Acid-Catalyzed Rearrangement of Tricyclic Alcohol 34.—To a solution of 194 mg of tricyclic alcohol **34** in 10 ml of spectroquality pentane was added 5 ml of a 50% aqueous sulfuric acid solution. The two phase system was stirred for 14 hr at room temperature. The pentane layer was separated from the aqueous layer, washed with water, and dried over magnesium sulfate. The pentane was removed by evaporation to afford 113.8 mg of tricyclic alcohol **8** as a white solid (53.6% yield). The spectral properties were identical with those of alcohol **8** prepared by rearrangement of alcohol **4**.

Acid-Catalyzed Rearrangement of Tricyclic Carbinol 35.—To a solution of 72.6 mg of tricyclic carbinol **35** in 3 ml of spectroquality pentane was added 1.5 ml of 50% aqueous sulfuric acid. The two-phase system was stirred at room temperature for 18 hr. The pentane layer was separated and washed with water. The combined aqueous layers were extracted with ether, and ether extracts were washed with water. The combined organic extracts were dried over magnesium sulfate and evaporated at reduced pressure to give 48.9 mg (75%) of a clear liquid having a camphorous odor. The spectral properties of this material were identical with those of tricyclic hydrocarbon **5** prepared from compound **1**.

3,6-Dimethyltricyclo[4.4.0.0^{2,7}]dec-3-ene (32) and 3-Methylene-6-methyltricyclo[4.4.0.0^{2,7}]decane (33).—To a solution of 180 mg of alcohol **1** in 1 ml of pyridine was added 0.25 ml of phosphorus oxychloride. The solution was slowly warmed to 90° and then allowed to cool to room temperature. The partially crystalline mixture was mixed with 25 ml of ice water and extracted with ether (three 30-ml portions). The combined ether extracts were washed with 5% HCl (50 ml), 10% K_2CO_3 (10 ml), and saturated NaCl (50 ml). After drying over $MgSO_4$, the ether was evaporated under reduced pressure to yield 135.5 mg of colorless liquid. Glpc analysis (10% NPGS, 135°) showed the product to be a mixture of **32** and **33** in a ratio of 80:20. The major product (endocyclic double bond isomer **32**) had the following spectral properties: ir (CCl_4) 3050, 3025, 2930, 2830, 1480, 1450, 1385, 1370, 1270, 1225, 1190, 1040, 982, 960, 940, 880, 860 cm^{-1}; pmr (CCl_4) δ 0.92 (s, 3, angular Me), 5.17 (m, 1, vinyl H). The minor product (exocyclic double bond isomer) had the following spectral properties: ir (CCl_4) 3030, 1680, 1500, 1480, 1470, 1465, 1400, 883 cm^{-1}; pmr (CCl_4) δ 0.87 (s, 3, angular Me), 2.60 (s, 1, C-2 H), 2.45 (broad t, 2, C-4 H's), 4.52 (q, 2, vinyl H's).

A solution of 199 mg of the olefin mixture, prepared as above, in 10 ml of pentane was layered over 5 ml of 50% aqueous sulfuric acid. After stirring vigorously for 16 hr, the pentane layer was decanted, dried, and evaporated to yield 181 mg of clear oil. Analysis by glpc and pmr showed that no reaction had occurred.

Registry No.—**5**, 32980-12-4 **6**, 32970-82-4; **7**, 32980-13-5; **7** 2,4-DNP, 32980-14-6; **8**, 32970-83-5; **9**, 32970-84-6; **10**, 32970-85-7; **11**, 32970-86-8; **12**, 32970-87-9; **13**, 32970-81-3; **13** epimer, 32970-88-0; **14**, 32970-89-1; **14** epimer, 32970-90-4; **16**, 32970-91-5; **16** epimer, 33020-76-7; **19**, 13351-29-6; **19** 2,4-DNP, 32970-93-7; **20**, 32970-94-8; **32**, 33015-39-3; **33**, 33015-40-6; **34**, 33020-77-8; **35**, 33020-78-9.

Acknowledgment.—We thank the National Science Foundation and the Alfred P. Sloan Foundation for financial support.

Synthesis and Chemistry of Some 2-Substituted Tricyclo[3.3.0.0^{3,7}]octane Derivatives[1]

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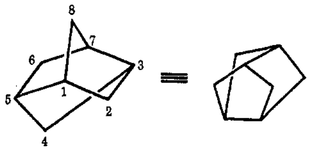
Received July 22, 1971

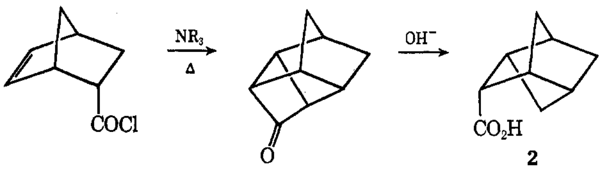
A survey of the chemistry of 2-substituted tricyclo[3.3.0.0^{3,7}]octyl derivatives was initiated. Experiments were conducted which produced the following reactive intermediates at the 2 position: free radicals, carbanions, and carbonium ions. It was found that those reactions which involved formation of cationic intermediates yielded rearranged products *via* a formal ring contraction of a five- to a four-membered ring. Analysis of solvolysis data of the 2-brosylate suggests that this rearrangement proceeds with a rate enhancement of the order of *ca.* 10^8.

Exploitation of the unique properties of strained molecules has provided physical organic chemists with significant insights into the mechanistic details of organic transformations. In addition, there has been a special fascination with the synthesis and behavior of molecules which possess a high degree of symmetry: *e.g.*, tetrahedrane, cubane, adamantane. These three molecules are notable in that the smallest rings in each system are all of the same size, three-, four-, and six-membered, respectively. We have for some time been interested in the most symmetrical all five-membered ring homolog: tricyclo[3.3.0.0^{3,7}]octane (1).[2-4] In this report we wish to detail the synthesis of several derivatives of **1** and to report the results of a survey of some of the chemistry of this system.



1

The key intermediates used in this study were the acid **2** and the alcohol **3**. The detailed procedure for



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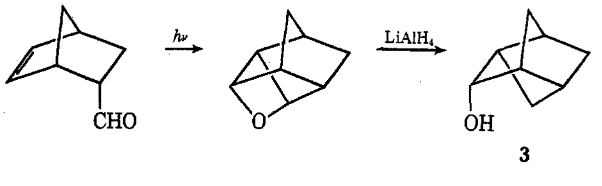

3

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[1] Presented in part at the 158th National Meeting of the American Chemical Society, New York, N. Y., Sept 1969, Abstracts, ORGN 74; see also R. R. Sauers and B. R. Sickles, *Tetrahedron Lett.*, 1067 (1970).

