Carbonium Ion Rearrangements in the Deltacyclane Ring System. IV. Solvolytic Reactions of *exo*-7-Isodeltacyclyl Brosylate[1]

Peter K. Freeman,* Brian K. Stevenson, Dean M. Balls, and Donald H. Jones

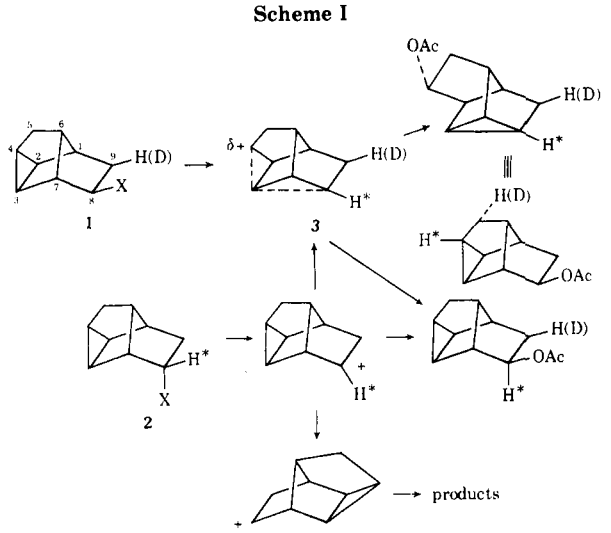
Departments of Chemistry, Oregon State University, Corvallis, Oregon 97331, and University of Idaho, Moscow, Idaho 83843

Received August 8, 1973

The synthesis of *exo*-7-isodeltacyclyl acetate was accomplished by conversion of the appropriate Diels–Alder adduct of ethyl *trans*-β-acetoxyacrylate and cyclopentadiene to *exo*-5-acetoxy-*endo*-6-chlorocarbonylnorbornene, which was used to prepare *exo*-7-acetoxyisodeltacyclan-5-one, *via* intramolecular carbenoid addition brought about by Cu(II)-catalyzed decomposition of *exo*-5-acetoxy-*endo*-6-diazoacetylnorbornene. Reduction of the ethanedithiol ketal of *exo*-7-acetoxyisodeltacyclan-5-one with Raney nickel gave *exo*-7-isodeltacyclyl acetate. Acetolysis of *exo*-7-isodeltacyclyl brosylate generated *exo*-8-deltacyclyl acetate and *exo*-7-isodeltacyclyl acetate in a ratio of 96.3:3.7. Acetolysis of *exo*-7-isodeltacyclyl brosylate deuterated at C-5 produces *exo*-8-deltacyclyl acetate with deuterium distributed between C-9 and C-5 in a ratio of 1:1.8. These results are rationalized in terms of the direct generation of a norbornonium ion (**13**), which then leaks to the dissymmetric (C_2) delocalized 8-deltacyclyl ion (**3**), with both intermediates producing product. The implications of these results as they bear on the solvolytic reactions of *exo*- and *endo*-8-deltacyclyl substrates are discussed.

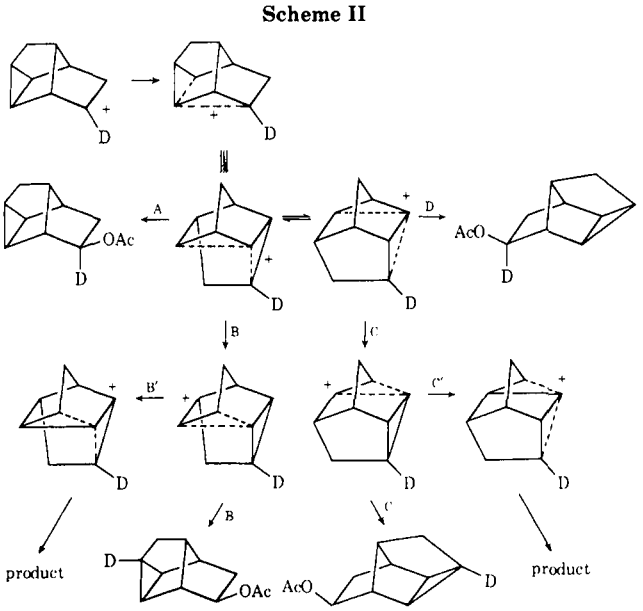
Our previous studies on the stereochemistry of the acetolyses of *exo*- and *endo*-8-deltacyclyl substrates (**1** and **2**), the distribution of deuterium tracer during acetolysis, the rates of acetolysis, the nmr spectra of the 8-deltacyclyl carbonium ion in FSO_3H–SO_2, the stereochemistry as revealed by acetolysis of optically active **1**-OBs and **2**-OBs, the secondary deuterium isotope effects on the acetolysis of **1**-OBs and **2**-OBs, and the effect of substitution of electron-withdrawing substitutents at C-5 on the rates of acetolysis of substituted *exo*- and *endo*-8-deltacyclyl brosylates[1-3] provide a rather clear-cut case for the suggestion that acetolyses of *exo*-8-deltacyclyl substrates generate delocalized nonnorbornonium ion **3** directly (Scheme I). For example, acetolysis of **1**-OBs labeled with deuterium at the exo-C-9 position generates **1**-OAc with label distributed 50:50 over the exo-C-9 and C-5 positions (Scheme I), acetolysis of optically active **1**-OBs results in 99% retention of optical activity and the rate of acetolysis of **1**-OBs ($k = 2.61 \times 10^{-4}$ sec^{-1} at 25.68°) appears to be anchimerically assisted ($10^{5.3}$). In contrast, acetolysis of **2**-OBs labeled with deuterium at the exo-C-8 position produces **1**-OAc with label distributed over the endo-C-8 and C-4 positions (60:40) and acetolysis of optically active **2**-OBs produces **1**-OAc with 57% loss of optical activity, while the rate of acetolysis of **2**-OBs is 4.62×10^{-6} sec^{-1} at 25.68°, which corresponds to a less dramatic calculated rate enhancement ($10^{3.1}$).

Scheme I



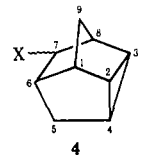
It seems certain that the reaction course followed in the solvolytic reactions of endo substrates **2** is more complex than that for the exo epimers **1** and that the question as to the details of the reaction course represents an intriguing mechanistic puzzle. On the basis of the studies described above, we have settled on the hypothesis that acetolysis of endo brosylate **2**-OBs generates a classical 8-deltacyclyl carbonium ion, which has three choices: (a) reaction with solvent to give exo acetate with retention and no deuterium migration; (b) leakage to a nonclassical ion of type **3** which generates exo acetate with retention and 50:50 deuterium scrambling between C-4 and C-8, and (c) rearrangement by a series of alkyl shifts to product of inverted configuration. The sequence of shifts might well be those of routes C and D in Scheme II. Thus, inversion might proceed with distribution of the deuterium between C-4 and C-8 (routes C and D) or with no migration of deuterium label (D only). If routes C and D are operative, then routes A and B must necessarily be in use giving scrambling of deuterium label with retention of configuration.

Scheme II



At this stage of our studies of the chemistry of the deltacyclane ring system, it seemed clear that there was an excellent chance to elucidate the interesting nature of the

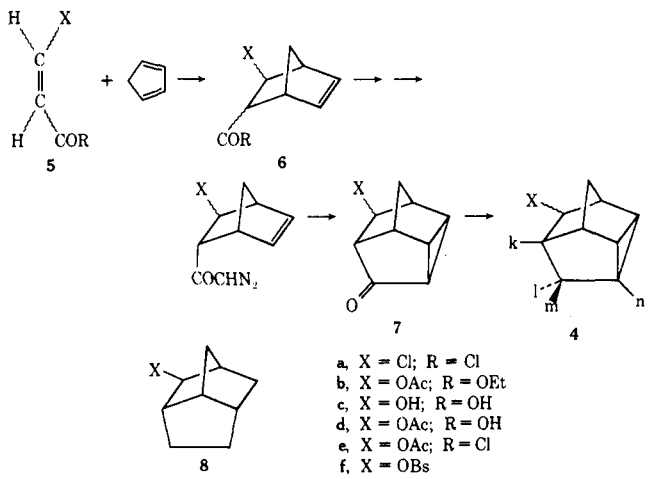
ionization route(s) used in the solvolytic reaction of *endo*-8-deltacyclyl derivatives by carrying out an investigation of carbonium ion rearrangements of 7-tetracyclo-[4.3.0.$0^{2,4}$.$0^{3,8}$]nonyl (7-isodeltacycly)[4] derivatives (4) using deuterated substrates.



4

Synthesis. The best approach to the synthesis of 7-substituted isodeltacyclane substrates appeared to be through the introduction of the eventual C-7 substitutent by appropriate choice of dienophile (5) and then use of the method developed by Nickon[5] for the preparation of isodeltacyclan-5-one (7-H). Deuteration might be conveniently introduced into the C-5 position at the ketone reduction stage (7 → 4) (Scheme III).

