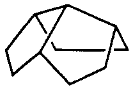
Functionalization Reactions of Tricyclo[5.2.1.$0^{4,10}$]decane. The Tricyclo[5.2.1.$0^{4,10}$]decane to Adamantane Rearrangement

Leo A. Paquette, George V. Meehan,[1a] and Sandra J. Marshall[1b]

Contribution from the Department of Chemistry, The Ohio State University, Columbus, Ohio 43210. *Received June 16, 1969*

Abstract: Treatment of tricyclo[5.2.1.$0^{4,10}$]decane (**1**) with carbomethoxynitrene leads chiefly to insertion into the tertiary C–H bonds (when evaluated on a per-hydrogen basis). A reactivity ratio of 4.0:3.8:1.0 for the tertiary apical, tertiary nonapical, and methylene positions is observed. Similarly, chromyl acetate oxidation of **1** results in preferential attack at tertiary carbons. However, the tertiary apical position does not undergo oxidation. These contrasting features are discussed. Exposure of **1** to aluminum chloride in refluxing hexane leads to adamantane. Treatment of several tricyclo[5.2.1.$0^{4,10}$]decanols with fluorosulfonic acid, followed by aqueous quenching, yields 1-adamantanol. These transformations are accommodated by a scheme involving nonbridgehead carbonium ions which rearrange only by 1,2-alkyl shifts.

The hydrocarbon tricyclo[5.2.1.$0^{4,10}$]decane (**1**) is so constructed that each cyclopentane ring shares three contiguous carbon atoms with the remaining two five-membered rings, the central carbon (C-10) being common to all three carbocyclic moieties. Such a bonding arrangement necessitates that the molecule be cup-shaped with eight equivalent methylene groups and three equivalent "edge" methine groups in addition to the unique central methine carbon. From the reactivity viewpoint, **1** may be considered a chemical model for the theoretically interesting dodecahedrane molecule (which is formally built up of two units of **1**[2]) and as a rigid, relatively strain-free, small ring isomer of adamantane. In connection with our developing interest in the chemistry of unusually constructed hydrocarbons,[3–6] we have sought to achieve functionalization of **1** with the intent of analyzing the relative reactivities of its various positions and examining possible structural rearrangements of the tricyclo[5.2.1.$0^{4,10}$]decane skeleton to the adamantane framework.[7]



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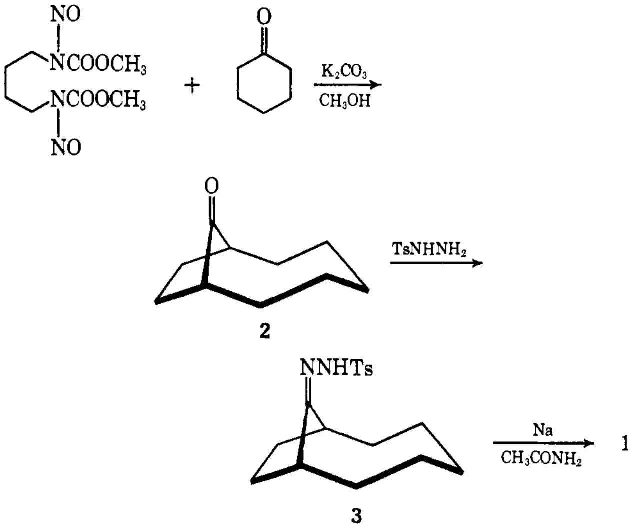
Functionalization Studies

The tricyclo[5.2.1.$0^{4,10}$]decane (**1**) employed in this study was prepared according to the procedure of Jacobson,[8] which relies upon the fact that tosylhydrazone **3** can be isolated in good yield and a high state of purity directly from the double ring expansion which affords crude **2**.[9] Decomposition of the sodium salt of **3** in acetamide at 170° gives **1** in 83–91% yield.



The reaction of alkanes and cycloalkanes with singlet nitrenes results in insertion into the various available C–H bonds by a concerted mechanism with essentially complete retention of configuration.[10] Because this technique provides a useful functionalization reaction, and in view of the present interest in nitrene insertion selectivities,[11] the thermal decomposition of methyl azidoformate in **1** has been examined. The decompositions were performed in 9 molar excess of **1** at 120° in sealed ampoules. After removal of the excess hydrocarbon by column chromatography, there was obtained a 70% yield of a mixture of four isomeric methyl urethans. Preparative scale gas chromatographic separation of this mixture provided analytical samples of **4**, **5**, and **6** (mixture of *exo* and *endo* isomers) shown to be produced in the ratio of 1.00:2.87:3.08, respectively.

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(1) (a) University Postdoctoral Fellow, 1967–1969; (b) National Science Foundation Undergraduate Research Participant, Summer 1968.

(2) This relationship was recognized by R. B. Woodward, T. Fukunaga, and R. C. Kelly [*J. Am. Chem. Soc.*, **86**, 3162 (1964)], who have described the synthesis of the triply unsaturated congener of **1** which they named triquinacene.

(3) L. A. Paquette and J. C. Philips, *Tetrahedron Lett.*, 4645 (1967).

(4) L. A. Paquette and J. C. Philips, *Chem. Commun.*, 680 (1969).

(5) L. A. Paquette and J. C. Philips, *J. Am. Chem. Soc.*, **91**, 3973 (1969).

(6) L. A. Paquette, J. F. Kelly, and J. C. Stowell, unpublished observations.

(7) H. W. Whitlock, Jr., and M. W. Siefken [*J. Am. Chem. Soc.*, **90**, 4929 (1968)] have recently defined a basis set of sixteen C-10 tricyclic structures (including **1**) and have discussed their potential interconvertibility.