[2] (a) R. R. Sauers, W. Schinski, and M. M. Mason, *ibid.*, 79 (1969); (b) R. R. Sauers and K. W. Kelly, *J. Org. Chem.*, **35**, 3286 (1970).

[3] For other syntheses of this ring system see (a) O. W. Webster and L. H. Sommer, *ibid.*, **29**, 3103 (1964); (b) P. K. Freeman, V. N. M. Rao, and G. E. Bigam, *Chem. Commun.*, 511 (1965); (c) B. R. Vogt, S. R. Suter, and J. R. E. Hoover, *Tetrahedron Lett.*, 1609 (1968).

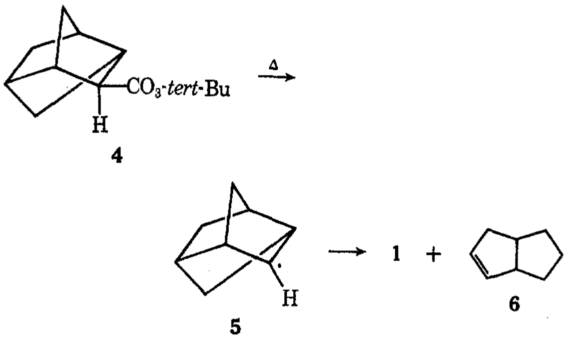
[4] This molecule may be regarded as a bis nor homo log of adamantane or twistane depending on whether the methylenes are inserted at the zero-carbon bridges or at the appropriate methylene sites, respectively. The symmetry of this molecule (D_{2d}) precludes both structural isomerism and optical activity in monosubstituted derivatives.

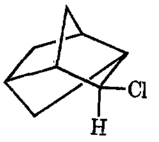
the preparation of 2 has been published[2b] and the details for the preparation of 3[2a] may be found in the Experimental Section.

Results and Discussion

The survey of the chemistry of 1 was designed to include some representative reactions from three major categories: free radical reactions, reactions involving carbanionic intermediates, and solvolyses and other carbonium ion reactions. It was felt that the results of these studies would provide a reasonable overview of the behavior of this system.

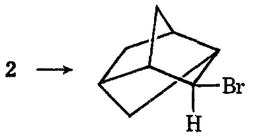
Radical Reactions.—Our interest in exploring this area was stimulated by two previous reports dealing with the behavior of the 2-tricyclo[3.3.0.0^{3,7}]octyl radical. In our earlier study[2b] it was shown that **5** underwent cleavage in competition with chain transfer (eq 1). On the other hand, it was reported that chlorination of **1** gave chloride **7** exclusively.[5] It was of interest to examine more fully the dependency of product distribution on reaction conditions and the nature of the termination step.





7

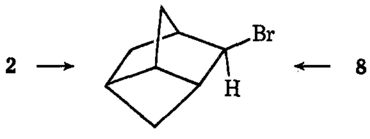
The first and simplest results were obtained on treatment of acid **2** with lead tetraacetate and lithium bromide.[6] There was obtained a 29% yield of a bromide whose spectral properties [nmr δ 4.11 (t)] and elemental analysis were compatible with those expected for **8**.



8

In addition, this substance could be converted to **1** by reduction (*vide infra*). The analogous reaction with lithium chloride proved to be considerably more complex in that a mixture of at least six products was obtained,[7] including a 36% yield of unrearranged chloride **7**. The yield of **7** was doubled if a molar excess of lithium chloride was used.

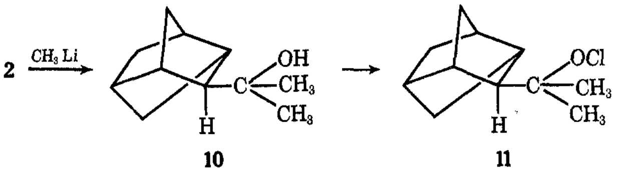
Attempts to prepare **8** by either the conventional Hunsdiecker procedure or the Cristol–Firth modification[8] led to the formation of the bromide **9**. In both cases, it is likely that the ultimate product was formed from **8** *via* metal ion catalyzed rearrangements.



9

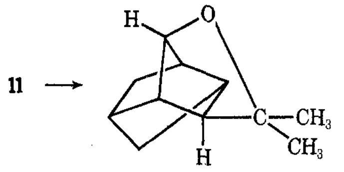
The feasibility of this sequence was demonstrated in the second case in that it was found that **8** could be transformed into **9** on treatment with mercuric oxide–mercuric bromide under the reaction conditions. Rearrangements during Hunsdiecker reactions are rare[9] and are unprecedented in Cristol–Firth reactions.

The last radical reaction studied was the decomposition of the hypochlorite **11**, prepared according to eq 2.



(2)

Thermal and photochemical decompositions of hypochlorites are known to produce radicals by intramolecular hydrogen abstractions and/or by homolytic cleavages.[10] In the case at hand, both methods of decomposition gave a complex mixture of products in which only trace amounts of chloride **7** could be detected. An oxygen-containing product was isolated to which structure **12** is assigned on the basis of spectral data [nmr δ 3.94 (d, $J = 2.5$ Hz)] and elemental analysis.[11] Thus the intermediate alkoxy radical undergoes preferential intramolecular hydrogen abstraction rather than homolytic cleavage. In this respect this system resembles the behavior of the analogous *endo*-norbornyl derivative (eq 3) and stands in contrast to that of the exo system (eq 4). These differences are best rationalized in terms of the distances between the δ hydrogens and the oxy radicals. It is clear from models that this distance is significantly greater in the *exo*-norbornyl system than in the other two.



12

In general, it appears that the tricyclooctyl radical **4** is relatively stable and that ring cleavage is not expected except when the termination step requires significant activation energy. The fact that **4** does

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[5] P. K. Freeman, R. B. Kinnel, and T. D. Ziebarth, *Tetrahedron Lett.*, 1059 (1970).

[6] J. K. Kochi, *J. Org. Chem.*, **30**, 3265 (1965).

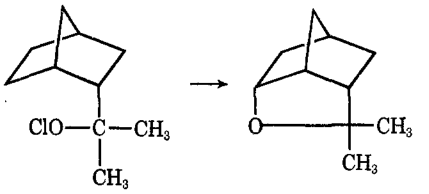
[7] In addition to **7**, the following components were identified: 2-acetoxytricyclo[3.2.1.0^{3,6}]octane (40%), 2-chlorotricyclo[3.2.1.0^{3,6}]octane (6%), and 2-acetoxytricyclo[3.3.0.0^{3,7}]octane (6%).

[8] S. J. Cristol and W. C. Firth, *J. Org. Chem.*, **26**, 280 (1961).

