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Reactions of *exo*- and *endo*-8-Carbenatricyclo[3.2.1.$0^{2,4}$]octane[1]

Peter K. Freeman,* Thomas A. Hardy, R. S. Raghavan, and Donald G. Kuper

Department of Chemistry, Oregon State University, Corvallis, Oregon 97331, and the Department of Chemistry, University of Idaho, Moscow, Idaho 83843

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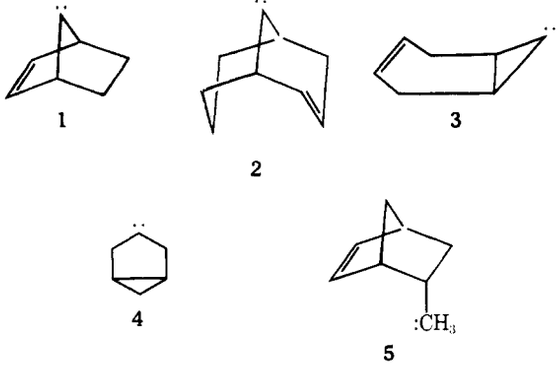
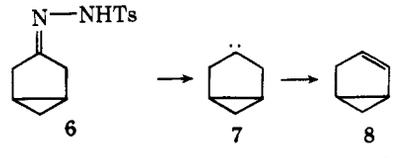
Decomposition of the tosylhydrazone of *exo*-8-tricyclo[3.2.1.$0^{2,4}$]octanone in bis(2-ethoxyethyl)ether/sodium methoxide produces a mixture of hydrocarbons (20%) composed of 65% of bicyclo[3.3.0]octa-1,6-diene and 35% of a mixture of two isomeric bicyclo[3.3.0]octadienes. The decomposition of the tosylhydrazone of *endo*-8-tricyclo[3.2.1.$0^{2,4}$]octanone (**17a**) in diglyme/sodium methoxide yields *endo-anti*- and *endo-syn*-tricyclo[3.2.1.$0^{2,4}$]-octan-8-yl methyl ether, *endo*-tricyclo[3.3.0.$0^{4,6}$]octan-2-yl methyl ether, tetracyclo[3.3.0.$0^{2,8}$.$0^{4,6}$]octane (**21**), and tricyclo[3.3.0.$0^{4,6}$]oct-2-ene (**22**) in an overall yield of 80%. The ratio of methyl ethers/hydrocarbons is dependent upon the concentration of methanol in the reaction medium. The decomposition of the 2-methyl derivative of tosylhydrazone **17a** (**35a**) in either diglyme/sodium methoxide or diglyme/sodium hydride generates a hydrocarbon mixture of 4-methylenetricyclo[3.3.0.$0^{2,8}$]octane (**36**) and 2-methyltetracyclo[3.3.0.$0^{2,8}$.$0^{4,6}$]octane (**37**). NMR and mass spectral analyses of the hydrocarbon products of decomposition of labeled tosylhydrazones using deuterated substrates, *exo,exo*-6,7-dideuterio-**17a** (**17c**), *exo,exo*-6,7-dideuterio-**35a** (**35b**), *exo*-4-deuterio-**35a** (**47**), and 4-*exo,exo*-6,7-trideuterio-**35a** (**48**) support an intermolecular carbene to carbene rearrangement for the generation of tetracyclooctanes **21** and **37**.

If one relates the state of the art of carbene chemistry[2] to our knowledge of carbonium ion chemistry,[3] it is easy to appreciate that the development of our understanding of the mechanistic features of carbene reactions is at a relatively primitive stage. A major facet of carbonium ion chemistry which we are pursuing in carbene chemistry is the importance of homoaromatic delocalization illustrated in the carbonium ion case by the bicyclo[3.1.0]hexyl carbonium ion.[4] In a number of studies, intriguing possibilities for homoaromatic character in carbene intermediates have surfaced. Moss and co-workers[5] have described the chemistry of 7-carbenanorbornene (**1**), Fisch and Pierce[6] have generated 9-carbenabicyclo[3.3.1]non-2-ene (**2**), Klumpp and Vrielink[7] have considered 7-carbenabicyclo[4.1.0]hept-3-ene (**3**), and we have reported on the chemistry of 3-carbenabicyclo[3.1.0]hexane (**4**)[8] and *endo*-5-norbornenylcarbene (**5**).[9]

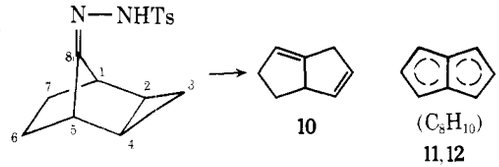


Evidence suggesting horoaromatic stabilization has been advanced for 7-carbenanorbornene (**1**), bivalent **2**, and *endo*-5-norbornenylcarbene (**5**). The simplicity of 3-carbenabicyclo[3.1.0]hexane (**4**) was appealing initially; however, the methoxide ion induced decomposition of the tosylhydrazone of 3-bicyclo[3.1.0]hexanone (**6**) generates bicyclo[3.1.0]hexene-2 (**8**) in 91% yield, most probably as a result of 1,2-hydrogen migration of 3-carbenabicyclo[3.1.0]hexane.[10] Thus, any trishomocyclopropenyl character which might actually be present in 3-carbenabicyclo[3.1.0]hexane is not revealed. If one were to bridge 3-carbenabicyclo[3.1.0]hexane across the C-2–C-4 positions with a small bridging unit, however, hydrogen migration would be prevented and transannular interactions might be revealed. For example, the incorporation of an ethano bridging unit would create the tricyclo[3.2.1.$0^{2,4}$]-octane ring system, which provides a very favorable geometry for interaction of remote cyclopropane with an empty p orbital at C-8 in the case of the endo arrangement. For these reasons, we chose to investigate *exo*- and *endo*-8-carbenatricyclo[3.2.1.$0^{2,4}$]octane (**13** and **28**).



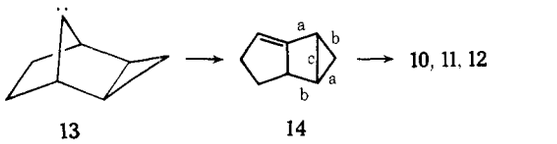
Decomposition of the tosylhydrazone of *exo*-8-tricyclo[3.2.1.$0^{2,4}$]octanone (**9**) in bis(2-ethoxyethyl) ether (3.3 equiv of $NaOCH_3$) at 160 °C gives a 20% yield of hydrocarbons, composed of 65% of bicyclo[3.3.0]octa-1,6-diene (**10**) and

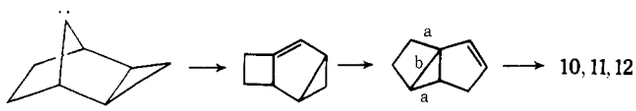
35% of a mixture of two isomeric bicyclo[3.3.0]octadienes (**11**, **12**). Two reasonable reaction courses can be suggested: mi-



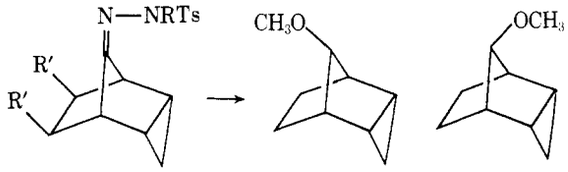
9

gration of C-2 (**13** → **14** → products), with **14** undergoing either a concerted ($_{\sigma}2_s + {}_{\sigma}2_a$ fission at bonds a or at bonds b)[11] or biradical ring opening to products (fission at a, b, or c), or migration of C-6 (**13** → **15** → **16** → products), with **15** undergoing a vinylcyclopropane rearrangement to **16** and **16** opening by a partly concerted (fission at bonds a), partly biradical (fission at b or b + a), or a completely biradical process.[12] In work reported subsequent to our own, Murashashi and coworkers[13] note that pyrolysis of the sodium salt of **9** generates **15** as the only significant product in 57% yield. Since no bicyclo[3.3.0]octadienes were observed in addition to **15**, the second alternative (migration of C-6) appears to occur exclusively in reactions of bivalent **13**.

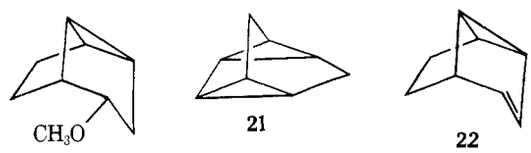




In sharp contrast, the decomposition of the tosylhydrazone of *endo*-8-tricyclo[3.2.1.0^{2,4}]octanone (**17a**) in diglyme (5.74 equiv of $NaOCH_3$) at 155 °C produces *endo-anti*- (**18**, 11%) and *endo-syn*-tricyclo[3.2.1.0^{2,4}]octan-8-yl methyl ether (**19**, 1%), *endo*-tricyclo[3.3.0.0^{4,6}]octan-2-yl methyl ether (**20**, 51%), tetracyclo[3.3.0.0^{2,8}.0^{4,6}]octane (**21**, 33%), and tricyclo-[3.3.0.0^{4,6}]oct-2-ene (**22**, 4%) in an overall yield of 80%. The



a, R = H; R' = H
b, R = D; R' = H
c, R = H; R' = D



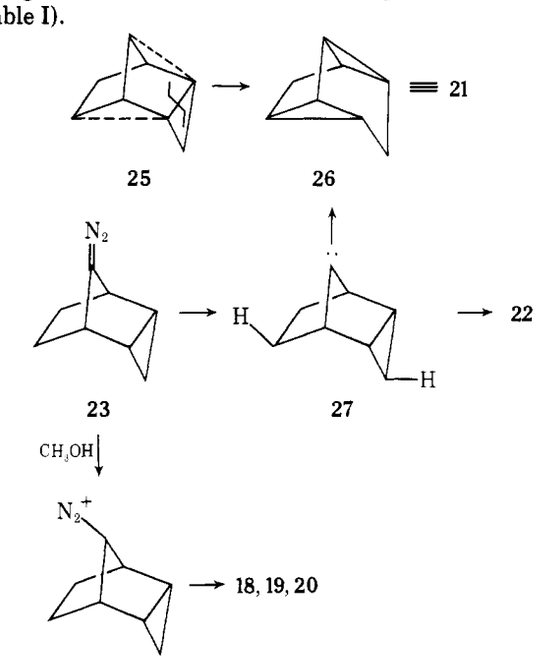
formation of methyl ethers **18**, **19**, and **20** suggests that the methanol of neutralization formed in the reaction of tosylhydrazone with sodium methoxide may have converted **23** to **24**, providing two major reaction routes, a carbonium ion pathway (from **24**) as well as a carbene pathway (from **23**).[14] By using either deuterated or undeuterated tosylhydrazone, various quantities of methanol-*d*, and taking advantage of the isotope effect, it is possible to separate the carbene and carbonium ion components of the reaction. Thus, keeping the concentration of the proton source to a minimum and using the fact that $k_H/k_D > 1$,[15] it is possible to retard the route **23**

Table I. Decomposition of Tosylhydrazone 17a in Diglyme/$NaOCH_3$/CH_3OH(D)

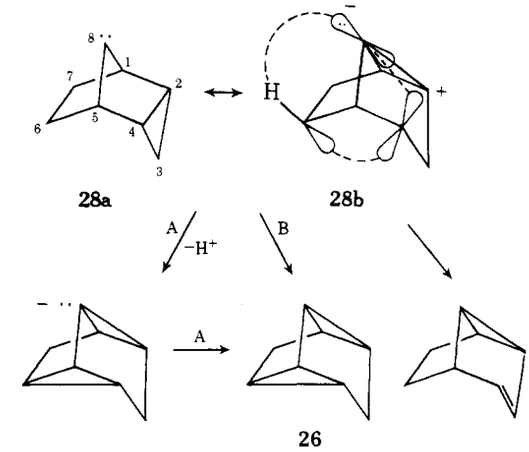
Run	17a equiv	$NaOCH_3$, equiv	CH_3OD,[b] equiv	20,[c] %	18,[c] %	21,[c] %	22,[c] %
1	1.00 **17b**[a]	5.82		6	3	81	10
2	1.00 **17a**	5.92	1.00	64	13	21	2
3	1.00 **17a**	5.75	11.9	81	11	7	1
4	1.00 **17a**	6.20	81.7	81	16	3	0

[a] 97% d_1. [b] 83% methanol-*d*. [c] ±2%.

