57711-28-1; **3** (R = Et; R_1, R_2, R_3 = H; R′ = Me), 66255-88-7; **3** (R = *n*-Pr; R_1, R_2, R_3 = H; R′ = Me), 66255-89-8; **3** (R = *t*-Bu; R_1, R_2, R_3 = H; R′ = Me), 73611-85-5; **3** (R = Me; R_1, R_2, R_3 = H; R′ = Et), 73611-86-6; **3** (R = Me; R_1, R_2, R_3 = H; R′ = *i*-Pr), 73611-87-7; **3** (R = Me; R_1 = Cl; R_2, R_3 = H; R′ = Me), 64743-30-2; **3** (R = Me; R_1 = Br; R_2, R_3 = H; R′ = Me), 64743-31-3; **3** (R = Me; R_1 = OMe; R_2 = Cl; R_3 = H; R′ = Me), 73611-88-8; **3** (R = Me; R_1 = OMe; R_2 = Cl; R_3 = NO_2; R′ = Me), 73611-89-9; **6**, 2114-03-6; **7**, 703-17-3; **8**, 2114-00-3; **9**, 63017-05-0; **10**, 63017-20-9; **11**, 21120-36-5; **12**, 63017-06-1; **21b** (X = Cl), 73611-90-2; **25**, 93-55-0; **26**, 6084-17-9; **27**, 73611-91-3; (*E*)-**28**, 73611-92-4; (*Z*)-**28**, 73611-93-5; **32**, 73611-94-6; (*E*)-**33**, 73611-95-7; (*Z*)-**33**, 73611-96-8; **34**, 73611-97-9; sodium methoxide, 124-41-4; trimethyl orthoformate, 628-90-0; 2,2-dimethoxy-1-phenyl-1-propanol, 73611-98-0; 1,1-dimethoxy-1-phenyl-2-propanol, 73611-99-1; 1-phenyl-1,2,2-trimethoxypropane, 73612-00-7; 1-phenyl-1,1,2-trimethoxypropane, 73612-01-8; methyl benzoate, 93-58-3; 1-phenyl-1,2-propanedione, 579-07-7.

Supplementary Material Available: Yield and boiling point data for 1-aryl-2,2-dialkoxy-1-alkanones **2** and 1-aryl-1,1-dialkoxy-2-alkanones **3** (Table II) and spectrometric data for 1-aryl-2,2-dialkoxy-1-alkanones **2** and 1-aryl-1,1-dialkoxy-2-alkanones **3** (Table III) (5 pages). Ordering information is given on any current masthead page.

Rearrangements of Tricyclo[3.2.1.$0^{3,6}$]octyl Systems

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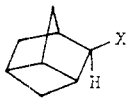
New 2,2-substituted derivatives of tricyclo[3.2.1.$0^{3,6}$]octane with the following sets of substituents were synthesized in a study designed to test their stability toward Wagner–Meerwein rearrangements: CH_3, OH; CH_3, Cl; C_6H_5, OH; Cl, Cl; Br, CO_2H. Epimerizations, but not skeletal rearrangements, were observed in some cases. The phenyl carbinol underwent self-reduction under vigorous conditions.

The first synthesis and some chemical studies of 2-substituted derivatives of the tricyclo[3.2.1.$0^{3,6}$]octyl system **1** were reported in 1963[1] at which time it was observed that



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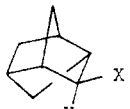
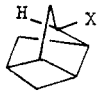


2



3

acetolysis of either the *exo*- or *endo*-2-tosylate resulted in clean formation of the *exo*-2-acetate. Similarly, no skeletal rearrangements were observed during deamination of the amine or during the transformation of the alcohol to the corresponding bromide with HBr–$ZnBr_2$.[2] We rationalized this behavior on the grounds that Wagner–Meerwein rearrangements[3] to systems **2** or **3** might be accompanied by an increase in ring strain. The facile rearrangement of derivatives of **2** to tricyclo[3.2.1.$0^{3,6}$]octanes[4,5] further supported our contention.