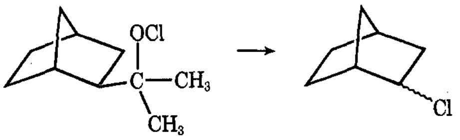
[9] W. V. E. Doering and M. Farber *J. Amer. Chem. Soc.*, **71**, 1514 (1949).

[10] F. D. Greene, M. L. Savitz, F. D. Osterholtz, N. H. Lau, W. N. Smith, and P. M. Zanet, *J. Org. Chem.*, **28**, 55 (1963).

[11] The by-products formed in this reaction are believed to arise from the reaction of unreacted alcohol **10** with the HCl liberated from the cyclization step.



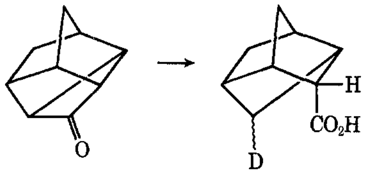
(3)



(4)

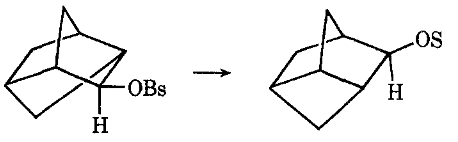
undergo ring opening under relatively mild conditions (*ca.* 125°) is evidence that strain relief provides a significant driving force in this system. The bornyl radical, for example, undergoes relatively minor ring cleavage at temperatures as high as 255°.[12]

Carbanion Reactions.—Carbanions of **1** were generated under two widely differing sets of conditions. The reduction of bromide **8** (*vide supra*) was carried out with metallic sodium in liquid ammonia and produced **1** of greater than 94% purity. The potassium *tert*-butoxide–water–ether cleavage of **13** was repeated in deuterium oxide to establish unequivocally the ultimate source of the carbon-bound hydrogen. The fact that one atom of deuterium was found in the product acid **14** confirms the presence of the postulated carbanion intermediate.[13] Although ring opening of carbanions in a fashion analogous to the radical cleavage (eq 1) would be expected to be exothermic, the reaction conditions in the above experiments were relatively mild.[14]

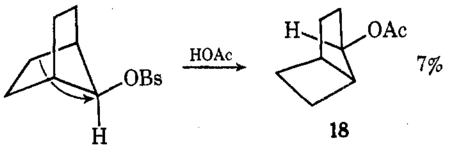


13 **14**

Carbonium Ion Reactions.—There are indications from the results of at least two of the reactions discussed above that rearrangements of the 2-tricyclo[3.3.0.0^{3,7}]octyl carbonium ion are remarkably facile: the mercuric salt catalyzed rearrangement of **8** and the formation of 2-acetoxytricyclo[3.2.1.0^{3,6}]octane from **2** on treatment with lead tetraacetate.[6,15] In order to examine this rearrangement more systematically, we chose to study the behavior of brosylate **15** under solvolysis conditions. Under either acetolysis or hydrolysis conditions the only detectable products were derivatives of the tricyclo[3.2.1.0^{3,6}]octyl system (**16**).[16] This remarkable rearrangement involves a formal ring contraction of a five- to a four-membered ring and is without precedent. In many respects (see below for details) the behavior of the 7-norbornyl system serves as a useful model for comparative analysis. In this system, kinetic and product studies led to the conclusion that the four-membered ring system **18** is *ca.* 14 kcal/mol less stable than the isomeric system **17**.[17]



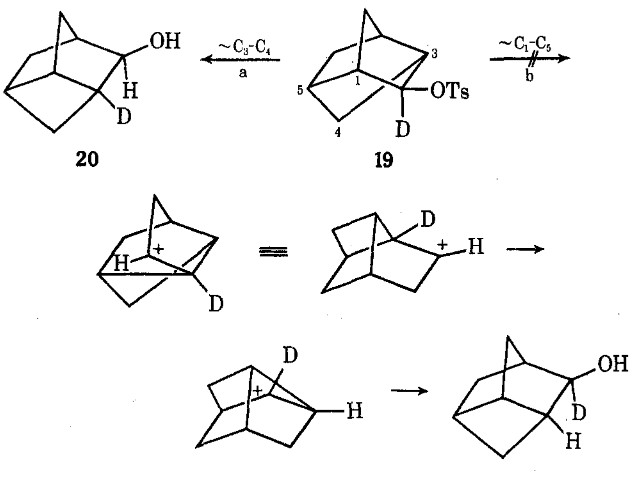
15 **16**



17 **18**

Further insight into the mechanism of the rearrangement **15** → **16** was provided by a labeling study and by measurement of the kinetics of acetolysis. The purpose of the labeling experiments was to differentiate between the direct pathway of migration (a) and a two-step sequence (b) which would lead to the same final product. As shown in Scheme I, these two paths lead to two differently labeled deuterated isomers starting with the deuterated tosylate **19**. The finding that the alcohol isolated from the hydrolysis of **19** had essentially no deuterium at C$_2$ strongly supports the direct migration pathway and unequivocally eliminates the two-step mechanism.

Scheme I



The kinetic analysis of the acetolysis of **15** was complicated by non-first-order behavior. During the first 28% of the reaction the calculated first-order rate constants drifted downward until a constant value of 1.3×10^{-5} sec^{-1} was attained. This behavior is typical of systems which solvolyze with internal return to form a less reactive substrate, the mathematical analysis having been worked out by Young, Winstein, and Goering.[18] Our results are most consistent with the situation described by Scheme II in which direct solvolysis (**15** → **16**) and internal return (**15** → **21**) are competitive processes. Freeman and coworkers[5] arrived at the

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(12) J. A. Berson, C. J. Olsen, and J. S. Walia, *J. Amer. Chem. Soc.*, **84**, 3337 (1962).

(13) P. G. Gassman and F. V. Zalar, *ibid.*, **88**, 2252 (1966); see also P. G. Gassman, J. T. Lumb, and F. V. Zalar, *ibid.*, **89**, 946 (1967).

(14) For discussions and literature analogies see E. A. Hill, R. J. Theissen, and K. Taucher, *J. Org. Chem.*, **34**, 3061 (1969), and P. K. Freeman, V. N. M. Rao, D. E. George, and G. L. Fenwick, *ibid.*, **32**, 3958 (1967).