→ **24** to such an extent that the carbene component is 91% (products **21** and **22**). In contrast to this, a concentration of nearly 82 equiv of methanol-*d* using undeuterated tosylhydrazone **17a** results in a process which proceeds principally through **24** and a carbonium ion (97%) (products **18** and **20**) (Table I).



Thus, decomposition of diazo compound **23** generates a bivalent intermediate, which appears to rearrange via bond formation between C-2 and C-8, fission at C-2–C-4, and bonding between C-4 and C-6, with concomitant hydrogen migration (**25**) to generate **26** (equivalent to **21**). Representing the bivalent intermediate as **28a** ↔ **28b**, two major alternatives may be viewed for the formation of tetracyclic **26** via a C-6 → C-8 hydrogen shift: (a) an intermolecular process (route A) or (b) an intramolecular process, a C-6 → C-8 hydrogen shift is a symmetry-allowed process ($_{\sigma}2_a + {}_{\omega}2_a + {}_{\omega}0_a$)[16] (route B) (eq 1). These alternatives were investigated through the



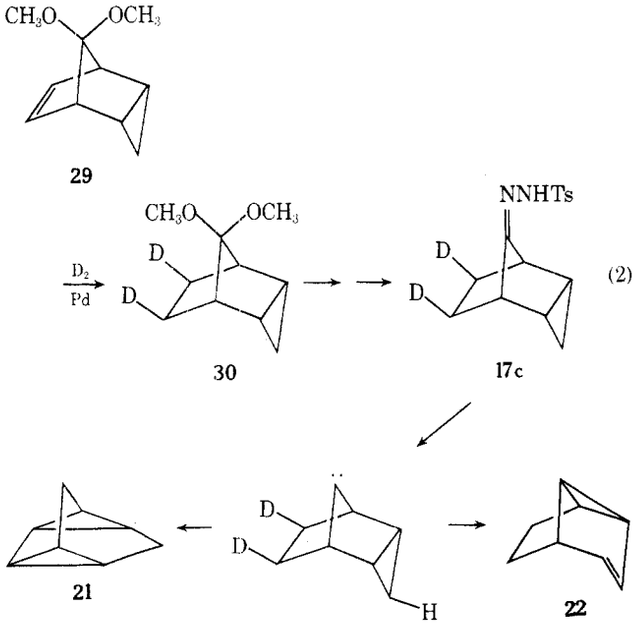
(1)

Table II. Mass Spectral Analysis of the Methoxide Ion Induced Thermal Decomposition of 17c

Run	Compd	% d_0	% d_1	% d_2
A	**17c**[a]	7.6 ± 0.5[c]	26.2 ± 0.5	66.2 ± 0.9
	22	8.5 ± 0.6	25.0 ± 0.7	66.5 ± 1.0
	21	11.9 ± 0.5	24.4 ± 0.5	63.7 ± 0.6
B	**17r**[b]	35.3 ± 0.5	33.0 ± 0.5	31.7 ± 0.7
	22	33.9 ± 0.7	35.8 ± 0.7	30.2 ± 0.5
	21	37.2 ± 0.5	34.0 ± 0.5	28.8 ± 0.6

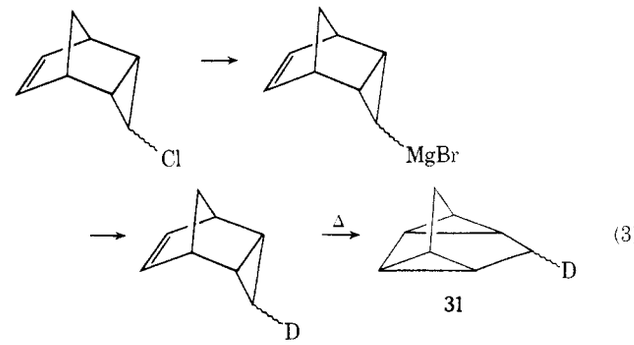
[a] Batch A. [b] *endo*-Tricyclooctane from $NaBH_4$ reduction of **17c**, batch B. [c] One standard deviation.

synthesis of **17c** and analysis of the fate of labeled intermediate *exo,exo*-6,7-dideuterio-**28.** Labeled carbene precursor **17c** was prepared by reduction of ketal **29** with D_2/Pd, hydrolysis of saturated ketal **30** to parent ketone, followed by conversion to **17c** (eq 2). Chemical-shift studies using $Eu(fod)_3$ combined with an analysis of spin decoupling on labeled parent ketone revealed that deuterium addition is entirely exo (>95%). Decomposition of *exo,exo*-dideuteriotosylhydrazone **17c,** using conditions (6.5 equiv of $NaOCH_3$/diglyme) similar to those described above for **17a,** generated tetracyclooctane **26** (**21**) and tricyclooctene **22** in 81 and 10% yields, respectively. Since the ratio of **21**:**22** is identical to that obtained with undeuterated substrate **17a,** no deuterium isotope effect is indicated as might have been anticipated in a competition of C-6 H (D) with C-3 H fission. Mass spectral analysis of **17c** and carbene products tetracyclooctane **21** and tricyclooctene **22** reveals that no deuterium is lost in the formation of **22** (<1%) and very little in the formation of **21** (<3%) (Table II). Since in an intermolecular exo C-6 deuterium shift, assuming complete *exo,exo*-dideuterio-**28,** $k_H/k_D \cong 1.0$ for neutralization of a carbanion,[17] and an initial equivalent of CH_3OH present, the ratio of **26**-d_1:**26**-d_2 resulting should be 63:37,[18] the retention of deuterium rules out intermolecular process A involving loss of an exo C-6 or C-7 hydrogen for formation of tetracyclic **26** (**21**). There remains the possibility that an

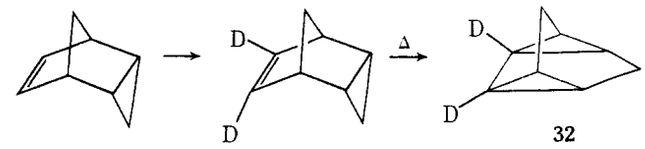


(2)

intermolecular endo C-6 hydrogen shift obtains.[19] With at least one variation of route A eliminated, route B is worthy of consideration. The deuterium distribution expected is illustrated in eq 5. The synthesis of deuterated standards **31** (eq 3) and **32** (eq 4) both relied upon the very clean thermal rearrangement of *endo*-tricyclo[3.2.1.$0^{2,4}$]octane[20] and allowed us to make the NMR assignments indicated in **33.** Starting

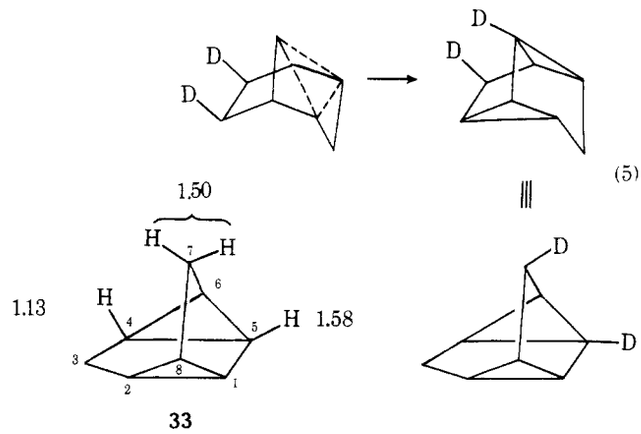


(3)



(4)

with **17c** which was 80% deuterated at the exo-6, exo-7 positions and assuming that k_H/k_D is ca. 1.00, the deuterium distribution in the tetracyclooctane **21** anticipated for a C-6 → C-8 shift would result in an NMR spectrum with a δ 1.58–1.50/δ 1.13 ratio of 4.4:4.0. The ratio found, 5.2:3.2, raises doubts concerning a C-6 → C-8 shift and suggests, instead, that there may be no migration of deuterium.



(5)

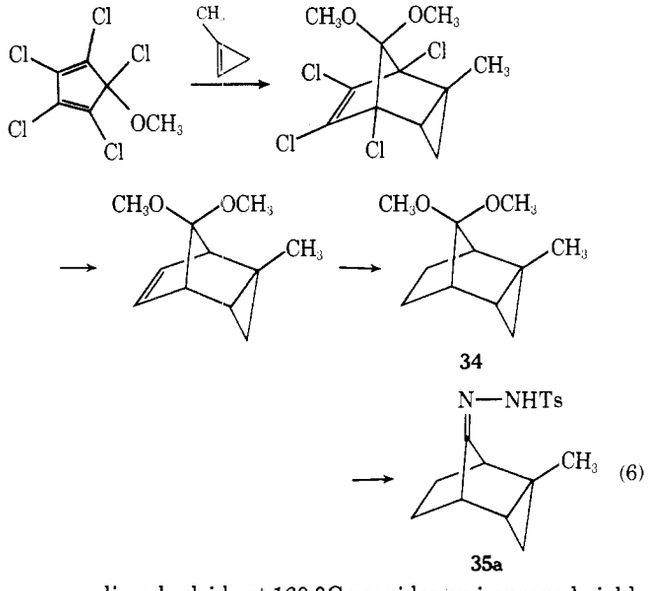
The C_{2v} symmetry of tetracyclic **21** makes the analysis of deuterium scrambling difficult. We found that the resolution of the mechanistic puzzle confronting us at this stage was simplified considerably by reducing the symmetry of the bivalent intermediate and the resulting tetracyclic product by introduction of a methyl group. The synthetic sequence used for the preparation of the tosylhydrazone of *endo*-2-methyltricyclo[3.2.1.$0^{2,4}$]octan-8-one (**35a**) is given in eq 6. Treatment of 5,5-dimethoxy-1,2,3,4-tetrachlorocyclopentadiene with methylcyclopropene produced Diels–Alder adduct in nearly quantitative yield. Reduction with sodium in *tert*-butyl alcohol–THF yielded alkene ketal (56%), which was hydrogenated to saturated ketal **34.** Difficulties in isolating the ketone precursor of tosylhydrazone **35a** were obviated by direct conversion of **34** to tosylhydrazone **35a.**

Decomposition of tosylhydrazone **35a** in diglyme/sodium methoxide (6.5 equiv) generates methylenetricyclooctane **36,** methyltetracyclooctane **37,** and methyl ethers in yields of 26, 3, and 10%, respectively. Ozonolysis of **36** produced the known tricyclooctanone **38,**[21] while pyrolysis of *endo*-2-methyltricyclooctene (**39**) yields **37**[20] providing confirmation of the structural assignments. The low yield of key product **37** provided the impetus to switch to sodium hydride in diglyme in order to eliminate the methanol of neutralization and thus enhance the carbene component of the reaction. Decomposition of tosylhydrazone **35a** in diglyme in the presence of

Table III. Mass Spectral Results of the Thermal Decomposition of the Sodium Salts of 35b, 47, and 48

