peak heights at mass numbers 96 and 97 are in the same ratio as the number of molecules of these approximate molecular weights in the ketone sample. There is no measurable peak at mass number 95. An equation has been derived (eq 1) for the determination of excess deuterium content in the bicyclo[3.1.0]hexan-3-one where R_0 is the ratio of peak heights at mass numbers 96 to that of 97 for ketone with normal isotopic distribution, R is the ratio of these same peaks for the sample under consideration, and P_d is the percentage of deuterated molecules in the sample.[6] Utilization of this equation produced the results listed in Table III. The analysis of

$$P_d = \frac{R - R_0}{1 + R - R_0} \times 100 \qquad (1)$$

the methyl ester was complicated by the formation of a substantial peak at mass number 139 due to the loss of one hydrogen. It was assumed that the fragmentation leading to this ion would not involve the abstraction of a proton from the methylene carbon of the cyclopropane ring which is substituted by deuterium in the ester under consideration. An equation can be derived (eq 2) involving the same reasoning as indicated above for the ketone where R_0 is the ratio of peak heights for mass numbers, 140 and 139, respectively, for the deuterated ester and R_4 is the same ratio for the undeuterated ester; R_1 is the ratio of peak heights for mass numbers, 141 and 139, respectively, for the deuterated species and R_3 is the same ratio for the standard ester; finally, R_2 is the ratio of peak heights for mass numbers, 142 and 139, respectively, for the deuterated methyl ester. The calculated percentage of deuterated

$$P_d = \frac{R_0 + R_1 + R_2 - R_3 - R_4}{1 + R_0 + R_1 + R_2} \times 100 \qquad (2)$$

methyl ester obtained from mass spectral data is in good agreement with a value of 64 ± 2% obtained from nmr analysis. A variation of ±1% from duplicate mass spectra of the compounds in question indicates no loss of deuterium in the rearranged alcohols obtained from electrolysis of *cis*- or *trans*-bicyclo[3.1.0]hexane-3-carboxylic acids-6-d_1.

***cis*-Bicyclo[3.1.0]hexane 3-*t*-Butyl Perester Synthesis and Decomposition.** To a solution of 1.8 g (0.016 mole) of sodium *t*-butyl peroxide in 20 ml of ether at 0° was slowly added 1.1 g (0.0076 mole) of *cis*-bicyclo[3.1.0]hexane-3 acid chloride, bp 79° (17 mm), dissolved in 10 ml of ether. The suspension was stirred for 3 hr at room temperature, then 5 ml of water was added and the solution was vigorously stirred for 15 min followed by extraction with 25 ml of pentane. The organic phase was successively washed with 10% cold sulfuric acid, 10% cold sodium bicarbonate, and cold water, dried over anhydrous magnesium sulfate, filtered, and concentrated in the cold. An infrared spectrum of the residue indicated the presence of residual *t*-butyl peroxide. The concentrate was redissolved in pentane, washed successively with cold water, and concentrated to a colorless, sweet-smelling liquid, the infrared spectrum of which contained a strong, sharp peak at 5.6 μ and no absorption in the hydroxyl region. The ester was dissolved in 20 ml of monoglyme (distilled from calcium hydride) and heated to reflux in a steady flow of oxygen for 30 hr. The solution was cooled to room temperature and slowly added to 0.8 g (0.021 mole) of lithium aluminum hydride in ether at 0°, stirred at room temperature for 2 hr, and slowly hydrolyzed with 3.2 ml of water. Additional stirring for 1 hr followed by filtration and concentration with a short column of glass helices gave a colorless liquid residue which was analyzed by vpc on a β,β′-oxydipropionitrile column at 80°. The chromatogram indicated the epimeric 3-alcohols were present but none of the rearranged 2-alcohols could be detected. The epimeric bicyclo[3.1.0]hexyl-3-carbinols were also present.

Acknowledgment. The authors are indebted to Drs. Kahler and Foltz of the Battelle Memorial Institute for the mass spectra determinations and to the National Science Foundation for Grant No. GP-4184 which partially supported this investigation.

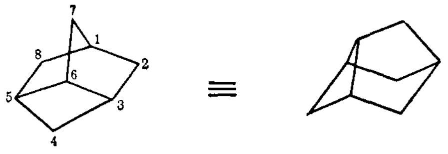
Synthesis and Chemistry of the Tricyclo[3.2.1.0^{3,6}]octane System

R. R. Sauers, R. A. Parent, and S. B. Damle

Contribution from the School of Chemistry, Rutgers, The State University, New Brunswick, New Jersey 08903. *Received January 19, 1966*

Abstract: The tricyclo[3.2.1.0^{3,6}]octane system (I) and several of its derivatives have been synthesized by a novel ring closure reaction. A study of reactions involving cationic intermediates at C_2 has revealed a remarkable resistance to rearrangement.

The chemistry of bridged polycyclic carbon systems has attracted the attention of innumerable investigators. In addition to the many challenging synthetic problems involved, many of these systems have exhibited interesting physical and chemical properties as well. We wish to expand and detail our earlier results on the synthesis and chemistry of the tricyclo[3.2.1.0^{3,6}]-octane system (I)[1,2] and some of its derivatives.



I

The key synthetic step in which the cyclobutyl ring is constructed is noteworthy owing to the potential generality of this procedure for the preparation of other strained ring systems. Additionally, the reactivity of strained systems is not well understood and data obtained in this study provide further insights and suggest other experimentation.