(8) I. T. Jacobson, *Acta Chem. Scand.*, **21**, 2235 (1967).

(9) C. D. Gutsche and T. D. Smith, *J. Am. Chem. Soc.*, **82**, 4067 (1960).

(10) (a) M. F. Sloan, T. J. Prosser, N. R. Newburg, and D. S. Breslow, *Tetrahedron Lett.*, 2945 (1964); (b) W. Lwowski and T. J. Maricich, *J. Am. Chem. Soc.*, **86**, 3164 (1964); (c) W. Lwowski and T. W. Mattingly, Jr., *ibid.*, **87**, 1947 (1965); (d) G. Smolinsky and B. I. Feuer, *ibid.*, **86**, 3085 (1964); (e) A. G. Anastassiou and H. E. Simmons, *ibid.*, **89**, 3177 (1967); (f) A. G. Anastassiou, *ibid.*, **89**, 3184 (1967).

(11) (a) J. Meinwald and D. H. Aue, *Tetrahedron Lett.*, 2317 (1967); (b) D. S. Breslow, E. I. Edwards, R. Leone, and P. von R. Schleyer, *J. Am. Chem. Soc.*, **90**, 7097 (1968).

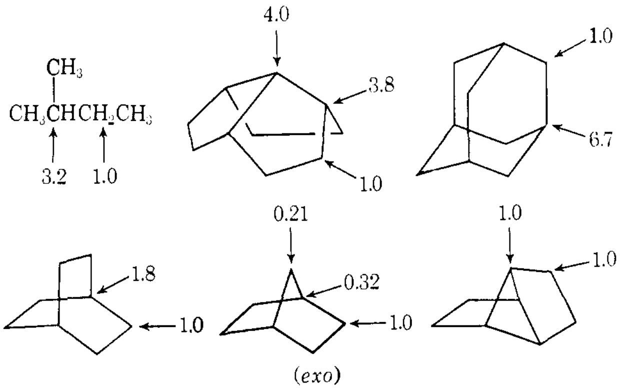
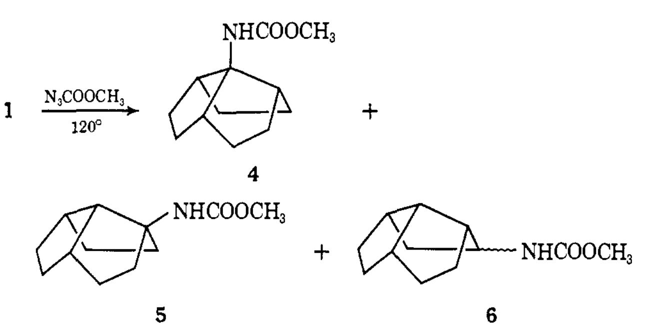


Figure 1. Relative reactivities (per H) of various hydrocarbons.

The structure of **4** follows from its elemental analysis, its infrared absorption maximum at 1730 cm^{-1}, and its nmr spectrum which reveals the absence of a proton on the carbon atom bearing the nitrogen substituent. In particular, this last spectrum is simplified by a coincidence of chemical shift values caused by the inherent symmetry of the molecule; whereas the twelve methylene protons appear in the δ 1.1–2.1 region as a multiplet split symmetrically into six major peaks centered at δ 1.67, the three equivalent methine protons are seen as a broad peak at δ 2.10–2.70.[12]



The second urethan to be eluted displayed a somewhat more complex nmr spectrum than **4**, indicative of its less symmetrical nature. The spectrum shows only two broad multiplets at δ 1.10–2.10 (12 H) and 2.30–2.90 (3 H); the absence of absorption due to a >C*H*N< proton is again uniquely consistent with tertiary substitution. These data are entirely consistent with structure **5**.

The nmr spectrum of the major product (two isomers) revealed a one-proton absorption due to the carbinylamine hydrogen (broad peak at δ 3.5–3.8) in addition to broad patterns at 1.10–1.95 (10 H) and 1.95–3.00 (4 H). This chemical shift profile is explainable if a methylene group bears a urethan functionality and offers confirmation of the proposed structure (**6**). The elemental analyses of **5** and **6**, as well as their infrared spectra, were consistent with these assignments.

Although a large difference in relative reactivity among the various positions of **1** is not seen, the tertiary centers are clearly more reactive than the secondary positions by a factor approximating 4. Since 2-methyl-2-butane demonstrates a 3.2:1 preference for methine over methylene attack[10a] and the tertiary positions in adamantane are 6.7-fold more reactive than the secondary sites,[11b] **1** appears to undergo "normal" nitrene insertion behavior. The decrease in relative tertiary/secondary reactivity ratios with increasing ring strain in the cyclic hydrocarbon (compare bicyclo[2.2.2]octane, norbornane, and tricyclo[3.3.0.0^{2,6}]octane) would seem to suggest further that **1** is strainless, as assumed earlier from examination of molecular models. The relative reactivities of several hydrocarbons are summarized in Figure 1.[13]