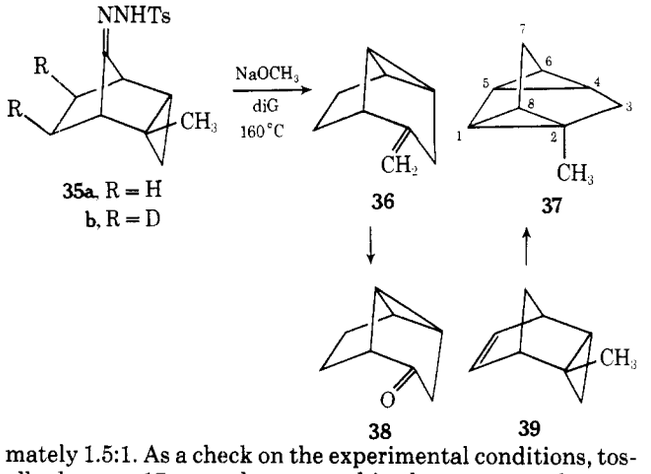
Compd	Registry no.	% d_0	% d_1	% d_2	% d_3	% d_4
35b[a]	63689-18-9	6.1 ± 0.7[d]	19.4 ± 0.7	74.5 ± 0.9		
37		5.3 ± 0.5	23.0 ± 0.5	71.7 ± 0.5		
36		4.1 ± 0.5	23.0 ± 0.6	71.5 ± 0.6	1.1 ± 0.6	
47	6389-19-0	4.3 ± 0.5	93.0 ± 0.4	2.7 ± 0.7		
37		84.0 ± 0.5	16.1 ± 0.5			
36		5.5 ± 0.6	79.5 ± 0.6	14.9 ± 0.7		
48[b]	63689-20-3	0.5 ± 0.4	3.9 ± 0.4	19.5 ± 0.5	74.5 ± 0.5	1.8 ± 0.7
37		2.5 ± 0.5	14.9 ± 0.5	71.9 ± 0.5	10.7 ± 0.5	
36		0.8 ± 0.6	2.9 ± 0.6	17.0 ± 0.5	71.5 ± 0.6	7.5 ± 0.7
47[b]		4.3 ± 0.4	93.0 ± 0.4	2.7 ± 0.7		
37[c]		93.2 ± 1.2	6.8 ± 0.9			
36[c]		9.8 ± 0.9	86.0 ± 1.1	4.2 ± 0.8		

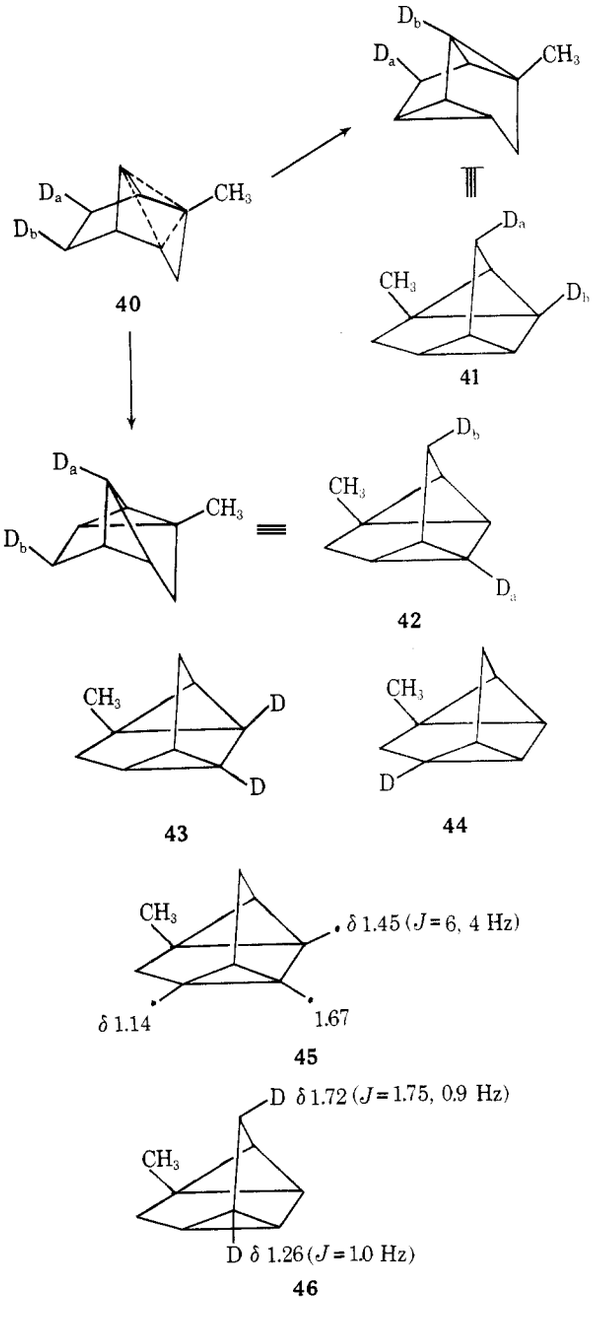
[a] Determined by mass spectral analysis of 2-methyl-*endo*-tricyclo[3.2.1.0^{2,4}]octane obtained by reduction of **35b**. [b] Determined by mass spectral analysis of the ketone precursor. [c] From sodium methoxide induced decomposition of **47**. [d] One standard deviation.



(6)

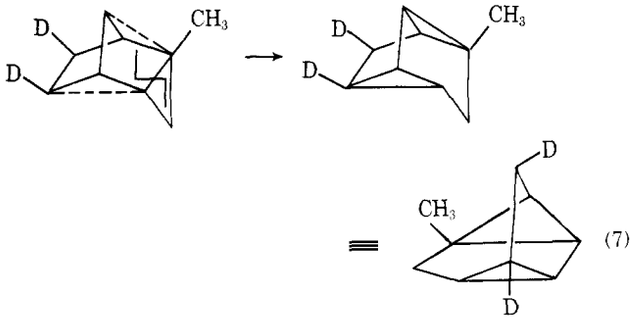
excess sodium hydride at 160 °C provides an improved yield (50–60%) of hydrocarbons **36** and **37** in a ratio of approximately 1.5:1. As a check on the experimental conditions, tosylhydrazone **17a** was decomposed in the presence of excess sodium hydride in diglyme at 160 °C and the same 8:1 ratio of **21:22** was obtained as in the methoxide ion induced decomposition (estimated to be 91% carbenoid, 9% cationic). Deuterated tosylhydrazone **35b** was prepared in a manner analogous to that described above for **17c**, and subsequent decomposition in diglyme/NaH (160 °C) produced deuterated





36 and 37. Mass spectral analysis revealed that little deuterium was lost in the generation of 36 (<4%) and 37 (<4%) (Table III).

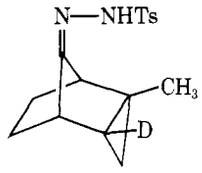
A reconsideration of the C-6 → C-8 hydrogen (deuterium) migration mechanism for carbene 40 provides a useful format for analysis. Due to the lack of symmetry in carbene 40, C-6 → C-8 migration of D_b generates 41, while a similar shift of D_a produces the alternative scrambling pictured in 42. Analysis of proton and deuterium NMR spectra of standards 43 and 44 and the ^1H NMR spectrum of methyltetracyclooctane 37 provided the assignments illustrated in 45 and the data necessary for determination of the deuterium scrambling in the deuterated methyltetracyclooctane 37 derived from decomposition of 35b. The proton NMR spectrum of deuterated 37 exhibits the doublet of doublets at δ 1.45 identical in intensity and splitting to undeuterated substrate. Thus, deuterium is not located at C-8, C-1, or C-5, and, therefore, the deuterium shifts illustrated by transformation 40 → 41 and 40 → 42 do not occur. The deuterium NMR data of deuterated 37 are given in structure 46. The chemical shift and the deuterium–proton coupling of the doublet of doublets at δ 1.72 (translating to proton–proton coupling of 11 and 6 Hz) and that of the triplet at δ 1.26 (proton–proton coupling ca. 6 Hz) fit very nicely the assignments indicated in 46. This surprising outcome corresponds to bond formation between C-2 and C-8, C-4 and C-6, and fission at C-2–C-4, with no migration of deuterium (eq 7). Such a result can be considered in terms of a carbene to carbene rearrangement (as illustrated in eq 8) or an intermolecular shift of an endo C-6 hydrogen (as in route A, eq 1).



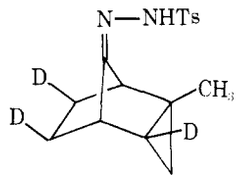
(7)

(8)

In order for a carbene to carbene rearrangement to occur, hydrogen must be lost from C-4 and gained at C-8. To test this possibility, 4-deuterio and 4-*exo*,*exo*-6,7-trideuteriotosylhydrazones 47 and 48 were prepared, using the chemistry of eq 6 and reagents D_2/Pd and 2-deuterio-1-methylcyclopropene; each was then decomposed in diglyme/sodium hydride (160 °C). The mass spectral analysis of tosylhydrazones 47 and 48 and the methyltetracyclooctane and methylenetricyclooctane products are presented in Table III. Thus, in viewing the results with 47, it appears that in the formation of tetracyclooctane 37 nearly all the deuterium is lost from C-4 (13% retained), while methylenetricyclooctane has picked up approximately 12%. The mass spectral data for the decomposition of 48 reinforce this picture. The deuterium NMR spectrum of methyltetracyclooctane 37 obtained from 47 provides significant insight, exhibiting a single absorption at δ 1.45. This demonstrates that *all* the deuterium (>99.5%) has been lost from C-4 in 47 and that the 13% retained is located at C-1 in methyltetracyclooctane 37 (equivalent to the C-8 position in the carbene derived from 47). To confirm that loss of hydrogen (deuterium) from C-4 is an intrinsic feature of the generation of tetracyclooctane 37, 4-deuterio-2-methyltetracyclooctane 44 was treated with 3 equiv of sodium hydride in diglyme at 160 °C. Mass spectral analysis of 44 initially (97.6 ± 1.0% d_1) and after treatment (99.1 ± 1.0% d_1) demonstrated that there was no loss of deuterium due to exchange with the medium. In addition, since tricycloalkene 36 has gained deuterium (12%) equivalent to that reincorporated by 37 at C-1, it is clear that precursor tosylhydrazone does not undergo exchange with the solvent.

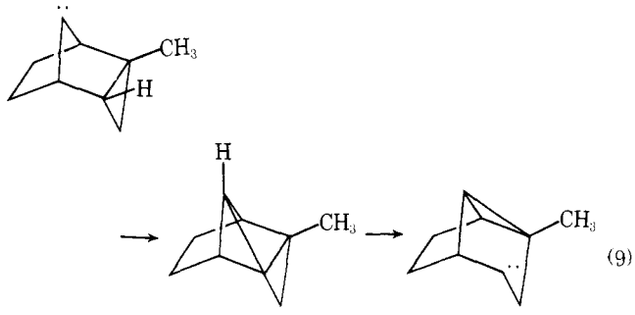


47



48

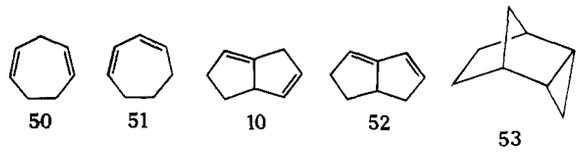
In order to answer the question as to whether the NaH/diglyme medium is unique, tosylhydrazone 47 was allowed to react with 5.6 equiv of sodium methoxide in diglyme at 160 °C. Hydrocarbon products 36 and 37 were formed in a 9:1 ratio and mass spectral analysis (Table III) suggests that the same process is in operation. Clearly, the experiments with tosylhydrazones 47 and 48 support the carbene to carbene rearrangement, rather than a loss of hydrogen from the endo C-6 position (route A, eq 1). The carbene rearrangemt pictured in eq 8 might be either an intramolecular process, perhaps involving C-4 insertion to form a spirane and subsequent cleavage as pictured in eq 9, or else an intermolecular process



(9)