Synthesis. The basic starting materials for the successful synthesis of this tricyclic system were the readily available 5-halomethylnorbornenes (IIa and IIb). Treatment of the olefins with buffered peracetic acid led to epoxides IIIa and IIIb.[3]

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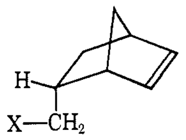
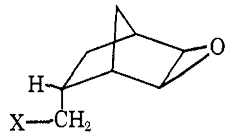
(1) R. R. Sauers and R. A. Parent, *J. Org. Chem.*, **28**, 605 (1963).

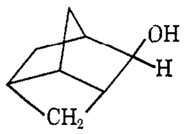
(2) P. K. Freeman, V. N. M. Rao, and G. E. Bigam, *Chem. Commun.*, **21**, 511 (1965).



IIa, X = Br
b, X = Cl



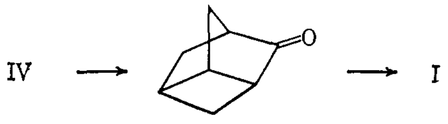
III



IV

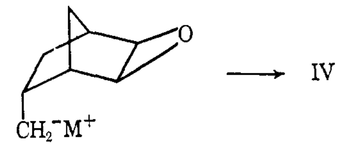
The cyclization step (III → IV) was studied in some detail with emphasis on choice of solvent and metal. The best results were obtained on treatment of IIIb with lithium in tetrahydrofuran. Under these conditions, the product IV was formed essentially free of by-products. Treatment of IIIa with sodium in toluene, on the other hand, led to considerable amounts of contaminants.[4]

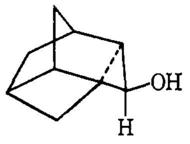
The parent hydrocarbon, tricyclo$[3.2.1.0^{3,6}]$octane (I), was readily prepared by oxidation of alcohol IV to the corresponding ketone (V) followed by Wolff–Kishner reduction.



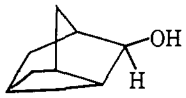
V

Structure. The structure proof of this novel hydrocarbon system is based on a combination of spectral and chemical methods. In addition to compound IV, we have considered three alternate possibilities: VI, VII, and VIII. The modes of formation of these follow from the assumption that the first intermediate in the cyclization step is the anion indicated. System VI would result by ring formation at the other end of the epoxide bridge. Compounds VII and VIII would be the results of ring expansion of the carbanions[5] in the two possible directions followed by cyclization. Fortunately, all three of these possibilities can be unambiguously eliminated. Compound VIII was recently prepared by LeBel and Huber[6] and was shown to be different by spectral comparison. Compounds VI and VII were eliminated by symmetry arguments. A consideration of the ketones derived from these molecules by oxidation leads to the conclusion that reduction back to alcohols could produce only the original alcohols. In actual fact, this sequence led mainly (85%) to an isomeric alcohol which must be the *endo* isomer IX.

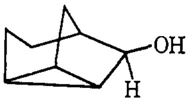




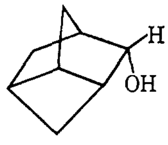
VI



VII



VIII



IX

All of the physical data which we have accumulated thus far is also in agreement with the assigned structures. The nmr spectrum of the hydrocarbon I, for example, shows no olefinic protons and has broad singlets at τ 7.2 (area 1), 7.6 (area 1), and 7.8 (area 3). Broad multiplets centered at τ 8.5 (area 3) and 8.7 (area 4) also were observed. Alcohol IV is interesting in that its nmr spectrum shows a remarkably sharp (width at half-height, *ca.* 2 cps) absorption line at τ 6.3 due to the HCO proton. That this is consistent with the assigned structure can be seen from a consideration of the dihedral angles that this proton makes with the adjacent protons on C_1 and C_3. The two angles in question are 66 and 92°, respectively, which lead to estimated[7] coupling constants of less than 1 cps in both cases. The mass spectra of IV, V, and IX have been determined.[8]

In addition to providing further evidence for the tricyclic nature of these systems, the spectra are of intrinsic interest. For example, both alcohols show $(M - 18)^+$ peaks which must be associated with loss of water at some stage. In agreement with the results of Biemann and Seibl[9] the *endo* alcohol (IX) shows a more intense ion current (5.2 *vs.* 4.3%) than the *exo* isomer. The strongest *m/e* peaks in the alcohol and hydrocarbon spectra appear at 66 and 67, corresponding to $C_5H_6^+$ and $C_5H_7^+$. These fragments result from three-bond cleavages, although not necessarily *via* a concerted process.

Reactions. At this time we have concentrated our efforts on carbonium ion reactions of these systems

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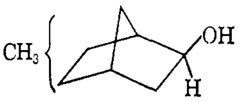
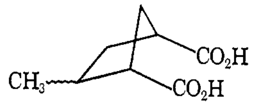
[3] It is assumed that the oxirane ring is predominantly *exo* although this point is not critical: *cf.* H. Kwart and T. Takeshita, *J. Org. Chem.*, **28**, 670 (1963).