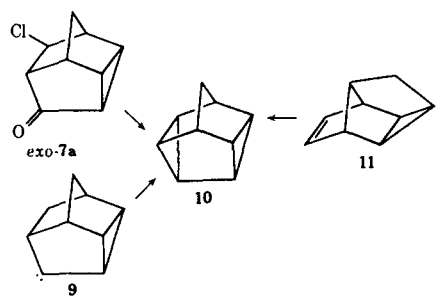
Scheme III



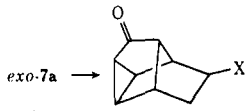
a, X = Cl; R = Cl
b, X = OAc; R = OEt
c, X = OH; R = OH
d, X = OAc; R = OH
e, X = OAc; R = Cl
f, X = OBs

Our first attempt at construction of 4 was through the preparation of 7-Cl. Addition of hydrogen chloride to propiolic acid, followed by treatment with thionyl chloride, afforded a mixture of *cis*- and *trans*-β-chloroacrylyl chloride (*cis*- and *trans*-**5a**) which was separable by distillation. The Diels–Alder addition of *trans*-**5a** to cyclopentadiene produced a mixture of trans adducts **6a** with a ratio of endo COCl to exo COCl of 90:10. Treatment of this mixture with diazomethane, followed by intramolecular carbenoid [Cu(II)] addition, generated *exo*-7-chloroisodeltacyclan-5-one (*exo*-**7a**). The nmr spectrum exhibits a sharp singlet for the endo C-7 hydrogen at τ 6.26. When *exo*-**7a** was subjected to the Huang-Minlon modification of the Wolff–Kishner reduction, an interesting intramolecular displacement of chloride by the carbanionic center at C-5 occurred, producing pentacyclo[4.3.0.$0^{2,4}$.$0^{3,8}$.$0^{5,7}$]-nonane[6] (**10**), rather than the desired *exo*-**4a**. The yield for this transformation is better (*ca.* 80%) than that which we have found for the alternative processes *via* 5-carbena-isodeltacyclane (**9**) (59% from precursor tosylhydrazone) and photoisomerization of deltacyclene (**11**) (24%) (Scheme IV).

Scheme IV



It appeared that if the acetolysis of *exo*-**7a** were to proceed without rearrangement, the anticipated product, *exo*-**7b**, would be a most convenient synthetic intermediate. The results foreshadow the eventual characteristics of the desired system (*exo*-**4**): acetolysis of *exo*-**7a** in HOAc–AgOAc generates a 4.5:1.0 ratio of *exo*-8-chloro- and *exo*-8-acetoxydeltacyclan-5-one (**12a** and **12b**).



12a, X = Cl
b, X = OAc
c, X = OH

Identification of the minor product **12b** was accomplished by nmr and infrared spectral comparison with an authentic sample available from a previous study,[1] and the internal return product **12a** was identified by nmr and infrared spectral analysis and by independent synthesis. Treatment of **12c** with thionyl chloride produced **12a** as the sole product.

At this point attention was turned to the preparation of the epimeric endo chloride, *endo*-**7a**, with the hope that with prohibition of both β-elimination and intramolecular displacement *endo*-**7a** might be a suitable precursor for the preparation of *endo*-**4**-Cl. The Diels–Alder addition of *cis*-β-chloroacrylyl chloride proceeded smoothly to the di-endo adduct (di-*endo*-**6a**) (75% yield) and subsequent treatment of di-*endo*-**6a** with diazomethane, followed by carbenoid ring closure, produced *endo*-7-Cl, as readily as in the case of the exo epimer. The nmr spectrum exhibits a doublet of doublets (J = 9, 2 Hz) at τ 5.83 for the proton α to chlorine. The last step was again a problem. Using the Huang-Minlon modification of the Wolff–Kishner reduction and two modified procedures, which have been successfully employed at lower temperatures (25–100°),[7,8] brought no success.

In the light of these unsuccessful attempts with the epimeric chlorides 7-Cl it was apparent that *exo*- or *endo*-7-acetoxyisodeltacyclan-5-one would be a superior precursor for the preparation of *exo*- or *endo*-7-isodeltacyclyl derivatives. Using a procedure of Pechman,[9] an 8:1 trans:cis mixture of ethyl β-acetoxyacrylate (*trans*- and *cis*-**5b**) was prepared. The cycloaddition of this mixture of *trans*- and *cis*-**5b** with cyclopentadiene produced a 48:46:6 ratio of *exo*-acetoxy-*endo*-carbethoxy-**6b**, *endo*-acetoxy-*exo*-carbethoxy-**6b**, and *endo*-acetoxy-*endo*-carbethoxy-**6b** in an overall yield of 79%. This mixture of Diels–Alder adducts was converted to a mixture of the corresponding hydroxy acids (**6c**) and the alcohol groups were protected by reconversion to acetates (**6d**) using acetic anhydride. Subsequent treatment with oxalyl chloride and diazomethane produced a mixture of diazomethyl ketones which was treated with cupric sulfate. At this stage only the *exo*-acetoxy-*endo*-diazoacetylnorbornene undergoes intramolecular carbenoid addition to provide the desired keto acetate **7b** (63% yield based on *exo*-acetoxy-*endo*-acid chloride **6e**). The nmr spectrum of keto acetate **7b** exhibits a singlet at τ 5.58 (CHOAc) and a study of spectra obtained using chemical shift reagent Eu(fod)$_3$ revealed the three nonequivalent cyclopropane protons at C-2, C-3, and C-4 (mutually coupled, J = 6 Hz), the endo fusion of the cyclopropane unit ($J_{1,2} \cong 6$, $J_{3,8} \cong 6$ Hz) and the appropriate stereochemistry for the protons at C-1, C-6, C-7, and C-8 ($J_{1,6} \cong 4$, $J_{6,7} = J_{7,8} \cong 0$ Hz).

Attempts to reduce *exo*-**7b** using Wolff–Kishner conditions were unsuccessful; however, conversion of *exo*-**7b** to the corresponding ethanedithiol ketal and reduction of the thioketal with Raney nickel gave *exo*-7-isodeltacyclyl acetate (*exo*-**4b**) and *exo*-2-brendyl acetate (**8b**) in equal abundance (48%). Brendyl acetate **8b** was identified by conversion to brendyl alcohol **8c** with lithium aluminum hydride, followed by oxidation of **8c** to brendan-2-one.[10] The nmr spectrum (100 MHz, CCl_4) of *exo*-**4b** exhibits a singlet for a proton α to acetoxy at τ 5.90, similar to that noted for the analogous proton of exo keto chloride **7a** and exo keto acetate **7b**. Spin-decoupling experiments carried out on *exo*-**4b**, complexed with $Eu(fod)_3$, provided evidence completely consistent with the structural assignment of *exo*-7-isodeltacyclyl acetate to this reduction component. The presence of an endo fused cyclopropane unit containing three nonidentical, mutually coupled protons (J = 6 Hz) as well as a methylene bridge connecting C-4 and C-6 (J_{lm} = 11, J_{km} = 6, $J_{nl} \cong$ 2 Hz, hydrogens denoted in 4) was revealed. *exo*-7-Isodeltacyclyl acetate was converted to alcohol *exo*-**4c** using lithium aluminum hydride and then to brosylate *exo*-**4f**.

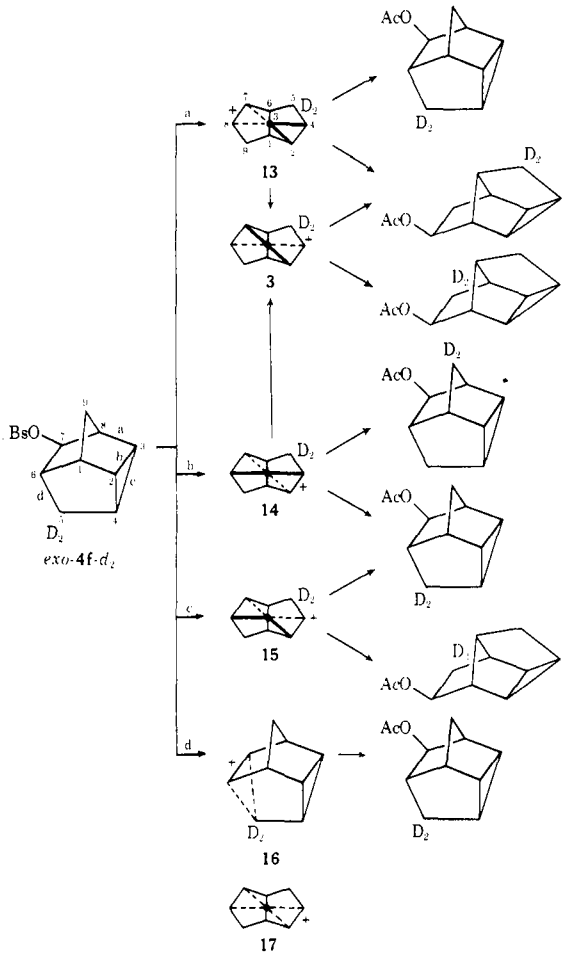
5,5-Dideuterio-*exo*-7-isodeltacyclyl acetate was prepared using the method of Fukushima.[11] The ethanedithiol ketal of *exo*-**7b** was reduced with deuterated Raney nickel and the C-5 deuterated *exo*-**4b** was separated from 2-brendyl acetate by vapor phase chromatography. Treatment of *exo*-**4b** with $Eu(fod)_3$ provides for the resolution of the geminal protons at C-5 in the nmr (100 MHz, CCl_4) spectrum and enables one to measure the extent of deuteration. Our measurements revealed that the extent of deuterium incorporation at C-5 in *exo*-**4b** was 0.70 ± 0.08 D, with no evidence for introduction of deuterium at other positions. Deuterated acetate *exo*-**4b** was converted to deuterated brosylate *exo*-**4f** as above.