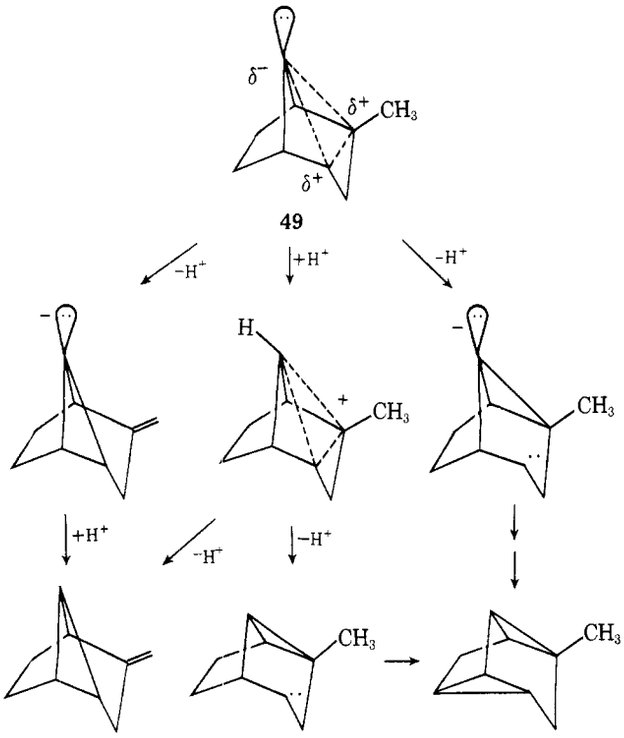
involving the solvent. Interestingly, the total loss of deuterium from C-4 and the gain of only some of that deuterium at C-8 in the bivalent intermediate generated is precisely the evidence required to support an intermolecular variation of the carbene to carbene rearrangement suggested in eq 8. As a working hypothesis, one can suggest proton (deuterium) loss at C-4 of the delocalized carbene, followed by proton (deuterium) gain at C-8, and insertion, or the reverse of this process, as outlined in Scheme I.

Murahashi and co-workers[13] in the study referred to above have reported that the dry salt pyrolysis of the sodium salt of 17a produces a mixture of toluene, 1,4-cycloheptadiene (50), 1,3-cycloheptadiene (51), 1,6-bicyclo[3.3.0]octadiene (10), 1,7-bicyclo[3.3.0]octadiene (52), and *endo*-tricyclo-[3.2.1.$0^{2,4}$]octane (53) and suggest that the different spectrum



50 51 10 52 53

Scheme I



of hydrocarbon products in their study and ours may be explained by invoking an energetic cation as the precursor for **21** and **22** and a carbene for hydrocarbons **10** and **50–53.** The simplest interpretation of this suggestion as it pertains to the formation of tetracyclooctanes **21** and **37** is clearly incorrect. Proton addition to the diazo intermediate related to **47** and subsequent 1,3 elimination[22] (loss of a proton from C-6) would result neither in the loss of deuterium from C-4 nor in the reincorporation of 13% of the deuterium at C-1 in product **37** as is observed.

Without the presence of solvent to act as a proton-transfer agent, the dry salt pyrolysis generates bivalent **28,** which apparently undergoes the unusual option of extruding carbon to form **50** and **51.**[23,5a] The bicyclooctadienes **10** and **52** are undoubtedly formed by alkyl migration, the options being similar to those described above for *exo*-8-carbenatricyclooctane. Although the migration of C-2 has been proposed,[13] the operation of rearrangement sequence **13** → **15** → **10, 11, 12** raises a question which must, for the moment, be considered along with the results of alkyl migration of 7-carbenanorbornene, which support C-2 migration.[5]

With solvent present, the evidence for the intermolecular process in the rearrangements of carbene intermediates **28** and **49** is particularly important in that such processes are rare for dialkyl carbene species.[2] This might well be the consequence of a longer lifetime for singlet carbene resulting from the extra stabilization provided by delocalization. This view of the nature of the singlet intermediate is supported by the fact that the normal 1,3 insertion observed by Moss and Whittle[17] for 7-carbenanorbornane does not occur either with or without solvent. The similarity of bivalent species **28** and **49** to 7-carbenanorbornene is clear in that <1% of the 1,3-insertion product is formed in the reaction of 7-carbenanorbornene.[5] In the absence of solvent, intermolecular processes of *endo*-8-carbenatricyclooctane are not competitive, allowing one to view intramolecular 1,2-alkyl migration and intersystem crossing to triplet (with eventual formation of **53**).[13]

Experimental Section

Melting points were determined using a Büchi melting point apparatus and are uncorrected. All boiling points are also uncorrected. Infrared spectra were recorded on either a Beckman IR-9 infrared spectrophotometer or a Perkin-Elmer 621 infrared spectrophotometer. Proton NMR spectra were recorded on a Varian Associates A-60 or HA-100 NMR spectrometer, and deuterium NMR were recorded on a Varian Associates XL-100 NMR spectrometer. Mass spectra were run on an Atlas CH-7 or Finnigan 1015 S/L mass spectrometer. Elemental analyses were performed by Alfred Bernhardt, Mikronanalytisches Laboratorium, 5251 Elback Uber Engelskirchen, Fritzpregl-strasse 14-26, West Germany. High-resolution mass spectra were carried out at the University of Oregon Chemistry Department on a CEC 110 B instrument. VPC analyses were carried out with an F and M Model 700 Chromatograph equipped with dual columns and thermal-conductivity detectors. The following columns were used: (A) 32 ft × 0.25 in. aluminum containing 20% Carbowax 20 M plus 2% XF-1150 on Anakrom 70–80 mesh ABS; (B) 20 ft × 0.375 in. aluminum containing 12% Carbowax 20 M on Anakrom 70–80 mesh ABS; (C) 9 ft × 0.25 in. aluminum containing 10% Carbowax 20M and 1% XF-1150 on Anakrom 70–80 mesh ABS; (D) 10 ft × 0.25 in. aluminum containing 10% UCON water soluble on 30–60 mesh Chromosorb W; (E) 18 ft × 0.125 in. stainless steel containing 10% UCW-98 on 80–100 mesh Diatoport S.

Product ratios and percentage yields calculated from chromatographic data are based on relative peak areas as measured by a Hewlett Packard 3373B integrator and are uncorrected for variations of thermal conductivity with molecular weight.

***exo*-Tricyclo[3.2.1.0^{2,4}]octan-8-one.** The title ketone was prepared from the corresponding alcohol by an oxidation procedure similar to that reported by Brown and Garg.[24] Thus, *exo*-tricyclo[3.2.1.0^{2,4}]octan-8-*syn*-ol (7.9 g, 0.064 mol) was dissolved in 26 mL of ether. To this solution, contained in a 100-mL flask fitted with a stirrer and dropping funnel, was added 6.36 g of sodium dichromate dihydrate (0.021 mol) dissolved in 4.77 mL of concentrated sulfuric acid and 31.8 mL of water. The oxidant was added dropwise at such a rate as to maintain a reaction temperature of 23–25 °C, the reaction mixture being cooled by means of a 12 °C water bath. After completing the addition of oxidant (20 min), the reaction mixture was stirred an additional 90 min at room temperature. The ether layer was decanted and the lower layer subjected to three 15-mL portion ether extractions. The total ether extracts were combined and washed with saturated sodium bicarbonate and water. After drying the ether solution over anhydrous magnesium sulfate, the ether was removed by rotary evaporation. The residue, along with the residue obtained from a similar oxidation of 6.80 g (0.055 mol) of *exo*-tricyclo[3.2.1.0^{2,4}]-octan-8-*syn*-ol, was distilled on an 18-in. spinning-band column. Product ketone was collected at 74 °C (20 mm) (7.6 g, 53% yield). Infrared analysis showed strong carbonyl absorption at 1770 cm^{-1}, and NMR analysis revealed the C-3 protons as a multiplet from δ 0.7 to 0.0, the C-2 and C-4 protons as a quartet at δ 1.1, the C-6 and C-7 protons as a singlet at δ 1.2, and the C-1 and C-5 protons as a singlet at δ 2.0.

Anal. Calcd for $C_8H_{10}O$: C, 78.63; H, 8.25. Found: C, 78.57; H, 8.29.

***exo*-Tricyclo[3.2.1.0^{2,4}]octan-8-one *p*-Toluenesulfonylhydrazone (9).** *p*-Toluenesulfonylhydrazine (10.9 g, 0.059 mol) was dissolved in 53 mL of 95% ethanol which contained 1.33 g of concentrated hydrochloric acid. The resulting solution was heated to 45–50 °C and *exo*-tricyclo[3.2.1.0^{2,4}]octan-8-one (7.0 g, 0.057 mol) was added. The solution was maintained at 45–50 °C for an additional 75 min with occasional shaking, after which it was allowed to stand overnight in the freezer. During this time crystals precipitated. The crystals were recovered by filtration and washed with absolute ethanol. After drying, the crystals weighed 11.9 g (0.041 mol, 71.5%) and had mp 161.5–162.5 °C (dec). The derivative could not be obtained without the acid catalyst.

Anal. Calcd for $C_{15}H_{18}N_2O_2S$: C, 62.04; H, 6.24. Found: C, 62.23; H, 6.30.

Decomposition of *exo*-Tricyclo[3.2.1.0^{2,4}]octan-8-one *p*-Toluenesulfonylhydrazone with Excess Sodium Methoxide. The apparatus for the decomposition consisted of a 500-mL, three-necked flask fitted with a pressure-equalizing dropping funnel, nitrogen sparge, magnetic stirring device, and a 10-cm Vigreux column heated to 100 °C by heating tape. Heating for the flask was provided by an oil bath. The Vigreux column was connected to a receiving flask which was cooled with dry ice–isopropyl alcohol.

A suspension of the title compound (13.1 g, 0.045 mol) in 125 mL of dry bis(2-ethoxyethyl) ether was added with stirring to a mixture of sodium methoxide (8.0 g, 0.15 mol) in 125 mL of bis(e-ethoxyethyl) ether solvent at 160 °C. The addition required 30 min and was accomplished under a nitrogen atmosphere. Heating was continued for about 8 h after the addition was completed.

The volatile material which collected in the cold receiving flask was washed thoroughly with water and then dried over magnesium sulfate. Subsequent analyses revealed the presence of C_8H_{10} hydrocarbon (1.0 g, 20%) which was made up of 65% bicyclo[3.3.0]octa-1,6-diene and 35% of incompletely defined bicyclo[3.3.0]octadienes.

Impure bicyclo[3.3.0]octa-1,6-diene was separated from the product mixture by means of a 3-m DC-200 column at 150 °C, the product eluting with a retention volume of 430 mL. Two additional hydrocarbons eluted together with a retention volume of 570 mL. Reinjection of the impure bicyclo[3.3.0]octa-1,6-diene into a 10-ft Carbowax 1500 column at 80 °C separated an ether impurity and provided pure bicyclo[3.3.0]octa-1,6-diene. Reinjection of the hydrocarbon mixture (35% component) into a 3-m 20 M column at 120 °C separated two hydrocarbons, the major constituent (80%) eluting with a retention volume of 960 mL and the minor one (20%) with a retention volume of 1200 mL.

Bicyclo[3.3.0]octa-1,6-diene was identified in part by its infrared and NMR spectral data. Infrared analysis showed C=C stretching at 1600 and 1590 cm^{-1}. Analysis by NMR showed no signals at a lower field than δ 1.0 and therefore precludes the presence of the cyclopropyl ring as it existed in the starting material. Two olefinic protons were found at δ 5.8 (singlet) and a third one at 5.4 (multiplet). Six methylene protons were indicated, two of which abosrobed at δ 2.8 while the remaining four complex bands exhibited a smear centered at δ 2.3 (2 H) and 1.42 (2 H). A final proton was found as a multiplet at δ 3.5. Hydrogenation of the material over platinum oxide provided *cis*-bicyclo[3.3.0]octane as the sole product, the material being identified by comparing its infrared and NMR spectra with the spectra of authentic material.[25,26]

Anal. Calcd for C_8H_{10}: C, 90.50; H, 9.50. Found: C, 90.39; H, 9.41.

