A number of explanations of this result were possible a priori; of these, reversion of nitrophenonium ion 3 to 1 or "encounter pair"[4] could be excluded as a major contributor to the rearrangement mechanism, since nitration of 1 gives such a drastically different isomer distribution (vide supra).[11] Other possible reaction pathways for 3 are outlined in Scheme I. Omitted

Scheme I

5- or 8-NO₂-1   5-NO₂-1   8-NO₂-1
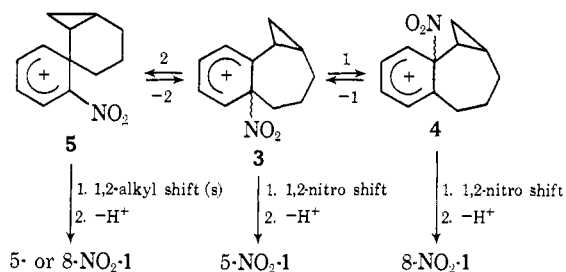
from this scheme are 1,3 shifts, on the basis of orbital symmetry considerations, and 1,2-alkyl shifts originating from 4, for momentary simplicity. Although alkyl migration (step 2) is rendered unlikely by the destabilizing effect of the nitro group in 5 (relative to 3), rigorous exclusion of this mechanism seemed desirable in view of the unprecedented nature of the transformations of 3. It should be stressed also that the conversion of 3 to 8-NO₂-1 may find parallels in such well-studied o-dialkylbenzenes as o-xylene,[4] indan,[3] and tetralin,[3] but that these parallels would be undetectable in the latter systems because of their symmetry properties.

The lack of symmetry in 1, however, in addition to allowing observation of extensive nitro shifts, enabled us to obtain experimental results essentially ruling out step 2 et sequelae. The monodeutero compound 1-7-d_1 was prepared[12] and converted to the corresponding crystalline ipso adduct. Exposure of the latter to 78% sulfuric acid afforded 5- and 8-NO₂-1-d_1 in which no change in the apparent position of the deuterium could be detected. The nitro group in 3 therefore must shift
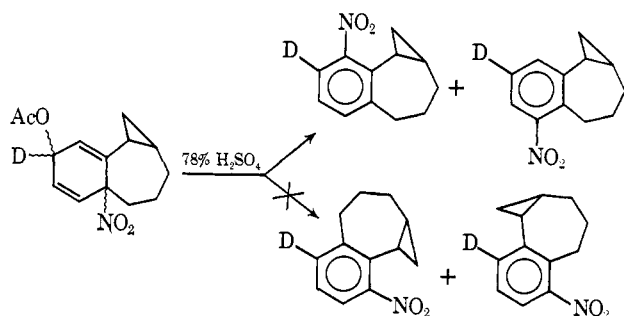
at least once, and since step 2 (Scheme I) and any subsequent alkyl shifts are excluded, a second nitro shift from 4 seems much more likely than any alkyl shifts in-

we conclude that some of the nitrophenonium ion 3 in acidic medium is transformed readily to products other than simple nitro compounds. Direct nitration of 1 in acidic medium gave ca. 75% overall yields of nitro compounds; the missing 25% again is consistent with diversion of half of the initially formed 3 to other products. The nitro derivatives of 1 were shown to be stable to all nitration and solvolysis conditions used.

(11) Reversible expulsion of NO₂⁺ from 3 cannot be excluded as a minor possibility. For this minor component, reattack would afford "normal" proportions of 6- and 7-nitro-1, sufficient to account for the observed 5% of these isomers. This possibility is under study.

(12) Deuterium incorporation was greater than 80% by pmr analysis; synthesis details will be given in our full paper.

volving that species.[13] The absence of detectable amounts of ipso adducts derived from ion 4 indicates that this is a considerably more energetic species than 3, although the transition-state barrier from 4 → 8-NO₂-1 must be slightly lower than the barrier from 3 → 5-NO₂-1.

Nitration of 1 in 82% sulfuric acid gave 18% of 5-nitro-1, 24% of 8-nitro-1, and 58% of 6- and 7-nitro-1, with no detectable acetoxylation products; this is the same isomer distribution, within experimental error, as that obtained from strong acid solvolysis of an acetyl nitrate–acetic anhydride nitration mixture containing 40% ipso adducts. The available evidence strongly suggests that the bulk of 5- and 8-nitro-1 isolated from sulfuric acid nitration is derived from initial ipso attack followed by nitro shifts and deprotonation; the caveat of Myhre[4] and Perrin[2] thus is underscored: true partial rate factors in aromatic substitution of certain substrates cannot be obtained without determination of the extent and consequences of ipso attack.[14]

Structural effects on the formation and rearrangement of ipso adducts are under further study.

