitively on tube size and sample size, and thus on pressure. More kinetic work undertaken in full awareness of this possibility would be necessary to define properly the kinetic aspects of the thermal isomerization of *trans*-cyclooctene to *cis*-cyclooctene and to 1,7-octadiene.

## Summary

The pyrolysis of *trans*-1,2-dideuteriocyclooctene at 291.6 °C in a well-seasoned ampules gives *cis*-1,2-dideuteriocyclooctene. A simple twist about C(1)–C(2) describes the process.[33] Other mechanisms which predict a different distribution of deuterium labels in the product, including

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[33] For theoretical treatments of the rotational process in ethylene, including configuration interaction, see: Buenker, R. J. *J. Chem. Phys.* **1968**, *48*, 1368–1379. Buenker, R. J.; Peyerimhoff, S. D. *Chem. Rev.* **1974**, *74*, 127–188.

radical-chain, [1,3] hydrogen shift, and [1,2] hydrogen shift processes, have been excluded. 2,3-Dideuterio-1,7-octadiene is produced as well, through retro-ene isomerization of either *trans*-1,2-dideuteriocyclooctene, vibrationally excited *cis*-1,2-dideuteriocyclooctene, or possibly both.

Pyrolyses in unconditioned ampules are complicated by secondary reactions which scramble the deuterium labels inter- and intramolecularly in *cis*-cyclooctene; *trans*-cyclooctene and active sites on the glass walls serve to initiate deuterium scrambling in the cis product. These secondary reactions are not detected by chromatographic analyses of reaction mixtures: only isotopic labeling brings them to light. Erroneous inferences which might have been made from proton NMR spectroscopic analyses alone were conclusively discredited as deuterium NMR and mass spectrometry were employed.

## Experimental Section

Deuterium nuclear magnetic resonance spectra were obtained by using Varian XL-100-12 or XL-100-15 spectrometers and a time-averaging data acquisition facility in conjunction with an 8K Varian 620/I computer and the Varian S-126X time-averaging program. Spectra of $C_8H_{13}D$ isomers were obtained with tetramethylsilane as an internal lock signal and $CDCl_3$ as a reference absorption; for the $C_8H_{12}D_2$ isomers an external fluorine lock was used. The peak areas in $^2$H NMR spectra were estimated by cutting and weighing at least five Xerox copies of the absorptions.

Mass spectra were obtained on a CEC-21-110B by Dr. S. Rottschaefer and Dr. R. Wielesek. Routine IR spectra were recorded with a Beckman IR7 spectrometer. Analytical GLC work was done with Varian Aerograph 1520-B, Perkin-Elmer F-11, and Hewlett-Packard 5771A chromatographs, with flame-ionization detection and either digital (Autolab 6300) or disc/integration. The $C_8$ hydrocarbons were analyzed on an aluminum, 3.2 mm × 5 m, 20% 1,2-bis(2-cyanoethoxy)propane (BCEP) on 60/80-mesh regular Chromosorb P column at 79 °C; the relative retention times from the point of injection were as follows: 1,7-octadiene, 1.0; *cis*-cyclooctene, 2.14; *trans*-cyclooctene, 2.78. Mole fractions obtained by using either the digital integrator or the disc integrator were uncorrected for detector response.

Preparative GLC for purification and isolation of the cycloolefins and other hydrocarbon pyrolysis products was carried out on a Varian Aerograph A-90P on a 6 mm × 3 m, aluminum, 20% 1,2,3,-tris(2-cyanoethoxy)propane (TCEP) on 50/80-mesh Chromosorb P column at 75 °C with a helium carrier gas flow rate of about 60 mL/min. Liquid nitrogen cooled collectors were necessary.

***cis*-1-Deuteriocyclooctene (5).** To 11.0 g (0.058 mol) of 1-bromocyclooctene[26] in 30 mL of hexane was added 1.25 g (0.18 mol) of freshly cleaned lithium ribbon; the mixture was heated to reflux for 24 h. As the reaction proceeded, areas of bright silvery yellow mirror formed on the lithium ribbon, and LiBr was deposited. The orange reaction mixture was very cautiously quenched with $D_2O$ until all the excess lithium had been consumed and the organic phase had turned pale yellow. The aqueous phase was separated and extracted with three 5-mL portions of ether. The combined hexane and ether extracts were washed with 30 mL of water, dried over $MgSO_4$, and filtered; the filtrate was condensed by distillation at atmospheric pressure. The residue was fractionally distilled at reduced pressure to give the crude product, bp 72–74 °C (85 mm). Preparative GLC separation on a 10 mm × 1 m aluminum column packed with 7.5% Apiezon L on a 1:1 mixture of 90/100-mesh Anakrom-ABS and 80/100-mesh non-acid-washed Chromosorb W gave 1.44 g (22%) of partially deuterated cyclooctene.