Lwowski[13,14] has recognized that, although the preference demonstrated by singlet nitrenes for insertion into tertiary C–H bonds may be indicative of partial cationic development on carbon in the particular transition state, the roughly comparable reactivity of norbornane bridgehead C–H bonds would seem to indicate "that only little, if any, positive charge is created on the carbon in the transition state."[14] Breslow and Schleyer[11b] have noted that nitrene insertion and *t*-butyl perester decomposition (a free-radical reaction) respond in very similar fashion to structural variations and suggest that the observed C–H insertion behavior of nitrenes is most nearly compatible with the free-radical character of the carbon atom involved. The results obtained with tricyclo[5.2.1.0^{4,10}]decane (**1**) are likewise suggestive of partial free radical rather than partial carbonium ion transition state characteristics at the reaction center. Thus, the nearly inflexible geometry of **1** demands that the tertiary carbon atom at C-10 remain in a state of sp^3 hybridization (or nearly so) and precludes the attainment of sp^2 character at that site. Molecular models therefore suggest that development of carbonium ion character at C-10 will be impeded by a significant energy barrier caused chiefly by the conformational rigidity of the molecule. The fact that nitrene insertion into the C$_{10}$-H bond of **1** is not disfavored necessitates the conclusion that the transition state for carbomethoxynitrene insertion is controlled substantially by the capability of the carbon atom to support free radical character.[15]

The reaction of hydrocarbons with chromyl acetate is known to result in oxidation of the substrate. Typically, attack at tertiary C–H bonds is more rapid than attack at methylene groups (methyl groups are quite unreactive), the former process affording alcohols and/or acetates and the latter generally yielding ketones.[18,19]

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[12] After completion of this portion of the work, a synthesis of tricyclo[5.2.1.0^{4,10}]decan-10-ol appeared [J. W. Baum and C. D. Gutsche, *J. Org. Chem.*, **33**, 4312 (1968)]. Although the nmr spectra of this alcohol and **4** are comparable, it is clear that the diamagnetic anisotropy of the carbonyl group in **4** serves to separate more clearly the respective absorptions of the methylene and methine protons.

[13] Although several of these nitrene insertions were performed in the absence of added solvent while others were carried out in methylene chloride solution, the comparison is valid in view of the known lack of solvent dependence established for this reaction; see footnote 13 of ref 11b and W. Lwowski, *Angew. Chem. Intern. Ed. Engl.*, **6**, 897 (1967).

[14] G. T. Tisue, S. Linke, and W. Lwowski, *J. Am. Chem. Soc.*, **89**, 6303 (1967).

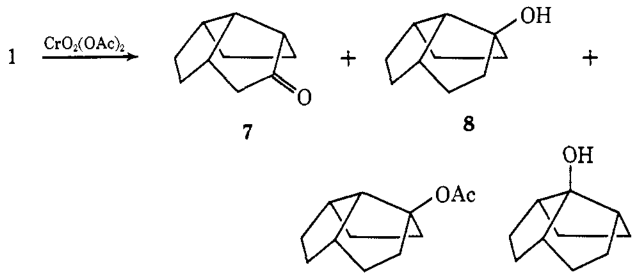
[15] Despite the fact that theoretical considerations predict that the most favorable hybridization for an alkyl radical is sp^3,[16] electron spin resonance investigations of alkyl radicals appear to be best interpreted by postulating a planar geometry.[17] As a result, it would seem that the energy difference between planar and pyramidal configurations of free radicals are much smaller than the energy differences between similar geometries of carbanions and carbonium ions. Therefore, the requirement that the developing free radical at C-10 must maintain tetrahedral character should obviously not be prohibitive.

[16] (a) J. W. Linnett and A. J. Poe, *Trans. Faraday Soc.*, **47**, 1033 (1951); (b) A. D. Walsh, *J. Chem. Soc.*, 2296 (1953).

[17] (a) H. M. McConnel and R. W. Fessenden, *J. Chem. Phys.*, **31**, 1688 (1959); (b) M. Karplus and G. K. Fraenkel, *ibid.*, **35**, 1312 (1961); (c) M. C. R. Symons, *Advan. Phys. Org. Chem.*, **1**, 283 (1963).

[18] R. Stewart, "Oxidation Mechanisms," W. A. Benjamin, Inc., New York, N. Y., 1964, pp 50–55.

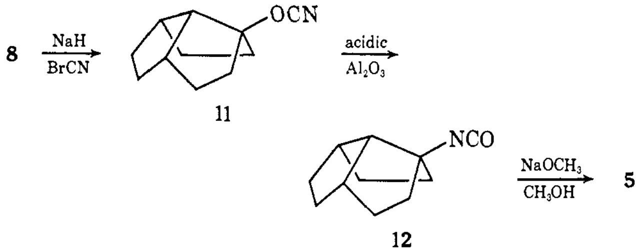
Oxidation of **1** with 2 equiv of chromyl acetate afforded a crude oxidation product containing ketone **7**, alcohol **8**, and acetate **9** in a ratio of 37:51:12 determined by vpc analysis. In addition, there was produced in 8.8% yield a pentane-insoluble bis oxidation product ($C_{10}H_{14}O_2$) which displayed infrared peaks at 1735 and 1700 cm^{-1}, but no bands above 3000 cm^{-1}. Its nmr spectrum was devoid of absorption due to the >CHO– group; this substance gave a negative ferric chloride test and afforded a crystalline product free of carbonyl and hydroxyl infrared absorptions upon Wolff-Kishner reduction, but was not further characterized.[20]



7 **8** **9** **10**

The structure of **7** follows from its elemental analysis, from its infrared carbonyl absorption at 1730 cm^{-1}, and from modified Wolff-Kishner reduction to **1** *via* its semicarbazone. The nmr spectrum of **7** is complex and the patterns of absorption proved not to be resolvable.