(13) Two 1,2-cyclopropyl shifts from 4 would produce 5-NO₂-1-d_1 with no apparent deuterium change, so that this possibility remains, though it is considered remote.

(14) Myhre has found (private communication) that acid solvolysis of 4-nitro-3,4,5-trimethylcyclohexa-2,5-dienyl acetate affords only 4-nitrohemimellitene
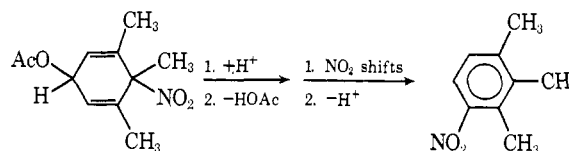
We thank Professor Myhre for this further example of a multistep nitro group migration.

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Stereospecific Rearrangement of Strained Cyclobutylcarbinyl Cations[1]

Sir:

By comparison with the extensively studied cyclopropylcarbinyl cation system,[2] a paucity of information exists concerning the cyclobutylcarbinyl cation. We now wish to report on a stereospecific rearrangement of a cyclobutylcarbinyl cation which involves the ring expansion of the four-membered ring of the tricyclo-[4.2.1.0¹,⁶]nonane skeleton.[3]

(1) Paper XLII in the series The Chemistry of Bent Bonds. For the preceding paper in this series, see: P. G. Gassman, R. N. Steppel, and E. A. Armour, *Tetrahedron Lett.*, in press.

(2) For recent reviews of this subject see, H. G. Richey, Jr., in "Carbonium Ions," Vol. III, G. A. Olah and P. v. R. Schleyer, Ed., Wiley-Interscience, New York, N. Y., 1972, pp 1201–1294; see also K. B. Wiberg, B. A. Hess, Jr., and A. J. Ashe, III, *ibid.*, pp 1295–1345.

(3) This ring system can also be named as a [4.2.1]propellane. For an explanation of propellane nomenclature see J. Altman, E. Babad, J. Itzchaki, and D. Ginsburg, *Tetrahedron, Suppl.*, No. 8, 279 (1966). See also D. Ginsburg, *Accounts Chem. Res.*, 2, 121 (1969); 5, 249 (1972).

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Table I. Rates of Solvolysis of Tricyclo[4.2.1.0^{1,6}]nonane Derivatives in 90:10 Acetone–Water Buffered with 2,6-Lutidine

Compd	Temp, °C (±0.02°)	Rate, sec⁻¹	ΔH‡, kcal/mol	ΔS‡, eu
1	80.00	(6.34 ± 0.06) × 10⁻⁴		
	70.00	(2.90 ± 0.01) × 10⁻⁴	20.5 ± 0.2	−15.4 ± 0.6
	60.00	(1.04 ± 0.01) × 10⁻⁴		
	25.0ᵃ	2.54 × 10⁻⁶		
2	100.00	(4.62 ± 0.02) × 10⁻⁴		
	90.00	(1.86 ± 0.02) × 10⁻⁴	23.2 ± 0.1	−12.1 ± 0.4
	80.00	(7.44 ± 0.02) × 10⁻⁵		
	25.0ᵃ	1.41 × 10⁻⁷		

ᵃ Extrapolated from higher temperatures.

Solvolysis of the epimeric carbinyl *p*-toluenesulfonates **1** and **2**⁴,⁵ was carried out in 90:10 v/v acetone–water.⁷ As shown in Table I, the rates of solvolysis, which were very similar, provide little indication of any difference in activation energy for the solvolyses of **1** and **2**. The observed difference of a factor of about 9 at 80° in the relative rates of solvolysis could be attributed to any one of a variety of effects. In contrast to the kinetic study, a product study indicated a high degree of involvement by the rest of the molecule in the ionization of **1** and **2**. After 10 half-lives **1** gave 91% of **3** and 5% of **4**. It would appear that this is the kinetic product mixture, since on treatment with acid **3** and **4** are interconverted to give an equilibrium mixture consisting of 55% of **3** and 45% of **4**. The structure of **4** was established on the basis of its spectral properties and through comparison of its mp (66.0–67.5°) and infrared spectrum with the reported values.⁸ The structure of **3** was established on the basis of its spectral properties. The ir spectrum of **3** showed both free and hydrogen-bonded O–H stretching bands at 2.70 and 2.92 μ, respectively. No absorption characteristic of a carbon–carbon double bond could be
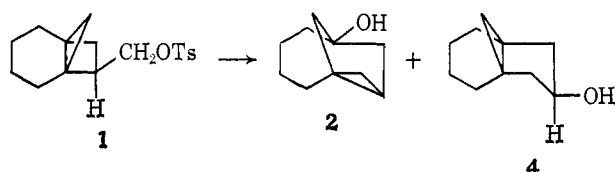
detected. The near-infrared spectrum of **3** showed an

