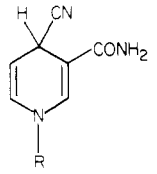
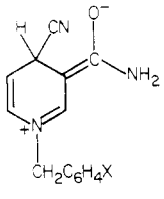


4

$-3.7 \times 0.326 = -1.2$ for X substituents in **3** by making use of the relationship of Ritchie and Sager[8] ($\sigma^*(XC_6H_4CH_2) = 0.326\ \sigma^n(X) + \sigma^*(C_6H_5CH_2)$). We believe that this value for $\rho$, which is somewhat more negative than our result, is less reliable than the $\rho$ values of eq 2 and 3 of the current work. The earlier work is based upon data for **4** (R = $CH_3$, $CH_3(CH_2)_2$, $C_6H_5CH_2$, 2,6-$Cl_2C_6H_3CH_2$, 4-$NO_2C_6H_4CH_2$, and 2-Cl-4-$NO_2C_6H_3CH_2$). For only three of these substituents (R = $CH_3$, $CH_3(CH_2)_2$, and $C_6H_5CH_2$) are both equilibrium constants and $\sigma^*$ values known with certainty. For R = 4-$NO_2C_6H_4CH_2$ and 2-Cl-4-$NO_2C_6H_3CH_2$, the equilibrium constant is admitted to be uncertain due to relatively rapid secondary reactions with these substituents. For R = 2,6-$Cl_2C_6H_3CH_2$ and 2-Cl-4-$NO_2C_6H_3CH_2$, only rough estimates of appropriate $\sigma^*$ values were available. Furthermore, for the above six R groups one cannot assume with certainty that variable solvation effects do not play a role in charge stabilization for the nicotinamide cations.

The values of $\rho = -0.88$ and $-0.95$ in eq 2 and 3 are somewhat smaller than the related $\rho$ values in Table I. This suggests that the net change in charge on N-1 in the current reaction is somewhat less than that in the reactions of Table I. In making such comparisons, it is important to keep in mind that, although the reactions of Table I and eq 1 are written as formally involving a nitrogen atom bearing a unit positive charge, the true electron deficiency of such nitrogen atoms will actually be smaller than +1 because of intramolecular electron polarization and charge neutralization by the dipoles of solvating molecules. It is exactly these factors which require comparisons of kinetic and equilibrium $\rho$ values to be made only for systems which resemble one another as closely as possible. For the reaction of eq 1, we note that **5** may be an important



5

resonance contributor to the electronic structure of the neutral cyanide adducts **3**. A significant contribution from **5** would reduce the magnitude of the net change in formal positive charge upon formation of the nicotinamide cations and so consequently reduce the magnitude of the $\rho$ value for X substituents in the *N*-benzyl group.

## Experimental Section

**Materials.** The bromide salts of 1-(substituted benzyl)-nicotinamide cations were synthesized by refluxing nicotinamide with the appropriate substituted benzyl bromide in acetone. The products were recrystallized several times from ethanol and characterized by $^1H$ NMR spectroscopy and molecular-weight determination by Volhard titration of bromide ion as X, mp dec, exptl mol wt (calcd mol wt): 4-$CH_3$, 238–239 °C, 309.1 (307.2); H, 206–208 °C (lit.[9] 205 °C), 291.6 (293.0); 4-F, 246–247 °C (lit.[10] 247–249 °C), 313.6 (311.2); 4-Br, 263–264 °C; 3-F, 240–241 °C, 312.3 (311.2); 3-CN, 256–258 °C, 321.1 (318.2); 4-CN, 275–276 °C, 319.3 (318.2).

Spectroscopic-grade acetonitrile was used for the preparation of acetonitrile–water mixtures. Potassium hydroxide, potassium cyanide, and potassium chloride were the best commercially available grades.

**Dissociation constants,** $K = [2][^-CN]/[3]$, were measured by the general method of Lindquist and Cordes[7] at pH 11.3 (KOH), 25 °C, and ionic strength 1.0 (KCl + KCN) in both water and 20% acetonitrile–80% water. The absorbances of solutions containing mixtures of nicotinamide cation ($8 \times 10^{-5}$ M) and cyanide ion were recorded as a function of time at 340 nm on a Varian Cary 210 spectrophotometer. At this wavelength, the absorbance initially increases due to formation of the cyanide adducts **3**, becomes constant after 2–7 min, depending upon the X substituent and the cyanide concentration, and then undergoes subsequent slower changes due to various base-catalyzed decomposition reactions. Detailed spectroscopic studies have shown[7] that the initial adsorbance increase is due to the formation of **3**. For each nicotinamide cation, the constant absorbance ($A$) at 340 nm was recorded at about eight cyanide ion concentrations in the range $[^-CN] = 0.04$–$0.5$ M for aqueous solutions and $[^-CN] = 0.004$–$0.1$ M for 20% acetonitrile–80% water. Values of $K$ were then evaluated[7] from the reciprocals of the slopes of plots of $-A/[^-CN]$ vs. $A$. The absorbance at 340 nm of each nicotinamide cation is negligible at the concentrations used in the present study.