The two remaining bicyclic octadienes were not isolated in sufficient quantity to afford their complete characterization. However, infrared analysis showed C=C stretching in the 1600–1650 cm^{-1} range for both isomers. Analysis of the mixture by NMR revealed no signals above δ 1.0 so that a cyclopropyl ring structure was not indicated. A broad methylene absorption in the region δ 3.7–1.2 showed some peaks at δ 1.6–1.2 which is characteristic of the bicyclo[3.3.0]octene-1 type. Olefinic proton signals were exhibited at δ 6.3, 5.7, and 5.2. Hydrogenation of the mixture over platinum provided *cis*-bicyclo[3.3.0]-octane as the sole product.

Preparation of *endo*-Tricyclo[3.2.1.$0^{2,4}$]octan-8-one Tosylhydrazone (17a). To 5.15 g (0.0422 mol) of the endo ketone in a 100-mL flask, provided with a magnetic stirrer and a reflux condenser, was added 45 mL of 95% ethanol, followed by 7.85 g (0.0422 mol) of tosylhydrazine and 2 drops of concentrated HCl. A white flocculent precipitate formed in about 5 min. The mixture was gently heated at reflux for 2.5 h. The flask was then cooled to room temperature and the solid product filtered and dried by suction, giving 7.25 g. An additional 0.3 g of the product was obtained by refrigerating the filtrate overnight. The total yield of the tosylhydrazone was 7.55 g (0.026 mol, 61.6% yield). Recrystallization from absolute ethanol gave the tosyhydrazone with mp 172–173 °C (dec), lit.[27], 172–173 °C (dec) (from methanol): IR (KBr pellet), 3200 (m, N–H stretching), 3080 (shoulder, cyclopropyl C–H stretching), 3056 (shoulder, cyclopropyl C–H stretching or aromatic C–H stretching), 3040 (m, cyclopropyl C–H stretching or aromatic C–H stretching), 1668 (m, aromatic C=C stretching), 1582 (m, aromatic C–H stretching), 1160 cm^{-1} (s, SO_2–N stretching).

Anal. Calcd for $C_{15}H_{18}N_2O_2S$: C, 62.05; H, 6.24. Found: C, 61.96; H, 6.16.

Decomposition of *endo*-Tricyclo[3.2.1.$0^{2,4}$]octan-8-one Tosylhydrazone (17a) in the Presence of Excess Sodium Methoxide. In a three-necked 250-mL flask provided with a magnetic stirrer, a nitrogen inlet, and a Vigreux column heated to 80 °C by means of a heating tape was placed 4.92 g (0.0911 mol) of dry sodium methoxide and 140 mL of anhydrous diglyme. The Vigreux column was connected to two dry ice–95% ethanol traps in series and then to a gas bubbler. The flask was heated to 82 °C by an oil bath and the tosylhydrazone (4.61 g, 0.0159 mol) was added. The temperature was then raised to and maintained at 150–155 °C for 4.5 h. At the end of this period, the Vigreux column was washed with pentane and the washings were added to the liquid collected in the traps. The pentane solution (ca. 35 mL) was washed repeatedly with water, dried ($MgSO_4$), and concentrated by distillation to about 1.3 g. VPC analysis of this concentrate (column A, 125 °C, 80 mL/min) showed that this material consisted almost exclusively of pentane.

The cloudy diglyme suspension in the pot was diluted with 200 mL of water and extracted with five 50-mL portions of pentane. The combined pentane extracts were washed with three 80-mL portions of water and dried ($MgSO_4$). Near-complete removal of pentane by distillation using a Vigreux column yielded 1.897 g of a pale-yellow liquid. VPC analysis of this liquid under conditions identical to those used previously revealed that the liquid consisted of, besides traces of pentane and diglyme, four components in the ratio 4:33:11:51 in the order of increasing retention times plus about 1% of unisolable products in a total yield of approximately 80%.

The 4% component was identified as tricyclo[3.3.0.$0^{4,6}$]oct-2-ene by comparison of its IR and NMR spectra with those of Zirner and Winstein[28] and Roth and Peltzer.[29]

The 33% component had VPC retention time, IR, NMR, and mass spectra identical to those of an authentic sample of tetracyclo[3.3.0.0.$^{2,8}0^{4,6}$]octane, reported by Freeman, Kuper, and Rao.[30,31]

The 11% component was identified as *anti*-6-methoxy-*endo*-tricyclo[3.2.1.$0^{2,4}$]octane on the basis of its spectral data: mass spectrum parent peak at *m/e* 138; IR (neat) 3090 (w), 3030 (m), and 3010 (m) (all assignable to cyclopropyl C–H stretching), 1195 (s), 1120 (shoulder), and 1110 cm^{-1} (s) (all assignable to C–O stretching); NMR (100 MHz, CCl_4) δ 3.5 (unresolved t, 1 H, the α-methoxy proton), 3.15 (s, 3 H, the methoxy protons) 2.2–2.0 (m, 2 H, the bridgehead protons), and 1.6–0.25 (complex m, the protons on C-6, C-7, C-2, C-4, and C-3). The structure assignment was confirmed by an independent synthesis of this compound.

Anal. Calcd for $C_9H_{14}O$: C, 78.21; H, 10.21. Found: C, 78.02; H, 10.37.

The 51% component was identified as *endo*-2-methoxytricyclo[3.3.0.$0^{4,6}$]octane on the basis of tis spectral data and confirmation by an independent synthesis: mass spectrum parent peak at *m/e* 138; IR (neat), 3035 (s), (assignable to cyclopropyl C–H stretching), 1115 (s) and 1097 cm^{-1} (s) (assignable to C–O stretching); NMR (100 MHz, CCl_4) δ 3.9–3.45 (six-peak signal, 1 H, the α-methoxy proton), 3.15 (s, 3 H, the methoxy protons), and 2.7–0.9 (m, 10 H, the remaining protons). The spectrum shows a striking similarity to those of *endo*-2-chloro- and *endo*-2-hydroxytricyclo[3.3.0.$0^{4,6}$]octane.

Anal. Calcd for $C_9H_{14}O$: C, 78.21; H, 10.21. Found: C, 78.15; H, 10.28.

Preparation of *syn*- and *anti*-8-Methoxy-*endo*-tricyclo[3.2.1.$0^{2,4}$]octane (19, 18). A mixture of *syn*- and *anti*-*endo*-tricyclo[3.2.1.$0^{2,4}$]octan-8-ol (64:36)[21] (1.06 g, 0.00954 mol) in ether solution was added dropwise to a suspension of sodium hydride [1.14 g (57.2% dispersion), 0.0272 mol] in pentane, in a nitrogen atmosphere, in a three-necked 150-mL flask provided with a reflux condenser and calcium chloride tube, a pressure-compensated addition funnel, a nitrogen inlet, and a magnetic stirrer. When the alcohol addition was complete, 9.39 g (0.0661 mol) of methyl iodide was added and the mixture stirred for 16 h. An additional 7.82 g (0.0552 mol) of methyl iodide was added about 13 h after the commencement of the reaction. Any unreacted sodium hydride was destroyed by addition of anhydrous methanol. A clear yellow solution resulted which was taken up in 40 mL of ether. The solution was repeatedly washed with water and then dried ($MgSO_4$). Removal of ether by rotary evaporation at room temperature gave 0.55 g (47% yield) of a yellow liquid. VPC analysis revealed that this liquid consisted of two methyl ethers in the ratio 37:63 in the order of increasing retention times. The 37% ether had VPC retention time, IR, and NMR spectra identical to those of the 11% component of the decomposition of tosylhydrazone **17a**.

The 63% ether which must be the syn ether gave spectral data consistent with the expected structure: IR (neat) 3095 (w), 3060 (w), 3030 (shoulder) (all assignable to cyclopropyl C–H stretching), 1209 (s), 1135 (s), and 1107 cm^{-1} (s), all assignable to C–O stretching; NMR (100 MHz, CCl_4) δ 3.75 (unresolved t, 1 H, the α-methoxy proton), 3.27 (s, 3 H, the methoxy protons), 2.15 (unresolved t, 2 H, the bridgehead protons), and 1.53–0.8 (complex m, 8 H, the remaining protons).

Anal. Calcd for $C_9H_{14}O$: C, 78.21; H, 10.21. Found: C, 78.12; H, 10.35.

Methanolysis of *anti*-8-Chloro-*endo*-tricyclo[3.2.1.$0^{2,4}$]octane. The antichloride (0.31 g, 22 mmol) was treated with 3 mL of anhydrous methanol and 0.22 g (22 mmol) of anhydrous calcium carbonate in a 10-mL flask provided with a magnetic stirrer and a reflux condenser. The mixture was heated to reflux for 13 h. After cooling to room temperature, the solid residue was filtered off and the filtrate subjected to VPC analysis (column A, 130 °C, 75 mL/min). The solvolysis was not complete. The only solvolysis product that was present had VPC retention time and IR spectrum identical to those of *endo*-2-methoxytricyclo[3.3.0.$0^{4,6}$]octane obtained in the methoxide ion induced decomposition of tosylhydrazone **17a**.

Study of the Effect of Added Methanol-*O-d* on the Composition of the Products in the Decomposition of the Endo Ketone Tosylhydrazone 17a. Several runs were made in which the decomposition of the tosylhydrazone was carried out at 145–150 °C in the presence of different amounts of added methanol-*O-d* (83% d_1) and

excess sodium methoxide in anhydrous diglyme in a nitrogen atmsophere in a three-necked flask, provided with a nitrogen inlet, a magnetic stirrer, and reflux condenser.

(1) The tosylhydrazone (0.40 g, 1.4 mmol) was decomposed with $NaOCH_3$ (0.44 g, 0.0081 mol) and methanol-*O*-d (45.5 mg, 1.38 mmol). The products were composed of 2% of the rearranged olefin **22**, 21% of the tetracyclic hydrocarbon **21**, 13% of the endo-antiether **18**, and 64% of the rearranged endo ether **20**.

(2) The tosylhydrazone (2 g, 7 mmol) was decomposed with sodium methoxide (2.14 g, 39.6 mmol) and methanol-*O*-*d* (2.70 g, 81.8 mmol) in 100 mL of anhydrous diglyme. The products consisted of 1% of the rearranged olefin, 7% of the tetracyclic hydrocarbon, 11% of the endo-anti ether and 81% of the rearranged endo ether.

(3) The tosylhydrazone (0.1040 g, 0.358 mmol) was decomposed with sodium methoxide (0.1200 g, 2.2 mmol) and methanol-*O*-*d* (0.9650 g, 29.2 mmol) in 7 mL of anhydrous diglyme. The products were composed of 0% (<1%) of the rearranged olefin, 3% of the tetracyclic hydrocarbon, 16% of the endo-anti ether, and 81% of the rearranged endo ether.

Deuteration of 8,8-Dimethoxy-*endo*-tricyclo[3.2.1.0^{2,4}]oct-6-ene (29). To 1.0 g (6.6 mmol) of the title ketal[21] in 6 mL of methanol was added 30 mg of 5% palladium on charcoal. The suspension was stirred under 1 atm of 98% deuterium. When deuterium uptake ceased, the methanol, after filtration, was removed by distillation, yielding 0.9 g of 6,7-dideuterio-8,8-dimethoxy-*endo*-tricyclo-[3.2.1.0^{2,4}]octane. The NMR spectrum is identical with that of 8,8-dimethoxy-*endo*-tricyclo[3.2.1.0^{2,4}]octane[21], except that the doublet at δ 1.60, due to the exo C-6 and C-7 protons, has nearly disappeared, integrating to 0.4 protons, and the doublet at δ 0.94 (endo protons) has collapsed to a singlet.