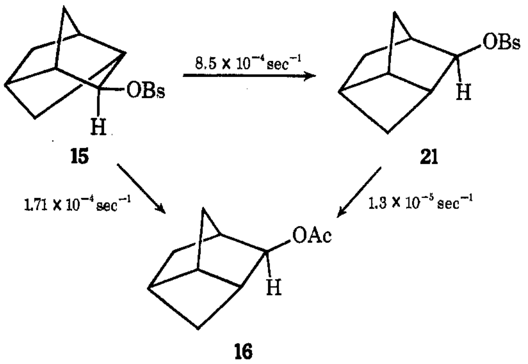
(15) Carbonium ion rearrangements have not generally been observed in these decarboxylations when lithium chloride is present owing to the rapid ligand transfer step. For example, neopentyl chloride can be prepared in high yield from β,β-dimethylbutyric acid.[6]

(16) R. R. Sauers, R. A. Parent, and S. B. Damle, *J. Amer. Chem. Soc.*, **88**, 2257 (1966).

(17) S. Winstein, F. Gadient, E. T. Stafford, and P. E. Klinedinst, Jr., *ibid.*, **80**, 5895 (1958).

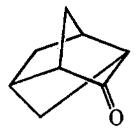
(18) W. G. Young, S. Winstein, and H. L. Goering, *ibid.*, **73**, 1958 (1951).

SCHEME II



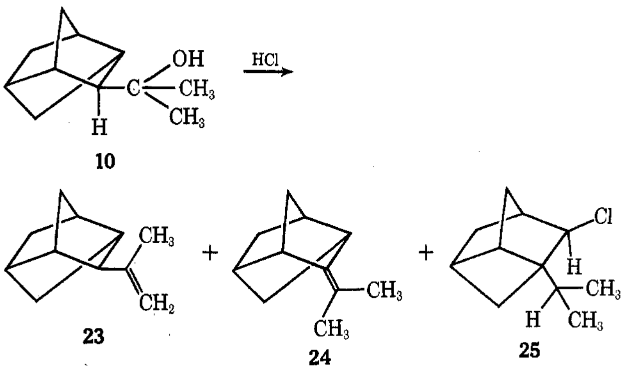
same conclusion on the basis of similar experimental results. The basis for the adoption of Scheme II rests on several additional observations. For one thing, there is good agreement between the calculated rate of disappearance of **21** and that observed: 1.4×10^{-5} sec^{-1} *vs.* 1.3×10^{-5} sec^{-1}.[16] Secondly, it was observed on monitoring the acetolysis by nmr spectroscopy that the rate of disappearance of **15** exceeded the rate of formation of **16** and that a new peak appeared in the region expected for protons bound to a secondary carbon bearing oxygen. It was shown by direct comparison that this peak had the same chemical shift as the CHO proton in **21**.

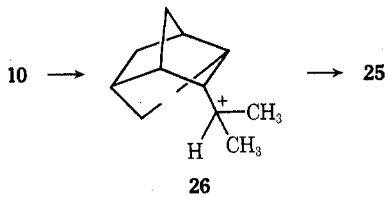
The significance of the rate data can be appreciated by comparison with model systems or by use of empirical correlations.[19] In the absence of steric complications[20] there is a good correlation between solvolysis rates and the stretching frequencies of the carbonyl derivatives located at the same sites in those cases which are believed to ionize without anchimeric assistance. On this basis it is estimated that **15** should solvolyze 10^{-7} times as fast as cyclohexyl brosylate. A rate enhancement of 10^9 may be calculated from the actual rate ratio at 53°.[21] Alternatively, one can compare rates directly with those from model systems. As mentioned earlier, the 7-norbornyl system appears to be closely related to **15** in view of the correspondence between bond angles in the ground states and at the trigonal centers. For example, the bond angles about C_7 in norbornanes range from 92 to 97°[22] compared with the value of 93° estimated from models for the C_1–C_2–C_3 angle in **15**. The similarity in carbonyl stretching frequencies between 7-ketonorbornane (1773 cm^{-1}) and 2-ketotricyclo[3.3.0.0^{3,7}]octane (**22**) (1771 cm^{-1}) is likewise suggestive of similar geometry at the trigonal centers in these two molecules. This analysis leads to a value of 10^7 for the rate enhancement factor.[23]



22

In view of the reservations which have arisen concerning the appropriateness of these calculations and analogies,[20,24,25] it was important to provide more compelling data to support the conclusions. It is known that alkyl groups stabilize carbonium ions to a relatively large degree. Factors as large as 10^8 have been reported for the rate ratios of tertiary/secondary solvolyses,[25] although more typical α-CH_3/H effects are in the range 10^4–10^5.[26] Substitution of a methyl group for hydrogen in the tricyclo[3.3.0.0^{3,7}]octyl system would thus not be expected to sufficiently stabilize the resulting tertiary carbonium ion to the extent that rearrangement would be inhibited. An indication that this conclusion is indeed correct comes from the results of the reaction of alcohol **10** with hydrochloric acid. Three products were isolated from this reaction: two olefins and a chloride. The two olefins were assigned structures **23** and **24** on the basis of analysis of infrared and nmr spectral data. More importantly, the chloride formed was not the product of direct hydroxyl replacement, since the nmr spectrum displayed a low-field singlet attributable to a CHCl moiety. This finding and the fact that an isopropyl group was also present lead us to propose structure **25** for this substance. This product could be formed by rearrangement of the tertiary ion **26**, itself the result of hydride shifts and/or protonation of **24**. While it has not been established whether **25** is formed in a kinetically controlled reaction or not, it should be pointed out that these products were also formed as by-products during the photochemical decomposition of **11** (15 min at −10°, 30 min at 25°). For comparison, the product of kinetic control was isolated under considerably more vigorous





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(19) (a) C. S. Foote, *J. Amer. Chem. Soc.*, **86**, 1853 (1964); (b) P. v. R. Schleyer, *ibid.*, **86**, 1854 (1964); (c) J. L. Fry, C. J. Lancelot, L. K. M. Lam, J. M. Harris, R. C. Bingham, D. J. Raber, R. E. Hall, and P. v. R. Schleyer, *ibid.*, **92**, 2538 (1970).

(20) H. C. Brown, W. J. Hammar, J. H. Kawakami, I. Rothberg, and D. L. Vander Jagt, *ibid.*, **89**, 6381 (1967).

(21) The value for cyclohexyl brosylate was taken from data given by H. C. Brown and G. Ham, *ibid.*, **78**, 2735 (1956).

(22) J. F. Chiang, C. F. Wilcox, Jr., and S. H. Bauer, *ibid.*, **90**, 3149 (1968).

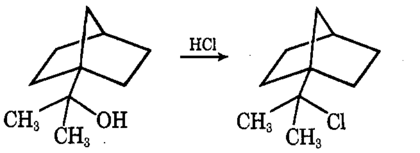
(23) The rate of acetolysis of **17** at 53° (*ca.* 10^{-11} sec^{-1}) was calculated from data given by H. Tanida, S. Ikegarni, and N. Ishitobi, *ibid.*, **89**, 2928 (1967).