**Registry No.** **3** (X = 4-$CH_3$), 75420-69-8; **3** (X = H), 19432-61-2; **3** (X = 4-F), 75420-70-1; **3** (X = 4-Br), 75420-71-2; **3** (X = 3-F), 75420-72-3; **3** (X = 3-CN), 75420-73-4; **3** (X = 4-CN), 75420-74-5.

(8) C. D. Ritchie and W. F. Sager, *Prog. Phys. Org. Chem.*, **2**, 323 (1964).

(9) J. A. Gautier and J. Renault, *C. R. Hebd. Seances Acad. Sci.*, **226**, 1736 (1948).

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# Unusual Long-Range Cyclopropyl Participation in 1-Substituted *exo*-Tricyclo[3.2.1.$0^{2,4}$]octanes

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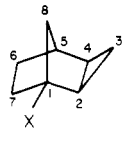
Our recent interest in inductive withdrawal by cyclopropanes[1] and continuing studies by a number of groups[2] on long-range effects of cyclopropane rings have prompted us to study 1-substituted *exo*- and *endo*-tricyclo[3.2.1.$0^{2,4}$]octanes **1** and **2**. Our earlier work on 4-substituted nortricyclenes[1] has convinced us that, especially in bridged bicyclic compounds, there is appreciable electron withdrawal by a cyclopropane when placed at a position which is $\gamma$ or $\delta$ from a reaction center. An increase in the acidity of carboxylic acids and a decrease in acetolysis rates of tosylates were the experimental proofs used. Since isolated inductive withdrawal with no apparent homoallylic or homobenzylic participation of double bonds



1

2

(1) Chenier, P. J.; McClure, J. R.; Golembeski, D. J. *J. Org. Chem.* **1978**, *43*, 4306–4310.

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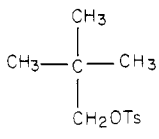
or aromatic rings has been successfully studied for 1-substituted norbornenes,[3,4] benzonorbornenes,[5] benzonorbornadienes,[6,7] and dibenzonorbornadienes,[7] we wondered if such isolated induction of a cyclopropane might also be studied with the ring fused to the 2,3 position of 1-substituted norbornanes.

The effect of a cyclopropane ring on the 8 position of tricyclo[3.2.1.$0^{2,4}$]octanes is quite dramatic, causing the *anti*-8-*endo*-tricyclo[3.2.1.$0^{2,4}$]octyl *p*-nitrobenzoate to solvolyze $10^{12}$ times faster than *anti*-8-*exo*-tricyclo[3.2.1.$0^{2,4}$]octyl *p*-nitrobenzoate.[8] Participation by the edge of this cyclopropane ring is even better than a double bond or aromatic ring similarly situated. Less dramatic but interesting rate increases for exo 6-substituents in solvolyses have been observed for this ring system when the cyclopropane ring is exo or endo.[9]

We therefore decided to test the only homocyclopropylcarbinyl ions in this tricyclic system not yet studied, those derived from the solvolysis of *exo*- and *endo*-tricyclo[3.2.1.$0^{2,4}$]octyl-1-carbinyl tosylates (1-$CH_2OTs$ and 2-$CH_2OTs$). The cyclopropane ring in these systems has severe geometric constraint and the ring is held at a fixed angle with the primary carbon. It is of interest therefore to compare these solvolytic rates and products to those of neopentyl tosylate **3** and related tosylates **4** and **5**. These three systems have been previously studied[10-12] and the cyclopropane ring of **5** has been shown to participate to a small extent.



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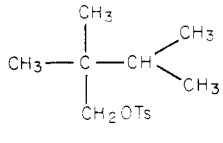

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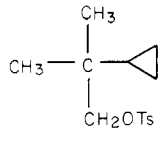
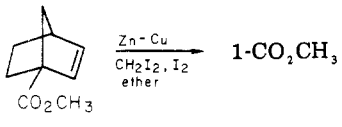


**5**

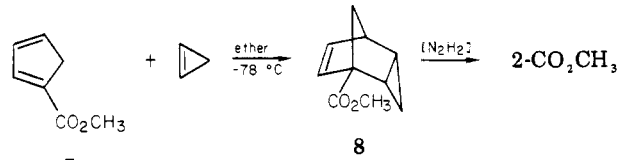
Methyl norbornene-1-carboxylate (**6**) proved to be a




**6**

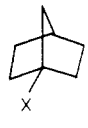
convenient precursor[13,14] for the exo ester 1-$CO_2CH_3$. The Simmons–Smith reaction[15] of ester **6** with zinc–copper couple, methylene iodide, and iodine in ether at reflux for 48 h gave a 53% yield of hitherto unknown adduct 1-$CO_2CH_3$, found to be only the exo isomer (as expected[15]) by GC, IR, and NMR.[16] Saponification gave acid 1-COOH. Lithium aluminum hydride reduction of ester 1-$CO_2CH_3$ yielded alcohol 1-$CH_2OH$. Reaction of alcohol 1-$CH_2OH$ with tosyl chloride in pyridine gave tosylate 1-$CH_2OTs$.