More recently, Freeman and co-workers[6] reported the results of two experiments which were believed to involve cationic rearrangements of **1** to system **3**: reaction of **1**-OH with thionyl chloride to give **3**-Cl and reductive solvolysis of **1**-OTs with lithium aluminum hydride to give **3**-H. In the former example, no direct evidence was given for the presence of **3**-Cl, but its presence was inferred since **3**-H was found among the hydrocarbon products after reduction with sodium in decane. Similarly, the reaction with lithium aluminum hydride produced a mixture of hydrocarbons which contained 27% **3**-H.

Table I. Strain Energies of Hydrocarbons and Cations (kcal/mol)

compd	hydrocarbon (X = H) EAS[7]	SH[8]	GD[9]	2-cation (X = +), SH[8]
1	41.96	38.44	41.26	48.10
2	47.15	42.38	25.14[a]	54.68
3	48.29		47.46	51.71

[a] An "improved" estimate of this value was given as 35.72 kcal/mol by the authors, and it was stated that further extensions are in progress.[9]

From a theoretical point of view the calculation of strain energies in polycyclic molecules has been a continuing challenge, and several groups have utilized empirical methods to estimate heats of formation, geometries, and strain energies. The molecular mechanics studies of Schleyer[7] are particularly comprehensive in this context, and strain energies calculated for **1**, **2**, and **3** are given in Table I. Also included are the strain energies calculated by Smith and Harris[8] for the 2-cations and the results of a different method used by Gasteiger and Dammer.[9]

These calculations support the contention that skeletal rearrangements of **1** are both kinetically and thermodynamically unfavorable with respect to transformations to systems **2** and **3** owing to increases in strain energies of ca. 4–6 kcal/mol.

At this time we wish to report the results of extensive studies which were designed to probe the stability of derivatives of **1** toward cationic rearrangements and to com-

(1) Sauers, R. R.; Parent, R. A. *J. Org. Chem.* **1963**, *28*, 605.
(2) Sauers, R. R.; Parent, R. A.; Damle, S. B. *J. Am. Chem. Soc.* **1966**, *88*, 2257.
(3) For a lucid summary of earlier work, see: Berson, J. A. "Molecular Rearrangements"; DeMayo, P., Ed.; Interscience: New York, 1963; Vol. 1, Chapter 3.
(4) Sauers, R. R.; Sickles, B. R. *Tetrahedron Lett.* **1970**, 1067. Sauers, R. R.; Kelly, K. W.; Sickles, B. R. *J. Org. Chem.* **1972**, *37*, 537.
(5) Freeman, P. K.; Kinnel, R. B.; Ziebarth, T. D. *Tetrahedron Lett.* **1970**, 1059.
(6) Freeman, P. K.; Ziebarth, T. D.; Rao, V. N. M. *J. Org. Chem.* **1973**, *38*, 3823.
(7) Engler, E. M.; Andose, J. D.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1973**, *95*, 8005.
(8) Smith, M. R.; Harris, J. M. *J. Org. Chem.* **1978**, *43*, 3588. Private communication from Professor Harris.
(9) Gasteiger, J.; Dammer, O. *Tetrahedron* **1978**, *34*, 2939.

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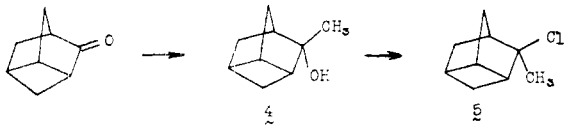
ment on the discrepancies mentioned above.

Results and Discussion

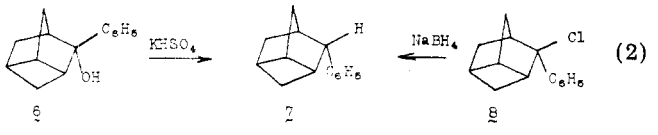
The initial studies involved experiments with tertiary derivatives of 1 because of the wealth of literature data on the behavior of analogous camphyl and norbornyl systems.[3,10] Accordingly, the carbinol 4 was synthesized via Grignard addition to the corresponding ketone (eq 1)