Characterization of **8** as a tertiary alcohol was made chiefly on the basis of its nmr spectrum which is free of >CHO– absorption, but which shows a twelve-proton multiplet at δ 1.00–2.25 due to the methylene protons and a broadened singlet pattern centered at δ 2.51 attributable to three methine hydrogens. This alcohol was not identical with authentic tricyclo[5.2.1.$0^{4,10}$]decan-10-ol (**10**)[12] and it was presumed to be the 1-isomer (**8**). This assignment was confirmed by conversion of **8** to its cyanate (**11**) through the agency of sodium hydride and cyanogen bromide, rearrangement of **11** to isocyanate **12** on acidic alumina, and ultimate conversion of **12** to **5** with sodium methoxide in methanol.[21]



11 **12**

The identity of the two urethans was established by spectral methods. The structure of the minor oxidation product (**9**) was readily established by means of lithium aluminum hydride reduction to **8**.

Lithium aluminum hydride reduction of **7** in ethereal solution at −78° afforded in high yield a single crystalline alcohol which, on the grounds of steric approach control,[22] was assigned the *endo* configuration **13**.

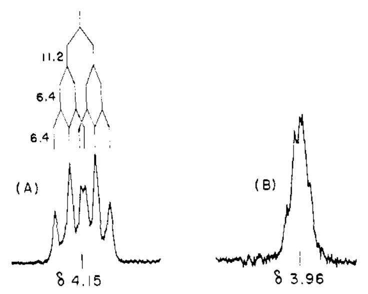
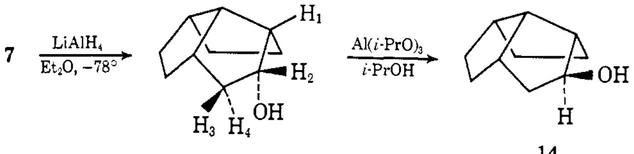


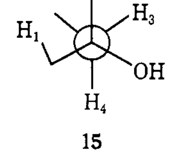
Figure 2. Partial 60-MHz nmr spectra of alcohols **13** (A) and **14** (B) showing the respective carbinol proton absorptions.

Equilibration of **13** with aluminum isopropoxide in isopropyl alcohol at 105–110° for 60 hr[23] gave a mixture of **13** and a new alcohol (**14**) in a ratio of 23:77. The skeletal integrity of **14** was confirmed by chromium trioxide–pyridine reoxidation to **7**. These results are consistent with the fact that *exo* alcohol **14** can be expected to be thermodynamically more stable than *endo* epimer **13** because of nonbonded 1,3 interactions present in the latter structure.



13 **14**

The nmr signal of the >CHO– proton of *endo* alcohol **13** is seen to be a symmetrical six-line multiplet centered at δ 4.15 (Figure 2A). First-order analysis of this pattern reveals appreciable vicinal coupling of H-2 to one proton ($J_{2,4}$ = 11.2 Hz) and additional vicinal spin–spin interaction with H-1 and H-3, each to the extent of 6.4 Hz. Because the magnitude of vicinal coupling constants is sensitive to the dihedral angles adopted by adjacent protons,[24] an analysis of the conformation of **13** seemed possible. The large coupling constant ($J_{2,4}$ = 11.2 Hz) may be explained if the previously mentioned 1,3-interaction of the hydroxyl group and an *endo* hydrogen combines with the energetically unfavorable eclipsing of -OH and H-4 to induce sufficient carbon–carbon bond rotation to give the conformation denoted by part structure **15**. In this conformation, the dihedral angle relationship between H-2 and H-4 approaches 180° which is consistent with the large observed coupling constant. A further direct result of conformation **15** is the near identity of the dihedral angles (approximately 60°) defined by



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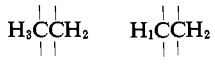

$$H_3\overset{|}{\underset{|}{C}}\overset{|}{\underset{|}{C}}H_2 \qquad H_1\overset{|}{\underset{|}{C}}\overset{|}{\underset{|}{C}}H_2$$

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[19] K. B. Wiberg in "Oxidation in Organic Chemistry," K. B. Wiberg, Ed., Academic Press, New York, N. Y., 1965, Chapter 2.

[20] This substance was not formed in significant yield when **1** was oxidized with 1.5 equiv of chromyl acetate.

[21] J. C. Kauer and W. W. Henderson, *J. Am. Chem. Soc.*, **86**, 4732 (1964).

[22] H. C. Brown and J. Muzzio, *ibid.*, **88**, 2811 (1966), and pertinent references cited therein.

[23] C. F. Wilcox, Jr., M. Sexton, and M. F. Wilcox, *J. Org. Chem.*, **28**, 1079 (1963).

[24] M. Karplus, *J. Chem. Phys.*, **30**, 11 (1959); M. Karplus, *J. Am. Chem. Soc.*, **85**, 2870 (1963).

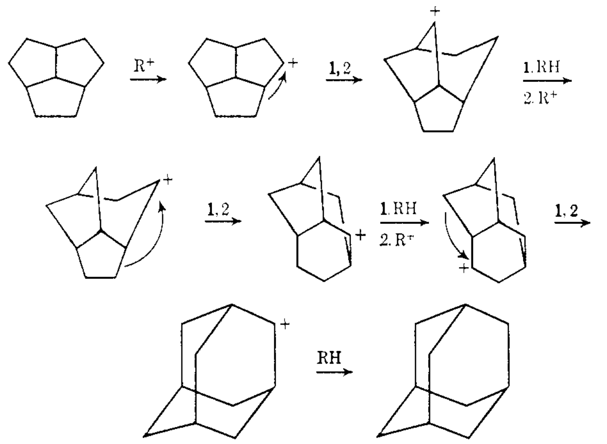
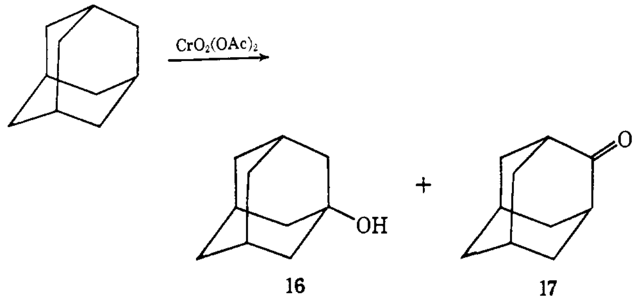