The endo system **2** was conveniently synthesized by taking advantage of the fact that cyclopentadiene and some of its derivatives react with cyclopropene to give Diels–Alder adducts which are exclusively endo.[17] Although methyl cyclopentadiene-1-carboxylate (**7**) dimerizes readily at 25 °C, a new procedure for its synthesis[13] and a good method of generating cyclopropene[18,19] made this route attractive. Freshly cracked ester **7** reacts with excess cyclopropene at −78 °C in ether to give a 20–47% yield of endo adduct **8**. Diimide reduction of the double bond gave endo ester 2-$CO_2CH_3$ from which acid 2-COOH, alcohol 2-$CH_2OH$, and tosylate 2-$CH_2OTs$ were readily obtained.




**7** **8**

The p$K_a$'s of acids 1-COOH and 2-COOH were determined in 50% ethanol at 28 °C along with that of norbornane-1-carboxylic acid (**9**-COOH). Results are found




**9**

in Table I. although the change in the acidity is small, the cyclopropane ring has a definite acid strengthening effect due to slight inductive withdrawal in 1-COOH and 2-COOH. This inductive effect is apparently not as strong as the withdrawal by the double bond in norbornene-1-carboxylic acid or by the aromatic ring in benzonorbornene-1-carboxylic acid, which have lower p$K_a$'s of 5.98 and 5.88, respectively.[5]

Kinetic studies of 1-$CH_2OTs$, 2-$CH_2OTs$, and **9**-$CH_2OTs$ in glacial acetic acid buffered with sodium acetate are summarized in Table II. Extrapolation of the data to 25 °C and comparison with neopentyl-like tosylates **3**, **4**, and **5** is given in Table III. Of utmost importance is the fact that, although the *endo*-tosylate 2-$CH_2OTs$ solvolyzes very near the rate of norbornyl-1-carbinyl tosylate, there is

Table I. p$K_a$ Studies at 28 °C

| acid | p$K_a$ ± 0.01 |
|---|---|
| norbornane-1-carboxylic, 9-COOH | 6.35[a] |
| *exo*-1-COOH | 6.25 |
| *endo*-2-COOH | 6.15 |

[a] Reference 5 reported a value of 6.37 at 25 °C.

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(9) (a) Wiberg, K. B.; Wenzinger, G. R. *J. Org. Chem.* **1965**, *30*, 2278–2284. (b) Colter, A. K.; Musso, R. C. *Ibid.* **1965**, *30*, 2462–2464. (c) Berson, J. A.; Bergman, R. G.; Clarke, G. M.; Wege, D. *J. Am. Chem. Soc.* **1968**, *90*, 3236–3238. (d) Berson, J. M.; Bergman, R. G.; Clarke, G. M.; Wege, D. *Ibid.* **1969**, *91*, 5601–5613.
(10) Winstein, S.; Marshall, H. *J. Am. Chem. Soc.* **1952**, *74*, 1120–1126.
(11) McElrath, E. N.; Fritz, R. M.; Brown C.; Le Gall, C. Y.; Duke, R. B. *J. Org. Chem.* **1960**, *25*, 2195–2200.
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(16) See the Experimental Section.
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We thank Professor Y. E. Rhodes for furnishing details and spectra.

Table II. Acetolysis Rates

| tosylate | temp,[a] °C | $k$,[b] $s^{-1}$ | $\Delta H^{\ddagger}$, kcal/mol | $\Delta S^{\ddagger}$, eu |
|---|---|---|---|---|
| *exo*-1-$CH_2OTs$ | 99.4 ± 0.1 | (8.70 ± 0.53) × $10^{-5}$ | 26.64 | −6.04 |
| | 129.9 ± 0.2 | (1.43 ± 0.08) × $10^{-3}$ | | |
| *endo*-2-$CH_2OTs$ | 99.9 ± 0.5 | (1.80 ± 0.26) × $10^{-5}$ | 27.78 | −6.26 |
| | 130.3 ± 0.2 | (0.323 ± 0.038) × $10^{-3}$ | | |
| norbornyl, 9-$CH_2OTs$[c] | 99.6 ± 0.3 | (1.58 ± 0.04) × $10^{-5}$ | 27.23 | −7.82 |
| | 130.2 ± 0.2 | (0.280 ± 0.007) × $10^{-3}$ | | |

[a] Error expressed as a standard deviation. [b] Error expressed at the 95% confidence level. All correlation coefficients were ≥0.992. [c] Reference 5 gives (0.27 ± 0.01) × $10^{-3}$ $s^{-1}$ at 133.0 °C and (1.13 ± 0.12) × $10^{-5}$ $s^{-1}$ at 99.5 °C for 9-$CH_2OTs$. Reference 26 gives 1.17 × $10^{-5}$ $s^{-1}$ at 99.7 °C.