4 5 (1)

and treated with acetic and sulfuric acids for 40 h at ca. 58 °C. The product consisted of an equimolar mixture of the starting alcohol and its epimer and no other products after reduction with lithium aluminum hydride. By comparison, *exo*-2-methyl-*endo*-norborneol can be converted to 1-methyl-2-*exo*-norborneol under similar conditions in 1 h.[10a] In addition, the chloride **5** formed from **4** on treatment with hydrochloric acid proved to be stable to aluminum chloride (except for epimerization) in strong contrast to the behavior of camphene hydrochloride.[3]

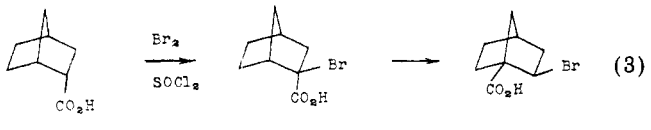
These studies were extended to the analogous phenyl compound **6** which was subjected to the above and much more vigorous conditions, namely, potassium bisulfate at 120–140 °C.[11] The latter experiment was conducted by removal of water as it was formed, and a low yield of a hydrocarbon was collected by distillation. It was shown that this substance was *endo*-2-phenyltricyclo[3.2.1.0^{3,6}]-octane (7) by an independent synthesis[12] (eq 2) from 8.



6 7 8 (2)

Presumably, the phenyl cation undergoes disproportionation or is reduced by abstraction of hydride ion from the starting material. Once again, no skeletally rearranged products were found.

It was reasoned that additional driving force for rearrangement might be provided if the starting material could be destabilized by electronic repulsive forces. For example, the rearrangement of 2,2-dichloronorbornane to 1,*exo*-2-dichloronorbornane takes place at room temperature in 3 days when catalyzed by aluminum chloride.[13] At least part of the driving force must involve the separation of the carbon–chlorine dipoles. Likewise, the rearrangement of 2-bromo-2-norbornanecarboxylic acid[14] (eq 3) involves a



(3)

similar separation of opposing dipoles.[15] Additional driving force in both cases is provided by relief of the nonbonded strain associated with the endo substituents.

We therefore undertook the synthesis and study of the appropriate tricyclic analogues **9** and **10**. The dichloride **9** did not undergo noticeable changes in the ^{1}H NMR spectrum on treatment for long periods with stannic chloride, boron trifluoride, or aluminum chloride.

9 10

Bromination of **11** under conditions which cause rearrangement of norbornane-2-carboxylic acid[14] produced a mixture of bromo acids **12** which could be converted back to **11** by Zn reduction (eq 4).

11 12 (4)

In summary, it has been shown that several derivatives of the tricyclo[3.2.1.0]octyl system were reluctant to undergo Wagner–Meerwein rearrangements under a wide variety of conditions. These results are consonant with the earlier conclusions[2] and with the expectations based on the calculated energy differences between **1** and its isomers **2** and **3**. They are at variance with the conclusions of Freeman et al.[6] We believe that the evidence presented[6] for carbonium ion rearrangements is inconclusive for several reasons: (1) rearranged chloride was not detected directly; (2) product stability was not demonstrated;[16] (3) other mechanisms were not excluded. In both cases, anionic intermediates should be considered in addition to cations since it is possible that the rearranged products arose during the reductions as a result of rearrangement of anions by a cleavage–readdition sequence.[17]

Experimental Section

Infrared spectra were determined on a Perkin-Elmer Model 157 or a Beckman IR-5A spectrometer. Nuclear magnetic resonance spectra were determined on a Varian A60 spectrometer in carbon tetrachloride solution or as noted. Gas chromatographic data were obtained on an Aerograph A-90-P instrument using the following columns: A, Carbowax 20-M (15 ft × 0.25 in.); B, SE-30 (10 ft × 0.25 in.); C, Apiezon L (9 ft × 0.25 in.). Capillary gas chromatograms were determined on a Barber-Colman Model 5000 instrument.