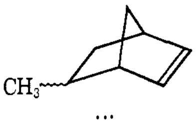
[4] The gross structures of these contaminants is best represented by structure i. Permanganate oxidation of these alcohols led to the same mixture of diacids (ii) as was obtained on oxidation of the methylnorbornenes iii. Since the halomethylnornenes used in the synthesis were *exo–endo* mixtures, at least part of these alcohols must have been formed by reduction of the *exo*-halomethyl component.



i



ii



iii

[5] Although ring expansion in the formal sense is unprecedented with purely alkyl systems, the added effect of relief of strain could conceivably tip the balance in this system. Alternatively, the same result would be obtained if the initial carbanion fragments to give unsaturated carbanions which recombine in the reverse direction: *cf.* P. K. Freeman, D. E. George, and V. N. M. Rao, *J. Org. Chem.*, **29**, 1682 (1964).

[6] N. A. LeBel and J. E. Huber, *J. Am. Chem. Soc.*, **85**, 3193 (1963). We are indebted to Professor LeBel for a sample of this material.

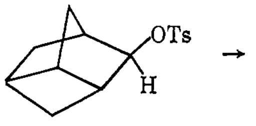
[7] M. Karplus, *J. Chem. Phys.*, **30**, 11 (1959).

[8] Spectra were determined on a CEC 21-103 mass spectrometer. We are deeply indebted to Mr. A. Struck, Dr. B. Mookherjee, and to Dr. S. Lemberg for obtaining these spectra.

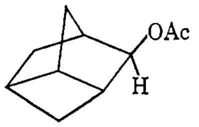
[9] K. Beimann and J. Seibl, *J. Am. Chem. Soc.*, **81**, 3149 (1959).

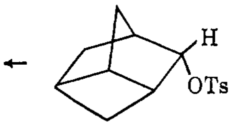
owing to the availability of suitable derivatives and current interest in this general area. It was anticipated that the high degree of strain in the ring structure would lead to facile rearrangement and/or ring cleavage.[10]

Accordingly, the *p*-toluenesulfonate esters (X and XII) of the *exo* and *endo* alcohols were synthesized and solvolyzed in buffered acetic acid. Surprisingly, *exo*-acetate XI was the sole product from either reaction.



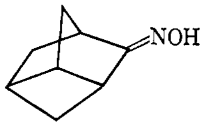
X

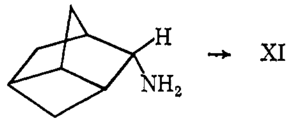




XI XII

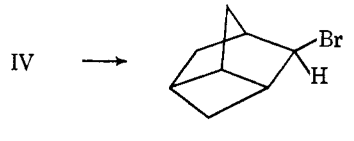
Likewise, the amine, presumably mainly XIV, produced on lithium aluminum hydride reduction of oxime XIII gave essentially exclusively XI on nitrous acid deamination.

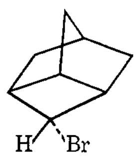




XIII XIV

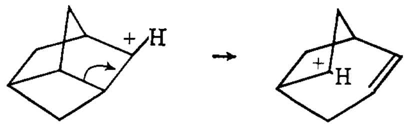
The most vigorous treatment to which we subjected the system involved refluxing alcohol IV in aqueous hydrobromic acid (with or without added zinc bromide). The only product isolated proved to be a monobromide which was still tricyclic as evidenced by the absence of unsaturation. That the gross structure of the ring system was unchanged was shown by reduction of this bromide with sodium in ammonia to hydrocarbon I. The HCBr proton showed a sharp unsplit absorption in the nmr spectrum similar to that of the HCO proton of alcohol IV. The only two bromides whose properties would be consistent with the data are XV and XVI.[7] Of these, XVI seems extremely unlikely on mechanistic grounds.





XV XVI

It seems pertinent at this juncture to consider in more detail the nature of the cationic intermediate(s) in these reactions. The remarkable reluctance of these intermediates to undergo any observable rearrangements was unexpected. It might be reasonably argued that Wagner–Meerwein shifts would lead to products with greater strain energy than the initial system.[11] At least one process, XVII → XVIII, leads to a rearranged system which is almost certainly more stable than the precursor. This process allows relief of the strain of the cyclobutane ring without any obvious change in stability of the cation, and should be exothermic to the extent of 9–14 kcal/mole. Opposed to this rearrangement is the misalignment of the axis of the p orbital of the carbonium ion with the C_3–C_6 bond. The two orbitals are nearly orthogonal and the rigidity of the system severely restricts any attempt to force them into a parallel orientation.

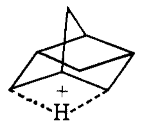


XVII XVIII

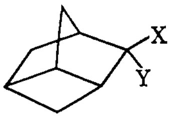
In this connection, it was pertinent to attempt to assess the importance of anchimeric assistance to ionization. The absence of assistance would tend to dispel consideration of intermediates other than classical ions. Since it is not inconceivable that both the *exo* and *endo* epimers might ionize with assistance in this system, it was decided to compare the absolute solvolysis rates with those calculated by the method of Schleyer.[12]

Interestingly, the calculated acetolysis rates for the two epimers were essentially identical, namely, $10^{-2.5}$ relative to the rate for cyclohexyl tosylate. The observed ratios were 10^{-2} ($k_{endo}/k_{\text{cyclohexyl}}$) and $10^{0.3}$ ($k_{exo}/k_{\text{cyclohexyl}}$). These results sugest that the *exo* isomer undergoes substantial ($10^{2.8}$) anchimeric assistance during the ionization stage.[13]

The possibility that hydrogen participation was responsible for the enhanced rate of the *exo* system was considered feasible in view of the lack of carbon skeletal rearrangements. Formula XIX symbolizes a possible transition state or intermediate for this process which would be expected to lead to interconversion between two equivalent ions. This alternative can be excluded from further consideration based on the results of labeling experiments. Acetolysis of both the *exo*- and *endo*-deuteriotosylates XX and XXI was unaccompanied by scrambling.