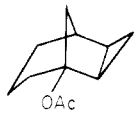
Table III. Relative Acetolysis Rates at 25 °C

| tosylate | $k_{rel}$ |
|---|---|
| *exo*-1-$CH_2OTs$[a] | 174 |
| *endo*-2-$CH_2OTs$[a] | 22.9 |
| norbornyl, 9-$CH_2OTs$[a] | 26.3 |
| c-$C_3H_5$-$C(CH_3)_2CH_2OTs$, **5**[b,c] | 141 |
| *i*-$C_3H_7$-$C(CH_3)_2CH_2OTs$, **4**[b,d] | 13.5 |
| $CH_3C(CH_3)_2CH_2OTs$, **3**[b,d] | 1.00 |

[a] This work. [b] Assuming $k_{OTs} = k_{OBs}/2.9$. [c] Reference 12. [d] Reference 11.

appreciable anchimeric assistance by an *exo*-cyclopropane ring. The exo/endo ratio at 25 °C is 7.6 and at 130.0 °C it is 4.6. It is interesting to note that the *exo*-cyclopropyl system in 1-$CH_2OTs$ is even faster than a plain cyclopropane ring substituted on the neopentyl group, as in **5**, although certainly some of this assistance is due to relief of ring strain in the norbornyl-type structure. But the severely geometrically constrained *exo*-cyclopropane ring still assists the ionization of the tosylate appreciably!

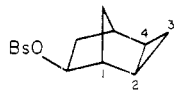
Product studies also prove unequivocally the participation by the *exo*-cyclopropane ring of 1-$CH_2OTs$, in contrast to no participation by the *endo*-cyclopropane ring of 2-$CH_2OTs$. Table IV lists the one major acetate product formed from each solvolysis in refluxing acetic acid with sodium acetate buffer after 10 half-lives or more. All three tosylates studied showed obvious ring expansion because of the lack of downfield NMR absorption characteristic of primary acetates. Acetates **11** and **12** were confirmed by comparison with the literature.[14a,19] For *exo*-tosylate 1-$CH_2OTs$, the major product is definitely not that which would have been formed from methano or ethano bridge expansion, namely, acetate **11** or **13**, by comparison of the



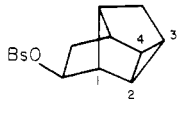

**13**

actual product with either the known acetates or their alcohols.[19] The major product is acetate **10**, formed by cyclopropano bridge expansion.

These kinetic and impressive product studies are in accord with participation by the cyclopropane ring during solvolysis. While "edge" participation by the cyclopropane ring is quite dramatic and also quite common in homocyclopropylcarbinyl systems and "face" participation has been shown not to exist, "corner" or "end-on" participation has been observed only rarely. It has been found to be effective though to a lesser extent than edge participation.[2] Molecules such as **14**[9] and **15**[20] display this type of corner

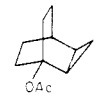
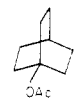



**14**



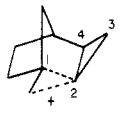

**15**

Table IV. Acetolysis Products

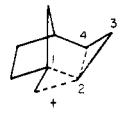
| tosylate | major product | percentage |
|---|---|---|
| *exo*-1-$CH_2OTs$ |  **10** | ≥95 |
| *endo*-2-$CH_2OTs$ |  **11** | ≥99 |
| norbornyl, 9-$CH_2OTs$[a] |  **12** | ≥98 |

[a] Reference 14a reported the same major product.

participation. The developing p orbital in these two brosylates does not interact with the edge of the three-membered ring, presumably because of the distortion that would be required. Instead, these two brosylates undergo assistance at the C-2 corner by the strategically placed back lobe of the 2,3 bond. We believe *exo*-1-$CH_2OTs$ also involves a rare corner participation since this geometrically constrained system would also be highly distorted by edge participation. Solvolysis probably occurs via an ion such as **16** or **17**, where the 2,4 bond aids the tosylate in leaving.

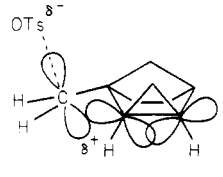



**16**




**17**

Models suggest that the back lobe of the 2,4 bond is in an excellent position to stabilize a developing positive charge on the primary carbon, as shown in structure **18**. It is




**18**

interesting to note that, although most cyclopropanes undergo electrophilic ring opening by edge attack, La Londe has found that this same 2,4 bond in *exo*-tricyclo-[3.2.1.$0^{2,4}$]octane prefers to be protonated by sulfuric acid-$d_2$ via an end-on or corner attack,[21] since the edge of