Results and Discussion

Nmr analysis of brosylate *exo*-**4f** described above revealed that 35% had isomerized during the reaction of *exo*-**4c** with brosyl chloride to *exo*-8-deltacyclyl brosylate. Acetolysis of this mixture of brosylates in sodium acetate buffered acetic acetate was carried out at 40° for 48 hr and generated two product acetates in a ratio of 97.6:2.4. The major product was identified by nmr and infrared spectral comparison as *exo*-8 deltacyclyl acetate (1-OAc), while the minor component was recognized as *exo*-7-isodeltacyclyl acetate by retention time comparison on three different vpc columns. Correcting for the composition of starting brosylate, acetolysis of *exo*-**4f** generates a ratio of *exo*-8-deltacyclyl acetate:*exo*-7-isodeltacyclyl acetate of 96.3:3.7. In our tracer experiment the deuterated *exo*-**4f**, described above, actually contained 24% deuterated, rearranged *exo*-8-deltacyclyl brosylate. Acetolysis in sodium acetate buffered acetic acid, carried out in the same manner as in the case of undeuterated *exo*-**4f**, generated a 96.7:3.3 ratio of *exo*-8-deltacyclyl acetate:*exo*-7-isodeltacyclyl acetate. *exo*-8-Deltacyclyl acetate was isolated and nmr analysis, employing $Eu(fod)_3$, indicated that deuterium was scrambled between C-9 and C-5 exclusively and in the ratio of 1:1.8, correcting for the amount of brosylate which had undergone rearrangement prior to solvolysis. The correction is made taking advantage of the fact that solvolysis of 1-OBs, whether deuterated unevenly at C-5 and C-9 or not, will produce *exo*-8-deltacyclyl acetate with 50:50 distribution over C-5 and C-9.[2]

In our analysis of the possible reaction pathways for the solvolytic course for *endo*-8-deltacyclyl substrates, we have suggested roles for alkyl migration in the 7-isodeltacyclyl carbonium ion involving bonds a, b, c, and d. The alternatives for ionization of deuterated *exo*-**4f** are outlined in Scheme V in terms of delocalized ions **13**, **14**, **15**, and **16**, which are sketched to emphasize that participation of bonds a and c might generate asymmetric ions **13** and **15**, while involvement of b produces dissymmetric (C_2) **14** and delocalization of d yields nondissymmetric species **16**. Thus a family of ions **13**, **3**, **14**, and **15** is possible and leakage of one to another within the family requires somewhat minimal electronic reorganization. If leakage occurs between **14** and **3**, the double norbornonium ion **17**, originally mentioned as a possible intermediate in the reactions of **1** and **2**, is a reasonable structure for the transition state.

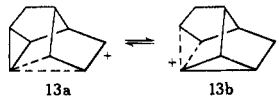
Scheme V



On the basis of product formation and deuterium scrambling in the acetolysis of *exo*-**4f** and *exo*-**4f**-d_2, one can rule out any one of the series, **13**, **3**, **14**, **15**, or **16**, as the sole product-determining intermediate. Some combination must be in effect and this combination must contain **13** as one component, since **13** is the only species which can distribute deuterium to C-5 to a greater extent than to C-9. Two major possibilities are apparent: (a) the generation of **13**, with rearrangement to **3**, and product formation from both or (b) generation of both **13** and **15** as product-determining intermediates. A role for **14** cannot be ruled out, since it could be generated and undergo leakage to **3** as the predominant reaction choice. Since *exo*-7-isodeltacyclyl acetate is stable to the reaction conditions, it is clear that **14** cannot be a significant (>4%) product-determining intermediate. The simplest rationalization is that *exo*-**4f** undergoes acetolysis to generate norbornonium ion **13**, which either forms products (27% to deltacyclyl acetate, 4% to isodeltacyclyl acetate) or leaks to **3**, which produces scrambled *exo*-8-deltacyclyl acetate

(69%). It is of interest to raise the question, however, as to whether this process might be equally well represented in terms of the formation of a classical 7-isodeltacyclyl carbonium ion and its rearrangement to a classical 8-deltacyclyl carbonium ion. At first glance this possible representation would appear to be easily evaluated, since the fate of a classical 8-deltacyclyl carbonium ion formed in the solvolysis of *exo*-**4f** should be the same as that formed in the ionization of endo brosylate **2**-OBs. Thus one would anticipate a deuterium scrambling ratio for C-9:C-5 for **1**-OAc formed from *exo*-**4f** in the range of 45:55 to 40:60,[2] which seems low in C-5 deuterium concentration, although not quite low enough to rule out this alternative route on this basis with confidence.

A major point of interest revealed in the results of acetolysis of *exo*-**4f** is that of the formation of *exo*-7-isodeltacyclyl acetate (*exo*-**4b**). Since *exo*-**4b** is stable to the acetolysis conditions and is not formed in the acetolysis of **1**-OBs, the benefit of some hindsight can be applied to a reconsideration of an alternative to the mechanistic picture presented for the acetolyses of **1**-OBs and **2**-OBs (Scheme I). We previously considered that ionization of exo brosylate **1**-OBs might generate a norbornonium ion directly and product formation occur *via* an equilibrium of equivalent norbornonium ions (**13a** and **13b**), while ionization of endo brosylate **2**-OBs might produce a classical 8-deltacyclyl carbonium ion initially, which then leaks to a norbornonium ion or reacts by the additional alternatives as described above. Such a picture would be consistent with the stereochemical course, the deuterium scrambling, the secondary deuterium isotope effects, and the rates of acetolysis found for **1**-OBs and **2**-OBs. However, the norbornonium ion **13** generated initially in the acetolysis of *exo*-**4f** should set up the same equilibrium of equivalent norbornonium ions as are created in the acetolysis of **1**-OBs. Thus the lack of formation of *exo*-7-isodeltacyclyl acetate in the acetolysis of exo brosylate **1**-OBs provides evidence against the intermediacy of **13a** ⇄ **13b** as product determiners in this instance. In addition the wide divergence in deuterium scrambling for acetolysis of **1**-OBs and *exo*-**4f** would have to be explained. Deuterium scrambling might differ in these two cases if the second major possibility for the solvolytic course of *exo*-**4f** is the better explanation: generation of product-determining intermediates **13** and **15**. While the scrambling would differ, we must postulate that the initally formed norbornonium ion **13** (from *exo*-**4f**) set up an equilibrium of equivalent norbornonium ions (**13a, 13b**), of necessity providing the same scrambling (50–50) as found when **13a** ⇄ **13b** is generated from **1**-OBs. An equilibrium of **13a** ⇄ **13b** and **15** serving as product-determining intermediates cannot account for the deuterium scrambling found in the acetolysis of *exo*-**4f**-d_2, and thus the creation of an equilibrium of equivalent norbornonium ions as a consequence of acetolysis of exo brosylate **1**-OBs can be ruled out no matter which mechanistic picture for solvolysis of *exo*-**4f** is adopted.



13a **13b**

In retrospect, the process favored for the acetolysis of *exo*-**4f**, generation of **13** and leakage to **3** with product formation from both, provides support for reaction pathways B and C of the picture presented to rationalize the stereochemistry and deuterium scrambling found for solvolysis of endo brosylate **2**-OBs (Scheme II) with the insertion of the delocalized deltacyclyl ions **3** (routes B′ and C′) in the mechanistic scheme.

Experimental Section

All melting points and boiling points are uncorrected. Infrared spectra were run on a Beckman Model IR-8 or a Perkin-Elmer 621 infrared spectrophotometer. Mass spectra were run on an Atlas CH7 or a Finnigan 1015 S/L mass spectrometer. Elemental analyses were performed by Alfred Bernhardt, Mikroanalytisches Laboratorium, 5251 Elback über Engleskirchen, West Germany. Vpc analyses were performed on a F & M Model 700 chromatograph equipped with dual columns and thermal conductivity detectors, or on a Varian Aerograph Series 1200 chromatograph equipped with a flame ionization detector. The following columns were used for vpc work: (1) 10 ft × 0.25 in. aluminum containing 10% Carbowax 20M on Anakrom 70–80 ABS, (2) 3 ft × 0.25 in. aluminum containing 10% Carbowax 20M on Anakrom 70–80 ABS. Nmr spectra were obtained using a Varian Associates A-60 or HA-100 nmr spectrometer.

Preparation and Separation of *cis*- and *trans*-β-Chloroacrylyl Chlorides. Propiolic acid (55 g, 0.78 mol) was added to an ice-cooled solution of 180 ml of concentrated hydrochloric acid. The stirred mixture was allowed to warm to room temperature. After 8 hr the solution was placed in a refrigerator for 12 hr. Crystals formed and were isolated by filtration. The filtrate was extracted twice with ether. The ether extracts were combined with the crystals, and solvent was removed by rotary evaporation. Water was azeotropically separated using a Dean–Stark trap. Thionyl chloride (95 g, 0.80 mol) was added, and the mixture was allowed to reflux for 12 hr. Distillation of solvent, followed by fractional distillation on a Teflon spinning-band column, gave two products, *trans*-β-chloroacrylyl chloride [21.9 g, 0.185 mol, 22% yield, bp 45° (70 mm)] and *cis*-β-chloroacrylyl chloride [12.3 g, 0.10 mol, 13% yield, bp 63° (70 mm)]. The assignment of geometry was based on the magnitude of the coupling constants for the olefinic protons (J = 13 Hz for the olefinic protons in the trans isomer, and J = 7.8 Hz for the cis isomer) revealed in the nmr spectra. The overall yield was 35%.