Figure 3. Shortest pathway between **1** and adamantane *via* 1,2 shifts.

in agreement with the fact that $J_{2,3}$ and $J_{1,2}$ are identical (6.4 Hz) and smaller than $J_{2,4}$. Unfortunately, the absorption of the >CHO– proton of **14** appears as a broad, poorly resolved multiplet centered at δ 3.96, which has not proven amenable to analysis (Figure 2B).

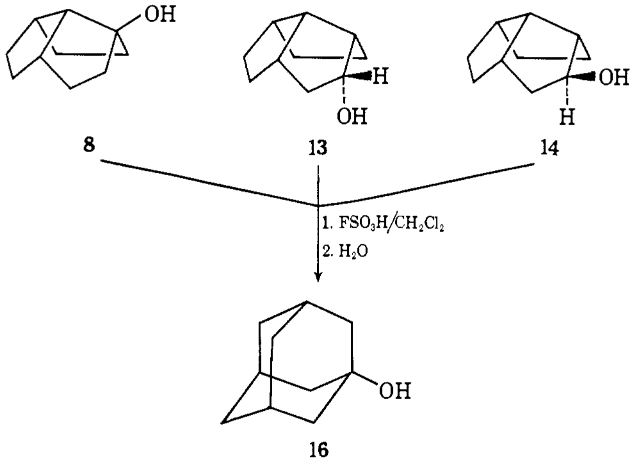
It will be observed that chromyl acetate oxidation of **1** does not result in oxidation at the C-10 methine position. Similar absence of bridgehead methine reactivity has been noted in like oxidation of norbornane,[25] bicyclo[2.2.2]octane,[25] bicyclo[3.2.1]octane,[25] and tricyclo[3.3.0.0^{2,6}]octane.[26] A significantly greater reactivity toward the chromyl acetate reagent is seen at the nonapical tertiary C–H bonds in **1**, oxidation at these three equivalent positions occurring seven times more rapidly (per H) than at the methylene positions. A similar tertiary/secondary reactivity ratio has been observed in the oxidation of adamantane which affords **16** and **17** in yields of 71 and 9%, respectively.[25] This behavior suggests that chromyl acetate oxidation of a hydrocarbon at a given position is controlled by the capability of that carbon atom to become trigonal in the activated complex. Thus, in adamantane where bond angle deformation is absent, the bridgehead site is known to be significantly more reactive in carbonium ion processes than the 2 position.[27] In contrast, the central carbon in **1** is prohibited from achieving sp^2 hybridization (see above); however, since both the nonapical methine positions and the methylene carbons of **1** can attain a trigonal configuration (see below), these positions are reactive in the oxidation. The above considerations lead to a mechanistic picture of the oxidation as one in which significantly greater cationic demands are placed on the reacting carbon at the transition state, at least when compared to nitrene insertion reactions. It could be primarily for this reason that bridgehead sites in strained molecules or constrained sites in strain-free structures are not subject to oxidation.[28]



Structural Rearrangements

Reaction of tricyclo[5.2.1.0^{4,10}]decane (**1**) with excess aluminum chloride in refluxing hexane results in smooth isomerization to adamantane, but at a rate (91% adamantane after 45 hr) somewhat slower than that reported[7] for the similar isomerization of twistane (85% adamantane after 2 hr at 70°). Careful vpc monitoring of the reaction mixture at various time intervals showed only **1** and adamantane to be present; apparently, therefore, no intermediate hydrocarbons were produced in detectable amounts. This observation parallels exactly the behavior of twistane.[7]

Extraction of **8**, **13**, and **14** from methylene chloride solutions into fluorosulfonic acid at –78° effected facile ionization and isomerization of each alcohol to the 1-adamantyl cation. Quenching of the acid solutions with water and isolation of the product by preparative vpc afforded 1-adamantanol (**16**) in each instance. These isomerizations were particularly clean in the sense that no by-products were observable by vpc. In the case of **13**, the 1-adamantanol was accompanied by approximately 20% of unchanged starting alcohol, thereby indicating that adamantanization of **13** is qualitatively more difficult than for its *exo* counterpart **14**.



Clearly, although rearrangement of the tricyclo[5.2.1.0^{4,10}]decane system to the adamantane framework is more facile than adamantanization of tetrahydrodicyclopentadience (THDCP),[29] the isomerization is somewhat less rapid than that observed in the case of twistane.[7] Whitlock has rationalized the slow rate of the THDCP–adamantane interconversion on the basis of the fact that one bridgehead carbonium ion interme-

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[25] P. von R. Schleyer and R. D. Nicholas, Abstracts, 140th National Meeting of the American Chemical Society, Chicago, Ill., Sept 1961, p 75Q.

[26] J. Meinwald and B. E. Kaplan, *J. Am. Chem. Soc.*, **89**, 261, (1967).

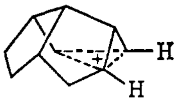
[27] R. C. Fort, Jr., and P. von R. Schleyer, *Chem. Rev.*, **64**, 277 (1964).