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the 2,4 bond is sterically hindered by the U-shaped environment of the endo face of the molecule. It is therefore reasonable to suggest that a proximate developing positive charge should take advantage of the back lobe of the 2,4 bond and be stabilized by such corner participation.[22]

## Experimental Section

Melting and boiling points are uncorrected. The melting points were taken on a Thomas-Hoover apparatus. The following instruments were used: a Varian T-60 NMR spectrometer, Perkin-Elmer 727 and 283 infrared spectrophotometers, and Varian Aerograph A-90-P and 700 Autoprep gas chromatographs. NMR data are given in parts per million ($\delta$) relative to internal $Me_4Si$. Only significant IR absorptions ($cm^{-1}$) are listed. Gas chromatography was performed on SE-30 and QF-1 columns with helium carrier gas. Microanalyses were performed by Micro-Tech Laboratories, Skokie, IL.

**Methyl Norbornene-1-carboxylate (6).** The ester was prepared from the acid by reaction with diazomethane according to the literature method,[14a] bp 59–62 °C (2 mm) [lit. bp 48–49 °C (0.15 mm),[14a] 40 °C (2.5 mm)[13]].

**Methyl *exo*-Tricyclo[3.2.1.$0^{2,4}$]octane-1-carboxylate (1-$CO_2CH_3$).** Zinc–copper couple[23] (9.81 g, 150 mmol), iodine (1.0 g), and anhydrous ether (40 mL) were stirred until the iodine color faded. Methylene iodide (22.7 g, 84.8 mmol) and ester **6** (10.75 g, 70.7 mmol) were added and washed down with anhydrous ether (10 mL). The mixture was magnetically stirred and refluxed for 48 h. The mixture was cooled and filtered and the filtrate was washed with saturated ammonium chloride (50 mL), twice with sodium bicarbonate (50 mL), and water (50 mL). The solution was dried with anhydrous magnesium sulfate and filtered, and the filtrate was evaporated. Vacuum distillation of the product gave a colorless oil (6.18 g, 37.2 mmol, 53%): bp 63–73 °C (1.0–1.3 mm); IR (neat) 3070 (cyclopropyl CH), 1728 (C=O), 1266 (asymmetric C—O), 1076 (symmetric C—O) $cm^{-1}$; NMR ($CCl_4$) $\delta$ 3.63 (s, 3, $CH_3O$), 2.2–2.4 (m, 1, bridgehead), 0.8–1.8 (m, 6, $CH_2$), −0.2–0.7 (m, 4, cyclopropyl). Gas chromatography (QF-1, 134 °C) showed trace impurities. An analytical sample was collected by GC. Anal. Calcd for $C_{10}H_{14}O_2$: C, 72.26; H, 8.49. Found: C, 72.29; H, 8.62.

***exo*-Tricyclo[3.2.1.$0^{2,4}$]octyl-1-carbinyl Tosylate (1-$CH_2OTs$).** Alcohol 1-$CH_2OH$ was formed by treating ester 1-$CO_2CH_3$ (4.48 g, 27.0 mmol) with lithium aluminum hydride (2.05 g, 54.0 mmol) in anhydrous ether (90 mL) under reflux for 2 h in the normal fasion.[24] Vacuum distillation of the product gave a colorless oil (2.32 g, 16.8 mmol, 62%): bp 72–78 °C (1.5–1.7 mm); IR (neat) 3340 (OH), 3065 (cyclopropyl CH), 1025 $cm^{-1}$ (C–O); NMR ($CCl_4$) $\delta$ 3.67 (s, 2, $CH_2O$), 3.50 (s, 1, OH), 2.2–2.3 (m, 1, bridgehead), 1.1–1.9 (m, 4, $CH_2$), −0.1–1.1 (m, 6, $CH_2$ and cyclopropyl).

Alcohol 1-$CH_2OH$ was converted into tosylate 1-$CH_2OTs$ without further purification. In the usual manner[25] alcohol 1-$CH_2OH$ (2.26 g, 16.4 mmol) was treated with tosyl chloride (0.40 g, 33.6 mmol) in pyridine (35 mL) at 0 °C overnight. Purification by ether extraction gave the crude white solid (4.35 g, 14.9 mmol, 91%). Pure material was obtained by six recrystallizations from petroleum ether (bp 30–60 °C): mp 57–59 °C; IR (neat) 1601 (C=C), 1365 and 1179 (S=O) $cm^{-1}$; NMR ($CDCl_3$) $\delta$ 7.2–8.0 (AA'XX', 4, Ar H), 4.17 (s, 2, $CH_2O$), 2.43 (s, 3, $CH_3$), 2.2–2.3 (m, 1, bridgehead), 1.2–1.7 (m, 4, $CH_2$), −0.1–1.1 (m, 6, $CH_2$ and cyclopropyl). Anal. Calcd for $C_{16}H_{20}SO_3$: C, 65.72; H, 6.89. Found: C, 65.74; H, 6.79.