(24) R. E. Davis, D. Grosse, and A. Ohno, *Tetrahedron*, **23**, 1029 (1967).

(25) J. L. Fry, J. M. Harris, R. C. Bingham, and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **92**, 2540 (1970).

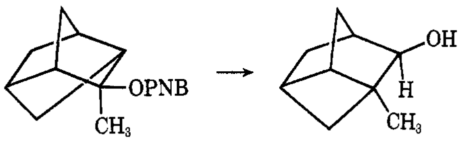
(26) K. L. Servis, S. Borčić, and D. E. Sunko, *Tetrahedron*, **24**, 1247 (1968).

conditions (30 min at 0°, 1 hr at 25°) in the case of dimethyl-1-norbornylcarbinol (eq 5).[27]



(5)

Finally, we have some preliminary results with the tertiary *p*-nitrobenzoate **27** which also undergoes rearrangement concurrent with hydrolysis.[28,29] In this case the unrearranged alcohol was shown to be stable toward the reaction conditions, and the rearranged alcohol was assigned structure **28** on the basis of its mass spectral fragmentation pattern and nmr data.



27 **28**

There can be little doubt that these cationic reactions proceed with great facility, the overall driving force being rearrangement to a more stable ring system. Although relief of nonbonded strains may be significant in promoting the rearrangements, it appears that the principal factor involves relief of bond angle strains at carbons **2** and **6**. It is estimated that the C–C–C angles at these positions expand by as much as 10–12° during the course of the rearrangements. None of the other C–C–C angles appear to change by more than a few degrees during the rearrangement. In any event, these results clearly demonstrate that carbon–carbon participation in strained saturated systems can produce rather large rate enhancements. Previously, rate enhancements of the magnitude discussed here have been observed only in systems in which double bonds or cyclopropyl rings were involved. A more complete discussion of the nature of the intermediates and transition states in these solvolyses will be deferred until data is available on the substituted systems.

Summary and Conclusions

The results discussed above present an interesting spectrum of behavior. Under the conditions examined the carbanionic species proved to be stable. The free radical, given sufficient activation, rearranged *via* cleavage of one of the bonds between adjacent bridgeheads. It is interesting that the same mode of cleavage is not found in carbonium ion reactions, especially when one considers the strain relief which must accompany this process. Instead, the carbonium ion invariably suffered ring contraction with the formation of the tricyclo[3.2.1.0^{3,6}]octyl system. This latter result highlights the complexities of the chemistry of strained polycyclic ring systems and provides stimulus for further experimentation.

Experimental Section

Elemental analyses were determined by Micro-Tech Laboratores, Skokie, Ill. Infrared spectral data was obtained from a Perkin-Elmer Model 137 spectrometer on thin films or as noted. Nuclear magnetic resonance spectra were obtained from a Varian Model A-60 spectrometer in carbon tetrachloride with tetramethylsilane as internal standard. Gas chromatograms were determined on an Aerograph A90P (analytical and preparative): (A) 15-ft 5% Carbowax 20M, (B) 12-ft 2% Carbowax 20M, (C) 12-ft 10% Apiezon L. Melting points were determined on a Mel-Temp apparatus and are uncorrected. Mass spectra were determined on an Hitachi RMU-7 mass spectrometer at 70 eV.

2-Bromotricyclo[3.2.1.0^{3,6}]octane (9).[8] A.—A solution of 0.54 g (3.1 mmol) of 2 and 0.54 g (3.4 mmol) of bromine in 5 ml of carbon tetrachloride was added over a 10-min period to an ice-cold suspension of 1.33 g (6.16 mmol) of red mercuric oxide in 1 ml of carbon tetrachloride. The resulting mixture was stirred at 26° for 17 hr and filtered to remove the mercury salts. Gc analysis (A, 150°) revealed a single component, which was isolated by evaporation of the solvent followed by distillation of the residue. The yield of product, bp 84° (8 mm), whose infrared and nmr spectra were identical with those of authentic[16] 9, was 0.196 g (34%).

B.—The silver salt of 2 was prepared[30] by treatment of 1.0 g (6.58 mmol) of the acid in 10 ml of water and 0.6 ml of 28% ammonium hydroxide solution with a solution of 1.1 g of silver nitrate in 15 ml of water. The precipate was collected, washed with water and ether, and dried at 100° (0.2 mm).

A suspension of the salt in 15 ml of dry petroleum ether (bp 30–60°) was cooled to −10° and treated with a solution of 0.705 g (4.42 mmol) of bromine in 5 ml of petroleum ether. The mixture was stirred for 30 min at −10°, 30 min at 25°, and 3 hr at reflux. The solvent was evaporated after filtration and the residue was distilled at 45° (0.1 mm) to give 0.275 g (38%) of bromide 9 whose infrared and nmr spectra were identical with those of authentic material.

2-Bromotricyclo[3.3.0.0^{3,7}]octane (8).—To a solution of 1.00 g (6.58 mmol) of acid 2 and 2.92 g (6.58) mmol of lead tetraacetate in 15 ml of dry benzene was added 0.805 g (6.58 mmol) of lithium bromide dihydrate.[6] The resulting mixture was flushed with nitrogen and placed in an oil bath at 80° for 4.5 hr. The solvent was then decanted, diluted with ether, and washed with sodium bicarbonate solution. The dried solvents were evaporated to give a residue which was distilled at 60° (1 mm) to give 0.35 g (29%) of a colorless oil: nmr δ 4.11 (t, 1 H, J = 1.7 Hz) broad singlets at 2.80, 2.65, and 2.38 (5 H), and a singlet at 1.47 (5 H); ir 10.07, 10.76, 11.72, 12.42 (s), 13.10, 13.70 μ (s).

Anal. Calcd for $C_8H_{11}Br$: C, 51.37; H, 5.93; Br, 42.73. Found: C, 51.13; H, 5.68; Br, 42.36.

2-Chlorotricyclo[3.3.0.0^{3,7}]octane (7). A.—A solution prepared from lead tetraacetate (2.92 g, 6.58 mmol), 1.00 g (6.58 mmol) of acid 2, and 0.293 g (6.92 mmol) of lithium chloride was flushed with nitrogen and heated at 80° for 4 hr. The reaction was processed as in the preceding experiment to yield 0.411 g of a complex product mixture. Gc analysis (A, 148°) revealed six compoenents in the area ratios i, 6%; ii, 2.5%; iii, 36%; iv, 40%; v, 10%; vi, 6%. Compound i had the same retention time as a sample of 2-chlorotricyclo[3.2.1.0^{3,6}]octane.[31] Compound iii was isolated by preparative gc and assigned structure 7: nmr δ 3.95 (t, 1 H, J = 1.7 Hz), 2.8–2.10 (m, 5 H), 1.7–1.17 (m, 5 H); ir 10.05, 10.69 (s), 11.64, 12.15 μ (s).