Hydrolysis of 6,7-Dideuterio-8,8-dimethoxy-*endo*-tricyclo[3.2.1.0^{2,4}]octane (30). The method of Pincock and Haywood-Farmer[21] was followed. A 10-mL flask was charged with 0.9 g (5.9 mmol) of deuterated ketal and 8 mL of glacial acetic acid, and the solution was stirred at 80 °C for 20 h. The solution was then diluted with 10 mL of pentane, and 6.4 g of sodium hydroxide in 15 mL of water was added slowly. About 15 mL of water was added and the aqueous phase was extracted with three 10-mL portions of pentane. The pentane layers were combined, washed with brine, and dried over anhydrous magnesium sulfate. The solvent was removed by rotary evaporation at room temperature yielding 0.7 g of crude deuterated ketone. The NMR spectrum was identical with that reported[20] except that the multiplet at δ 1.55 (*exo*-methylenes) now integrates out to 0.4 protons, and the doublet at δ 1.19 has collapsed to a singlet. Chemical-shift studies of the deuterated and undeuterated ketone using Eu(fod)$_3$ allowed a comparison of the absorption area of the endo C-6 and C-7 protons with the protons α to the carbonyl which revealed no detectable endo deuterium (<4%).

Preparation of 6,7-Dideuterio-*endo*-tricyclo[3.2.1.0^{2,4}]-octan-8-one Tosylhydrazone (17c). To 0.8 g (6.5 mmol) of deuterated endo ketone in a 25-mL flask was added 15 mL of 95% ethanol, 1.2 g (6.5 mmol) of tosylhydrazine, and 1 drop of concentrated hydrochloric acid. The solution was heated at 80 °C for 2 h. The flask was allowed to cool to room temperature and then was placed in a refrigerator overnight. The white crystals were collected and dried in a vacuum oven at 70 °C, yielding 1.0 g (3.4 mmol, 53%) of tosylhydrazone with mp 168–169 °C (dec). Mass spectral analysis using a low-ionizing potential (8.0 eV) yielded d_0 = 7.6 ± 0.5%, d_1 = 26.2 ± 0.5%, and d_2 = 66.2 ± 0.9%. (A second batch was synthesized which was determined to consist of d_0 = 35.3 ± 0.5, d_1 33.0 ± 0.5, and d_2 = 31.7 ± 0.7, by mass spectral analysis of the sodium borohydride reduction product 6,7-dideuterio-*endo*-tricyclo[3.2.1.0^{2,4}]octane at 11.0 eV.)

Decomposition of 6,7-Dideuterio-*endo*-tricyclo[3.2.1.0^{2,4}]-octan-8-one Tosylhydrazone (17c) with Excess Sodium Methoxide. A 25-mL flask equipped with a magnetic stirrer and reflux condenser was charged with 292 mg (1 mmol) of deuterated tosylhydrazone, 15 mL of dry diglyme, and 350 mg (6.5 mmol) of sodium methoxide. The resulting suspension was stirred at 160 °C for 2 h. After cooling, 15 mL of pentane was added and the solution was poured into 200 mL of water. Extraction by three 20-mL portions of pentane of the water layer was followed by combining the pentane layers, washing with two 100-mL portions of water and 50 mL of brine, drying over anhydrous sodium sulfate, and removal of most of the solvent by distillation through a Vigreux column. VPC analysis (column C, 100 °C, 60 mL/min) showed products identical to those from the undeuterated tosylhydrazone **17a**, except for deuterium content, in ratios of 4 ± 1:33 ± 1:6 ± 1:29 ± 1 (**22:21:18:20**). The 4% component, tricyclo[3.3.0.0^{4,6}]oct-2-ene, **22**, and the 33% component, tetracyclo[3.3.0.0^{2,8}.0^{4,6}]octane, **21**, were subjected to mass spectral analysis at low-ionizing potentials, and the resulting deuterium content is given in Table II.

Test for Hydrogen-Deuterium Exchange of Tetracyclo-[3.3.0.0^{2,8}.0^{4,6}]octane (21). To 5 mL of freshly distilled diglyme were added 110 mg (2.0 mmol) of sodium methoxide, 8 mg (0.24 mmol) of methanol-*O*-*d* (99% d_1), and 8 mg (0.07 mmol) of the title hydrocarbon. To this was added 0.5 mmol of cyclohexanone tosylhydrazone which had been prepared by the reaaction of cyclohexanone with tosylhydrazine in methanol-*O*-*d*. The solution was then stirred at 165 °C for 2 h. After cooling to room temperature, 5 mL of pentane was added and the solution was poured into 100 mL of water. The aqueous phase was extracted with three 10-mL portions of pentane; the pentane extracts were combined, washed with water and brine, and dried over anhydrous sodium sulfate. After removal of most of the solvent by distillation through a Vigreux column, VPC analysis (column D, 110 °C, 60 mL/min) showed only tetracyclooctane and cyclohexene. Low-voltage (10.2 eV) mass spectral analysis showed the cyclohexene to contain 61% d_4, 31% d_3, 7% d_2, and 1% d_1. The title hydrocarbon was found (10.2 eV) to contain 0.3% deuterium (95% confidence level).

Reaction of 5,5-Dimethoxy-1,2,3,4-tetrachlorocyclopentadiene with 1-Methylcyclopropene[32] The method of Magid and coworkers[33] was used to generate 1-methylcyclopropene. A 500-mL three-necked flask equipped with a magnetic stirrer, dropping funnel, and reflux condenser was charged with 100 mL of a 2.4 M solution of phenyllithium in 60:40 benzene–ether. Under nitrogen, 9.0 g (0.115 mol) of 3-chloro-2-methylpropene in 30 mL of pentane was added dropwise over 0.5 h. The solution turned milky white and was stirred at room temperature for 1 h. The solution was then cooled to 0 °C in an ice bath and 23 g (0.5 mol) of absolute ethanol was added dropwise. The reaction mixture was then gently refluxed overnight, and the 1-methylcyclopropene was carried through a length of Tygon tubing by a nitrogen flow over the solution, and then bubbled through a length of Tygon tubing by a nitrogen flow over the solution, and then bubbled through a solution of 13 g (0.053 mol) of 5,5-dimethoxy-1,2,3,4-tetrachlorocyclopentadiene and 20 mL of pentane at 0 °C. Removal of solvent by rotary evaporation yielded 16 g (100%) of 2-methyl-8,8-dimethoxy-1,5,6-7-tetrachloro-*endo*-tricyclo[3.2.1.0^{2,4}]-oct-6-ene (95% pure by VPC): IR (0.1 mm, CCl_4) 3030 (shoulder, cyclopropyl C–H stretching), 1603 (s, C=C stretching), 1381 (methyl bending), 1193 (shoulder), 1178 cm^{-1} (s) (all assignable to C–O stretching); NMR (100 MHz, CCl_4) δ 3.59 and 3.48 (s, 3 H each, methoxy protons), 1.53 (d of d, J = 3.5 and 6.5 Hz, 1 H, cyclopropyl methine at C-4), 1.41 (s, 3 H, methyl group on C-2), and 0.61 (m, 2 H, cyclopropyl methylene protons).

Anal. Calcd for $C_{11}H_{12}O_2Cl_4$: C, 41.54; H, 3.80. Found: C, 41.40; H, 3.98.

Dechlorination of 2-Methyl-1,5,6,7-tetrachloro-8,8-dimethoxy-*endo*-tricyclo[3.2.1.0^{2,4}]oct-6-ene, with Sodium.[32] The procedure of Gassman and Pape[34] was followed with minor experimental modifications. To a 500-mL three-necked flask equipped with magnetic stirrer, dropping funnel and reflux condenser was added 175 mL of reagent grade tetrahydrofuran, 40 mL (0.42 mol) of *tert*-butyl alcohol, and 20 g (0.9 mol) of 10-mm sodium cubes. The solution was heated to reflux and 16 g (0.053 mol) of the title ketal in 50 mL of tetrahydrofuran was added dropwise over 1 h. After heating at reflux for 26 h, the solution was decanted off the remaining sodium and 50 mL of methanol was added with cooling. The solution was then poured into a separatory funnel containing 1.5 L of ice and 500 mL of ether. The organic layer was separated, and the aqueous layer was extracted three times with 250 mL of ether. The ether layers were combined and washed with brine until the volume of the organic layer remained constant and the washings remained clear. The ethereal solution was dried with anhydrous magnesium sulfate and most of the solvent was removed under reduced pressure. Distillation (89–91 °C, 14 Torr) yielded 5.0 g (0.028 mol, 56%): IR (0.1 mm, CCl_4) 3086 (m, cyclopropyl C–H stretch), 3049 (shoulder, cyclopropyl or vinyl C–H stretching), 1565 (w, C=C stretching), 1374 (w, methyl bending), 1111 (s) 1092 (shoulder), and 1072 (s) (all assignable to C–O stretching), 1022 (m, cyclopropyl deformation), and 707 cm^{-1} (s, alkene C–H out of plane bending); NMR (100 MHz, CCl_4) δ 5.67 (m, 2 H, vinyl protons), 3.00 and 2.92 (s, 3 H each, methoxy protons), 2.82 (unresolved doublet, 1 H, J = 3 Hz, bridgehead C-5 proton), 2.46 (quintet, 1 H, J = 1.5 Hz, bridgehead C-1 proton), 1.33 (s, 3 H, methyl group on C-2), 0.93 (m, 1 H, cyclopropyl methine), 0.51 (d of d, J = 5 and 3.5 Hz, 1 H, *syn*-cyclopropylmethylene), and 0.37 (d of d, J = 5 and 7 Hz, 1 H, *anti*-cyclopropylmethylene protons).

Anal. Calcd for $C_{11}H_{16}O_2$: C, 73.30; H, 8.95. Found: C, 73.24; H, 9.06.

Preparation of 2-Methyl-8,8-dimethoxy-*endo*-tricyclo-

[3.2.1.0^{2,4}]octane (34). The unsaturated ketal, 2-methyl-8,8-dimethoxy-*endo*-tricyclo[3.2.1.0^{2,4}]oct-6-ene (2.0 g, 11.5 mmol) was dissolved in 15 mL of reagent grade methanol, and 50 mg of 5% paladium on charcoal was added. The solution was stirred under 1 atm of hydrogen until hydrogen uptake ceased. The solution was then filtered and used without further purification. VPC collection gives a sample with IR (0.1 mm, CCl_4) 3086 (w, cyclopropyl C–H stretch), 3030 (shoulder, cyclopropyl C–H stretch), 1377 (w, methyl bending), 1093 (shoulder), 1087 (s), and 1064 (all assignable to C–O stretching), 1028 cm^{-1} (m, cyclopropyl deformation); NMR (100 MHz, CCl_4) δ 3.25 and 3.13 (s, 3 H each, methoxy protons), 2.10 (m, 1 H, bridgehead C-5 proton), 1.82 (m, 1 H, bridgehead C-1 proton), 1.54 (broadened d, J = 6 Hz, 2 H, *exo*-methylene protons at C-6 and C-7), 1.21 (s, 3 H, methyl protons), 0.96 (d, J = 8 Hz, 2 H, *endo*-methylene protons at C-6 and C-7), 0.94 (m, under part of 0.96 absorption, 2 H, cyclopropylmethine and one cyclopropylmethylene), 0.44 (d of d, J = 7 and 8.5 Hz, 1 H, one of the cyclopropyl methylenes on C-3).

Anal. Calcd for $C_{11}H_{13}O_2$: C, 72.49; H, 9.96. Found: C, 71.40; H, 10.24.