[28] K. B. Wiberg and R. Eisenthal have reviewed much of the data on chromyl acetate oxidations prior to 1964 and have concluded that the reacting carbon develops a trigonal configuration with little change in electron distribution [*Tetrahedron*, **20**, 1151 (1964)]. More recent evidence, including the data presented herein, seems to suggest that such oxidations are more closely dependent upon the carbonium ion characteristics of the various sites in a saturated hydrocarbon.

[29] THDCP merely undergoes *endo–exo* isomerization under the conditions outlined in the Experimental Section: P. von R. Schleyer and M. M. Donaldson, *J. Am. Chem. Soc.*, **82**, 4645 (1960).

diate necessarily must be involved.[7] Neither twistane nor **1** suffer from this disadvantage. The shortest pathway between **1** and adamantane involving only 1,2-alkyl shifts is shown in Figure 3. The more rapid aluminum chloride catalyzed isomerization of twistane can logically be traced to its closer proximity to adamantane on the bridgehead-free map of C-10 tricyclic hydrocarbon interconversions.[7]

Since the tricyclo[5.2.1.$0^{4,10}$]decane-adamantane rearrangement is most efficiently triggered by migration of a peripheral rather than an internal carbon–carbon bond (Figure 3), one can nicely rationalize the qualitatively more rapid rearrangement of *exo* alcohol **14** relative to **13** on the basis of significant "nonclassical" σ-bond participation at the transition state (*cf.* **18**).



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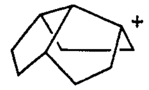

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Finally, attention should be called to the fact that, although alcohol **8** is seen to undero ready adamantanization *via* carbonium ion **19**, it is possible to trap **19** prior to skeletal change. For example, mention has already been made of the alumina-catalyzed rearrangement of cyanate **11** to isocyanate **12**, a transposition which is viewed as heterolytic C–O bond cleavage and rebonding of the nitrogen terminus of the ambident cyanate ion to the carbonium ion center.[30]

Experimental Section[31]

Decomposition of Methyl Azidoformate in 1. **1**[8] (20 g, 0.147 mole) and 1.46 g (0.014 mole) of methyl azidoformate were placed in a sealed tube and heated at 120° for 3.5 hr. The crude solid product (20.4 g) was chromatographed on 150 g of Woelm neutral alumina (activity I). Elution with pentane yielded 17.4 g of recovered **1**, whereas elution with chloroform afforded 2.07 g (71%) of a urethan mixture (four components, vpc analysis). Preparative scale vpc separation (5 ft × 0.25 in. Al column packed with 10% SE-30 on Chromosorb G) afforded pure samples of **4**, **5**, and **6** (*exo* and *endo* isomers).

Urethan **4** was obtained as white crystals: mp 65°; $\nu_{max}^{CCl_4}$ 3380 (NH) and 1730 cm^{-1} (>C=O); $\delta_{TMS}^{CCl_4}$ 1.1–2.1 (symmetrical six-line pattern centered at 1.67, 12 H, methylene protons), 2.10–2.70 (multiplet, 3 H, methine protons), 3.62 (singlet, 3 H, -OCH$_3$), and 5.42 (broad absorption, 1 H, >NH).

Anal. Calcd for $C_{12}H_{19}NO_2$: C, 68.86; H, 9.15; N, 6.69. Found: C, 69.19; H, 8.78; N, 6.61.

Urethan **5** was isolated as white crystals: mp 49.5–51.5°; $\nu_{max}^{CCl_4}$ 3365 (NH) and 1727 cm^{-1} (>C=O); $\delta_{TMS}^{CCl_4}$ 1.10–2.10 (multiplet, 12 H, methylene protons), 2.30–2.90 (multiplet, 3 H, methine protons), 3.60 (singlet, 3 H, -OCH$_3$), and 5.70 (broad absorption, 1 H, >NH).

Anal. Calcd for $C_{12}H_{19}NO_2$: C, 68.86; H, 9.15; N, 6.69. Found: C, 68.82; H, 9.14; N, 6.59.

The mixture of *exo*- and *endo*-urethans **6** was obtained as a white semicrystalline substance: $\nu_{max}^{CCl_4}$ 3378 (>NH) and 1727 cm^{-1} (>C=O); $\delta_{TMS}^{CCl_4}$ 1.00–1.95 (multiplet, 10 H, methylene protons), 1.95–3.00 (multiplet, 4 H, methine protons), 3.5–3.8 (multiplet, 1 H, >C*H*-N<), 3.61 (singlet, 3 H, -OCH$_3$), and 5.70 (broad absorption, 1 H, >NH).

Anal. Calcd for $C_{12}H_{19}NO_2$: C, 68.86; H, 9.15; N, 6.69. Found: C, 68.56; H, 9.39; N, 6.32.

Chromyl Acetate Oxidation of 1. **1** (16 g, 0.118 mole) was added in small portions to a stirred, cooled (ice–isopropyl alcohol) solution of chromyl acetate [prepared from 23.6 g (0.236 mole) of chromium trioxide and a mixture of 118 ml each of acetic acid and acetic anhydride] at such a rate that the temperature did not rise above 5°. After the addition was complete, the reaction mixture was allowed to warm to room temperature, stirred for 30 hr, and 118 ml of water was added slowly with stirring. The mixture was heated at 100° for 2 hr and allowed to cool, when 213 g of sodium hydroxide in 300 ml of water was added slowly with cooling and the products were isolated by extraction with six 300-ml portions of methylene chloride. Evaporation of the solvent *in vacuo* afforded 11.0 g of a semicrystalline material which by trituration with pentane deposited 1.13 g (8.8%) of a white solid. Careful recrystallization of this substance from ether-pentane gave 440 mg of pure bis oxidation product: mp 133–134.5°; $\nu_{max}^{CCl_4}$ 1735 and 1700 cm^{-1}; negative ferric chloride test. This substance was not further characterized.