A $^2$H NMR spectrum of this material obtained by A. H. Andrist showed only one resonance, $\delta$ 5.70 [$C_6D_6$ at $\delta$ 7.37, Freon-11 as solvent and lock signal]. The $^1$H NMR spectrum of the product was similar to that of unlabeled *cis*-cyclooctene except that the olefinic resonance was reduced. Through comparison of olefinic and allylic integrations, the material was estimated to be 62% monodeuterated.

***trans*-Cyclooctenes (1 and 6)** were prepared from the labeled or unlabeled cis isomers through photolysis at 2537 Å under nitrogen in the presence of freshly prepared cuprous chloride,[34] as detailed by Deyrup and Betkouski.[28,35] The trans isomer, purified by preparative GLC on an Apiezon L column, had $^1$H NMR absorptions[12] at $\delta$ 0.8–2.0 (m, 10 H, H(4,5,6,7) and one diasteriotopic pair of allylic hydrogens), $\delta$ 2.39 (m, 2 H, the other diasteriotopic pair of allylic hydrogens) and 5.51 (m, 2 H, H(1) and H(2)).

**1,2-Dideuterio-1,2-cyclooctanediol (9)** was prepared through reduction of 1,2-cyclooctanedione[32] with $LiAlD_4$. A 100-mL, three-necked, round-bottomed flask was charged with 25 mL of dry THF and 1.00 g (23.8 mmol, 1.02 equiv) of $LiAlD_4$ (Alfa Ventron Products). To this slurry under nitrogen was added dropwise with stirring over a period of 45 min 6.52 g of 86.1% pure 1,2-cyclooctanedione (contaminated with 13.9% cyclooctanone; 40.1 mmol of dione) in 50 mL of THF. Vigorous reflux was maintained throughout the addition. The mixture was allowed to stir overnight and was worked up in the usual way. After gravity filtration, drying over $MgSO_4$, and another filtration, the slightly yellow solution was concentrated by means of a rotary evaporator to give 6.55 g of a very slightly yellow oil. Removal of the remainder of the solvent at 0.1 mm caused the oil to deposit a mass of white crystals (4.59 g). This material proved to be 83.8% diol by GLC analysis on a 10% UCW-98 column at 130 °C; the main impurity was cyclooctanol.

In another reduction using 94% pure dione and $LiAlD_4$, the diol (72% yield) had the following $^1$H NMR spectrum: no measurable signal at $\delta$ 3.86 and 3.48, the positions of the methine protons in nondeuterated diol, a broad singlet at $\delta$ 2.95 (2 H), and a broad signal split into two uneven peaks at $\delta$ 2.71 and 2.50 (12 H).

**1,8-Dideuterio-10-phenyl-9,11-dioxabicyclo[6.3.0]undecane (10)** was prepared by a modification of a published procedure.[29g] A 100-mL round-bottomed flask was charged with the dideuterio diol described immediately above (4.59 g, 83.8% pure, 26.6 mmol) and 25 mL of toluene. After the system was equipped with a Dean–Stark trap and flushed with nitrogen, 6.68 g (62.8 mmol) of benzaldehyde, freshly distilled under nitrogen, was added by syringe. The addition of 60 mg of *p*-toluenesulfonic acid monohydrate brought on immediate reaction. After 6 h at reflux, the reaction mixture was cooled, $K_2CO_3$ (44 mg) was added to neutralize the acid, and filtration, concentration by rotary evaporation, and purification by Kugelrohr distillation under high vacuum ($\sim10^{-5}$ mm) at 110 °C gave 5.78 g (93%) of the pure white solid acetal. Analysis by $^1$H NMR showed this to be a mixture of the two acetals derived from the *cis*-diol and the one coming from the *trans*-diol. The $^1$H NMR spectrum was in agreement with data given in the literature:[29g] complex aromatic signal at $\delta$ 7.6–7.3 (5 H); three very sharp benzylic hydrogen signals corresponding to the three isomeric acetals at $\delta$ 5.88 (0.21 H), 5.68 (0.30 H), and 5.47 (0.49 H); the two types of methine protons giving rise to complex signals centered at $\delta$ 4.0 and 3.8, with an approximate ratio of 0.72:0.29, respectively, observed in the undeuterated compounds were completely absent in the spectrum of the dideuterated analogues; a broad complex signal was observed from $\delta$ ~1.0 to 2.2 (12 H).