***exo*-Tricyclo[3.2.1.$0^{2,4}$]octane-1-carboxylic Acid (1-COOH).** Ester 1-$CO_2CH_3$ (1.25 g, 7.53 mmol) was saponified with 10% sodium hydroxide (30 mL) under reflux for 3 h. Acidification with concentrated hydrochloric acid at 0 °C and filtration gave a white solid (0.88 g, 5.79 mmol, 77%). Three recrystallizations from petroleum ether (bp 20–40 °C) gave the pure material: mp 39–40 °C; IR (KBr) 2500–3500 (OH), 1702 (C=O), 1312 (C—O) $cm^{-1}$; NMR ($CDCl_3$) $\delta$ 12.0 (s, 1, COOH), 2.2–2.3 (m, 1, bridgehead), 0.8–2.0 (m, 6, $CH_2$), −0.1–0.7 (m, 4, cyclopropyl). Anal. Calcd for $C_9H_{12}O_2$: C, 71.03; H, 7.95. Found: C, 71.47; H, 7.87.

**Norbornane-1-carboxylic acid (9-COOH)** was made by hydrogenation of norbornene-1-carboxylic acid (6-COOH) by the literature method,[14a] mp 109–110 °C [lit. mp 111–112 °C,[14a,b] 113.8–115.5 °C[26]].

**Norbornyl-1-carbinyl tosylate (9-$CH_2OTs$)** was made from the corresponding acid by the literature method, [14a,26] mp 76–77 °C [lit. mp 76–78 °C,[14a] 78.9–80 °C[26]].

**Methyl cyclopentadiene-1-carboxylate (7)** was prepared by the published procedure,[13] bp 60–69 °C (4.0 mm) [lit.[13] bp 60–62 °C (5 mm)], and contained a small percentage of methyl cyclopentadiene-2-carboxylate but was suitable for the reactions below. Monomer **7** rapidly dimerizes at room temperature and must be freshly distilled and kept at liquid nitrogen temperatures when used for the following synthesis.

**Methyl *endo*-Tricyclo[3.2.1.$0^{2,4}$]oct-6-ene-1-carboxylate (8).** Ester **7** (10.27 g) was freshly recracked and vacuum distilled through a small Vigreux column and collected (9.57 g, 77.2 mmol) at liquid nitrogen temperatures in a three-necked 500-mL flask. A cyclopropene generator was set up, using a scale of 200 g of sodium amide and 425 mL of allyl chloride.[19] Ester **7** was dissolved and magnetically stirred in anhydrous ether (300 mL) which was precooled to −78 °C. Generation of cyclopropene commenced immediately and it was bubbled through the solution of **7** at −78 °C for 4 h during the addition of allyl chloride to sodium amide. The resulting solution was stirred for an additional 2 h at −78 °C and allowed to warm slowly overnight. Evaporation of the ether and vacuum distillation of the product gave adduct **8** as a colorless oil (2.51 g, 15.3 mmol, 20%), bp 53–63 °C (2.2–2.4 mm), and a higher boiling fraction, bp 63–126 °C (1.6–2.4 mm), which solidified and was identified as the dimer of **7**. Gas chromatographic analysis (QF-1, 128 °C) showed that the main isomer **8** was contaminated with a second isomer in a ratio of 87.3:12.7. The mixture of the two esters can be used for the reactions below. For purposes of identification the two isomers were separated by GC and the minor isomer was identified as methyl *endo*-tricyclo[3.2.1.$0^{2,4}$]oct-6-ene-6-carboxylate (**20**), formed by reaction of methyl cyclopentadiene-2-carboxylate with cyclopropene.

Ester **8**: IR (neat) 3072 (cyclopropyl CH), 1741 (C=O), 1601 (very weak, C=C), 1277 (asymmetric C—O), 1121 (symmetric C—O) $cm^{-1}$; NMR ($CCl_4$) $\delta$ 5.6–5.9 (m, 2, vinyl), 3.67 (s, 3, $CH_3O$), 2.7–2.9 (m, 1, bridgehead), 2.1–2.3 (d of d, 1, H of C-8 syn to C=C), 1.3–2.0 (m, 3, two cyclopropyl CH and H on C-8 syn to cyclopropyl), 0.3–0.8 (m, 2, cyclopropyl $CH_2$). Anal. Calcd for $C_{10}H_{12}O_2$: C, 73.15; H, 7.37. Found: C, 73.10; H, 7.32.

Ester **20**: IR (neat) 3070 (cyclopropyl CH), 1720 (conjugated C=O), 1600 (medium, C=C), 1279 (asymmetric C—O), 1090 (symmetric C—O) $cm^{-1}$; NMR ($CCl_4$) $\delta$ 6.4–6.6 (m, 1, vinyl), 3.63 (s, 3, $CH_3O$), 3.0–3.3 (m, 1, bridgehead next to $CO_2CH_3$), 2.7–2.9 (m, 1, bridghead), 1.8–2.0 (m, 2, two H on C-8), 1.3–1.6 (m, 2, two cyclopropyl CH), 0.1–0.7 (m, 2, cyclopropyl $CH_2$). Anal. Calcd for $C_{10}H_{12}O_2$: C, 73.15; H, 7.37. Found: C, 72.97; H, 7.34.