Hydrolysis of 2-Methyl-8,8-dimethoxy-*endo*-tricyclo[3.2.1.0^{2,4}]octane (34). Saturated ketal **34** (1 mL of hydrogenated mixture, containing 133 mg) was placed in a 5-mL flask with 2 mL of methanol and 0.1 mL of a solution of 5% sulfuric acid in water. The solution was stirred at 70 °C for 4 h, followed by dilution with 10 mL of water and 1 mL of a 10% Na_2CO_3 solution. The mixture was extracted three times with 5 mL of pentane; the pentane extracts were combined, washed twice with 10 mL of water and once with 10 mL of brine and dried over anhydrous sodium sulfate. Following removal of most of the pentane by distillation through a Vigreux column, the ketone, 2-methyl-*endo*-tricyclo[3.2.1.0^{2,4}]octan-8-one, was collected by preparative VPC for IR and NMR analysis: IR (0.1 mm, CCl_4) 3096 (s, cyclopropyl C–H stretching), 3040 (shoulder, cyclopropyl C–H stretching), 1761 (vs, C=O stretching), 1385 (w, methyl bending), 1042 (m, cyclopropyl deformation), 972 (m) and 877 cm^{-1} (m); NMR (100 MHz, CCl_4) δ 2.17 (broadened s, $W_{1/2}$ = 9 Hz, 1 H, bridgehead proton on C-5), 1.86 (broadened d, J = 2 Hz, 1 H, bridgehead proton on C-1), 1.70 (unresolved m, 2 H, *exo*-methylene protons on C-6 and C-7), 1.28 (s, 3 H, methyl protons), 1.25 to 0.75 (unresolved m, 5 H). Analyses were unsatisfactory, probably due to loss of carbon monoxide.[21]

Preparation of 2-Methyl-*endo*-tricyclo[3.2.1.0^{2,4}]octan-8-one Tosylhydrazone (35a). Into a 25-mL flask containing 2-methyl-8,8-dimethoxytricyclo[3.2.1.0^{2,4}]octane (**34**) (1.9 g, 11 mmol) and 14 mL of methanol was placed 1 mL of water, 20 mg of *p*-toluenesulfonic acid, and 1.86 g (11 mmol) of *p*-toluenesulfonylhydrazine. The solution was then heated at 65 °C for 2 h and then placed on a steam bath, and water was added until the solution began to cloud. Upon cooling, crystals formed [2.2 g, 65%, mp 119–121 °C (dec)]. Recrystallization from methanol–water yielded mp 125–126 °C: IR (0.1 mm $CHCl_3$) 3236 (s, N–H stretching), 3090 (shoulder, aromatic or cyclopropyl C–H stretching), 3030 (shoulder, aromatic or cyclopropyl C–H stretching), 1681 (s, C=N stretching), 1597 (aromatic C=C stretching), 1335 (s, S–O stretching), 1163 (vs. S–O stretching), and 1019 cm^{-1} (w, cyclopropyl deformation); NMR (100 MHz, $CHCl_3$) δ 2.98, 2.70, 2.47, and 2.14 (broadened singlets, 0.5 H each, bridgehead protons at C-1 and C-5), 2.39 (s, 3 H, aromatic methyl), 1.02 and 0.96 (both s, 1.5 H each, methyl group on C-2), 1.70 to 0.70 (complex m, 7 H). Half protons are due to syn and anti forms of the tosylhydrazone, which arise because of lack of rotation around the C=N bond.

High-resolution mass spectra calcd for $C_{16}H_{20}SO_2N_2$: 304.125; found: 304.126.

Decomposition of 2-Methyl-*endo*-tricyclo[3.2.1.0^{2,4}]octan-8-one Tosylhydrazone (35a) with Excess Sodium Methoxide in Diglyme. Into a 10-mL flask equipped with a reflux condenser, drying tube, and magnetic stirrer was placed 125 mg (0.41 mmol) of tosylhydrazone and 200 mg (2.6 mmol) of sodium methoxide, along with 5 mL of dry diglyme. The flask was then placed in an oil bath maintained at 160 °C for 2 h. After cooling to room temperature, the solution was diluted with 5 mL of pentane and 100 mL of water, and extracted four times with 5 mL of pentane. The pentane extracts were combined, washed three times with 75 mL of water, once with 50 mL of brine, and dried over anhydrous sodium sulfate. Most of the pentane was removed by distillation through a Vigreux column, and the residue was analyzed by VPC (column D, 100 °C, 60 mL/min). VPC analysis showed six peaks. Three were of fairly long retention time, had m/e 152, corresponding to methyl ethers, were present only to the extent of about 10% total yield, and were not characterized further. There were three peaks in the hydrocarbon region of the VPC. Their yields as determined by internal VPC standard, in order of increasing retention time, were 0.5, 3, and 28%. The 0.5% component could not be isolated in sufficient amounts or purity to characterize.

The 3% component was identified as 2-methyltetracyclo[3.3.0.0^{2,8}.0^{4,6}] octane (**37**) on the basis of its spectral data: mass spectrum parent peak at m/e 120; IR (0.1 mm CCl_4) 3050 (shoulder, cyclopropyl C–H stretch), 3020 (m, cyclopropyl C–H stretch), 1378 (w, methyl bending), 1281, 1248, 858 and 827 cm^{-1} (all w, skeletal vibrations); NMR (C_6H_6, 100 MHz) δ 1.75 to 1.08 (complex series of m, 9 H), 1.00 (s, 3 H, methyl). The structure assignment was confirmed by an independent synthesis of this compound.

High-resolution mass spectra calcd for C_9H_{12}: 120.094; found: 120.093.

The 28% component was identified as 2-methylenetricyclo[3.3.0.0^{4,6}]octane (**36**) on the basis of its spectral data: mass spectrum parent peak at m/e 120; IR (0.1 mm, CCl_4) 3096 (shoulder), 3077 (shoulder) and 3049 (m, all three attributable to either cyclopropyl or vinyl C–H stretch), 1647 (m, C=C stretch), and 877 cm^{-1} (s, terminal vinyl group C–H out of plane bending); NMR (100 MHz, CCl_4) δ 4.54 (s, 2 H, vinyl protons), 2.90 (d of t, J_d = 1 Hz, J_t = 5 Hz, 1 H, bridgehead proton at C-1), 2.75 to 1.2 (complex series of m, 10 H). The structure was confirmed by ozonolysis to the known ketone (see below).

Anal. Calcd for C_9H_{12}: C, 89.93; H, 10.06. Found: C, 89.87; H, 10.07.

Preparation of Tricyclo[3.3.0.0^{4,6}]octan-2-one (38) by Ozonolysis of 2-Methylenetricyclo[3.3.0.0^{4,6}]octane (36). A solution of 20 mg of the unsaturated hydrocarbon in 0.5 mL of CCl_4 and 1.5 mL of $HCCl_3$ was placed in a 5 mL pear-shaped flask. Three percent ozone in oxygen from a Welsback Ozonator was passed through the solution at a rate of 80 mL/min at −5 °C and then into a solution of 2% potassium iodide and 2% sulfuric acid. After 15 min, iodine began to be liberated and the reaction was stopped. Half the solvent was removed under reduced pressure and 5 mL of ether was added. The organic layer was washed with three 50-mL portions of water and one 30-mL portion of brine. After drying with anhydrous sodium sulfate, the single product was collected by preparative VPC and identified as tricyclo[3.3.0.0^{2,4}]octan-2-one by comparison of VPC retention time, infrared, and NMR with an authentic sample, which was prepared by oxidizing a sample of *endo*-tricyclo[3.3.0.0^{4,6}]octan-2-ol (supplied by Tanida)[35] with the procedure of Haywood-Farmer and Pincock.[21]

Decomposition of 2-Methyl-*endo*-tricyclo[3.2.1.0^{2,4}]octan-8-one Tosylhydrazone (35a) with Sodium Hydride in Diglyme. Tosylhydrazone **35a** (71.5 mg, 0.24 mmol) and 12 mg of sodium hydride (0.50 mmol) were placed in 4 mL of freshly distilled (from $LiAlH_4$) diglyme. After heating at 160 °C for 2 h, the solution was cooled and diluted with 100 mL of water, *p*-cymene was added, and the solution was extracted with four 10-mL portions of pentane. The pentane extracts were combined, washed with three 50-mL portions of water and one 50-mL portion of brine, and dried over anhydrous sodium sulfate. After distilling most of the pentane through a Vigreux column, the solution was analyzed by VPC (column C). Along with the *p*-cymene internal standard, there were three products in 50–60% overall yield in ratios of 1:6:8. The shortest retention time product could not be isolated in sufficient amounts of purity for identification. The second product was identified as 2-methyltetracyclo[3.3.0.0^{2,8}.0^{4,6}]octane (**37**) and the third product identified as 2-methylenetricyclo[3.3.0.0^{4,6}]octane (**36**). The ratio of **36** to **37** was not constant, but varied from 1:1.5 to 1:3 in various runs.

Decomposition of *endo*-Tricyclo[3.2.1.0^{2,4}]octan-8-one Tosylhydrazone (17a) with Sodium Hydride. The title tosylhydrazone (50 mg, 0.16 mmol) was treated with 8 mg (0.3 mmol) of sodium hydride in 3 mL of dry diglyme. After stirring at 160 °C for 1 h, the solution was cooled, cumene was added as an internal standard, and the reaction was worked up as described for the reaction of **35a** with sodium hydride (above). VPC analysis (columns B and E) indicated two products along with the internal standard. The shorter retention-time product, produced in 5% yield, was identified as tricyclo[3.3.0.0^{4,6}]-oct-2-ene, and the longer retention-time product, formed in 39% yield, was identified as tetracyclo[3.3.0.0^{2,8}.0^{4,6}]octane.

Preparation of 2-Methyl-*endo*-tricyclo[3.2.1.0^{2,4}]oct-6-ene (37). 2-Methylcyclopropene (0.1 mol) was bubbled through a solution of 13.2 g (0.2 mol) of freshly cracked cyclopentadiene at 0 °C. After 6 h, the unreacted cyclopentadiene was removed under reduced pressure, yielding, after distillation (bp 78–80 °C, 100 Torr), 9.0 g (0.75 mol, 75%) of the title hydrocarbon.[33]

Preparation of 4-Deuterio-2-methyl-*endo*-tricyclo[3.2.1.0^{2,4}]oct-6-ene. 1-Methyl-2-deuteriocyclopropene[33] was bubbled through cyclopentadiene as described above. Mass spectral analysis showed the Diels–Alder product to contain 1.2–1.0% d_0 and 98.8–99.0% d_1, and in the NMR spectrum (CCl_4, 100 MHz) the pentet at δ 1.03 had completely disappeared.

Preparation of 6,7-Dideuterio-2-methyl-*endo*-tricyclo-

[3.2.1.$0^{2,4}$]oct-6-ene. The procedure of Zimmerman and co-workers was used with some modification.[36] 2-Methyl-*endo*-tricyclo-[3.2.1.$0^{2,4}$]oct-6-ene (120 mg, 1 mmol) was added to a solution of 100 μL of 21.5% butyllithium (in hexane, Alpha) in 2 mL of cyclohexylamine-d_2 (ca. 95% N–D). The solution was stirred at 90 °C for 12 h, quenched with D_2O, and extracted with pentane. The pentane was washed with dilute hydrochloric acid, water, and brine, and the title hydrocarbon was collected by preparative VPC. Mass spectral analysis at 12.6 eV indicated the alkene to consist of 3.4 ± 0.9% d_0, 29.0 ± 1.0% d_1, 66.6 ± 1.0% d_2, and 1.0 ± 1.1% d_3. The NMR spectrum of the title compound showed olefinic proton absorption greatly diminished (ca. 10–20% H).

Preparation of 6,7-Dideuterio-*endo*-tricyclo[3.2.1.$0^{2,4}$]oct-6-ene. The title alkene was deuterated in the same manner as the methylated alkene (above). Mass spectral analysis at 12.0 eV indicated that the product consisted of 3.0 ± 0.8% d_0, 30.3 ± 1.1% d_1, and 66.6 ± 1.0% d_2. NMR integration of the olefinic proton absorption showed ca. 15% olefinic hydrogen.