Anal. Calcd for $C_8H_{11}Cl$: C, 67.39; H, 7.78; Cl, 24.85. Found: C, 67.49; H, 7.69; Cl, 24.62.

Compound iv was isolated and shown to be 2-acetoxytricyclo[3.2.1.0^{3,6}]octane[10] by comparitive ir and nmr spectra. Compound v had an infrared spectrum which was identical with that of 2-acetoxytricyclo[3.3.0.0^{3,7}]octane.

B.—The reaction was repeated with a twofold excess of lithium chloride. The gas chromatogram showed the following percentages of the products: i, 7.2%; ii, 1.1%; iii, 70.0%; iv, 16.1%; v, 2.6%; vi, 2.6%.

Reaction of 2 with Lead Tetraacetate.—A solution of acid 2 (0.132 g, 0.87 mmol) and 3.86 g (0.87 mmol) of lead tetraacetate in 2 ml of benzene was heated for 6 hr at 80°. The gas chromatogram showed three components in the area ratios 79:10:11.

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[27] R. R. Sauers and D. H. Ahlstrom, *J. Org. Chem.*, **32**, 2233 (1967).

[28] B. R. Sickles, M.S. Thesis, Rutgers University, 1970.

[29] Kinetic studies are in progress whose objective is to determine the magnitude of the α-CH_3/H effect. Complete details of the syntheses, products, and kinetics of these reactions will be presented in a subsequent communication.

[30] R. R. Sauers and R. J. Kiesel, *J. Amer. Chem. Soc.*, **89**, 4695 (1967).

[31] Prepared and characterized by C. Weston, Ph.D. Thesis, Rutgers University, New Brunswick, N. J., 1967.

The major component had the same retention time as compound iv above. The retention time of the next major compound was identical with that of vi in the preceding experiment.

Dimethyl-2-tricyclo[3.3.0.0^{3,7}]octylcarbinol (10).—A 1.67 *M* solution of methyllithium in ether (24 ml, 40 mmol) was added to a solution of 1.52 g (10 mmol) of **2** in 30 ml of ether. The mixture was stirred and heated at reflux for 2 hr. The reaction mixture was poured onto ice and the ethereal layer was separated and washed with sodium bicarbonate solution. Gc analysis (A, 180°) revealed two components in nearly equal quantities. The mixture was treated with a second quantity of methyllithium (18 ml) for 2 hr. After work-up, gc analysis showed one peak and evaporation of ether gave an oil which distilled at 58.5° (0.25 mm): yield 1.34 g (81%); nmr δ 2.52–2.0 (m, 5 H), 1.24–1.15 (m, 6 H), 1.18 (s), 1.12 (s), and 0.75 (m, 7 H); ir 2.83, 7.73, 8.58, 10.50, and 12.11 μ.

Anal. Calcd for $C_{11}H_{18}O$: C, 79.46; H, 10.92. Found: C, 79.68; H, 11.02.

Decomposition of 11.[10] **A. Photochemical.**—The hypochlorite **11** was prepared in 5.5 ml of carbon tetrachloride from 0.50 g (3.0 mmol) of **10**. The solution was cooled to −10° and irradiated with a 250-W sun lamp for 15 min in a nitrogen atmosphere. The solution was allowed to stand at 25° for 30 min after which time it gave a negative starch–iodide test. Gc analysis (A, 152°) indicated the presence of six products, three of which were derived from the alcohol **10** (see below). Essentially no chloride **7** was present in the products. The major product proved to be alcohol **10**. The next most significant product (**12**) was isolated by preparative gc: nmr δ 3.94 (d, 1 H, J = 2.5 Hz), 2.55–1.85 (m, 5 H), 1.22 (s, 3 H), 1.00 (s, 3 H), 1.62–0.90 (m, 4 H); ir 9.22 (s), 11.98, and 12.28 μ.

Anal. Calcd for $C_{11}H_{16}O$: C, 80.44; H, 9.82. Found: C, 80.20; H, 9.71.

The three minor products were isolated and shown to be **23**, **24**, and **25**. Compound **24** showed the following spectral data: nmr δ singlets at 2.61 (2 H), 2.30 (2 H), 1.55 (6 H) and a multiplet (6 H) at 1.30; no strong ir bands below 8 μ.

Anal. Calcd for $C_{11}H_{16}$: C, 89.12; H, 10.88. Found: C, 89.28; H, 11.07.

Compound **23** gave δ 4.67 (s, 1 H), 4.55 (s, 1 H), 2.27 (m, 5 H), 1.58 (s), and 1.78–0.90 (m, 9 H); ir 6.06 and 11.30 μ (s).

Anal. Found: C, 89.21; H, 10.82.

Compound **25** gave nmr identical with that found below except for a small impurity peak at δ 3.82; ir 11.55 and 13.25 μ.

Anal. Calcd for $C_{11}H_{17}Cl$: C, 71.53; H, 9.28; Cl, 19.20. Found: C, 71.71; H, 9.36; Cl, 19.30.

B. Thermal Decomposition.—On heating a carbon tetrachloride solution of **11** for 20 hr at reflux a similar product mixture was obtained.

Reduction of 8.—A solution of 0.306 g (1.64 mmol) of **8** in 1 ml of ether was added to a suspension of 0.50 g (22 mg-atom) of sodium in 15 ml of liquid ammonia. The mixture was allowed to warm to 25° over a period of 4 hr, at which time the reaction was quenched with a small amount of ethanol. Water was then added and the product was extracted into ether. The ether was evaporated carefully to a volume of 1.5 ml and then analyzed by gc (C, 168°). The major component (94%) was collected by preparative gc to yield 0.072 g (41%) of **1**. The nmr spectrum showed two singlets at δ 2.24 (4 H) and 1.30 (8 H) in agreement with the literature.[3b] The retention time of the minor product was close to that of **6** but positive identification was not made.

Deuteriotricyclo[3.3.0.0^{3,7}]octane-2-carboxylic Acid (14).—The cleavage of ketone **13** was repeated[2b] except that deuterium oxide was substituted for water in the first step. An 84% yield of **14** was isolated which showed a carbon–deuterium stretching band at 4.56 μ in the infrared spectrum. The nmr spectrum displayed singlets at δ 12.13 (1 H) and 1.40 (5 H) and a multiplet at 2.70–2.25 (5 H).