Preparation of *exo*-5-Chloro-*endo*-6-chlorocarbonylnorbornene. Freshly cracked cyclopentadiene was distilled from a spinning-band column into an ice-cooled flask containing 25.0 g (0.20 mol) of *trans*-β-chloroacrylyl chloride, while stirring with a magnetic stirring bar. The addition was continued until 13.2 g (0.20 mol) had been added. Short-path distillation of the product, bp 45–50° (0.2 mm), gave 19.1 g (0.10 mol, 50% yield) of clear, colorless product. The nmr spectrum has absorptions at τ 6.05 and 5.42 (t, J = 2.2 and 3.5 Hz, respectively), which are assigned to endo CHCl and exo CHCl, in a ratio of 90:10: ir (90:10 mixture, neat) 3086 (olefinic C–H stretching), 1786 (carbonyl stretching), 1333, 1015, 741, 691 cm^{-1}; nmr (90:10 mixture, 60 MHz, CCl_4) τ 8.26 (doublet of triplets, 1 H, J = 10, 3 Hz, methylene proton), 7.95 (d, 1 H, J = 10 Hz, methylene proton), 6.95 (broad singlet, 1 H), 6.53 (m, 2 H, bridgehead protons), 6.05 (t, 1 H, J = 2.2 Hz, -CHCl), 3.83 (m, 2 H, olefinic protons).

Reaction of *exo*-5-Chloro-*endo*-6-chlorocarbonylnorbornene with Diazomethane. An ethereal solution of diazomethane was prepared from 30 g (0.29 mol) of *N*-methyl-*N*-nitrosourea,[12] 90 ml of 50% aqueous KOH, and 300 ml of dry ether. The diazomethane formed was codistilled with ether and dried over KOH pellets (−10°) for 1 hr. The drying process was repeated twice by nitrogen transfer of the liquid to fresh KOH pellets. After drying, the diazomethane solution was transferred to a flask immersed in a Dry Ice–acetone bath. Extreme care was taken to exclude water from the system. Acid chloride (8.0 g, 0.042 mol) was slowly dropped in, while the solution was stirred. The resulting solution was stirred for 45 min at −78° and finally for 0.5 hr at 0°. Rotary evaporation of the solvent at room temperature gave 6.9 g (0.035 mol, 83% yield) of bright yellow liquid whose ir spectrum shows no C=O acid chloride stretch and exhibits absorption bands appropriate for the desired diazomethyl ketone product: 3086 (olefinic C–H stretching), 2105 (=N=N stretching), 1631 (carbonyl stretching), 1366, 745 cm^{-1}. The product was used immediately after preparation.

Preparation of *exo*-7-Chloroisodeltacyclan-5-one. To a rapidly stirred solution of *n*-hexane (100 ml) and anhydrous $CuSO_4$ (15 g) was added 3.0 g (0.0155 mol) of *exo*-5-chloro-*endo*-6-diazoacetylnorbornene. A slow evolution of gas was monitored by an inverted cylinder filled with water. An additional 15 g of $CuSO_4$ was added after 30 min and after 1 hr of reaction time. After 2 hr the evolution of gas ceased. The bright yellow solution was decanted, and the remaining solid was extracted with ether. Washing the combined organic phases with saturated salt water,

drying ($MgSO_4$), and distilling off solvent using a rotary evaporator gave 2.1 g (0.014 mol, 88% yield) of yellow product. Vpc analysis (column 1, 180°, 75 ml/min, 17 min) indicated only one product, assigned to exo keto chloride by ir, mass spectral, and nmr analysis. Vpc collection gave a white, waxy solid: mp 30–33°; ir (neat) 3055 (cyclopropyl C-H stretching), 1724 (carbonyl stretching), 1282, 907, 813, 741, 702 cm^{-1}; nmr (100 MHz, CCl_4) τ 7.8–8.3 (m, 3 H, cyclopropyl protons), 7.3–7.7 (m, 3 H, bridgehead proton at C-1 and methylene protons at C-9), 7.1–7.3 (broad singlet, 2 H, bridgehead protons at C-6 and C-8), 6.26 (s, 1 H, -CHCl).

Anal. Calcd for C_9H_9OCl: C, 64.10; H, 5.38. Found: C, 63.91; H, 5.36.

Preparation of Pentacyclo[4.3.0.0^{2,4}.0^{3,8}.0^{5,7}]nonane. Starting with *exo*-5-chloro-*endo*-6-chlorocarbonylnorbornene (19 g, 0.10 mol), diazomethyl ketone was prepared as described above and then converted by intramolecular carbenoid addition (copper-bronze powder, 0.5 g) to *exo*-7-chloroisodeltacyclan-5-one. The crude chloro tetracyclic ketone, employed without purification, was added to 200 ml of ethylene glycol containing a pellet of potassium hydroxide and 5 g of 95% aqueous hydrazine. The resulting mixture was heated to 90–100° and held at that temperature for 1 hr. Potassium hydroxide (10 g, 0.15 mol) was cautiously added and the reaction mixture was then heated to 140–150° for 30 min. Steam distillation of the black solution caused 5.8 g (49%) of a waxy, white solid (mp 85–86°) to become lodged in the condenser. Infrared and vpc analysis proved that this product was identical with an authentic sample of title pentacyclononane and that no other isomeric hydrocarbons were present.

Solvolysis of *exo*-7-Chloroisodeltacyclan-5-one in Acetic Acid Containing Silver Acetate. A solution of exo chloro ketone (1.8 g, 0.017 mol) in acetic acid was added to a mixture of silver acetate (3 g, 0.0179 mol) and sodium acetate (1.5 g, 0.0182 mol) in 150 ml of glacial acetic acid. The stirred mixture was heated to 114° for 21 hr. The inorganic salts were removed by filtration, followed by rotary evaporation of acetic acid. The resulting oil was diluted with ether and filtered, and the ethereal solution was washed successively with 5% Na_2CO_3, water, and saturated salt solution. Drying with anhydrous magnesium sulfate, followed by rotary evaporation of solvent, gave 0.59 g of oil. Vpc analysis indicated the formation of two compounds in the ratio of 4.5:1 (column 1, 190°, 150 ml/min, 4 min, 5.8 min). The minor product was collected and found to be identical with *exo*-5-keto-8-deltacyclyl acetate by spectral comparison. Spectra of the major product demonstrate that it is different from starting chloro ketone, but still contains chlorine. A doublet of doublets (τ 5.77, 1 H, J = 6.5, 2.5 Hz) is present in the nmr spectrum, characteristic of exo 8-substituted deltacyclyl compounds; ir (neat) 3055 (cyclopropyl C-H stretching), 1751 (carbonyl stretching), 1241, 837, 666 cm^{-1} (C-Cl stretching); nmr (100 MHz, CCl_4) 8.72 (t, 1 H, J = 5 Hz), 7.8–8.5 (m, 4 H), 7.5 (doublet of doublets, 1 H, J = 14, 6.5 Hz, methylene proton), 7.1–7.4 (m, 2 H), 5.78 (doublet of doublets, 1 H, J = 6.5, 2.5 Hz, -CHCl).

Anal. Calcd for C_9H_9ClO: C, 64.10; H, 5.38. Found: C, 63.91; H, 5.36.

Reaction of *exo*-8-Hydroxydeltacyclan-5-one with Thionyl Chloride. Thionyl chloride (1.98 g, 0.020 mol) was slowly added to 0.44 g (0.0029 mol) of *exo*-8-hydroxydeltacyclan-5-one in a 25-ml, three-necked flask equipped with a condenser, drying tube, and magnetic stirring bar. The reaction solution was allowed to stir at ambient temperature for 3 hr and then the solution was diluted with 5 ml of water and extracted with ether. Drying ($MgSO_4$) and rotary evaporation of solvent gave 0.25 g (0.0016 mol, 55% yield) of an oil. Vpc collection (column 1, 150 ml/min, 4 min) of the resulting product and spectral comparison (nmr, ir) showed that the product obtained was identical with the major product obtained on solvolysis of isodeltacyclyl keto chloride.

Preparation of *endo*-5-Chloro-*endo*-6-chlorocarbonylnorbornene. *endo*-5-Chloro-*endo*-6-chlorocarbonylnorbornene was prepared in a similar fashion to that described for the exo-5-chloro epimer. Addition of 14.0 g (0.21 mol) of cyclopentadiene to 20.0 g (0.16 mol) of *cis*-β-chloroacrylyl chloride gave 22.5 g (0.12 mol, 75% yield) of product after distillation [90° (0.6 mm)]. Examination of the nmr spectrum indicated that the di endo adduct was the exclusive product: ir (neat) 3086 (olefinic C-H stretching), 1788 (carbonyl stretching), 1038, 783 cm^{-1}; nmr (60 MHz, CCl_4) τ 8.63 (d, 1 H, J = 10 Hz, methylene proton), 8.34 (doublet of triplets, J = 10, 3 Hz, methylene proton), 6.78 (broad singlet, 2 H, bridgehead protons), 6.25 (doublet of doublets, 1 H, J = 9 Hz, -CHCOCl), 4.35 (doublet of doublets, 1 H, J = 9, 3.5 Hz, -CHCl), 3.85 (m, 1 H, olefinic proton), 3.65 (m, 1 H, olefinic proton).

Preparation of *endo*-7-Chloroisodeltacyclan-5-one. Endo chloro diazo ketone was prepared in a similar manner to that described above for exo diazo ketone. Addition of 10.0 g (0.052 mol) of the *endo*-5-chloro-*endo*-6-chlorocarbonylnorbornene to diazomethane (prepared from 38 g of *N*-nitroso-*N*-methylurea) gave a nearly quantitative yield of yellow solid diazo ketone. No acid chloride could be detected by ir, indicating complete conversion: ir (neat) 3145 (olefinic C-H stretching), 2101 (=N=N stretching), 1647 (carbonyl stretching), 1366, 1095 cm^{-1}.

endo-7-Chloroisodeltacyclan-5-one was prepared as described above for the epimeric exo chloro ketone. Intramolecular carbenoid addition was accomplished by slowly adding the endo chloro diazo ketone, described above, to a refluxing mixture of 200 ml of *n*-hexane and 15 g of anhydrous $CuSO_4$. Evolution of gas ceased after 30 min. Work-up afforded 4.80 g (0.027 mol, 52% yield) of yellow semisolid product. Vpc analysis (column 1, 180°, 75 ml/min, 39 min) indicated that only one product was formed, which was identified as *endo*-7-chloroisodeltacyclan-5-one by nmr, ir, and mass spectral analysis. Vpc collection gave a white, crystalline solid: mp 130–134°; mass spectrum parent peaks at m/e 168 and 170; ir (neat) 3055 (cyclopropyl C-H stretching), 1730 (carbonyl stretching), 1279, 928, 903, 879 cm^{-1}; nmr (100 MHz, $CHCl_3$) τ 8.23 (d, 1 H, J = 10 Hz, methylene proton), 7.6–8.0 (m, 4 H, methylene, cyclopropyl protons), 7–7.4 (m, 3 H, bridgehead protons), 5.83 (doublet of doublets, 1 H, J = 9, 2 Hz, -CHCl).