Anal. Calcd for $C_{10}H_{14}O_2$: C, 72.26; H, 8.49. Found: C, 72.07; H, 8.47.

The original pentane solution was now chromatographed on 120 g of neutral alumina. Elution with hexane afforded 5.68 g (35.5%) of unchanged **1**. Continued elution with chloroform gave 3.32 g of a viscous oil which consisted to **7**, **8**, and **9** in the ratio 36.7:51.6:11.7. Preparative scale vpc separation on the above column yielded the purified constituents.

Alcohol **8** was obtained as a white crystalline solid: mp 98.5–100.5°; $\nu_{max}^{CCl_4}$ 3270 cm^{-1} (-OH); $\delta_{TMS}^{CCl_4}$ 1.00–2.25 (multiplet, 12 H, methylene protons), 2.51 (broad singlet, 3 H, methine protons), and 4.30 (singlet, 1 H, -OH).

Anal. Calcd for $C_{10}H_{16}O$: C, 78.89; H, 10.59. Found: C, 78.99; H, 10.53.

Ketone **7** was isolated as a white crystalline solid: mp 68.5–70.5°; $\nu_{max}^{CCl_4}$ 1730 cm^{-1} (>C=O).

Anal. Calcd for $C_{10}H_{24}O$: C, 79.95; H, 9.39. Found: C, 79.86; H, 9.25.

The semicarbazone of **7** was prepared in 76% yield, mp 187.5–190° dec.

Anal. Calcd for $C_{11}H_{17}N_3O$: C, 63.74; H, 8.27; N, 20.27. Found: C, 63.49; H, 8.29; N, 20.13.

Acetate **9** was not purified. However, a solution of 125 mg (0.65 mmole) of crude **9** in 5 ml of anhydrous ether was added dropwise to a cooled, stirred slurry of 152 mg (4.0 mmoles) of lithium aluminum hydride in 5 ml of anhydrous ether. The reaction mixture was refluxed for 3 hr and worked up by the successive addition of water (0.15 ml), 30% sodium hydroxide (0.15 ml), and water (0.45 ml). After filtration of the salts, the ether was removed to give 96 mg (98%) of a substance identical in all respects with **8**.

In a separate run in which 10.00 g (0.0735 mole) of **1** and 13.00 g (0.13 mole) of chromium trioxide were employed, there was obtained 6.7 g of crude oxidation product. Chromatography of 4.7 g of this material as described above gave 3.45 g (49%) of recovered **1** and a 1.30-g fraction which contained **7**, **8**, and **9** in the ratio 38.4:50.0:11.6.

Wolff-Kishner Reduction of 7. The semicarbazone of **7** (150 mg, 0.725 mmole), 0.10 ml of hydrazine hydrate, and 137 mg (2.45 mmoles) of potassium hydroxide in 5 ml of ethylene glycol were heated in an oil bath at 200° for 3 hr. During this time, a small amount of solid sublimed to the top of the microdistillation apparatus used and was removed by washing with pentane at the end of the reaction. The reaction mixture was diluted with water (20 ml) and extracted with two 20-ml portions of pentane. The combined pentane solutions were washed with water and dried. Most of the solvent was removed by distillation at atmospheric pressure and the residue (*ca.* 1 ml) was submitted to preparative vpc. Only a single volatile product was noted (10 mg) which was identical in all respects with authentic **1**.

Correlation of 8 with Urethan 5. **A.** A solution of 304 mg (2.0 mmoles) of **8** in 5 ml of anhydrous tetrahydrofuran was added dropwise during 30 min to a stirred suspension of 120 mg (5.0 mmoles) of sodium hydride in 5 ml of the same solvent under nitrogen. After the mixture was refluxed for 5 hr, it was cooled to 0° and a solution of 530 mg (5.0 mmoles) of cyanogen bromide in 5 ml of anhydrous tetrahydrofuran was added dropwise during 20 min. After stirring for 1 further hr at room temperature, the salts were filtered and the solvent was removed *in vacuo*. Extraction of the crude residue with pentane removed *ca.* 30 mg of a yellow solid and afforded, after removal of solvent, 320 mg (90%) of a yellow oil which partially crystallized, $\nu_{max}^{CCl_4}$ 2250 cm^{-1} (weak doublet, -OCN).[21]

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[30] J. W. Timberlake and J. C. Martin, *J. Org. Chem.*, **33**, 4054 (1968).

[31] The microanalyses were performed by the Scandinavian Microanalytical Laboratory, Herlev, Denmark, and Galbraith Laboratories, Knoxville, Tenn. The nmr spectra were recorded with Varian A-60 and A-60A spectrometers purchased with funds made available through the National Science Foundation.

B. A 130-mg of sample of the crude cyanate was dissolved in anhydrous ether and this solution was passed down a short (2 × 10 cm) column of acidic alumina. Evaporation of the solvent afforded 40 mg (31%) of a yellowish oil; ν_{max}^{neat} 2242 cm^{-1} (sharp singlet of *ca.* twice the intensity of the doublet at 2250 cm^{-1} in the corresponding cyanate, -N=C=O).