***exo*-2-Methyl-*endo*-2-tricyclo[3.2.1.0^{3,6}]octanol (4).** A solution of 23.0 g (0.189 mol) of tricyclo[3.2.1.0^{3,6}]octan-2-one[2] in 130 mL of dry ether was added over 1.25 h to a stirred solution of the Grignard reagent prepared from 52.9 g (0.364 mol) of methyl iodide and 8.7 g (0.36 mol) of magnesium in 110 mL of ether. After being stirred for 4 days at 25 °C, the reaction was quenched with ammonium chloride solution followed by dilute hydrochloric acid. The aqueous layer was extracted with pentane, and the combined organic layers were washed with sodium bicarbonate solution and

(10) (a) Berson, J. A.; Walia, J. S.; Remanik, A.; Suzuki, S.; Reynolds-Warnhoff, P.; Willner, D. *J. Am. Chem. Soc.* **1961**, *83*, 3896. (b) Rei, M.-H.; Brown, H. C. *Ibid.* **1966**, *88*, 5335. (c) Bartlett, P. D.; Sargent, G. D. *Ibid.* **1965**, *87*, 1297. (d) Toivonen, N. J.; Siltanen, E.; Ojala, K. *Ann. Acad. Sci. Fenn., Ser. A2* **1955**, *No. 64*.

(11) Kleinfelter, D. C.; Schleyer, P. v. R. *J. Org. Chem.* **1961**, *26*, 3740.

(12) Brown, H. C.; Bell, H. M. *J. Am. Chem. Soc.* **1964**, *86*, 5006; *J. Org. Chem.* **1962**, *27*, 1928.

(13) (a) Wilt, J. W.; Parsons, C. F.; Schneider, C. A.; Schultenover, S. J.; Wagner, W. J. *J. Org. Chem.* **1968**, *33*, 694. (b) Bixler, R. L.; Niemann, C. *Ibid.* **1958**, *23*, 742. (c) Fry, A. J.; Farnham, W. B. *Ibid.* **1969**, *34*, 2314.

(14) Boehme, W. R. *J. Am. Chem. Soc.* **1959**, *81*, 2762. Kwart, H.; Null, G. *Ibid.* **1959**, *81*, 2765.

(15) Some evidence for this contention may be found in the heat of combustion data reported by: Smith, L.; Bjellerup, L.; Krook, S.; Westermark, H. *Acta Chem. Scand.* **1953**, *7*, 65. The heat of combustion of α-chloropropionic acid is 6.1 kcal/mol higher than that reported for β-chloropropionic acid. 1,1-Dichloroethane has about the same heat of combustion as does 1,2-dichloroethane, however.

(16) The tetracyclic hydrocarbon also isolated by Freeman[6] could be the source of **3**-H.

(17) Anions have been suggested as intermediates in related reductions by LiAlH$_4$: Jefford, C. W.; Kirkpatrick, D.; Deloy, F. *J. Am. Chem. Soc.* **1972**, *94*, 8905.

water and then dried. After evaporative distillation the residue was sublimed at 0.5 mm to give 22.8 g (88%) of a white solid, mp 40–45 °C. GC analysis (A) revealed a major component (98%) and two minor ones, one of which was shown to be the epimeric alcohol. The NMR spectrum showed a singlet at δ 1.17 attributed to the methyl group.

Anal. Calcd for $C_9H_{14}O$: C, 78.22; H, 10.21. Found: C, 78.25; H, 10.20.

The *p*-nitrobenzoate ester had a melting point of 141–141.5 °C after crystallization from ethanol–cyclohexane.

Anal. Calcd for $C_{16}H_{17}NO_4$: C, 66.88; H, 5.96; N, 4.88. Found: C, 67.17; H, 6.15; N, 5.27.

2-Chloro-2-methyltricyclo[3.2.1.0^{3,6}]octane (5). A solution of 2.0 g (0.14 mol) of **4** in 12 mL of concentrated hydrochloric acid was stirred for 17 h at 25 °C. The product was extracted into ether which was washed with aqueous calcium chloride and water. A white solid (mp 72–77 °C) was obtained on evaporation of the ether. Repeated sublimation at 1 mm did not alter the melting point. GC analysis (A) revealed two components in a ratio of ca. 1:11. The NMR spectrum showed two singlets at δ 1.75 and 1.50 with an area ratio of 10:1, respectively.

Anal. Calcd for $C_9H_{13}Cl$: C, 69.00; H, 8.37; Cl, 22.63. Found: C, 68.97; H, 8.43; Cl, 22.54.