Anal. Calcd for C_9H_9OCl: C, 64.10; H, 5.38. Found: C, 63.84; H, 5.33.

Preparation of Ethyl β-Acetoxyacrylate. The procedure of Pechmann was followed with minor modifications.[9] To a 3-l., three-necked flask, equipped with a mechanical stirrer, N_2 inlet, reflux condenser, and dropping funnel, was added 1.5 l. of dry ether and 115 g (5.00 mol) of cut sodium. The temperature was maintained at 0–10° with external cooling using a cooling coil immersed in a water bath and connected to an external refrigeration unit. A mixture of 440 g (5.0 mol) of ethyl acetate and 370 g (5.00 mol) of ethyl formate was slowly dropped in over a period of 4–5 hr; a copious amount of hydrogen gas was given off and a pale yellow precipitate was formed in the reaction. The reaction solution was allowed to stir for an additional 36 hr. The product was collected by vacuum filtration and washed several times with ether until the ether washings were clear. Vacuum drying gave 301 g (2.18 mol, 44% yield) of white, powdery product. Utilizing the same set-up described above, the product (300 g, 2.17 mol) was added to 1.5 l. of dry ether and cooled to 0–10°, and 160 g (2.18 mol) of acetyl chloride was slowly dropped in over a period of 1 hr. The reaction was stirred overnight, maintaining the temperature at 0°. A white precipitate remained (NaCl) which was removed by vacuum filtration. The solid was washed with ether and the washings were combined with the filtrate. The ether solution was neutralized by shaking with saturated $NaHCO_3$ (Na_2CO_3 cannot be used, as the product will decompose), washed with saturated salt solution, and dried over anhydrous $MgSO_4$. Rotary evaporation and distillation [55–65° (2.2–2.3 mm), lit.[9] 126° (46 mm)] gave 54 g (0.34 mol, 16% yield) of yellow ethyl β-acetoxyacrylates. The ratio of trans to cis product was found to be 8:1 by integration of the absorptions of the protons α to -OAc or -COOEt. The isomer with the smaller splitting (7 Hz) was assigned as cis: ir (isomeric mixture of cis and trans) (neat) 3115 (olefinic C-H stretching), 1776 (carbonyl stretching in carbethoxy group), 1724 (carbonyl stretching in β-acetoxy group), 1656 (C=C stretching), 1366, 951 cm^{-1}; nmr (100 MHz, CCl_4) τ (trans isomer) 8.77 (t, 3 H, J = 7 Hz, $-OCH_2CH_3$), 7.85 (s, 3 H, $-OCOCH_3$), 5.89 (q, 2 H, J = 7 Hz, $-OCHCH_3$), 4.43 (d, 1 H, J = 10 Hz, -CHCOOEt), 1.86 (d, 1 H, J = 10 Hz, -CHOAc); nmr (cis isomer) 8.77 (t, 3 H, J = 7 Hz, $-OCH_2CH_3$), 7.79 (s, 3 H, $-COCH_3$), 5.89 (q, 2 H, J = 7 Hz, $-OCH_2CH_3$), 4.85 (d, 1 H, J = 7 Hz, =CHCOOEt), 2.58 (d, 1 H, J = 7 Hz =CHOAc).

Condensation of Ethyl β-Acetoxyacrylate with Cyclopentadiene. Preparation of *exo*-5-Acetoxy-*endo*-6-carbethoxynorbornene. To 80 ml of dry benzene and 8.0 g (0.063 mol) of pyrogallol in a 3-l., three-necked flask equipped with a nitrogen inlet, stirrer, and condenser was added 120 g (0.76 mol) of ethyl β-acetoxyacrylate (8:1 trans to cis isomeric mixture obtained above). The mixture was heated to 60–65° and 100 ml of freshly cracked cyclopentadiene was added. Addition of cyclopentadiene was repeated three times a day for 6 days (1.8 l. total). The solution was then distilled at atmospheric pressure until all excess dicyclopentadiene was removed. Final distillation [bp 78–82° (0.1 mm)] gave

135 g (0.60 mol, 79% yield) of clear, colorless product. The product was found to be composed of three Diels–Alder adducts in the ratio of 46:48:6, in order of increasing retention times by vpc analysis (column 1). No other products were detected. Vpc collection and nmr analysis indicated the products to be *endo*-5-acetoxy-*exo*-6-carbethoxy-, *exo*-5-acetoxy-*endo*-6-carbethoxy-, and *endo*-5-acetoxy-*endo*-6-carbethoxynorbornene (order of increasing retention times). No further attempt was made to separate the isomers prior to distillation of *exo*-7-acetoxyisodeltacyclan-5-one. The spectral properties for the three isomers are as follows: (*exo*-acetoxy, *endo*-carbethoxy) mass spectrum *m/e* (rel intensity) 179 (0.23), 164 (0.21), 159 (12.15), 137 (5.55), 117 (28.34), 79 (15.65), 66 (100), 43 (45.24); ir (neat), 3086 (=CH stretching), 1724 (carbonyl stretching), 1236, 1100 cm^{-1}; nmr (100 MHz, CCl_4) τ 8.74 (t, 3 H, J = 7 Hz, $-OCH_2CH_3$), 8.38 (d, 1 H, J = 10 Hz, methylene proton), 8.24 (d, 1 H, J = 10 Hz, methylene proton), 7.98 (s, 3 H, $-OCOCH_3$), 7.34 (t, 1 H, 3 Hz, -CHCOOEt), 7.06 (broad singlet, 1 H, bridgehead proton), 6.90 (broad singlet, 1 H, bridgehead proton), 5.91 (q, J = 7 Hz, $-OCH_2CH_3$), 5.24 (s, 1 H, endo -CHOAc), 3.86 (broad singlet, 2 H, olefinic protons); (*endo*-acetoxy, *endo*-carbethoxy) nmr (100 MHz, CCl_4) τ 8.81 (t, 3 H, J = 7 Hz, $-OCH_2CH_3$), 8.80 (d, 1 H, J = 10 Hz, methylene proton), 8.63 (d, 1 H, J = 10 Hz, methylene proton), 8.13 (s, 3 H, $-OCOCH_3$) 7.8–8.1 (m, 3 H, bridgehead protons, exo CHCOOEt), 6.02 (q, 2 H, J = 7 Hz, $-OCH_2CH_3$), 4.51 (doublet of doublets, 1 H, J = 9, 4 Hz, exo CHOAc), 4.07 (m, 1 H, olefinic proton), 3.61 (m, 1 H, olefinic proton); (*endo*-acetoxy, *exo*-carboethoxy) nmr (100 MHz, CCl_4) τ 8.60 (t, 3 H, J = 7 Hz, $-OCH_2CH_3$), 8.1–8.7 (m, 3 H, methylene protons at C-7, endo CHCOOEt), 8.04 (s, 3 H, $-OCOCH_3$), 7.06 (broad singlet, 1 H, bridgehead), 7.86 (broad singlet, 1 H bridgehead proton), 6.88 (q, 2 H, J = 7 Hz, $-OCH_2CH_3$), 4.72 (t, 1 H, J = 3 Hz, exo CHOAc), 3.92 (m, 1 H, olefinic proton), 3.68 (m, 1 H, olefinic proton).

Anal. Calcd for $C_{12}H_{16}O_4$ (mixture of **6b** isomers): C, 64.28; H, 7.19. Found: C, 64.10; H, 7.27.

Hydrolysis of *exo*-5-Acetoxy-*endo*-6-carbethoxynorbornene. To 80 g (1.43 mol) of potassium hydroxide in 670 ml of water was added 200 g (0.89 mol) of the isomeric mixture of 5-acetoxy-6-carbethoxynorbornene Diels–Alder adducts obtained above. The heterogeneous mixture was mechanically stirred for 15 hr. A dark solution resulted which was extracted three times with ether to remove any starting material. The aqueous layer was acidified with dilute H_2SO_4 and continuously extracted for three days using continuous ether extraction. The resulting solution was dried ($MgSO_4$) and the solvent was distilled off using a rotary evaporator. Removal of acetic acid was accomplished by vacuum distillation and further drying in a vacuum desiccator. A dark solid was obtained (135 g, 0.88 mol, 99% yield) which was easily decolorized by boiling in ethanol with decolorizing carbon. The product was used for subsequent reaction without further purification: ir (isomeric mixture, KBr pellet) 3425 (OH stretching), 2985 (broad, acid OH stretching), 1695 (C=O), 1031 cm^{-1}; nmr (*exo*-5-hydroxy-*endo*-6-carboxynorbornene) (100 MHz, DMSO-d_6) τ 8.48 (d, 1 H, J = 10 Hz, methylene proton), 8.36 (d, 1 H, J = 10 Hz, methylene proton), 8.46 (t, 1 H, J = 3 Hz, -CHCOOH), 7.10 (broad singlet, 1 H, bridgehead proton), 7.00 (broad singlet, 1 H, bridgehead proton), 6.74 (s, 1 H, -CHOH), 6.10 (s, 1 H, -CHOH), 3.88 (broad singlet, 2 H, olefinic protons).