Preparation of *exo*-*exo*-6,7-Dideuterio-2-methyl-*endo*-tricyclo[3.2.1.$0^{2,4}$]octan-8-one Tosylhydrazone (35b). Addition of 98% deuterium to 2-methyl-8,8-dimethoxy-*endo*-tricyclo[3.2.1.$0^{2,4}$]-oct-6-ene as described above for the nonmethylated ketal yielded *exo,exo*-6,7-dideuterio-**34**, and subsequent treatment with tosylhydrazine, water, methanol, and acid, as described for **34**, yielded **35b**. A small amount of *exo,exo*-6,7-dideuterio-**34** was hydrolyzed to the ketone precursor of **35b** and chemical-shift studies carried out with Eu(fod)$_3$ indicated entirely exo,exo-6,7 deuteration.

Preparation of 4-Deuterio-2-methyl-*endo*-tricyclo-[3.2.1.$0^{2,4}$]octan-8-one Tosylhydrazone (47). Addition of 2-deuterio-1-methylcyclopropene[33] to 1,2,3,4-tetrachloro-5,5-dimethoxycyclopentadiene yielded 4-deuterio-2-methyl-1,5,6,7-tetrachloro-8,8-dimethoxy-*endo*-tricyclo[3.2.1.$0^{2,4}$]oct-6-ene. Subsequent treatment in a manner identical to that described for **35a** yielded the title tosylhydrazone **47**.

Preparation of 4-*exo*-6-*exo*-7-trideuterio-2-methyl-*endo*-tricyclo[3.2.1.$0^{2,4}$]octan-8-one Tosylhydrazone (48). The title compound was prepared in a manner analogous to that used for **35b** and **47**.

Decomposition of 4-Deuterio-2-methyl-*endo*-tricyclo-[3.2.1.$0^{2,4}$]octan-8-one Tosylhydrazone (47) with Excess Sodium Methoxide. Decomposition was effected in an identical manner to the decomposition of **35a** with sodium methoxide. Mass spectral analyses of the product **36** and **37** along with the deuterium content of the tosylhydrazone precursor are given in Table III.

Decomposition of Deuterated Tosylhydrazones 35b, 47, and 48 with Sodium Hydride. Decomposition of **35b, 47,** and **48** were effected in an identical manner to the sodium hydride decomposition of **35a.** Mass spectral analysis of the products and tosylhydrazone precursors are presented in Table III.

Pyrolysis of *endo*-tricyclo[3.2.1.$0^{2,4}$]oct-6-ene Derivatives. Following the procedure of Kinnel[20], VPC purified tricyclooctenes (6,7-dideuterio; 2-methyl-6,7-dideuterio; 2-methyl-4-deuterio) (ca. 25 mg/run) were pyrolyzed in a sealed Pyrex tube at 240–260 °C for 20–30 h. VPC analysis on column C (100 °C, 60 mL/min) indicated >97% of the expected tetracyclooctane derivatives **32, 43,** and **44.**

Test for Exchange of 4-Deuterio-2-methyltetracyclo-[3.3.0.$0^{2,8}$.$0^{4,6}$]octane (44). The title hydrocarbon (2.2 ± 1.0% d_0, 97.8 ± 1.0% d_1, 20 mg) was placed in 5 mL of freshly distilled (from $LiAlH_4$) diglyme along with 80 mg of sodium hydride. The solution was heated at 160–170 °C for 2 h, cooled, diluted with water, and extracted with pentane. The pentane was washed with water and brine and dried over anhydrous sodium sulfate, and the hydrocarbon was collected by preparative VPC. Mass spectral analysis indicated 0.8 ± 1.0% d_0 and 99.2 ± 1.0% d_1.

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Registry No.—**9a,** 33978-29-9; **9a** ketone, 7076-83-7; **10,** 51088-75-6; **17a,** 22389-15-7; **17a** ketone, 14224-86-3; **17c,** 63689-08-7; **17c** ketone, 63669-09-8; **18,** 63729-79-3; **19,** 63729-80-6; **20,** 63689-10-1; **29,** 14224-84-1; **30,** 63689-11-2; **34,** 63689-12-3; *syn*-**35a,** 63689-13-4; *anti*-**35a,** 63729-81-7; **35a** ketone, 63689-14-5; **36,** 63689-15-6; **37,** 63689-16-7; *exo*-tricyclo[3.2.1.$0^{2,4}$]octan-8-*syn*-ol, 7076-80-4; *p*-toluenesulfonylhydrazine, 1576-35-8; *cis*-bicyclo[3.3.0]octane, 694-72-4; *syn-endo*-tricyclo[3.2.1.$0^{2,4}$]octan-8-ol, 7076-81-5; *anti-endo*-tricyclo[3.2.1.$0^{2,4}$]octan-8-ol, 16384-97-7; methyl iodide, 74-88-4; deuterium, 7782-39-0; 5,5-dimethoxy-1,2,3,4-tetrachlorocyclopentadiene, 2207-27-4; 1-methylcyclopropene, 3100-04-7; 2-methyl-8,8-dimethoxy-1,5,6,7-tetrachloro-*endo*-tricyclo[3.2.1.$0^{2,4}$]oct-6-ene, 53867-59-7; 2-methyl-8,8-dimethoxy-*endo*-tricyclo[3.2.1.$0^{2,4}$]oct-6-ene,42824-80-6;6,7-dideuterio-2-methyl-*endo*-tricyclo[3.2.1.$0^{2,4}$]-oct-6-ene, 63689-17-8; 2-methyl-*endo*-tricyclo[3.2.1.$0^{2,4}$]oct-6-ene, 55980-68-2.

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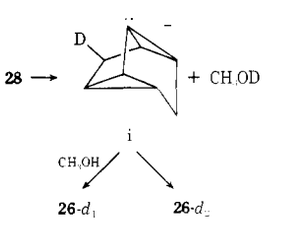
$$\frac{d[\mathbf{26}\text{-}d_2]}{dt} \Big/ \frac{d[\mathbf{26}\text{-}d_1]}{dt} = \frac{k_D}{k_H} \frac{[\mathbf{26}\text{-}d_1]}{(C_0 - [\mathbf{26}\text{-}d_1])}$$

Using the assumptions listed in the text above, integration reveals that [**26**-d_2] = C_0/e at the completion of the reaction (C_0 = initial concentration of methanol).



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Synthesis of Medium-Ring Cycloalkene-1-carboxylic Acids and Thermodynamic Properties of the Cycloundecene-1-carboxylic Acid System[1]

Augustine Silveira, Jr.,* Yashpal R. Mehra, and William A. Atwell

Department of Chemistry, State University of New York, College at Oswego, Oswego, New York 13126

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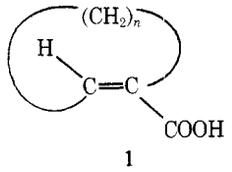
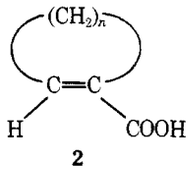
Cyclononene-1-carboxylic acid (*E* isomer), (*E*)-cyclodecene-1-carboxylic acid, (*E*)- and (*Z*)-cycloundecene-1-carboxylic acid, and (*E*)- and (*Z*)-cyclododecene-1-carboxylic acid were synthesized by aqueous alkaline hydrolysis of the corresponding 4-chloro-3,4-poly(methylene)-2-pyrazolin-5-ones. The stereochemistry of the *E*/*Z* acid pairs formed was determined by NMR data and showed the *Z* isomer as the predominant product. The standard free energies, enthalpies, and entropies of isomerization for the*E*/*Z* cycloundecene-1-carboxylic acids (acetic acid anhydrides) were determined at various temperatures using an acetic anhydride–triethylamine mixture as an isomerization medium. The thermodynamic data showed that the (*E*)-cycloundecene-1-carboxylic acid product is the more stable isomer.

Previous studies[2-5] have demonstrated the generality of the conversion of aryl and alkyl 4-halo-3,4-disubstituted-2-pyrazolin-5-ones to the acyclic trisubstituted α,β-unsaturated carboxylic acids. This method of preparation represents a useful synthetic route to acids difficult to obtain by other methods in that the labile acyclic (*Z*)-α,β-alkenoic acid is formed in predominant amounts in both the alkyl and aryl series. In the cyclic series, the *E* isomer was the *exclusive* product formed for cyclohexene through cyclooctene-1-carboxylic acid.[6] The object of this investigation is to determine if this method is applicable to the synthesis of medium-ring (*Z*)-cycloalkene-1-carboxylic acids **1** and, if a mixture of acids is formed, to determine at least in one case their relative stabilities. General methods for the preparation of (*E*)- and (*Z*)-cycloalkene-1-carboxylic acids **1** and **2** have not been readily available.[7] The cycloalkene-1-carboxylic acids that have been prepared are of interest to others because their salts have shown to be very powerful cholertics and these compounds have been used in the treatment of heptovascular conditions and hepatic insufficiency.[7] The methyl and ethyl esters of these acids are pleasant smelling and are of interest to the cosmetic industry as additives.[7]



1

Z isomer



2

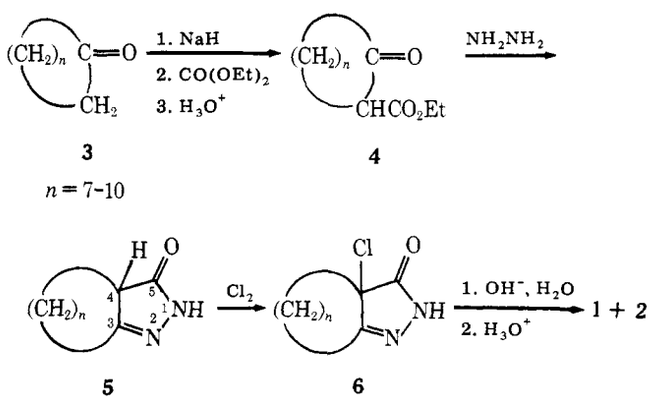
E isomer

n = 7–10

Accordingly, an attempt was made to synthesize the (*E*)- and (*Z*)-cycloalkene-1-carboxylic acids and, for purposes of clarity, the overall synthetic route is shown.

The first step in the synthesis (Scheme I) involved the conversion of the cycloalkanone **3** to the respective β-keto ester **4**, which was readily accomplished by reaction of **3** with sodium hydride and diethyl carbonate. The second step involved reaction of **4** with hydrazine hydrate to form the corresponding 3,4-poly(methylene)-2-pyrazolin-5-one (**5**). Compound **5** was converted to the 3,4-poly(methylene)-4-halo-2-pyrazolin-5-one **6** by chlorination. The presence of the 4,4-disubstituted product **6** was detected by the strong infrared absorption of the carbonyl group between the 1710- and 1730-cm^{-1} region. None of the 4-monsubstituted pyrazolones **5** showed any carbonyl absorption in this region and absorbed at lower frequencies, probably due to the C-4 hydrogens being involved in the corresponding tautomeric enol forms of **5**. These data are summarized in Table I. The final reaction involved treatment of the resultant 4-chloropyrazolone with dilute aqueous alkali followed by acifidication.

Scheme I



In the cases of cyclononene- and cyclodecene-1-carboxylic acids, only the *E* isomers **2** were formed. For the cycloundecene-1-carboxylic acids a *Z*/*E* isomer ratio of 3:1 was obtained, while the cyclododecene-1-carboxylic acids were formed in a 4:1 *Z*/*E* ratio. The quantitative determination of acids was readily accomplished using proton magnetic resonance. In an analysis of a mixture of *E* and *Z* isomers utilizing proton magnetic resonance, the vinyl proton peaks were well separated and the relative areas under these peaks were propor-