**Methyl *endo*-Tricyclo[3.2.1.$0^{2,4}$]octane-1-carboxylate (2-$CO_2CH_3$).** Potassium azodicarboxylate was prepared fresh by Thiele's method.[27] By the general procedure of Baird, Franzus, and Surridge[28] ester **8** (5.70 g, 34.8 mmol) and potassium azodicarboxylate (23.5 g, 122 mmol) in anhydrous methanol (100 mL) were reacted with acetic acid (14.6 g, 244 mmol) in methanol (50 mL) over 1 h. The usual purification procedure and vacuum

(22) A referee has suggested an alternate explanation of the kinetic results involving relief of interaction between the hydrogens at C-8 and C-3 in 1-$CH_2OTs$ due to the boat-like shape of the ring system. Tosylate **19** is now being studied in order to determine the effect of relieving this interaction of flagpole-like hydrogens.

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distillation gave 2-$CO_2CH_3$ as a colorless oil (2.9 g, 17.5 mmol, 50%): bp 62–64 °C (4.5–5.0 mm); IR (neat) 3075 (cyclopropyl CH), 1738 (C=O), 1272 (asymmetric C—O), 1088 (symmetric C—O) $cm^{-1}$; NMR ($CCl_4$) δ 3.57 (s, 3, $CH_3O$), 0.4–2.7 (m, 11). No exo ester 1-$CO_2CH_3$ was found to be present. An analytical sample was collected by GC (QF-1, 132 °C). Anal. Calcd for $C_{10}H_{14}O_2$: C, 72.26; H, 8.49. Found: C, 71.82; H, 8.37.

***endo*-Tricyclo[3.2.1.0$^{2,4}$]octyl-1-carbinyl Tosylate (2-$CH_2OTs$).** Alcohol 2-$CH_2OH$ was made by lithium aluminum hydride reduction of ester 2-$CO_2CH_3$. Vacuum distillation gave a 79% yield of a colorless oil: bp 82–94 °C (2.0 mm); IR (neat) 3330 (OH), 3070 (cyclopropyl CH), 1013 (C–O) $cm^{-1}$. The crude alcohol was treated with tosyl chloride and pyridine and tosylate 2-$CH_2OTs$ was formed in 82% yield after one recrystallization from petroleum ether (bp 30–60 °C). Seven recrystallizations gave a pure sample: mp 81.5–83 °C; NMR ($CDCl_3$) δ 7.2–8.0 (AA'XX', 4, Ar H), 4.17 (s, 2, $CH_2O$), 2.43 (s, 3, $CH_3$), 2.2–2.3 (m, 1, bridgehead), 0.6–2.1 (m, 10). Anal. Calcd for $C_{16}H_{20}SO_3$: C, 65.72; H, 6.89. Found: C, 65.62; H, 6.91.

***endo*-Tricyclo[3.2.1.0$^{2,4}$]octane-1-carboxylic Acid (2-COOH).** Ester 2-$CO_2CH_3$ was saponified with 10% sodium hydroxide under reflux for 3 h to give a 68% yield of acid 2-COOH. Purification can be accomplished by chromatography on silica gel with chloroform as eluant or by recrystallization from petroleum ether (bp 30–60 °C). Three recrystallizations gave a pure sample: mp 98–98.5 °C; IR (KBr) 2500–3600 (OH), 1687 (C=O), 1294 (C—O) $cm^{-1}$; NMR ($CDCl_3$) δ 12.1 (s, 1, COOH), 0.6–2.5 (m, 11). Anal. Calcd for $C_9H_{12}O_2$: C, 71.03; H, 7.95. Found: C, 70.91; H, 7.96.

**p$K_a$ Studies.** The p$K_a$ of acids 1-COOH, 2-COOH, and 9-COOH was taken by dissolving 0.30 mmol in 50% ethanol (50 mL, 1:1 absolute ethanol–distilled water, v/v) and titrating with 0.05 N aqueous sodium hydroxide at ambient temperature while the pH was measured vs. increments of base added. The p$K_a$ was obtained from the pH at the half-neutralization point. Results are given in Table I.

**Kinetic Studies.** Standard procedures were followed for the acetolysis studies. Standardized 0.05 M sodium acetate in glacial acetic acid containing 0.3% acetic anhydride was the solvent, with a tosylate concentration of 0.025 M. Aliquots (2 mL) were sealed in ampules and heated to the reaction temperature. The excess sodium acetate was back titrated in the ampule with standard 0.014 *p*-toluenesulfonic acid in acetic acid, using bromophenol blue indicator (yellow to colorless end point). The first-order plots were linear to at least 75% completion. Infinity titers were at least 94%. All correlation coefficients were at least 0.992. Results are given in Tables II and III.