***endo*-2-Methyl-*exo*-2-tricyclo[3.2.1.0^{3,6}]octanol.** A mixture of 1.0 g (6.4 mmol) of chloride **5** and 13 mL of 1 N sodium hydroxide solution was stirred at 25 °C for 21 h. The solution was saturated with salt and extracted with ether, which was dried (Na_2SO_4) and evaporated to give 0.74 g (84%) of a white solid, mp 124–127 °C (sealed capillary tube) after sublimation at 0.3 mm. GC analysis (A) showed one peak, and the NMR spectrum showed a sharp singlet at δ 1.32 attributed to the methyl group. The melting point rose to 130–131 °C after crystallization from hexane.

Anal. Calcd for $C_9H_{14}O$: C, 78.22; H, 10.21. Found: C, 77.78; H, 10.02.

The acetate ester was prepared from acetyl chloride and pyridine (75 °C, 4.5 h) and purified by GC (A); IR 5.79 μm.

Anal. Calcd for $C_{11}H_{16}O_2$: C, 73.30; H, 8.95. Found: C, 73.33; H, 9.08.

Treatment of 4 with Acetic and Sulfuric Acids. A solution of 1 g of **4** in a mixture containing 10 mL of glacial acetic acid, 1 mL of sulfuric acid, and 1 mL of water was heated at 55–60 °C for 40 h. The reaction was quenched with sodium bicarbonate solution and extracted with pentane. The dried extracts were evaporated to give an oil which was molecularly distilled at 0.5 mm to give 1.15 g of clear distillate. Reduction of this product with lithium aluminum hydride in ether gave 0.80 g (80%) of a 1:1 mixture of the *exo*- and *endo*-methyl carbinols as shown by GC (A) and by comparing the infrared spectra of the components.

Treatment of 5 with $AlCl_3$. A solution of 0.10 g of **5** in 0.6 mL of nitromethane was monitored by NMR spectroscopy. After 6 h at 25 °C no changes were observed. Addition of a small amount of $AlCl_3$ caused no change at 25 °C for 17 h. When the tube was heated on a steam bath for 60 h, the major change was in the ratio of the methyl peaks. The final ratio was ca. 1.3:1. GC analysis (A) showed only the two original peaks.

***exo*-2-Phenyl-*endo*-2-tricyclo[3.2.1.0^{3,6}]octanol (6).** A solution of 9.25 g (0.0758 mol) of tricyclo[3.2.1.0^{3,6}]octan-2-one in 100 mL of dry ether was added to the phenyllithium reagent prepared from 2.28 g (0.33 mol) of lithium ribbon and 15.42 g (0.0983 mol) of bromobenzene in 100 mL of dry ether. After 1.5 h of reflux, the mixture was quenched with dilute hydrochloric acid and the product extracted into ether. After evaporation there was obtained 13.3 g (88%) of a waxy solid which was crystallized from petroleum ether (bp 30–60 °C): mp 72–74 °C; IR 3.0, 13.2, 13.55, 14.4 μm.

Anal. Calcd for $C_{14}H_{16}O$: C, 83.96; H, 8.05. Found: C, 83.72; H, 8.17.

The *p*-nitrobenzoate had a melting point of 187–188 °C.

Anal. Calcd for $C_{21}H_{19}NO_4$: C, 72.19; H, 5.48; N, 4.01. Found: C, 72.04; H, 5.58; N, 4.01.

***endo*-2-Phenyl-*exo*-2-tricyclo[3.2.1.0^{3,6}]octanol.**[18] A small sample of chloride **8** was prepared by treating 1.44 g (0.0072 mol) of **6** with 17 mL of concentrated hydrochloric acid at 5 °C for 1.75 h. After neutralization of the solution with sodium bicarbonate, the product was extracted into ether, dried, and evaporated to give 1.38 g (88%) of an amber liquid.

Solvolysis of the chloride was accomplished at 25 °C by stirring it in a solution made up of 0.5 g of sodium carbonate and 35 mL of 80% acetone–20% water. The reaction was quenched with saturated ammonium sulfate solution followed by extraction with ether. After the mixture was dried and the solvent evaporated, there was obtained 0.64 g of an oil which gave 0.35 g of a white solid after sublimation. Crystallization from petroleum ether (bp 30–60 °C) gave a product with the following: mp 65–66 °C; IR (mull) 2.97, 13.2, 14.36 μm.