**1,2-Dideuterio-*cis*-cyclooctene (11) and 1,2-dideuterio-*trans*-cyclooctene (12)** were prepared in the manner described by Whitham and co-workers.[29g] The dideuterated acetal (5.74 g, 24.5 mmol) was dissolved in 26 mL of pentane and allowed to stir at room temperature under a nitrogen atmosphere after the addition of 30.6 mL of *n*-BuLi solution (1.6 M in hexane, 40 mmol, 2 equiv). The reaction was quenched after 43 h when conversion of the acetal to product had ceased (monitored by GLC on a 3.2 mm × 3 m 10% UCW-98 column at 130 °C; acetals diminished as phenyl butyl ketone increased). The reaction mixture was diluted with 150 mL of water; the aqueous layer was extracted with pentane, and the organic extract was dried over $MgSO_4$, filtered, and concentrated by distillation through a 30-cm Vigreux column. Final separation and purification of the two dideuterated cycloolefins was accomplished by preparative GLC. On the basis

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(34) Jolly, W. J. "Synthetic Inorganic Chemistry"; Prentice-Hall: Englewood Cliffs, NJ, 1960; pp 142–143.

(35) For quantitative work on the relative $K_{Ag^+}$ constants for cyclic olefins, see: Bach, R. D.; Richter, R. F. *Tetrahedron Lett.* **1973**, 4099–4102.

of material isolated in this way, the yield was 51% of a mixture of cis- and trans-dideuterated olefins in a 7:3 ratio.

**Thermolyses: Apparatus and Methods.** A 15-cm-diameter stainless-steel beaker mounted with three asbestos-cement plates and firebrick halves in a cubical plywood container was surrounded by a commercial insulative diatomacious filler ("Celatom" diatomite, Eagle-Picker Industries, Inc.) and fitted with stainless-steel immersion heaters and a stirrer. The bath held approximately 7 kg of molten $NaNO_2$ and $KNO_3$,[36] maintained at temperature with a Model 253 precision temperature controller (0–500 °C, Bailey Instrument Co.). The temperature was measured by a frequently calibrated Hewlett-Packard 2802A thermometer accurate to ±0.05 °C.

Thermolysis tubes for initial kinetic work were constructed from 1-mm wall thickness, 5-mm o.d. borosilicate glass tubing; they were detergent washed, acid washed, base washed, and dried at 200 °C prior to use. Later work employed Pyrex ampules made from 6-mm tubing (11–13 cm long, 1.4–1.6 mL volume). Large-scale pyrolyses were carried out in "20 mL" (volume 29 mL) and "50 mL" (volume 65 mL) ampules (Kontes) with 6-mm tubing butted on for sealing under vacuum. All ampules were subjected to the following washing procedure: 12 h of soaking in concentrated HCl(aq); rinsing with water; soaking in concentrated $NH_3$(aq)/EDTA solution for 24–72 h; copious rinsing with water; drying in an oven for at least 24 h at ~250–275 °C and pumping under high vacuum ($<10^{-4}$ mm).

Olefins to be pyrolyzed were freshly purified by preparative GLC and then introduced into the ampules by (conditioned) capillary tubing or by syringe; each ampule was subjected to freeze–pump–thaw cycles and sealed under high vacuum. Samples in ampules were suspended in the salt bath in a wire cage, removed after a determined period of time, and then cooled in water or under a stream of air. The pyrolysate was condensed in the small end of the ampule with liquid $N_2$, and the ampule was opened. The contents were diluted, after weighing, with 3–4 volumes of isooctane. Recovery of material ranged from 83% to 100%; no polymer was observed. A few microliters were utilized for GLC analyses, and the rest of the solution was subjected to preparative GLC to isolate the various isomers for NMR analyses. Kinetic data were obtained by analyzing the condensed, diluted pyrolysate at least three times by GLC.