(4) The synthesis of **1** and **2** involved the addition of methylene to bicyclo[4.3.0]non-1(6)-en-7-one⁶ to produce tricyclo[4.3.1.0^{1,6}]decan-7-one (36%), followed by conversion of this ketone into 8-hydroxymethylenetricyclo[4.3.1.0^{1,6}]decan-7-one (73%) *via* condensation with ethyl formate. Reaction of the hydroxymethylene derivative with *p*-toluenesulfonyl azide in the presence of base gave *ca.* 90% of 8-diazotricyclo[4.3.1.0^{1,6}]decan-7-one, which on irradiation in dry methanol gave a 75:25 mixture (52%) of the methyl esters resulting from the photochemical Wolff rearrangement. Lithium aluminum hydride reduction of the mixture of esters gave the epimeric carbinols which could be preparatively separated and converted into the corresponding tosylates **1** and **2**. Stereochemical assignments were based on a study of the nmr spectra of all the compounds in the series, in analogy to the assignments of related structures in the literature [see P. R. Brook and B. V. Brophy, *Tetrahedron Lett.*, 4187 (1969); and P. K. Freeman, M. F. Grostic, and F. A. Raymond, *J. Org. Chem.*, **30**, 771 (1965)].
(5) The tricyclo[4.2.1.0^{1,6}]nonane ring system has been previously prepared by the addition of dichlorocarbene to bicyclo[4.2.0]octa-1(6),3-diene [P. Warner and R. LaRose, *Tetrahedron Lett.*, 2141 (1972)] and by the addition of methylene to the same diene (P. G. Gassman and E. A. Armour, unpublished work).
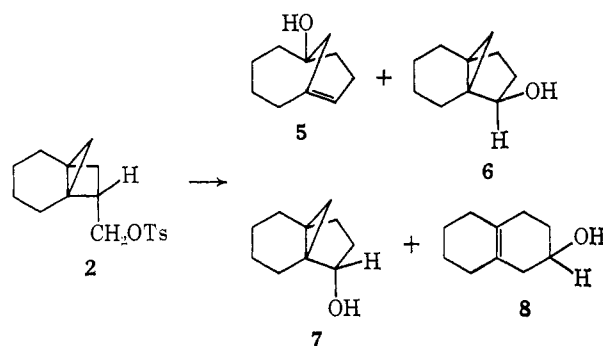(6) D. W. Mathieson, *J. Chem. Soc.*, 3248 (1953).
(7) Acetone–water was used as the solvolytic medium rather than the more common buffered acetic acid because the highly strained tricyclic ring system was susceptible to acetic acid addition.
(8) J. E. Starr and R. H. Eastman, *J. Org. Chem.*, **31**, 1393 (1966). These authors report a mp of 61–68° for **4** indicating that their material may not be isomerically pure. However, their method of synthesis should give **4** with the stereochemistry shown.

absorption at 1.651 μ (ε 0.248) characteristic of a cyclopropylmethylene unit.⁹ The nmr spectrum of **3** showed a complex pattern of overlapping multiplets extending from τ 7.61 to 9.63 for the carbon-bonded protons. No evidence for the presence of either vinylic hydrogens or protons bonded to a carbinol carbon could be detected. Thus, the alcohol must have been tertiary and a cyclopropyl ring must have been present. The spectral data, coupled with the interconversion of **3** and **4**, were consistent only with structure **3**.