Anal. Calcd for $C_{14}H_{16}O$: C, 83.96; H, 8.06. Found: C, 83.79; H, 8.01.

Treatment of 6 with Acetic and Sulfuric Acids. Alcohol **6** was treated with the same mixture of acids as before for 4 h at 60–70 °C and was worked up as before. There was obtained a 1:1 mixture of the *exo*- and *endo*-2-phenyl carbinols as shown by GC (A).

Reaction of 6 with Sodium Bisulfate. A mixture 1.04 g (0.0052 mol) of **6** and 3.81 g (0.028 mol) of sodium bisulfate was heated at 120–140 °C under a 35-mm vacuum. After 20 h the pressure was lowered to 1.2 mm at which point 0.321 g of a viscous liquid distilled. GC analysis indicated one major component: **7** (ca. 98–99%); IR (neat) 3.43, 3.52, 6.73, 6.95, 12.76, 13.86, 14.4 μm; NMR δ 2.2 (m, 11 H), 7.2 (s, 5 H); λ_{max} (C_6H_{12}) 260 nm (ϵ 295).

Anal. Calcd for $C_{14}H_{16}$: C, 91.25; H, 8.75. Found: C, 91.04; H, 8.75.

An authentic sample of **7** was prepared from **8** by the method of Brown and Bell.[12,19] There was obtained a crude product whose NMR spectrum was very similar to that of the *exo*-phenyl carbinol. GC analysis (A) gave two main products in a ratio of 1:2. The minor component of short retention time was collected and shown to have an infrared spectrum identical with the product formed from the sodium bisulfate reaction. The major component had the same retention time as the authentic *endo*-2-phenyl-*exo*-2-tricyclo[3.2.1.0^{3,6}]octanol prepared above.

2,2-Dichlorotricyclo[3.2.1.0^{3,6}]octane (9). An ice-cold mixture of 4.7 g (0.038 mol) of tricyclo[3.2.1.0^{3,6}]octan-2-one and 2.3 mL of phosphorus trichloride was treated with 11.9 g (0.057 mol) of phosphorus pentachloride over 0.5 h. The resulting mixture was stirred at 25 °C for 60 h and was quenched by being poured onto ice. After extraction with pentane the crude product (3.5 g, 51%) was isolated by evaporation of the dried extracts. The product was purified by distillation (40–50 °C at 4 mm) followed by GC (A): mp 85–87 °C; NMR δ 1.38 (d, J = 12.5 Hz, 1 H), 3.15–1.57 (m, 9 H).

Anal. Calcd for $C_8H_{10}Cl_2$: C, 54.26; H, 5.69; Cl, 40.05. Found: C, 54.53; H, 5.87; Cl, 40.22.

Attempted Rearrangements of 9. The following reaction conditions failed to effect significant rearrangement as monitored by GC or NMR: CH_2Cl_2, BF_3, 4 days, 25 °C; CH_2Cl_2, $AlCl_3$, 9 days, 25 °C; CH_2Cl_2, $SnCl_4$, 9 days, 25 °C; C_6H_6, $SnCl_4$, 5 days, 35–70 °C.

***exo*-2-Chlorotricyclo[3.2.1.0^{3,6}]octane.** A mixture of 28.6 g (0.21 mol) of *exo*-tricyclo[3.2.1.0^{3,6}]octan-2-ol and 170 mL of concentrated hydrochloric acid was heated at 40–48 °C for 6 h. After the mixture was quenched with water, the product was extracted with petroleum ether. The combined extracts were washed with sodium bicarbonate solution and water and then dried. The residue obtained after evaporative distillation of the solvent was distilled at 78–80 °C (25 mm) to yield 24.0 g (76%) of the chloride; NMR δ 3.95 (s, 1 H) (lit.[6] δ 3.98); GC analysis on a 150-ft Castorwax or a 50-ft Ucon 50 HB2000 capillary column failed to resolve any other component.

Anal. Calcd for $C_8H_{11}Cl$: C, 67.37; H, 7.77; Cl, 24.86. Found: C, 67.68; H, 7.84; Cl, 24.69.