Conditioned ampules were made by pyrolyzing *cis*-cyclooctene in the ampules (pressure ~250–830 mm) at 291.6–350 °C for periods of 2–9 days. The ampules were then broken open, emptied, and pumped under high vacuum. When these ampules were used, care was taken to seal them so that all the surface had been conditioned.

Treatment of kinetic data to obtain rate constants was carried out by using a standard least-squares program on the University of Oregon PDP-10 computer.

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**Registry No. 1**, 931-89-5; **4**, 4103-11-1; **5**, 79839-59-1; **6**, 79839-60-4; **8**, 3008-37-5; *cis*-**9**, 79839-61-5; *trans*-**9**, 79839-62-6; **10**, 79839-63-7; **11**, 79839-64-8; **12**, 79839-65-9; benzaldehyde, 100-52-7.

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(36) Cason, J.; Rapoport, H. "Laboratory Text in Organic Chemistry"; Prentice-Hall: Englewood Cliffs, NJ, 1962; p 279.

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# Cycloaddition and Polymerization Reactions of *N*-Ethyl-3-vinylcarbazole with Electron-Poor Olefins

M. Abdelkader and H. K. Hall, Jr.*

*The Chemistry Department, University of Arizona, Tucson, Arizona 85721*

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Reaction of *N*-ethyl-3-vinylcarbazole (**1**) and trimethyl ethylenetricarboxylate (**2**) yielded the cyclobutane adduct trimethyl 1-(*N*-ethyl-3-carbazyl)-2,2,3-cyclobutanetricarboxylate (**3**) and homopoly(*N*-ethyl-3-vinylcarbazole) (**4**). The formation of **3** was favored by polar solvents and high temperatures. Formation of homopolymer **4** was suppressed by dimethyl sulfoxide but unaffected by the addition of radical inhibitors. With AIBN as initiator, the alternating copolymer **5** was obtained (as well as some cycloadduct **3**). Dimethyl cyanofumarate (**6**), more reactive than **2**, reacted with **1** at room temperature to yield cyclobutane adduct dimethyl 1-(*N*-ethyl-3-carbazyl)-2-cyano-2,3-cyclobutanedicarboxylate (**7**) and homopolymer **4**. Reaction of **1** with tetramethyl ethylenetetracarboxylate (**8**) at high temperature resulted in cyclobutane adduct tetramethyl 1-(*N*-ethyl-3-carbazyl)-2,2,3,3-cyclobutanetetracarboxylate (**9**). These reactions were interpreted as proceeding via predominantly zwitterionic tetramethylene intermediates.

## Introduction

Functionally substituted olefins react thermally with themselves or with other olefins to produce a variety of products, both small molecules and polymers. Small molecules include cyclobutanes, 1-butenes and cyclohexanes; polymers include homopolymers of either or both olefins and alternating 1:1 copolymers.[1-4] Various mechanisms have been suggested for these reactions. We have been using the concept of a tetramethylene intermediate,[2,5,6] produced by bond formation between the β-carbons of the two olefin molecules, which is a resonance hybrid of zwitterion and spin-paired biradical forms. The various small molecules derived from collapse of various conformations of the intermediate tetramethylene T, and do not diagnose the relative contributions of the two resonance forms. The polymer products are more diagnostic. Homopolymers of one or the other monomer can form by cationic or anionic initiation at either end of a predominantly zwitterionic tetramethylene, whereas alternating copolymers will form from a predominantly biradical

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(1) Huisgen, R. *Acc. Chem. Res.* **1977**, *10*, 117.
(2) Huisgen, R. *Acc. Chem. Res.* **1977**, *10*, 199.
(3) Stille, J. K.; Oguni, N.; Chung, D. C.; Tarvin, R. F.; Aoki, S.; Kamachi, M. *J. Macromol. Sci. Chem.* **1975**, *A9(5)*, 745.
(4) Hall, H. K., Jr.; Ykman, P. *J. Am. Chem. Soc.* **1975**, *97*, 800.
(5) Salem, L.; Rowland, C. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 92.
(6) Chmurny, A. B.; Cram, D. J. *J. Am. Chem. Soc.* **1973**, *95*, 4237.

0022-3263/82/1947-0292$01.25/0