Solvolysis of **2** gave **5** (56%), **6** (12%), **7** (12%), and **8** (11%) after 10 half-lives when a 2,6-lutidine buffer was used in 90:10 v/v acetone–water.¹⁰ The structure of **8** was established through comparison with an authentic sample prepared according to the literature procedure,¹¹ while **6** and **7** were identified by comparison with independently synthesized samples.¹² Estab-

lishing the structure of **5** was a more formidable task. A combination of nmr and ir spectral data established that **5** was an unsaturated tertiary alcohol. The one-proton triplet at τ 4.46 (J = 5.5 Hz) indicated that the double bond was trisubstituted.¹³ In addition, the nmr spectrum showed six allylic-type protons at τ 7.66–8.15. Catalytic reduction of **5** gave a saturated tertiary alcohol, whose ir spectrum compared well with that reported for bicyclo[4.3.1]decan-1-ol.¹⁴ Product composition changed during the course of the solvolysis of

(9) P. G. Gassman and F. V. Zalar, *ibid.*, **31**, 166 (1966).
(10) In unbuffered 90:10 v/v acetone–water only **8** was obtained. It was demonstrated that **5**, **6**, and **7** were readily converted into **8** in the presence of acid.
(11) H. O. House and C. J. Blankley, *J. Org. Chem.*, **33**, 47, 53 (1968).
(12) The details of the synthesis of **6** and **7** will be provided in a future publication.
(13) The position and coupling constant for this absorption were very similar to those reported for bicyclo[3.3.1]non-1-ene. J. R. Wiseman and W. A. Pletcher (*J. Amer. Chem. Soc.*, **92**, 956 (1970)) report τ 4.38 (t, J = 7 Hz). J. A. Marshall and H. Faubl (*ibid.*, **92**, 948 (1970)) report τ 4.48 (t, J = 3.5 Hz). The isolation and identification of the bicyclo[4.2.1]non-1(8)-ene system [J. R. Wiseman, H.-F. Chan, and C. J. Ahola, *ibid.*, **91**, 2812 (1969)] indicates that our system, which should be less highly strained, may not be very destabilized as a result of the bridgehead double bond.
(14) S. H. Graham and D. A. Jones, *J. Chem. Soc. C.*, 188 (1969).

2, presumably as a result of acid catalysis by the 2,6-lutidine tosylate. The primary products of the solvolysis of 2 appear to be 5 and 6, since the amounts of 7 and 8 increase as the solvolysis proceeds.

The data presented support the contention that 1 and 2 solvolyze to give two completely different ions. It appears that 1 gives products based on the migration of C_6 to the incipient cationic center to give 9, while 2 is converted into products resulting from the migration of C_8 to the site of developing charge to yield 10. Since there is no crossover of products, these rearrangements must be extremely stereospecific. The degree of stereospecificity is presumably controlled by the stability of the developing cation. Migration of C_6 in the solvolysis of 1 should lead to 9, which is stereochemically well arranged for stabilization by the neighboring
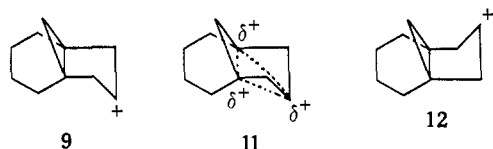
cyclopropyl ring as shown in 11. Only products with the stereochemistry required by the intermediacy of 11 were found in the solvolysis of 1. Migration of C_6 in the solvolysis of 2 would produce 12, which is not well situated for stabilization by the neighboring cyclopropyl group.

In the solvolysis of 2, migration of C_8 should give the cyclopropylcarbinyl cation 10. Support of this contention was provided by the solvolysis of each of the
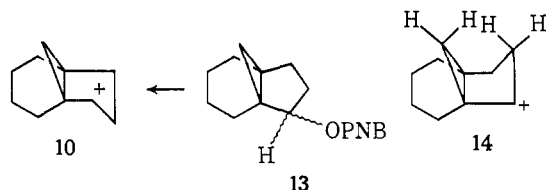
epimeric p-nitrobenzoates 13, which gave a mixture of the same products as were obtained from 2.[15] The derivation of 5, 6, and 7 from 10 is readily rationalized. Only the details of the conversion of 2, 5, 6, and 7 into 8 remain to be elucidated.[16] Migration of C_8 in the solvolysis of 1 would produce 14, which would be expected to have a destabilizing interaction of the hydrogens at C_8 and C_{10} of 14.

In summary, this study demonstrated that the ring expansion from a cyclobutylcarbinyl to a cyclopentyl type cation can be an extremely selective process. In compounds such as 1 and 2, where the cyclobutane moiety is part of a more highly strained ring system, interactions with the rest of the molecule can lead to products with unusual carbon skeletons due to the overall relief of ring strain.