Tricyclo[3.2.1.0^{3,6}]octane-2-carboxylic Acid (11). The Grignard reagent was prepared from 24.6 g (0.173 mol) of the

(18) For the analogous reaction in the norbornyl series, see: Brown, H. G.; Chloupek, F. J.; Rei, M.-H. *J. Am. Chem. Soc.* **1964**, *86*, 1246.

(19) It could be argued that this preparation does not constitute proof of the structure of **7** since carbenium ion reactions were involved in both cases. It is highly unlikely, however, that the *alcohol* produced in this sequence would have a different skeleton than the *hydrocarbon*.

chloride and 4.24 g (0.176 mol) of magnesium turnings in 100 mL of dry tetrahydrofuran. The reaction was initiated with a few crystals of iodine and the mixture allowed to react for 8 h at 60 °C. It was poured onto solid carbon dioxide, after which dilute hydrochloric acid was added. The aqueous layers were extracted with ether, and the combined extracts were evaporated to give a residue which was distilled at ca. 0.2 mm to give 18.2 g (69%) of a waxy solid.

The mixture of acids was converted to the methyl esters by means of diazomethane in ether. GC analysis on a 150-ft Apiezon L capillary column revealed two peaks in a 2:1 ratio: NMR δ 3.57 (s) and 3.52 (s), area ratio 37:63, respectively.

Anal. Calcd for $C_{10}H_{14}O_2$: C, 72.26; H, 8.49. Found: C, 72.18; H, 8.42.

Bromination of Tricyclo[3.2.1.0^{3,6}]octane-2-carboxylic Acid. A solution of 7.9 g (0.052 mol) of acid **11**, 9.5 g (0.059 mol) of bromine, and 0.224 mL (0.0025 mol) of phosphorus trichloride was heated for 17 h at 76 °C. Another 0.05 mL of PCl_3 was added, and the solution was heated for 24 h at 90–95 °C. The syrupy oil was triturated with pentane to yield 1.5 g of a tan solid, mp 130–140 °C. On crystallization from nitromethane the melting point was 152–155 °C.

Anal. Calcd for $C_9H_{11}O_2Br$: C, 46.77; H, 4.80; Br, 34.58. Found: C, 46.94; H. 4.85; Br, 34.53.

Treatment of the pentane filtrate with charcoal and reevaporation gave another 1.65 g of crystalline bromo acid. The oily residue was esterified with diazomethane and shown by GC (B) to contain only the methyl esters of **11** and the methyl esters of the bromo acids in a 60:40 ratio as determined by the ratio of the NMR peaks at δ 3.80 and 3.74.

Hydrogenolysis of Methyl Esters of 12. A mixture of the bromo esters (3.5 g, 0.0143 mol) and 4.7 g (0.072 mol) of granular zinc was stirred in 35 mL of glacial acetic acid at 40–50 °C for 40 h. The reaction mixture was poured into water and extracted with pentane. The dried extracts were evaporated, and the residue was distilled at 0.2 mm to yield 2.27 g (95%) of the esters of **11** as shown by GC (150-ft Apiezon L column), IR, and NMR comparisons.

Proof of Structure of 11. Preparation of 2-Acetylbicyclo[3.2.1.0^{3,6}]octane (13). A stirred solution of 2.0 g (0.013 mol) of **11** in 125 mL of anhydrous ether was treated dropwise with 16 mL of 1.67 M methyllithium solution over a period of 1.5 h. After an additional 0.5 h of vigorous stirring, the reaction was quenched with 25 mL of water. The aqueous layer was washed with ether, and the combined extracts were dried and evaporated to yield 2.0 g (100%) of an oil with a carbonyl absortpion at 5.90 nm and two closely spaced singlets in the NMR at δ 1.96 and 2.02 (relative area ca. 40:60). GC analysis (A or capillary) revealed one major peak (>96%).

Anal. Calcd for $C_{10}H_{14}O$: C, 79.95; H, 9.40. Found: C, 80.16; H, 9.70.