XIX



XX, X = OTs
Y = D
XXI, X = D
Y = OTs

Thus there is a striking parallelism of these solvolysis results with those obtained with the norbornyl system. The high degree of stereospecificity of product forma-

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[10] The ring structure and geometry can be considered as a composite of the norbornyl and nopinyl systems, both of which rearrange extensively in carbonium ion reactions. For leading references, see P. von R. Schleyer, W. E. Watts, and C. Cupas, *J. Am. Chem. Soc.*, **86**, 2722 (1964); E. C. Friedrich and S. Winstein, *ibid.*, **86**, 2721 (1964),; J. A. Berson and A. Remanick, *ibid.*, **86**, 1749 (1964).

[11] The basic ring systems for three of the possible rearranged systems are known: see ref 2, and G. Büchi and I. M. Goldman, *ibid.*, **79**, 4741 (1957).

[12] P. von R. Schleyer, *ibid.*, **86**, 1854 (1964). We are deeply indebted to Professor Schleyer and Mr. C. Cupas for determination of the rates and for valuable discussions. See the Experimental Section for details.

[13] See, however, R. E. Davis, Abstracts of papers presented at the 150th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept. 1965, p 39S.

tion and the *exo*/*endo* rate ratio ($10^{2.3}$) are closely analogous. Although the behavior of this system could conveniently be rationalized by postulation of nonclassical or rapidly equilibrating ions, it would seem to be prudent to remain noncommittal until more data are available.

Experimental Section

Analyses are by G. Robertson, Florham Park, N. J., and W. Manser, Herliberg, Switzerland. Infrared spectra were determined on a Perkin-Elmer Model 21 spectrophotometer in carbon tetrachloride unless otherwise noted. Nuclear magnetic resonance spectra were determined on a Varian Model A-60 spectrometer in carbon tetrachloride using tetramethylsilane as internal standard.

exo,endo-**5-Bromomethylbicyclo[2.2.1]heptene-2 (IIa)** was prepared essentially by the method of Alder and Windemuth[14] and had bp 80–83° (13.5 mm) (lit.[14] bp 75–77° (13 mm)). The *exo–endo* mixture (1:4) was used as such for the subsequent steps.

6-Bromomethyl-3-oxatricyclo[3.2.1.0^{2,4}] octane (IIIa). A solution of sodium acetate (20.0 g, 0.24 mole) in 100 ml of 40% peracetic acid was added dropwise over 20 min to a solution of 74.8 g (0.40 mole) of IIa in 30 ml of chloroform at *ca.* 5°. The reaction mixture was stirred vigorously for an additional 2.5 hr at 0° at which point the layers were separated. The upper phase was extracted with chloroform and the combined extracts were washed with sodium hydroxide solution and water. After drying over magnesium sulfate the solvent was evaporated and the residue was distilled. The fraction boiling between 83 and 85° (1.25 mm) weighed 26.8 g (33%), and had the correct analysis for IIIa.

Anal. Calcd for $C_8H_{11}OBr$: C, 47.29; H, 5.42. Found: C, 47.21; H, 5.66.

The infrared spectrum showed a stong absorption at 848 cm^{-1} (film) typical of epoxides.[15] The nmr spectrum showed complex groups centered at τ 6.6 (2 H), 7.0 (2 H), and 8.3 (7 H).

Cyclization of IIIa with Sodium in Toluene. A suspension of 0.5 g (0.0022 g-atom) of sodium metal in 10 ml of dry toluene was heated to reflux with vigorous stirring under nitrogen. A drop of BF_3–etherate was added followed by dropwise addition of a solution of IIIa (1.0 g, 4.9 mmoles) in 5 ml of dry toluene. The resulting mixture was heated at reflux for 4 hr. After cooling, the reaction mixture was poured over Dry Ice to carbonate any unreacted lithium compounds. The salts were decomposed with 20 ml of 20% hydrochloric acid solution. Separation of the layers was followed by ether extraction and the combined toluene–ether extracts were washed with sodium hydroxide solution and water. The dried ($MgSO_4$) extracts were evaporated to give 0.51 g of an oil. Gas chromatography of this product on an 8-ft Carbowax 20M column at 185° showed a single peak and a group of several unresolved peaks in an area ratio of 2.8 to 1. The major peak proved to be alcohol IV. Preparative gas chromatography afforded pure IV, mp 155–157°.

Anal. Calcd for $C_8H_{12}O$: C, 77.37; H, 9.74. Found: C, 76.90; H, 9.78.

The mass spectrum showed a molecular ion at 124 in agreement with the tricyclic structure.

The infrared spectrum (mull) showed strong absorption at 3160 cm^{-1}. The nmr spectrum displayed two sharp singlets at τ 6.3 and 6.6 of area equal to one proton. The latter was identified as the OH proton by deuterium exchange and the former is assigned to the HCO proton. The remainder of the spectrum was complex with several broad absorptions between τ 7.3 and 8.3 (total area, 9 H).

The **p-toluenesulfonate** derivative had mp 64° and was prepared in the usual way and crystallized from pentane.

Anal. Calcd for $C_{15}H_{18}O_3S$: C, 64.75; H, 6.48. Found: C, 64.73; H, 6.65.