(15) P. G. Gassman and E. A. Armour, unpublished work. The details of the solvolysis of 13 will be presented elsewhere.
(16) We are continuing to investigate this aspect of the problem.
(17) The Ohio State University Dissertation Fellow, 1972–1973.

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Tetrabutylammonium Cyanoborohydride. A New, Exceptionally Selective Reducing Reagent

Sir:

The ever-present requirement for accomplishing reductions of specific functional groups with a minimum of damage to other sensitive portions of molecules has stimulated considerable interest in reagents capable of such selective conversions.[1] One successful approach to this problem has involved the modification of borohydride anion by the replacement of a hydrogen with a cyanide substituent. This strongly electron-withdrawing group increases the Lewis acidity of the corresponding cyanoborane and thus the cyanoborohydride anion is more reluctant to deliver a hydride. The result is a toned down reducing capability (and an increased stability) which allows more discriminate selection among functional groups.[2–5]

This communication reports the unique ability in this regard of tetrabutylammonium cyanoborohydride (TBAC), a new, versatile reducing agent.[6,7] In hexamethylphosphoramide (HMPA) solvent at 25°, TBAC is an exceptionally mild reagent which reduces only primary iodides and, to a lesser extent, bromides to the corresponding hydrocarbons. Figure 1 illustrates the rate plots for primary halides and tosylate. Thus, 1-iododecane afforded an 81% yield of decane in 21 hr with no olefin or other side products detected while the corresponding bromo, chloro, and tosyl derivatives suffered less nucleophilic attack (Figure 1). In addition, other normally sensitive groups including aldehydes, ketones, esters, amido, cyano, and aromatic nitro were practically inert to the reaction conditions.[8]

Remarkably, the addition of acid to the medium drastically alters the reducing ability of the reagent and permits the selective reduction of aldehydes to be performed facilely in the presence of most other functional groups including ketones. In Figure 2 are plotted the results from competitive reduction experiments of nonaldehyde and 2-undecanone using excess TBAC and varying acid concentration. As seen, increasing the

(1) For a stimulating and educational review of selective reductions see H. C. Brown, "Boranes in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1972, Chapters 12 and 13.
(2) Recent applications of selective reductions with sodium cyanoborohydride include the reductive amination of aldehydes and ketones,[3] the selective reduction of alkyl halides and tosylates,[4] and the selective conversion of carbonyl tosylhydrazones to hydrocarbons.[5]
(3) R. F. Borch, M. Bernstein, and H. Durst, *J. Amer. Chem. Soc.,* 93, 2897 (1971); R. F. Borch and A. Hassid, *J. Org. Chem.,* 37, 1673 (1972); M. Boutigue and R. Jacquesy, *Bull. Soc. Chim. Fr.,* 750 (1973); A. Harmon and C. Hutchinson, *Tetrahedron Lett.,* 1293 (1973).
(4) R. O. Hutchins, B. E. Maryanoff, and C. A. Milewski, *Chem. Commun.,* 1097 (1971).
(5) R. O. Hutchins, C. A. Milewski, and B. E. Maryanoff, *J. Amer. Chem. Soc.,* 93, 1793 (1971); 95, 3662 (1973); B. Ganem, *Tetrahedron Lett.,* 4105 (1971).
(6) The reagent was prepared in a similar manner as described for the corresponding borohydride.[7] Thus, 0.1 mol of Bu_4NHSO_4 suspended in 50 ml of water was treated with 35 ml of 5 N NaOH, and a solution of 0.11 mol of $NaBH_3CN$ in 40 ml of water was added at room temperature. After 15 min, the mixture was extracted three times with CH_2Cl_2 which was dried (K_2CO_3), decolorized with carbon, and concentrated at reduced pressure to afford white crystalline product (78%) which was recrystallized from ethyl acetate. The material (mp 144–145°) gave a satisfactory elemental analysis for $C_{17}H_{39}N_2B$.
(7) A. Brandstrom, U. Junggren, and B. Lamm, *Tetrahedron Lett.,* 3173 (1972).
(8) For instance, nonaldehyde gave 3% reduction in 59 hr while 2-undecanone was 5% reduced in 72 hr. Heptanenitrile, ethyl decanoate, dodecamide, and 4-nitrobiphenyl were virtually unaffected in 72 hr under the conditions described in Figure 1. Sodium cyanoborohydride in HMPA offers similar discrimination between alkyl iodides and other functional groups; see ref 4.