Acetylation of *endo*-6-Carboxy-*exo*-5-hydroxynorbornene with Acetic Anhydride. To a solution of 91.4 g (0.59 mol) of the isomeric mixture of hydroxy acids obtained above in 300 ml of pyridine was slowly added 127 g (1.25 mol) of acetic anhydride. The solution was stirred for 12 hr. After neutralization with dilute hydrochloric acid, the solution was extracted with ether. Washing the extracts with dilute acid and saturated salt solution, drying ($MgSO_4$), and evaporation of solvent using a rotary evaporator, followed by removal of acetic acid by vacuum distillation, gave 73.1 g (0.37 mol, 63% yield) of product. Distillation on a high vacuum line gave a clear, colorless glass [99–105° (1–5 × 10^{-5} mm)]: ir (isomeric mixture, neat) 3080 (broad, acid OH stretching), 1733 (C=O from acetoxy carbonyl), 1698 (C=O from carboxylic acid carbonyl), 1239, 1034 cm^{-1}; nmr (*exo*-5-acetoxy-*endo*-6-carboxynorbornene, 100 MHz, CCl_4) τ 8.33 (d, 1 H, J = 10 Hz, methylene proton), 8.21 (d, 1 H, J = 10 Hz, methylene proton), 7.93 (s, 3 H, $-OCOCH_3$), 7.19 (t, 1 H, J = 2 Hz, exo CHCOOH), 7.01 (broad singlet, 1 H, bridgehead proton), 6.87 (broad singlet, 1 H, bridgehead proton), 5.21 (s, 1 H, endo CHOAc), 3.87 (broad singlet, 2 H, olefinic protons).

Anal. Calcd for $C_{10}H_{12}O_4$: C, 61.22; H, 6.17. Found: C, 61.08; H, 6.26.

Preparation of *exo*-5-Acetoxy-*endo*-6-chlorocarbonylnorbornene. To a solution of 52.5 g (0.027 mol) of the acetoxy acids obtained above in 150 ml of dry benzene in a three-necked flask equipped with a reflux condenser, drying tube, and magnetic stirrer was added 69 g (0.54 mol) of oxalyl chloride. The mixture was allowed to stir overnight at room temperature. Atmospheric distillation of the benzene followed by vacuum distillation of the acid chloride [bp 73° (0.25 mm)] gave 38.5 g (0.18 mol, 67% yield) of clear, colorless product. The product could be stored for a considerable length of time in a refrigerator without significant decomposition: ir (isomeric mixture, neat) 3086 (olefinic C–H stretching), 1792 (C=O stretching for acetoxy carbonyl), 1230, 1029 cm^{-1}; nmr (*exo*-5-acetoxy-*endo*-6-chlorocarbonylnorbornene, 100 MHz, CCl_4) τ 8.33 (d, 1 H, J = 10 Hz, methylene proton), 8.18 (d, 1 H, J = 10 Hz, methylene proton), 8.00 (s, 3 H, $OOCCH_3$), 7.51 (t, 1 H, J = 3 Hz, -CHCOCl), 7.00 (broad singlet, 1 H, bridgehead), 6.99 (broad singlet, 1 H, bridgehead), 5.31 (s, 1 H, -CHOAc), 3.83 (broad singlet, 2 H, olefinic protons).

Reaction of *exo*-5-Acetoxy-*endo*-6-chlorocarbonylnorbornene with Diazomethane. An ethereal solution of diazomethane was prepared from 45 g (0.44 mol) of *N*-methyl-*N*-nitrosourea, 100 ml of 50% aqueous KOH, and 300 ml of ether. Diazomethane was codistilled with ether and dried over KOH at −10° for 1 hr. This drying process was repeated twice, transferring the ethereal solution under nitrogen. The diazomethane was then transferred to a 500-ml erlenmeyer flask equipped with a small addition funnel and drying tube. Extreme care was taken to exclude water from the system. The isomeric mixture of exo and endo acid chlorides obtained above (12.0 g, 0.059 mol) was slowly added with stirring. The resulting solution was allowed to stand at −80° for 45 min, and finally for 1 hr at 0°. Rotary evaporation of the solvent at room temperature gave a bright yellow liquid whose ir spectrum indicated that no acid chloride remained. A new carbonyl absorption appeared at 1724 cm^{-1}, and an intense diazo peak at 2105 cm^{-1} was also present. The product was used immediately after preparation: ir (neat) 3086 (olefinic C–H stretching), 2105 (=N=N stretching), 1724 (carbonyl stretching from acetoxy carbonyl), 1634 (carbonyl stretching from diazo keto group), 1370, 1242, 1031 cm^{-1}; nmr (100 MHz, CCl_4) τ 8.38 (d, 1 H, J = 10 Hz, methylene proton), 8.22 (d, 1 H, J = 10 Hz, methylene proton), 7.96 (s, 3 H, $OCOCH_3$), 7.40 (t, 1 H, J = 3 Hz, $-CHCOCHN_2$), 7.06 (broad singlet, 1 H, bridgehead proton), 6.88 (broad singlet, 1 H, bridgehead proton), 5.26 (s, 1 H, -CHOAc), 4.37 (s, 1 H, $-COCHN_2$), 3.88 (m, 2 H, olefinic protons).

Preparation of *exo*-7-Acetoxyisodeltacyclan-5-one. The diazo ketone mixture obtained above was added dropwise to a rapidly stirred suspension of 12 g of anhydrous $CuSO_4$ in refluxing *n*-hexane. A nearly quantitative volume of nitrogen was given off over a period of 45 min. The solution was filtered and the solid residue was extracted with ether. The combined ethereal hexane solution was transferred to a separatory funnel and washed with saturated sodium bicarbonate (10%) and salt water. Drying over anhydrous magnesium sulfate and rotary evaporation gave a dark oil. Distillation on a high vacuum line [100° (1–5 × 10^{-5} mm)] gave 3.6 g (0.019 mol, 63% yield, based on *exo*-5-acetoxy-*endo*-6-chlorocarbonylnorbornene, correcting for the amount of *endo*-5-acetoxy-*exo*-6-chlorocarbonyl present). The product was determined to be *exo*-7-acetoxyisodeltacyclan-5-one by analysis of physical and spectral data: mass spectrum *m/e* (rel intensity) 192 (1), 150 (23), 132 (39), 77 (21), 43 (100); ir (neat), 3055 (cyclopropyl C–H stretching), 1727 (carbonyl stretching), 1232, 1035, 724 cm^{-1}; nmr (100 MHz, CCl_4) τ 8.04 (s, 3 H, $OCOCH_3$), 7.7–8.3 (m, 5 H, methylene protons, cyclopropyl protons), 7.42 (m, 1 H, bridgehead proton), 7.22 (broad singlet, 2 H, bridgehead protons), 5.58 (s, 1 H, -CHOAc).

Anal. Calcd for $C_{11}H_{12}O_3$: C, 68.74; H, 6.29. Found: C, 68.68; H, 6.46.

Preparation of *exo*-7-Acetoxyisodeltacyclan-5-one Ethanedithiol Ketal. Hydrogen chloride was rapidly bubbled into a stirred solution of 5.8 g (0.030 mol) of *exo*-7-acetoxyisodeltacyclan-5-one and 75 ml of ethanedithiol. The solution turned cloudy. Addition was continued for 2 min, followed by stirring for another 2 min. The reaction was quenched by pouring into 200 ml of 10% NaOH solution and then extracted with chloroform. The combined extracts were washed several times with 10% NaOH to remove excess ethanedithiol, once with 10% $NaHCO_3$, and once with saturated salt water. Drying ($MgSO_4$), rotary evaporation, and final drying in a vacuum desiccator gave 5.9 g of solid crystalline thioketal acetate. Vpc analysis (column 2, 190°, 60 ml/min, 16 min) indicated that 10% of the product had suffered electrophilic

addition of HCl to the cyclopropane ring, resulting in a decreased yield of 5.3 g (0.20 mol, 66% yield) of desired product: mp 84–86.5° (vpc collected); mass spectrum parent peaks at *m/e* 268 and 270; ir (CCl_4) 3055 (cyclopropyl C–H stretching) 1727 (C=O), 1222, 1044 cm^{-1}; nmr (100 MHz, CCl_4) τ 8.42 (t, 1 H, J = 6 Hz, cyclopropyl proton), 8.06 (s, 3 H, $OCOCH_3$), 7.7–8.2 (m, 5 H, cyclopropyl protons, methylene protons at C-9, bridgehead proton), 7.44 (broad singlet, 1 H, bridgehead proton), 7.26 (broad singlet, 1 H, bridgehead proton), 6.76 (m, 4 H, $-SCH_2CH_2S-$), 5.40 (s, 1 H, -CHOAc).

Anal. Calcd for $C_{13}H_{16}O_2S_2$: C, 58.18; H, 6.01. Found: C, 57.99; H, 6.14.