The **3,5-dinitrobenzoate** had mp 91–92° and was crystallized from ether.

Anal. Calcd for $C_{15}H_{14}N_2O_6$: C, 56.60; H, 4.40; N, 8.80. Found: C, 56.75; H, 4.79; N, 8.92.

exo, endo-**5-Chloromethylnorbornene-2 (IIb).** The material used was either the commercially available mixture (1:4) or was prepared from *exo,endo*-5-hydroxymethylnorbornene-2 by the following procedure.

A solution of 12.4 g (0.1 mole) of 5-hydroxymethylnorbornene in 25 ml of benzene and 10.9 g (0.12 mole) of pyridine was cooled to 5°. Over 1 hr, 14.3 g (0.12 mole) of thionyl chloride was added and the resulting mixture was heated at reflux for 6 hr. The reaction was quenched with water and extracted with ether. The combined extracts were washed with dilute hydrochloric acid, sodium bicarbonate solution, and water. The dried extracts were evaporated and distilled to give 8.6 g (61%) of IIb, bp 66–68° (2 mm) (lit.[14] bp 54–57° (11 mm)).

Gas chromatography of this product (12-ft Carbowax 20M) indicated the presence of only the *exo* and *endo* chlorides.

6-Chloromethyl-3-oxatricyclo[3.2.1.0^{2,4}]octane (IIIb). This epoxide was prepared in essentially the same way as was IIIa. From 35.6 g (0.25 mole) of chloride there was obtained 31.7 g (80%) of epoxide, bp 73–75° (0.9 mm).

Anal. Calcd for $C_8H_{11}OCl$: C, 60.57; H, 6.94. Found: C, 60.48; H, 6.80.

The infrared spectrum shows epoxide absorption at 851 cm^{-1}. The nmr spectrum shows two uneven doublets at τ 6.6 (2 H), a quartet at 6.9 (2 H), and a complex multiplet centered 8.3 (7 H).

Cyclization of IIIb with Lithium in Tetrahydrofuran. Under a nitrogen atmosphere, lithium ribbon (2.8 g, 0.4 g-atom) was cut into small pieces and placed in a flask with 20 ml of dry tetrahydrofuran. About 0.5 ml of BF_3–etherate was added followed by a solution of 15.85 g (0.10 mole) of IIIb in 25 ml of tetrahydrofuran over 1 hr. After heating at reflux for 24 hr the reaction mixture was filtered onto crushed Dry Ice. Dilute hydrochloric acid was added followed by ether extraction. The extracts were washed with sodium bicarbonate solution and water. After drying over sodium sulfate, the ether was evaporated to give 10.2 g of product, mp 155–156°, which was essentially pure (>95% by glpc) IV.[16]

exo-**Tricyclo[3.2.1.0^{3,6}]oct-2-yl Acetate (XI).** A 6.2-g (0.05 mole) sample of IV was acetylated by refluxing with 6.25 g (0.06 mole) of acetic anhydride and 0.5 g of sodium acetate for 2 hr. Addition of 100 ml of water was followed by ether extraction.

The extracts were washed with sodium bicarbonate solution and water. Evaporation of the ether gave 6.7 g (81%) of an oil which was pure XI as shown by glpc. The boiling point on an 18 × 0.4 in. spinning-band column was 88–89° (10 mm).

Anal. Calcd for $C_{10}H_{14}O_2$: C, 72.29; H, 8.43. Found: C, 72.44; H, 8.51.

Strong carbonyl absorption appeared at 1715 cm^{-1} (film) and the nmr spectrum showed broad singlets (area 1) at τ 5.3, 7.2, and 7.4. The CH_3 group appeared at τ 8.1. Complex absorption (5 H) was centered at τ 8.3.

Tricyclo[3.2.1.0^{3,6}]octan-2-one (V). Pyridine–Chromium Trioxide Procedure.[17] *exo*-Tricyclo [3.2.1.0^{3,6}]octan-2-ol (248 mg, 2 mmoles) was added in one portion to a stirred mixture of cold reagent prepared from 0.7 g (7 mmoles) of chromium trioxide in 7.8 ml of pyridine. The resulting mixture was stirred for 22 hr at 25° after which 80 ml of water was added to stop the reaction. Pentane extraction removed the product. The combined extracts were washed with hydrochloric acid, water, sodium bicarbonate solution, and water. Evaporation of the dried extracts gave 188 mg (77%) of crude ketone which was purified by gas chromatography. The retention time and spectral properties of this product were identical with those of the ketone prepared below.

Dichromate–Sulfuric Acid Procedure.[18] Oxidation of 12.4 g (0.1 mole) of IV with 8.7 g of potassium dichromate and 9.0 ml of sulfuric acid diluted to 50 ml according to the Brown and Garg procedure gave 11.0 g (90%) of crude ketone V. Purification by gas chromatography on a 6-ft Carbowax 20M column at 190° gave a solid, mp 126–127° (sealed capillary).

The **2,4-dinitrophenylhydrazone** melted at 189–190° after several crystallizations from acetone.

Anal. Calcd for $C_{14}H_{14}N_4O_4$: C, 55.63; H, 4.64; N, 18.54. Found: C, 55.50; H, 4.96; N, 18.68.

The **oxime XIII** was prepared from hydroxylamine hydrochloride and potassium hydroxide in aqueous methanol and was crystallized from *n*-hexane, mp 110–111°.