Oxidation of 13 with Trifluoroperacetic Acid. A solution of trifluoroperacetic acid was prepared by addition of 6.8 mL (0.041 mol) of trifluoroperacetic anhydride with cooling over 1 h to a solution of 1.04 mL (0.038 mol) of 90% hydrogen peroxide in 13.2 mL of methylene chloride. The resulting solution was stirred for 10 min and then added dropwise to a solution of 3.2 g (0.021 mol) of ketone **13** in a slurry of 40 mL of methylene chloride–potassium hydrogen phosphate (15.6 g, 0.11 mol). The resulting mixture was refluxed for 8 h and filtered to remove salts, and the filtrate was evaporated to give 3.5 g of crude product. GC analysis (A) revealed one major component (90%) which was isolated and shown by NMR to consist of a mixture of 2-*exo*- and 2-*endo*-tricyclo[3.2.1.0^{3,6}]octyl acetates[2] in a ratio of ca. 2:1. Lithium aluminum hydride reduction of the mixture gave a 2:1 mixture of 2-*exo*- and 2-*endo*-tricyclo[3.2.1.0^{3,6}]octanols as shown by NMR comparison of the area ratios of the carbinol protons at δ 3.7 and 4.1.[2]

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Registry No. 4, 73770-57-7; **4** *p*-nitrobenzoate ester, 73770-58-8; **5** (isomer 1), 73770-59-9; **5** (isomer 2), 73803-41-5; **6**, 73770-60-2; **6** *p*-nitrobenzoate ester, 73770-61-3; **7**, 73770-62-4; **8**, 73770-63-5; **9**, 73770-64-6; **11**, 25679-33-8; **11** methyl ester (isomer 1), 73770-65-7; **11** methyl ester (isomer 2), 73803-42-6; **12**, 73770-66-8; **12** methyl ester (isomer 1), 73770-67-9; **12** methyl ester (isomer 2), 73803-43-7; **13** (isomer 1), 73770-68-0; **13** (isomer 2), 73803-44-8; *endo*-2-methyl-*exo*-2-tricyclo[3.2.1.0^{3,6}]octanol, 73803-45-9; *endo*-2-methyl-*exo*-2-tricyclo[3.2.1.0^{3,6}]octanol acetate ester, 73770-69-1; *endo*-2-phenyl-*exo*-2-tricyclo[3.2.1.0^{3,6}]octanol, 73803-46-0; *exo*-2-chlorotricyclo[3.2.1.0^{3,6}]octane, 41564-23-2; *exo*-tricyclo[3.2.1.0^{3,6}]octan-2-ol, 6239-90-3; 2-*exo*-tricyclo[3.2.1.0^{3,6}]octyl acetate, 6239-95-8; 2-*endo*-tricyclo[3.2.1.0^{3,6}]octyl acetate, 73803-47-1; tricyclo[3.2.1.0^{3,6}]octan-2-one, 6239-87-8; 2-*endo*-tricyclo[3.2.1.0^{3,6}]octanol, 6239-89-0.

Acid- and Base-Catalyzed Isomerization of Androst-5-ene-3,17-dione and 17α-Ethynyl-17β-hydroxy-5-estren-3-one

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Isomerization of androst-5-ene-3,17-dione (**1**) to androst-4-ene-3,17-dione (**2**) and of 17α-ethynyl-17β-hydroxy-5-estren-3-one (**3**) to 17α-ethynyl-17β-hydroxy-4-estren-3-one (**4**) is kinetically general acid–base catalyzed; **1** is more reactive than **3**. Deuterium solvent kinetic isotope effects, $k(H_2O)/k(D_2O)$, of ca. 6 for tertiary amine catalyzed isomerization indicate rate-determining protonation of dienolate ions. The greater reactivity of **1** than **3**, catalyzed by tertiary amines, is probably due to a greater concentration of the **1** dienolate ion than of the **3** dienolate ion. Ethanolamine, but not tris(hydroxymethyl)aminomethane, catalyzes isomerization of **1** and **3** via Schiff-base formation. Curvilinear pseudo-first-order plots for isomerization of **1** and **3** catalyzed by DCl/D_2O indicate that partitioning of dienols is kinetically important.

Two kinetics studies of base-catalyzed isomerization of Δ^5-3-keto steroids to Δ^4-3-keto steroids (eq 1) have been reported[1,2] and they are limited to lyate species catalysis.[3] The present study is concerned primarily with the kinetics

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