C. The isocyanate (40 mg, 0.23 mmole) was stirred for 15 hr with 2.0 ml (0.23 mmole) of methanolic sodium methoxide [from 61 mg (1.13 mmoles) of sodium methoxide in 10 ml of methanol]. Acetic acid (2 drops) was added and most of the solvent was removed *in vacuo*. Preparative scale vpc purification of the residue (5.5 ft × 0.25 in. Al column packed with 10% SE-30 on Chromosorb G) yielded 6.3 mg of **5**, identical in all respects with material prepared earlier.

***endo*-Tricyclo[5.2.1.0^{4,10}]decan-2-ol (13).** A solution of 150 mg (1.0 mmole) of **7** in 5 ml of anhydrous ether was added dropwise during 10 min to a stirred slurry of 190 mg (5.0 mmoles) of lithium aluminum hydride in 5 ml of the same solvent cooled to −78°. The reaction mixture was stirred at −78° for a further 50 min, allowed to warm to 0°, and worked up as above. There was obtained 150 mg (99%) of a waxy, homogeneous (vpc analysis) solid which was purified by preparative vpc (above column) to give 93 mg (61%) of pure **13**: mp 101–102°; $\nu_{max}^{CCl_4}$ 3345 and 3255 cm^{-1} (-OH); $\delta_{TMS}^{CDCl_3}$ 0.85–2.05 (multiplet, 10 H, methylene protons), 2.05–2.90 (multiplet, 5 H, methine and hydroxyl protons), and 4.15 (symmetrical six-line multiplet, J = 11.2, 6.4, and 6.4 Hz, 1 H, >C*H*OH).

Anal. Calcd for $C_{10}H_{16}O$: C, 78.89; H, 10.59. Found: C, 78.70; H, 10.54.

***exo*-Tricyclo[5.2.1.0^{4,10}]decan-2-ol (14).** A mixture of 65 mg (0.43 mmole) of **13** and 300 mg (1.47 mmoles) of aluminum isopropoxide in 2 ml of dry isopropyl alcohol containing 0.005 ml of acetone was heated in a sealed tube at 105–110° for 60 hr. The cooled contents were dissolved in the minimum quantity of cold 3 *N* hydrochloric acid and the product was extracted with three 10-ml portions of ether. The ether solution was washed with 15 ml of a saturated aqueous sodium bicarbonate solution and two 10-ml portions of water, dried, and evaporated. Vpc analysis showed the presence of two components in the ratio 77:23 with the minor component corresponding in retention time to unchanged **13**. Preparative vpc separation of the crude product (11 ft × 0.25 in. Al column packed with 10% SF-96 on Chromosorb G) afforded 42 mg (65%) of **14**: mp 82–83°; $\nu_{max}^{CCl_4}$ 3560 and 3280 cm^{-1} (-OH); $\delta_{TMS}^{CDCl_3}$ 0.85–2.0 (multiplet, 10 H, methylene protons), 2.0–3.2 (multiplet, 5 H, methine and hydroxyl protons), and 3.83–4.10 (multiplet, 1 H, >C*H*OH).

Anal. Calcd for $C_{10}H_{16}O$: C, 78.89; H, 10.59. Found: C, 78.55; H, 10.49.

Oxidation of 14. Alcohol **14** (10 mg, 0.066 mmole) was added at 0° to the complex prepared from 50 mg (0.5 mmole) of chromium trioxide and 0.5 ml of pyridine. The reaction mixture was stirred under nitrogen for 12 hr during which time it was allowed to warm to room temperature. Ether was added, the chromium salts were removed by filtration, the ether solution was washed with two 20-ml portions of 1 *N* hydrochloric acid and two 20-ml portions of water, dried, and carefully evaporated at atmospheric pressure. The residue was purified by preparative scale vpc (SE-30 column) to give 5.7 mg (58%) of a white solid identical in all respects with authentic **7**.

Isomerization of 1. A mixture of 100 mg (0.735 mmole) of **1** and 1.0 g (7.5 mmoles) of aluminum chloride in 20 ml of purified hexane was stirred at reflux under a nitrogen atmosphere. Aliquots (*ca.* 1 ml) of the reaction mixture were removed at appropriate intervals, shaken with water (1 ml), dried, and analyzed by vpc. Adamantane was found to be the only product of this reaction. A typical time/product distribution result is shown in Table I.

Table I

Time, hr	% **1**	% adamantane
8	45	55
21	20	80
30	13	87
45	9	91

Work-up of the residual reaction mixture after 60 hr afforded a white solid identical in all respects with authentic adamantane.

Rearrangement of 8. Fluorosulfonic acid (3.0 ml) was added dropwise *via* a syringe under a nitrogen atmosphere to a stirred solution of 30 mg of **8** in 5 ml of anhydrous methylene chloride cooled in an acetone–Dry Ice bath. The reaction mixture was stirred vigorously at −78° for 30 min and the methylene chloride layer was removed with a syringe. The acid layer was added slowly to 60 ml of vigorously stirred ice water. The resulting solution was neutralized with solid sodium carbonate and extracted with three 40 ml portions of ether. The ether solution was washed with saturated brine, dried, and carefully evaporated at atmospheric pressure. Vpc analysis of the residual solution (*ca.* 1 ml) showed the presence of a single component. Preparative vpc (above SE-30 column) afforded 7 mg of a crystalline solid, identical in all respects with authentic 1-adamantanol (**16**).

Treatment of **13** (30 mg) in the same manner afforded 6.5 mg of **16**. In this instance, the crude product contained 19% of unchanged **13**.

Similar treatment of **14** (30 mg) yielded 6.0 mg of **16**.