Preparation of *exo*-7-Isodeltacyclyl Acetate by Reduction of *exo*-7-Acetoxyisodeltacyclan-5-one Ethanedithiol Ketal with Raney Nickel. The title thioketal acetate (1.55 g, 0.0058 mol) was added to a stirred mixture of Raney nickel and 30 ml of dry ethanol. The mixture was stirred for 1 hr at room temperature. Filtration and partial removal of solvent by fractional distillation gave 244 mg (0.0014 mol, 24% yield by internal standard, column 1, 155°, 50 ml/min, 24 min). An additional 255 mg (0.0014 mol, 24% yield, column 1, 155°, 50 ml/min, 16 min) was obtained of a second product in the reaction. Subsequent reduction of the latter with lithium aluminum hydride and oxidation (Jones reagent) gave a product whose ir was identical with that of an authentic sample of brendanone. *exo*-Isodeltacyclyl acetate has the following spectral properties: mass spectrum *m/e* (rel intensity) 178 (2), 150 (3), 149 (2), 136 (10), 135 (9), 117 (50), 118 (50), 91 (39), 77 (34), 70 (35), 43 (100); ir (CCl_4) 3039 (cyclopropyl C–H stretching), 1727 (carbonyl stretching), 1360, 1240, 1028 cm^{-1}; nmr (100 MHz, CCl_4) τ 8.75 (t, 1 H, J = 6 Hz, cyclopropyl proton), 8.50 (m, 1 H, cyclopropyl proton), 8.10 (s, 3 H, $-OCOCH_3$), 7.8–8.3 (m, 6 H, methylene protons at C-5, C-9, cyclopropyl proton, bridgehead proton at C-1), 7.52 (broad singlet, 2 H, bridgehead protons at C-6, C-8), 5.90 (s, 1 H, -CHOAc).

Anal. Calcd for $C_{11}H_{14}O_2$: C, 74.12; H, 7.91. Found: C, 74.02; H, 8.05.

Reduction of *exo*-Isodeltacyclyl Acetate with Lithium Aluminum Hydride. To a stirred solution of *exo*-7-isodeltacyclyl acetate (189 mg, 1.06 mmol) in 100 ml of anhydrous ether, lithium aluminum hydride (0.10 g, 2.6 mmol) was added. The reaction mixture was allowed to stir at room temperature for 12 hr. Saturated ammonium chloride was added, followed by extraction with ether. The ether extracts were washed with saturated salt water and dried over anhydrous magnesium sulfate. Fractional distillation of solvent gave 123 mg (0.90 mmol, 85% yield by internal standard) of waxy product: mp 104–106° (vpc collected); ir (neat) 3340 (broad OH stretching), 1290, 1062 cm^{-1}; nmr (100 MHz, CCl_4) τ 8.88 (t, 1 H, J = 6 Hz, cyclopropyl proton), 8.4–8.6 (m, 1 H, cyclopropyl proton), 7.9–8.4 (m, 7 H, methylene protons at C-5, C-9, cyclopropyl proton, bridgehead proton at C-1, and -CHOH), 7.76 (broad singlet, 1 H, bridgehead proton), 7.52 (broad singlet, 1 H, bridgehead proton), 6.72 (s, 1 H, -CHOH).

Anal. Calcd for $C_9H_{12}O$: C, 79.37; H, 8.88. Found: C, 79.17; H, 9.01.

Preparation of *exo*-7-Isodeltacyclyl Brosylate. *p*-Bromobenzenesulfonyl chloride (125 mg, 0.50 mmol) was added portionwise to a stirred solution of 0.5 ml of dry pyridine and 34 mg (0.25 mmol) of *exo*-7-isodeltacyclyl alcohol, maintaining the temperature at −20° with an ice–salt bath. After stirring for 1 hr, the solution was allowed to stand in a refrigerator for 3 days. Pyridine was then removed by vacuum, cooling the flask in an ice bath, and the crude brosylate was extracted with several 2-ml portions of pentane. The extracts were quickly transferred to a 25-ml flask. Evaporation of pentane under vacuum gave 72.5 g (0.21 mmol, 84% yield) of *exo*-7-isodeltacyclyl brosylate (correcting for the amount of unreacted alcohol remaining), which was used immediately without further purification. Nmr analysis indicated that 35% of the product had rearranged to deltacyclyl brosylate prior to solvolysis, evidenced by the appearance of small absorptions assignable to deltacyclyl brosylate, the most characteristic at τ 5.24 (doublet of doublets, J = 6 Hz, 2 Hz) for -CHOBs. Complete rearrangement could be achieved by allowing the brosylate to remain in pyridine for 2 weeks: ir (isomeric mixture, CCl_4) 3039 (cyclopropyl C–H stretching), 1575 (aromatic C=C stretching); nmr (*exo*-7-isodeltacyclyl brosylate), 100 MHz, CCl_4) τ 8.3–8.9 (m, 2 H), 7.6–8.3 (m, 5 H), 7.2–7.6 (broad, 3 H, bridgehead protons), 5.96 (s, 1 H, -CHOBs); *m/e* 353.988 (calcd for $C_{15}H_{15}O_3SBr$, 353.993).

Solvolysis of *exo*-7-Isodeltacyclyl Brosylate. Product Study. To 72.5 mg (0.210 mmol) of *exo*-7-isodeltacyclyl brosylate was added 8 ml of 0.04 *M* NaOAc–HOAc solution and the resulting solution was allowed to react at 40° for 48 hr. The contents of the flask were then neutralized by pouring into 50 ml of saturated sodium bicarbonate solution and extracted with 4 × 50 ml of ether. The organic phase was washed with salt water and dried over anhydrous $MgSO_4$. Two products, in the ratio of 97.6:2.4, were detected by vpc (column 1, 155°, 66 ml/min, 17 min, 15 min). The minor product was too small to isolate, but its retention time corresponded to that of isodeltacyclyl acetate on three different vpc columns. Vpc collection of the major product gave 14 mg (0.104 mmol, 48% yield) of product. Comparison of its ir and nmr with an authentic sample of *exo*-8-deltacyclyl acetate demonstrated the two to be identical.

To check the stability of *exo*-7-isodeltacyclyl acetate to the solvolytic conditions, 16 mg (0.089 mmol) of acetate was added to 3.3 ml of 0.04 *M* NaOAc–HOAc and allowed to stand for 48 hr at 40°. Working the reaction up as above and using vpc isolation afforded 5 mg (31% recovery) of *exo*-7-isodeltacyclyl acetate. No rearranged *exo*-8-deltacyclyl acetate could be detected by vpc analysis (<1%).

Preparation of Deuterated Raney Nickel. Deuterated Raney nickel was prepared by the method of Fukishima, Leiberman, and Pratz.[11] To a 2-l., three-necked flask equipped with a Hersberg stirrer was added 130 ml of ethanol–Raney nickel catalyst sludge. One liter of methylcyclohexane was added, and the contents were stirred at 70°. Ethanol, water, and methylcyclohexane were azeotropically distilled at 200 mm pressure. Distillation was discontinued and 15 ml of D_2O (99.9% pure) was added. The mixture was rapidly stirred for 30 min, at which time equilibrated water and deuterium oxide were azeotropically distilled as above. This process was repeated an additional six times with 15-ml portions of deuterium oxide. Anhydrous methylcyclohexane was added occasionally to maintain the original volume. Deuterium gas (95%) was finally added for 2 hr, maintaining the rate of addition commensurate with the absorption of gas. The Raney nickel was transferred and stored under methylcyclohexane.

Reduction of *exo*-7-Acetoxyisodeltacyclan-5-one Ethanedithiol Ketal with Deuterated Raney Nickel. The title thioketal acetate (2.0 g, 0.0074 mol) was added to 5 ml of deuterated Raney nickel sludge in 50 ml of anhydrous ether. The heterogeneous mixture was stirred at room temperature for 12 hr. The reaction mixture was filtered, concentrated by fractional distillation of solvent, and distilled in a short-path still. The Raney nickel reduction was repeated on the material left in the pot. A combined yield of 431 mg (2.42 mmol, 33% yield) of deuterated *exo*-7-isodeltacyclyl acetate was obtained (determined by vpc on column 1, 155°, 40 ml/min, 24 min, using an internal standard). Nmr analysis utilizing chemical shift reagent $Eu(fod)_3$ and comparison of the spectrum of complexed alcohol with an undeuterated sample under similar conditions demonstrated that the amount of deuterium at C-5 was 0.70 ± 0.08 D: ir (CCl_4) 3039 (cyclopropyl C–H stretching), 2105 (C–D stretching), 1727 (carbonyl stretching), 1360, 1340, 1028 cm^{-1}; nmr (100 MHz, CCl_4) τ 8.75 (t, 1 H, J = 6 Hz, cyclopropyl proton), 8.50 (m, 1 H, cyclopropyl proton), 8.10 (s, 3 H, $-OCOCH_3$), 7.8–8.3 [m, <6 H, methylene protons at C-5 (1.30 H, 0.70 D), C-9, cyclopropyl proton, bridgehead proton at C-1], 7.52 (broad singlet, 2 H, bridgehead protons at C-6, C-8), 5.90 (s, 1 H, -CHOAc).

Reduction of 5,5-Dideuterio-*exo*-7-isodeltacyclyl Acetate with Lithium Aluminum Hydride. The procedure for reduction of deuterated *exo*-7-isodeltacyclyl acetate was identical with that for the parent isodeltacyclyl acetate. 5,5-dideuterio-*exo*-7-isodeltacyclyl acetate (206 mg, 1.15 mmol, 0.70 D), upon reaction with 0.1 g (2.6 mmol) of lithium aluminum hydride in 100 ml of anhydrous ether, gave 126 mg (0.93 mmol, 80% yield) of alcohol: ir (CCl_4) 3340 (broad, -OH stretching), 3039 (cyclopropyl C–H stretching), 2105 (C–D stretching), 1062 cm^{-1}; nmr (100 MHz, CCl_4) τ 8.88 (t, 1 H, J = 6 Hz, cyclopropyl proton), 8.4–8.6 (m, 1 H, cyclopropyl proton), 7.9–8.4 [m, <7 H, methylene protons at C-5 (1.30 H, 0.70 D), C-9, cyclopropyl proton, bridgehead proton at C-1, and -CHOH], 7.76 (broad singlet, 1 H, bridgehead proton), 7.52 (broad singlet, 1 H, bridgehead proton), 6.72 (s, 1 H, -CHOH).