Reaction of 10 with Hydrochloric Acid.—A solution of 50 mg of **10** in 0.5 ml of carbon tetrachloride was stirred for 20 hr with 50 μl of concentrated hydrochloric acid. The gas chromatogram showed three of the components which were formed from the hypochlorite photolysis in the ratios **23** (4%), **24** (19%), and **25** (77%). The nmr spectrum of **25** showed singlets (1 H) at δ 4.01 and 2.66 (2 H), doublets at 0.87 (3 H), J = 6 Hz) and 0.77 (3 H, J = 6 Hz), and a multiplet at 2.32–1.05 (8 H).

4-Oxatricyclo[4.2.1.0^{2,5}0^{3,7}]nonane.[2a]—A solution of 68 g (0.555 mol) of norbornene-5-carboxaldehyde[32] (75% endo) and 38 g of piperylene in 1 l. of ether was irradiated for 160 hr with a 450-W Hanovia immersion lamp equipped with a Vycor filter. The resulting solution was evaporated and the residue was sublimed. Crystallization of the sublimate from pentane give 28.9 g (57%) of the oxetane, mp 134–137° (lit.[2a,33] mp 136–137.5°).

Tricyclo[3.3.0.0^{3,7}]octan-2-ol (3).—A slurry of 20 g (0.19 mol) of lithium aluminum hydride in 175 ml of *N*-methylmorpholine was heated to reflux and a solution of 10 g (82 mmol) of the above oxetane in 75 ml of *N*-methylmorpholine was added over 1 hr. The reaction was heated and stirred for 5 days. The excess hydride was decomposed by dropwise addition of a solution of 70 g of sodium potassium tartrate in 70 ml of water. The resulting mixture was filtered and extracted three times with pentane and three times with ether. The combined organic extracts were washed with water, dried, and concentrated. The resulting solid was recrystallized from pentane, mp 132–135° (lit.[2a] mp 134–135°), yield 6.2 g (61.5%).[34]

The *p*-nitrobenzoate had mp 96–98°.

Anal. Calcd for $C_{15}H_{15}NO_4$: C, 65.92; H, 5.53; N, 5.12. Found: C, 66.03; H, 5.75; N, 5.33.

The brosylate ester **15** had mp 45.5–47° after crystallization from pentane at −78°.

Anal. Calcd for $C_{14}H_{15}BrO_3S$: C, 48.98; H, 4.40; S, 9.34. Found: C, 48.94; H, 4.67; S, 9.26.

The acetate ester was prepared from the alcohol by heating a solution of **3** in acetic anhydride–pyridine: bp 101–103° (10 mm); ir 5.75, 8.00, 9.48, and 10.95 μ (m); nmr δ 4.5 (s, 1 H), 1.91 (s, 3 H), 2.25 (m, 4 H), and 1.4 (m, 7 H).

The *p*-toluenesulfonate ester was a viscous oil which did not crystallize. The infrared spectrum did not show OH absorptions and strong bands appeared at 6.92 and 8.51 μ.

Tricyclo[3.3.0.0^{3,7}]octan-2-one (22).—To an ice-cold solution of 4.0 g (3.2 mmol) of alcohol **2** in 25 ml of ether was added 24 ml of sodium dichromate sulfuric acid soltuion[35] and the resulting mixture was stirred at 0° for 1 hr. The layers were separated and the aqueous phase was extracted with ether. The combined ether extracts were washed with sodium carbonate solution and water and then dried. Evaporation of the ether gave 2.5 g (62%) of ketone **22**. The melting point was 106–110° after purification by gas chromatography. Nmr had three complex groups centered at δ 1.58, 2.12, and 2.50; ir (CCl_4) 5.64 μ. The carbonyl absorption was also examined more carefully on a grating spectrometer (Perkin-Elmer Model 521); two bands appeared (5.64 and 5.68 μ) whose weighted average position was 5.65 μ.

Anal. Calcd for $C_8H_{10}O$: C, 78.65; H, 8.25. Found: C, 78.51; H, 8.28.

Acetolysis of 15.—The acetolysis of **15** was followed by nmr spectroscopy by monitoring the region near δ 4.5. A solution of 0.0547 g of **15** in 0.5 ml of acetic acid (0.1 *N* in sodium acetate) was placed in the probe of the spectrometer which had been equilibrated at 56°. Within 1 min a new peak appeared (δ 4.45) adjacent to that of the H–C–O proton of **16** (δ 4.34). The area of the new peak gradually increased at the expense of the starting material. A third peak at δ 4.58 also appeared in *ca.* 2 min and increased in size at a rate *ca.* one-third that of the other. Within 18 min the starting material had completely disappeared and only the two new peaks remained with relative areas *ca.* 3:1, respectively. The peak at δ 4.45 was assigned to the H–C–O proton of **21** by direct comparison of the chemical shift with that of an authentic sample. The peak at δ 4.58 was attributed to the H–C–O proton of acetate **16**.[16] This assignment was supported by the observation that complete acetolysis (40 hr, 100°) produced a high yield of *ca.* 97% pure **16** as shown by gc and nmr comparisons.

Hydrolysis of **15** in 80% acetone–water (120°, 5 hr) likewise gave a nearly quantitative yield of pure **16** (S = H) as shown by gc and ir comparisons with authentic samples.[16]

Preparation and Hydrolsysis of 19.—A solution of 1.07 g (8.75 mmol) of ketone **22** in 10 ml of isopropyl alcohol was added dropwise to a stirred solution of 0.40 g (9.6 mmol) of sodium borodeuteride[36] in 15 ml of ice-cold isopropyl alcohol. The resulting solution was stirred at 25° for 17 hr. The reaction was

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[32] O. Diels and K. Alder, *Justus Liebigs Ann. Chem.*, **460**, 117 (1928).

[33] This material was first isolated and characterized by W. Schinski, Ph.D. Thesis, Rutgers University, New Brunswick, N. J., 1968.

[34] We have since found that this reduction is more expeditiously effected by means of lithium metal in ethylenediamine: E. O'Hara, unpublished results.

[35] H. C. Brown and C. P. Garg, *J. Amer. Chem. Soc.*, **83**, 2952 (1961).