**Acetolysis Products.** All three tosylates were studied by dissolution in acetic acid with 2 equiv of anhydrous sodium acetate and refluxing for a number of half-lives. Water was added and the products were extracted with ether. The combined ether layers were washed with 10% sodium bicarbonate, water, and brine. The resulting solution was dried with anhydrous magnesium sulfate and filtered, and the filtrate was rotary evaporated. Only one major product of each tosylate was found, as shown in Table IV.

For the products of *exo*-tosylate 1-$CH_2OTs$ gas chromatography (SE-30, 157 °C, and QF-1, 124 and 151 °C) showed two acetates with ratios varying from 99.0:1.0 to 95.4:4.6. The mixture was vacuum distilled, bp 66–67 °C (1.0 mm), and a pure sample was obtained by GC. Anal. Calcd for $C_{11}H_{16}O_2$: C, 73.30; H, 8.95. Found: C, 73.37; H, 8.83. NMR analysis of the major product indicated that a tertiary acetate was apparent. Comparison of its spectrum with that of known acetate **11**[19] conclusively eliminated this structure: IR (neat) 3085 (cyclopropyl CH), 1747 (C=O), 1258 (asymmetric C—O), 1058 (symmetric C—O) $cm^{-1}$; NMR ($CCl_4$) δ 1.83 (s, 3, $CH_3CO_2$), 1.3–2.6 (m, 9), 0.1–1.0 (m, 4, cyclopropyl).

Acetate **13** was eliminated as a possible structure by saponifying the acetate products and comparing the spectra with those of the alcohol corresponding to **13**.[19] The IR and NMR were different: NMR ($CCl_4$) δ 3.63 (s, 1, OH), 2.2–2.5 (m, 1, bridgehead), 0.9–2.0 (m, 8), 0–0.9 (m, 4, cyclopropyl). Thus the major product was unequivocally established as acetate **10**, formed by cyclopropano ring expansion.

For the products of *endo*-tosylate 2-$CH_2OTs$, gas chromatography (QF-1 at 154, 121, and 100 °C) showed only one major acetate product, 99.1:0.9. The IR and NMR spectra matched those of acetate **11**.[19]

For the products of norbornyl tosylate 9-$CH_2OTs$, gas chromatography (QF-1, 151 °C) showed only one major acetate with a percentage varying from 97.7-98.3. The IR and NMR showed that the major acetate was **12**, as shown previously by Wilt[14a] in this solvolysis.

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**Registry No.** 1 ($CO_2CH_3$), 75420-99-4; 1 ($CH_2OH$), 75421-00-0; 1 ($CH_2OTs$), 75421-01-1; 1 (COOH), 75421-02-2; 2 ($CO_2CH_3$), 75494-56-3; 2 ($CH_2OH$), 75444-02-9; 2 ($CH_2OTs$), 75444-03-0; 2 (COOH), 75444-04-1; 6, 15023-46-8; 7, 35730-27-9; 8, 75421-03-3; 9 (COOH), 18720-30-4; 9 ($CH_2OTs$), 13866-80-3; 10, 75421-04-4; 11, 75421-05-5; 12, 56714-23-9; 20, 75421-06-6; cyclopropene, 2781-85-3.

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## Structure Proof by Synthesis of Unusual Secodehydroabietanes from Tall Oil[1]

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A noncrystalline substance to which Conner and Rowe have assigned the unusual secodehydroabietanolide formula **1** (9,10-secoabieta-8,11,13-trien-18,10-olide) is a minor component of the neutral fraction of distilled tall oil. It also occurs in the bark of jack pine and western pine.[2,3] As identification of the very limited sample was based only on spectroscopic evidence and on biogenetic arguments, an unambiguous synthesis of optically active material was needed to provide conclusive evidence for the proposed structure. This has now been accomplished. We have also shown, by synthesis, that the structure of a second secodehydroabietane, presumed to be **12**, from the acid fraction of tall oil and from thermal rearrangement of methyl levopimarate must be revised to **11** and have confirmed the structure of a third secodehydroabietane from the thermal rearrangement as **10**.

The successful approach to the synthesis of **1** was initiated with a Diels–Alder–retro-Diels–Alder condensation of levopimaric acid (**2a**) with ethyl propiolate, giving **3b**.[5] The yield was improved to 90% from the reported[5] 35% by raising the temperature to 160 °C. After hydrolysis to **3a**, decarboxylation was effected in 53% yield by heating with Cu powder in quinoline giving **4a**. The purity of the basic solvent was crucial in raising the yield to this figure; under somewhat different conditions ($Cu_2O$, triply distilled quinoline) **4a** was accompanied by appreciable quantities of lactone **5**.

Ester **4b** was prepared from **4a** in 99% yield by treatment of the sodium salt with MeI in HMPA. Although **4b** could be converted to **6b** in two stages by osmylation–

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