Preparation of 5,5-Dideuterio-*exo*-7-isodeltacyclyl Brosylate. Preparation of 5,5-dideuterio-*exo*-7-isodeltacyclyl brosylate was accomplished as above for the parent isodeltacyclyl brosylate. *p*-Bromobenzenesulfonyl chloride (80 mg, 0.313 mmol) was added to 30 mg (0.22 mmol) of 5,5-dideuterio-*exo*-7-isodeltacyclyl alcohol (0.70 D) in 0.7 ml of pyridine. Work-up afforded 51.5 mg (0.151 mmol, 68% yield) of brosylate. Nmr analysis indicated that

24% of the product had rearranged to deltacyclyl brosylate. Solvolysis of the brosylate was carried out immediately: ir (neat) 3039 (cyclopropyl C-H stretching), 2105 (C-D stretching), 1575 (aromatic C=C stretching), 1183 cm^{-1}; nmr (100 MHz, CCl_4) τ 8.3-8.9 (m, 2 H), 7.6-8.3 (m, 5 H), 7.2-7.6 (broad, 3 H, bridgehead protons), 5.96 (s, 1 H, -CHOBs).

Solvolysis of 5,5-Dideuterio-*exo*-7-isodeltacyclyl Brosylate Product Study. The solvolysis of 5,5-dideuterio-*exo*-7-isodeltacyclyl brosylate was accomplished following the same procedure as for isodeltacyclyl brosylate. Brosylate (43 mg, 0.12 mmol, 0.70 D) was added to 3.2 ml of 0.04 *M* NaOAc-HOAc solution and allowed to solvolyze at 40° for 48 hr. After work-up, two products were detected by vpc in the ratio of 3.3:96.7 (column 1, 155°, 66 ml/min, 17 min, 15 min). The minor product was not isolated, but had the same retention time as isodeltacyclyl acetate. Nmr analysis utilizing $Eu(fod)_3$ indicated that deuterium was scrambled between C-9 and C-5 exclusively, in the ratio of 1:1.8, respectively, correcting for the amount of brosylate which had undergone rearrangement prior to solvolysis. The sum of the deuterium content at the two positions was 0.86 ± 0.05 D.

Acknowledgment. The authors gratefully acknowledge the generous support of this work by the National Science Foundation.

Registry No. *exo*-**4b**, 43187-23-1; *exo*-**4b**-*5,5-d*$_2$, 43187-24-2; *exo*-**4c**, 43187-25-3; *exo*-**4c**-*5,5-d*$_2$, 43187-26-4; *exo*-**4f**, 43187-27-5; *exo*-**4f**-*5,5-d*$_2$, 43187-28-6; *cis*-**5a**, 3721-35-5; *trans*-**5a**, 3721-36-6; *cis*-**5b**, 16506-98-2; *trans*-**5b**, 16544-46-0; 5-*endo*-6-*endo*-**6a**, 43187-30-0; 5-*exo*-6-*endo*-**6a**, 43187-31-1; 5-*endo*-6-*endo*-**6b**, 43187-32-2; 5-*endo*-6-*exo*-**6b**, 43187-33-3; 5-*exo*-6-*endo*-**6b**, 43187-34-4; 5-*exo*-6-*endo*-**6c**, 43187-35-5; 5-*exo*-6-*endo*-**6d**, 43187-36-6; 5-*exo*-6-*endo*-**6e**, 43187-37-7; *endo*-**7a**, 43187-38-8; *exo*-**7a**, 43187-39-9; *exo*-**7b**, 43187-40-2; *exo*-**7c**, 43187-41-3; **10**, 13084-56-5; *exo*-**12a**, 43187-43-5; *exo*-**12b**, 41850-57-1; propiolic acid, 471-25-0; diazo ketone (X = Cl), 43187-45-7; diazo ketone (X = OAc), 43187-46-8; *exo*-7-acetoxyisodeltacyclan-5-one ethanedithiol ketal, 43187-47-9.

References and Notes

(1) For part III, see P. K. Freeman and B. K. Stevenson, *J. Amer. Chem. Soc.*, **95**, 2890 (1973).
(2) P. K. Freeman, D. M. Balls, and J. N. Blazevich, *J. Amer. Chem. Soc.*, **92**, 2051 (1970); P. K. Freeman and D. M. Balls, *Tetrahedron Lett.*, 437 (1967).
(3) P. K. Freeman and J. N. Blazevich, *Chem. Commun.*, 1357 (1969).
(4) We have found it to be most convenient to refer to tetracyclo-[4.3.0.$0^{2,4}$.$0^{3,7}$]nonane as deltacyclane [A. Nickon, G. P. Pandit, and R. O. Williams, *Tetrahedron Lett.*, 2851 (1967), and ref 10] and now suggest the name isodeltacyclane for ring system tetracyclo-[4.3.0.$0^{2,4}$.$0^{3,8}$]nonane, which is related to deltacyclane by a Wagner-Meerwein rearrangement.
(5) A. Nickon, H. Kwasnik, T. Swartz, R. O. Williams, and J. B. DiGiorgio, *J. Amer. Chem. Soc.*, **87**, 1615 (1965).
(6) P. K. Freeman and D. M. Balls, *J. Org. Chem.*, **32**, 2354 (1967); H. Prinzbach and D. Hunkler, *Angew. Chem., Int. Ed. Engl.*, **6**, 247 (1967); E. Wiskott and P. v. R. Schleyer, *ibid.*, **6**, 694 (1967).
(7) M. F. Grundon, J. B. Henbest, and M. P. Scott, *J. Chem. Soc.*, 1855 (1963).
(8) D. J. Cram, M. R. V. Sahyun, and G. R. Knox, *J. Amer. Chem. Soc.*, **84**, 1734 (1962).
(9) H. V. Pechmann, *Chem. Ber.*, **25**, 1040 (1892).
(10) H. R. Kwasnik, Ph.D. Dissertation, Johns Hopkins University, 1966.
(11) D. K. Fukushima, S. Lieberman, and B. Praetz, *J. Amer. Chem. Soc.*, **72**, 5205 (1950).
(12) F. Arndt in A. H. Blatt, "Organic Syntheses," Collect. Vol. II, Wiley, New York, N. Y., 1943, p 165.

Pathways in the Base-Catalyzed Decomposition of Cyclic *N*-Nitroso Carbamates[1]

Alfred Hassner* and Robert H. Reuss[1b]

Department of Chemistry, University of Colorado, Boulder, Colorado 80302

Received June 25, 1973

The scope and stereochemical aspects of the base-catalyzed decomposition of 3-nitroso-2-oxazolidones are examined. Though certain 3-nitroso-2-oxazolidones (**3**) when treated with base in alcohol produce vinyl ethers **5** in good yield, the reaction is not general. Vinyl ethers are obtained only when a vinyl diazonium ion **3** can be produced readily. This occurs if a proton at the 4 position of **1** can be readily lost from intermediate **2** and when the 5 position is substituted such that the carbonate of intermediate **2** becomes a good leaving group. If the 4 carbon is primary, then the 5 carbon must be tertiary or benzylic, whereas, if the 4 carbon is secondary, then the 5 carbon must be benzhydrylic for formation of a vinyl ether as the major product. If these conditions are not met, many different products, in particular carbonates and ketones, are formed presumably by loss of N_2 from **2** to afford an intermediate carbonium ion **24**. Thus, 3-nitroso-2-oxazolidones **9a-f** afford primarily products formally derived from **24** and even **9g** yields a significant amount of such compounds. However, **10b** gives only a trace of such derivatives, furnishing, instead, products derived from vinyl diazonium ion **3**.

The base-catalyzed decomposition of *N*-nitroso carbamates is a well-known source of diazo and diazonium species.[2] Their cyclic analogs, the *N*-nitroso-2-oxazolidones contain an interesting feature. On base treatment, the original alcohol portion of the carbamate remains part of the same molecule that contains the diazo or diazotate group; hence neighboring group effects in these reactions can be evaluated. Earlier studies on the reaction of 3-nitroso-2-oxazolidones indicated that ketones, acetylenes, and vinyl ethers were among the products isolated.[3] Recent work by Newman and coworkers[4] has extended this reaction to a good yield synthesis of vinyl ethers **5** as a result of treatment of alcoholic solutions of certain 3-nitroso-2-oxazolidones (**1**) with base. The reaction was assumed to proceed by the elimination of monoalkyl carbonate and nitrogen from the diazonium intermediate **2**[5] to afford vinyl cation **4** which in alcohol is converted to **5** (Scheme I). When R_1 = H, evidence has been presented that an alkylidene carbene **6** is generated in aprotic media.[6]

Newman and coworkers have shown[6] that in the case of the *tert*-butyloxazolidone **1** (R_1 = H, R_2 = CH_3, R_3 = *tert*-butyl) there is a stereochemical preference leading mainly to the trans vinyl ether **5a** (or equivalent product of trapping cation **3** with a nucleophile). However, it has not been established whether stereochemistry is maintained in the conversion of stereoisomers of **1** into stereoisomeric **5**. Since our studies on INCO additions to olefins have provided a stereospecific entry into 4,5-disubstituted oxazolidones,[7] we decided to investigate the chemistry of such systems, *i.e.*, **1** (R_2 or R_3 = H), in order to relate the stereochemistry of the reactants and products.