[36] Purchased from Merck, Sharp and Dohme (98% minimum deuterium content).

quenched by addition of 6 *N* hydrochloric acid and 50 ml of water. Extraction with three portions of ether gave 0.70 g of alcohol 3-*d* on evaporation of the extracts. The nmr spectrum displayed no appreciable absorption near δ 3.8. This material was converted into the corresponding *p*-toluenesulfonate ester and solvolyzed in a mixture of 12 ml of water and 18 ml of acetone (3 hr at 140°). The product displayed two peaks on gc analysis. The minor product showed the same retention time as the starting alcohol 3-*d* and is believed to have been carried over due to incomplete tosylation. The major product (>80%) was assigned structure **20**, nmr δ 3.64 (s, 1 H), 2.79–1.1 (m, 10 H). The location of the deuterium atom could not be unambiguously established, but mass spectral analysis was consistent with the assigned structure. Thus, both deuterated and undeuterated **3** showed a base peak at m/e 67 which corresponds to the loss of carbons C_2, C_3, and C_4. No isotopic shift was observed for this fragmentation. On the other hand the ions formed *via* related cleavage of C_4, C_5, and C_8 did show an isotopic shift from m/e 83 to 84, a result which is consistent with deuteration at C_3.[37]

Kinetic Experiments.—A solution of sodium acetate in acetic acid (0.1 *N*) was prepared by refluxing purified[38] reagent grade acetic acid (500 ml) with 2.65 g (0.0251 mol) of anhydrous sodium carbonate and 2.56 g (0.0251 mol) of acetic anhydride for 5 hr. Perchloric acid (0.05 *N*) was prepared from 2.1 ml of 70% perchloric acid, 2.2 ml of acetic anhydride, and enough acetic acid to bring the total volume to 500 ml. The exact normality was determined before each run by titration with standard potassium hydrogen phthalate solution in acetic acid using *p*-bromophenol as an indicator. The solvolyses were carried out in sealed ampoules into which were placed 2.5-ml samples of a *ca.* 0.1 *M* solution of brosylate **15** in the acetic acid–sodium acetate solution. At the appropriate time intervals ampoules were withdrawn from the oil bath and cooled before opening. A 2.00-ml aliquot was removed and quenched in 5 ml of purified dioxane.[39] The samples were then titrated with standardized perchloric acid. Infinity titers were obtained after warming samples to 120–130° for 2 hr and values obtained agreed to within 5% of the expected values. The first-order rate consant for production of acid drifted downward with time and remained constant for 4–5 half-lines. The values for the rate of solvolysis of the rearranged brosylate were determined at four temperatures and are recorded as follows: 47.68° (0.96×10^{-5} sec^{-1}); 53.08° (1.30×10^{-5} sec^{-1}); 61.37° (4.77×10^{-5} sec^{-1}); 83.90° (53.0×10^{-5} sec^{-1}). The rate constant for this reaction (k_3) at 25° was obtained by extrapolation: 3.79×10^{-7} sec^{-1}.

The rate constants at 53.08° for direct acetolysis (k_1) and for rearrangement (k_2) were obtained by the method of Young, Winstein, and Goering,[18] and found to be k_1, 1.71×10^{-4} sec^{-1}; k_2, 8.51×10^{-4} sec^{-1}. These rate constants were used to calculate the instantaneous brosylate ion concentrations and were found to yield values within ±4% of those determined experimentally.

Registry No.—**3** *p*-nitrobenzoate, 32980-15-7; **3** brosylate, 27011-51-4; **3** acetate, 32980-17-9; **7**, 26955-51-1; **8**, 32980-18-0; **10**, 32980-19-1; **12**, 32980-20-4; **22**, 32980-21-5; **23**, 32980-22-6; **24**, 32980-23-7; **25**, 32980-24-8.

Acknowledgments.—We wish to acknowledge useful discussions with P. K. Freeman. Financial aid (to K. W. K.) from Merck and Company, the donors of the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged. We also wish to thank the Rutgers University Research Council for partial financial support. Funds toward the purchase of the mass spectrometer were obtained from the National Science Foundation.

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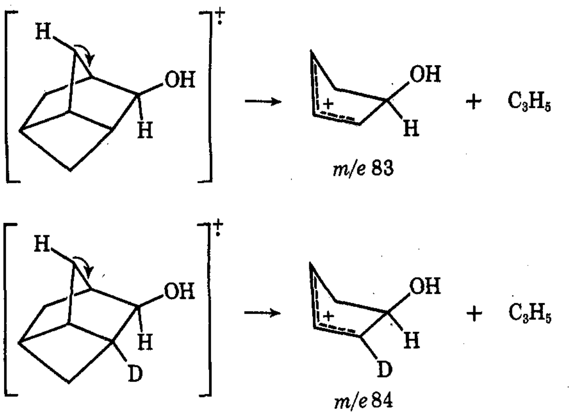
[37] Schematically, these cleavages may be symbolized as follows.



[38] H. Tanida, T. Tsuji, and J. Ishitobi, *J. Amer. Chem. Soc.*, **86**, 4901 (1964).

[39] Commercial dioxane was passed over a column of neutral alumina.

Addition of Nitrosyl Chloride to Some Strained Bicyclic Olefins

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Received June 9, 1971

Norbornene, norbornadiene, 5-methylene-2-norbornene (**1**), and 5-ethylidene-2-norbornene (**5**) add nitrosyl chloride to give exo-cis nitrosochlorides which dimerize to azodioxy compounds. In the latter two cases, addition does not occur at the exocyclic double bond, but 1,2 addition of nitrosyl chloride to the ring double bond occurs in two directions to give, after hydrolysis, a mixture of isomeric chloro ketones. In all cases, no rearrangement products were observed. 1,2,3,4,7,7-Hexachlorobicyclo[2.2.1]hepta-2,5-diene (**13**) does not add nitrosyl chloride in solution, but 1,2,3,4,7,7-hexachloro-5-methylenebicyclo[2.2.1]hept-2-ene (**14**) reacts very slowly under pressure to give addition to the exocyclic double bond. Addition to norbornene in a two-step process involving addition of nitrosonium tetrafluoroborate followed by addition of a chloride salt leads to small yields of chloro oximes instead of an azodioxy compound.

The reaction of nitrosyl chloride with alkenes to give nitrosochlorides, which dimerize if unhindered, has been known since 1875[2a] and has been adequately reviewed.[2b,c] Addition of the chloride to the carbon which can best support a positive charge is generally observed[3] and unstrained cyclic olefins give the products of trans addition.[4,5] A mechanism involving initial attack by NO$^+$ to form a strong olefin–electrophile

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[1] NDEA Fellow, 1965–1968; University of Alabama Fellow, 1969.

[2] (a) W. A. Tilden, *J. Chem. Soc.*, **28**, 514 (1875); (b) L. J. Beckham, W. A. Fessler, and M. A. Kise, *Chem. Rev.*, **48**, 319 (1951); (c) M. Plungian and F. E. DeVry, "Nitrosyl Chloride," An Annotated Bibliography, Hercules Technical Information Center, 1970, p 39.

[3] C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, p 669.

[4] J. Meinwald, Y. E. Meinwald, and T. N. Baker, *J. Amer. Chem. Soc.*, **86**, 4074 (1964).

[5] B. W. Ponder, T. E. Walton, and W. J. Pollock, *J. Org. Chem.*, **33**, 3957 (1968).