Anal. Calcd for $C_8H_{11}NO$: C, 70.04; H, 8.08; N, 10.21. Found: C, 70.16; H, 8.29; N, 10.31.

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(14) K. Alder and E. Windemuth, *Ber.*, **71**, 1939 (1938).

(15) S. B. Soloway and S. J. Cristol, *J. Org. Chem.*, **25**, 327 (1960).

(16) We have since found that more reliable results are obtained with lithium dispersion and a helium atmosphere; unpublished results with C. Weston.

(17) G. I. Poos, G. E. Arth, R. E. Beyler, and L. H. Sarett, *J. Am. Chem. Soc.*, **75**, 422 (1953), and Y. Mazur, N. Danieli, and F. Sondheimer, *ibid.*, **82**, 5889 (1960).

(18) H. C. Brown and C. P. Garg, *ibid.*, **83**, 2951 (1961).

The ketone V showed carbonyl absorption at 1750 cm^{-1} and displayed nmr absorptions at τ 6.8 (1 H) and complex multiplets between 7.2 and 8.5 (9 H); molecular ion at 122 (calcd 122).

Treatment of V with pyridine, potassium hydroxide, and deuterium oxide for 40 hr on a steam bath did not effect any deuterium incorporation. Norcamphor exchanged *ca.* one proton (nmr) under these conditions.

***endo*-Tricyclo[3.2.1.0^{3,6}]octan-2-ol (IX).** A solution of 3.175 g (0.026 mole) of ketone V in 50 ml of ether was slowly added to a slurry of 265 mg (0.0068 mole) of lithium aluminum hydride in 50 ml of ether. The resulting mixture was heated at reflux for 20 hr. The reaction mixture was decomposed with water and the salts were removed by filtration. The salts were washed with ether and the combined extracts were dried and evaporated to give 2.74 g (86.5%) of IX, mp 184–185° (sealed capillary).

The nmr spectrum of IX shows complex multiplets centered at τ 5.9 (1 H), 7.2 (1 H), and 6.4 (1 H). Complex absorption (9 H) also appeared centered at 8.3. A small sharp absorption peak at τ 6.3 is attributed to the HCO proton of the *exo* alcohol. The relative area of this peak indicated that about 15% of IV was present. Gas chromatography of this product on a 0.01 in. × 150 ft Castorwax column also indicated a mixture of the two epimers in a ratio of 85:15. The mass spectrum indicated a molecular ion at 124 (calcd 124).

The ***p*-toluenesulfonate** ester was prepared, in the usual way from the alcohol in pyridine and had mp 43.5–44.5° after crystallization from low-boiling petroleum ether (bp 30–60°).

Anal. Calcd for $C_{15}H_{18}O_3S$: C, 64.75; H, 6.48. Found: C, 64.36; H, 6.65.

The **3,5-dinitrobenzoate** ester was prepared and crystallized from ether, mp 112–113°.

Anal. Calcd for $C_{15}H_{14}N_2O_6$: C, 56.60; H, 4.40; N, 8.80. Found: C, 56.37; H, 4.64; N, 8.90.

Tricyclo[3.2.1.0^{3,6}]octane (I). A solution of 2.48 g (0.02 mole) of ketone V in 5 ml of ethylene glycol containing 5 ml of hydrazine hydrate and one drop of acetic acid was heated at 108° for 3 hr and then gradually heated to 160°. The solution was cooled and 4.0 g of sodium methoxide in 4 ml of methanol was added. The temperature was slowly raised to 180° over 3 hr. Nitrogen evolution was observed during the heating and a solid sublimed into the condenser. When cool, the reaction mixture was poured onto ice and extracted with ether. Evaporation gave *ca.* 1.5 g of crude product. Purification by preparative gas chromatography gave 0.84 g (40%) of pure hydrocarbon, mp 111–112° (sealed capillary). This material was homogeneous on a 150-ft capillary column of Ucon 50 HB 2000. The infrared spectrum showed a strong absorption at 1263 cm^{-1}[19] and no carbonyl or hydroxyl absorption. The nmr spectrum showed a complex multiplet superimposed on a singlet at τ 8.7 (area 3), a singlet (area 4) at 8.5, and broad singlets with fine structure at 7.8 (area 3), 7.6 (area 1), and 7.2 (area 1).

The molecular ion appeared at *m/e* 108 in agreement with the assigned structure. Strong peaks appeared at *m/e* 66 and 67.

Reaction of IV with HBr. A solution of 2.48 g (0.02 mole) of IV in 25 ml of 48% aqueous hydrobromic acid was heated at 80° for 6 hr. Dilution with 100 ml of water was followed by ether extraction. The combined extracts were washed with sodium bicarbonate solution and water. After drying (Na_2SO_4), the extracts were evaporated to give 2.6 g (61%) of a dark oil. Analysis on a 12-ft Craig column at 150° indicated only one product (XVI) which was collected and submitted for analysis.

Anal. Calcd for $C_8H_{11}Br$: C, 51.41; H, 5.92. Found: C, 51.35; H, 5.74.

The nmr spectrum showed a sharp singlet at τ 5.8 (area 1) and a complex multiplet centered at 7.9 (area 10).

Repetition of the experiment in the presence of 2.0 g of zinc bromide led to the same product, 2-bromotricyclo[3.2.1.0^{3,6}]-octane.

Reduction of 2-Bromotricyclo[3.2.1.0^{3,6}]octane with Sodium. The bromide (XVI, 1.87 g, 0.01 mole) was reduced by 1.0 g of sodium in 25 ml of liquid ammonia. After warming to room temperature, ether and water were added to the residue. Separation of the ether and further extraction gave 0.5 g (48%) of crude I after evaporation. The retention time and infrared and nmr spectra were all identical with the corresponding data for the Wolff–Kishner product.

2-Aminotricyclo[3.2.1.0^{3,6}]octane (XIV). To a stirred solution of 4.8 g (0.035 mole) of oxime XIII in 100 ml of dry ether was added 3.0 g (0.08 mole) of lithium aluminum hydride in small portions. The reaction mixture was heated at reflux for 48 hr and then hydrolyzed with water. The salts were removed by filtration and washed with ether. The dried (potassium carbonate) extracts were evaporated to give 2.60 g (61%) of amine which was purified by a molecular distillation, bp 94–96° (20 mm). The infrared spectrum showed absorptions at 3580 (sh) and 3280 (broad) cm^{-1} for the NH_2 group. Other prominent absorptions appeared at 1012, 909, 885, and 863 cm^{-1}. The nmr spectrum showed a sharp singlet at τ 6.2 of area 1 and a very broad absorption at 4.1 (area 1). Very complex absorption appeared at higher field. The product absorbed carbon dioxide rapidly and could not be analyzed for carbon and hydrogen.

The **phenylthiorurea** derivative was prepared and had mp 147–147.5°.

Anal. Calcd for $C_{15}H_{18}N_2S$: C, 69.67; H, 7.02; N, 10.85. Found: C, 69.51; H, 7.11; N, 10.61.

Deamination of XIV. A solution of 1.5 g (0.012 mole) of amine XIV in 25 ml of glacial acetic acid was cooled to 17 ± 1° and treated with 1.5 g (0.22 mole) of sodium nitrite over 1 hr. The resulting mixture was stirred overnight at room temperature. An additional 0.5 g of sodium nitrite was added followed by stirring for 1 hr. Crushed ice was added followed by ether extraction. The extracts were washed with dilute hydrochloric acid solution and sodium bicarbonate solution. The dried solution gave 1.6 g of an oil on evaporation. Glpc analysis on a 12-ft Craig column showed one major peak with the same retention time as authentic acetate XI and a minor peak (<10%). The nmr spectrum of the major peak was identical with that of an authentic sample of XI.

Solvolysis of *p*-Toluenesulfonates XX and XXI. A. Products. The *exo-p*-toluenesulfonate was solvolyzed by heating 0.162 g in 10 ml of 0.075 *N* sodium acetate–glacial acetic acid solution for 19 hr at 105°. Addition of water followed by ether extraction gave 0.085 g (88%) of essentially (>95%) pure acetate XI as shown by comparative retention times, infrared spectra, and nmr spectra. Gas chromatography on Carbowax 20M and Craig columns indicated only one major component. Gas chromatographic analysis of the derived alcohol on the 150 ft × 0.01 in. Castorwax column indicated alcohol IV as the only product.

The ***endo-p*-toluenesulfonate** (0.45 g) was solvolyzed under similar conditions (114° for 18 hr). The crude product (0.24 g) was again essentially pure acetate XI. The alcohol prepared from this acetate proved to have the same infrared spectrum as the original sample of IV.

B. Kinetics. The acetolysis data was furnished by Professor von R. Schleyer[12] and was obtained in the usual manner.[20] The data for X are as follows: k_1 (111°) = $1.75 \pm 0.12 \times 10^{-3}$; k_1 (93°) = $3.52 \pm 0.12 \times 10^{-4}$; k_1 (70°) = $3.19 \pm 0.15 \times 10^{-5}$; $k_{ext}{}^{25°} = 9.12 \times 10^{-8}\ sec^{-1}$; $\Delta H^* = 24.27$ kcal/mole; $\Delta S^* = -8.37$ eu. The data for XII are as follows: k_1 (111°) = $2.88 \pm 0.26 \times 10^{-5}$; k_1 (93°) = $4.16 \pm 1.32 \times 10^{-6}$; $k_{ext}{}^{25°} = 4.75 \times 10^{-10}\ sec^{-1}$; $\Delta H^* = 29.4$ kcal/mole; $\Delta S^* = -2.6$ eu.

The calculated[12] rate constants utilized the following data. Torsional strain relief for X was calculated using angles of 52° and 27° for the C_1H–CO and C_3H–CO angles, respectively. For XII, the angles were estimated to be 60° for the C_1C_8–CO interaction and 42° for the C_3C_4–CO projection. No nonbonded strain relief was deemed necessary in the *exo* case and a value of 1.4 kcal/mole was assumed for the relief of the nonbonded strain between the CH_2 of the cyclobutane ring and the *p*-toluenesulfonate moiety.

Preparation and Solvolyses of 2-Deuterio Systems XX and XXI. The *endo-p*-toluenesulfonate-2-*d* (XXI) was synthesized from the corresponding alcohol which, in turn, was prepared from reduction of ketone V with lithium aluminum deuteride (96.2%). The nmr spectrum of this alcohol showed essentially no HCO absorption at τ 5.9. Acetolysis gave the *exo*-acetate XXII which was converted to the deuterioalcohol. The nmr spectrum showed a very slight peak at τ 6.3, presumably the HCO proton of IV. The relative area was *ca.* 5% of the area of the OH proton. This product was converted to the *p*-toluenesulfonate ester XX and subjected to acetolysis. The nmr spectrum of the acetate obtained was very similar to that of the undeuterated material (XI) except that the HCO proton area was again only about 5% of the area expected for one proton. Thus, after two passes through the carbonium ion less than 2.5% exchange could have occurred per pass. The over-all yields were high in these steps.

Mass Spectral Data.[8] The complete data can be found in the thesis of R. A. P., Rutgers, 1963. The spectra of alcohols IV and

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(19) No regularities in this region were noted for these systems.

(20) S. Winstein, E. Grunwald, and L. Ingraham, *J. Am. Chem. Soc.*, **70**, 821 (1948).

IX were very similar showing ion current percentages for M^+ of 0.27 and 0.23, respectively. Both showed large $(M - 18)^+$ peaks (see text) and $C_5H_6^+$ and $C_5H_7^+$ peaks. These latter represent the base peaks in IX and IV, respectively. Both systems likewise show moderate $C_7H_7^+$ peaks. Ketone V shows a base peak at 66 ($C_5H_6^+$), a strong peak at 79, and a weak peak at 94 $(M - CO)^+$.

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Small-Ring Compounds. XLVII. Reactions of Optically Active Cyclopropylmethylcarbinyl Derivatives[1,2a]

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Abstract: Cyclopropylmethylcarbinylamine and cyclopropylmethylcarbinol were resolved into optical antipodes and their configurations were related. The former was deaminated with aqueous nitrous acid to give the latter with 0–4% net inversion of configuration. Solvolysis of N-methyl-4- alkoxypyridinium salts was investigated as a means of providing a leaving group which would not undergo "internal return." Solvolysis rates for N-methyl-4-(cyclopropylcarbinyloxy)pyridinium iodide and perchlorate in water and in 80% ethanol and of N-methyl-4-(cyclopropylmethylcarbinyloxy)pyridinium iodide in water were measured. The first-order rate constant for the hydrolysis of N-methyl-4-(cyclopropylmethylcarbinyloxy)pyridinium iodide at 30° was calculated to be 6×10^3 times that of N-methyl-4-(cyclopropylcarbinyloxy)pyridinium iodide. The hydrolysis of optically active N-methyl-4-(cyclopropylmethylcarbinyloxy)pyridinium iodide produced cyclopropylmethylcarbinol with 4.4 ± 1.5% inversion of configuration. The stereochemistry of the deamination of cyclopropylmethylcarbinylamine and of the hydrolysis of N-methyl-4-(cyclopropylmethylcarbinyloxy)pyridinium iodide and the ratio of rate constants for the cyclopropylmethylcarbinyl and cyclopropylcarbinyl pyridinium salts are discussed with respect to the possible intervention of nonclassical carbonium ion intermediates in these reactions.

Considerable interest attends the nature of the intermediates in carbonium ion type interconversion reactions of cyclopropylcarbinyl, cyclobutyl, and allylcarbinyl derivatives. Evidence regarding these intermediates has come principally from studies of solvolysis rates and product distributions in such interconversion reactions.[3]

In general, carbonium ion type reactions of both cyclopropylcarbinyl and cyclobutyl derivatives give similar relative amounts of products with the cyclopropylcarbinyl, cyclobutyl, and allylcarbinyl structures, almost independently of which of the two starting structures is employed. Such reactions include the reaction of cyclopropylcarbinylamine and cyclobutylamine with nitrous acid, the solvolysis of cyclopropylcarbinyl and cyclobutyl derivatives, and the reactions of cyclopropylcarbinol and cyclobutanol with thionyl chloride and of cyclopropylcarbinol with hydrogen bromide or phosphorus tribromide. This behavior suggests that all the above reactions go through common cationic intermediates; small variations in product composition may be accounted by specific effects of each reaction and do not require postulation of a drastic change in mechanism.

The solvolyses of cyclopropylcarbinyl and cyclobutyl derivatives are unusually fast. For instance, in 50% aqueous ethanol at 50°, cyclopropylcarbinyl chloride is 40 times more reactive than β-methylallyl chloride and cyclobutyl chloride is 15 times more reactive than isopropyl chloride.[4] Unusually high solvolysis rates are often indicative of nonclassical cationic intermediates.[5] The weight of the evidence is such, therefore, that the common intermediate(s) in the solvolyses of cyclopropylcarbinyl and cyclobutyl derivatives has (have) been inferred to be nonclassical in nature.[6]

The effect of methyl substitution at the methylene groups of the intermediate cations has been investigated in the deamination of the appropriate amines with aqueous nitrous acid.[7] The results fit reasonably well into a scheme similar to that presented for the unmethylated amines with some understandable differences due to the presence of the added methyl group. The isomeric methyl-substituted ions are, of course, not equal in stability, and their order of stability appears to be I $>$ II $\gg$ III. Two of the amines studied, 2-methylcyclobutylamine and 2-methylcyclopropylcarbinylamine, could form directly either of two non-

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(2) (a) From the Ph.D. Thesis of M. Vogel, California Institute of Technology, 1961. Presented in part at Sixteenth National Organic Chemistry Symposium of the American Chemical Society, Seattle, Washington, June 15, 1959; (b) National Science Foundation Predoctoral Fellow, 1958–1960.

(3) *Cf.* K. L. Servis and J. D. Roberts, *J. Am. Chem. Soc.*, **87**, 1331 (1965), and references cited therein.

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