of Merck acid-washed alumina (CH_2Cl_2–Skellysolve F, 1:1) gave 2.22 g (52%) of 2β-azido-3β-bromocholestane (**14**): mp 88–89° (from CH_2Cl_2–acetone); nmr (CCl_4) τ 5.70 (s, 1, half-width 6 Hz), 5.93 (s, 1, half-width 8 Hz), 9.01 (C-19); ir 2941, 2882, 2110, 1468, 1447, 1385, 1250, 1215, 960, and 758 cm^{-1}. *Anal.* Calcd for $C_{27}H_{46}BrN_3$: C, 65.83; H, 9.41. Found: C, 65.85; H, 9.40.

erythro-**2-Azido-3-bromobutane (17b).** A solution of bromine azide (50 mmol), prepared as in procedure 1, was added to 200 ml of nitromethane containing 4.0 g (excess) of *trans*-2-butene (**15b**) at 0°. The dichloromethane was removed under reduced pressure at room temperature and the remaining 200 ml of nitromethane removed by distillation through a 12-in. Vigreux column at room temperature. The residue was distilled to give 3.11 g (35%) of *erythro*-2-azido-3-bromobutane (**17b**): bp 56–58° (15 mm); nmr τ 8.63 (d, 3, J = 7 Hz), 8.32 (d, 3, J = 7 Hz), 6.38 (q, 1, J = 7 Hz, of d, J = 5 Hz), 5.88 (q, 1).

cis-**3-Azido-2-butene (18b).** To a cooled (−10°) and stirred solution of 0.655 g (3.68 mmol) of *erythro*-2-azido-3-bromobutane (**17b**) in 20 ml of anhydrous ether was added 0.5 g (4.46 mmol) of potassium *t*-butoxide. The reaction was stirred for 16 hr and allowed to warm to room temperature. The mixture was poured into 20 ml of ether and 30 ml of water. The ether layer was washed once with 30 ml of water, separated, and dried ($MgSO_4$). Evaporation of the ether under reduced pressure gave 0.223 g (57%) of crude *cis*-3-azido-2-butene (**18b**). The low yield was presumably due to the volatility of the vinyl azide. The nmr was identical with that reported.[3]

threo-**2-Azido-3-bromobutane (17a).** The adduct was prepared from *cis*-2-butene (**15a**), exactly as for the *erythro* adduct: yield, 3.14 g (35%); bp 54–59° (15 mm); nmr τ 8.62 (d, 3, J = 7 Hz), 8.30 (d, 3, J = 7 Hz), 6.40 (q, 1, J = 7 Hz, of d, J = 4 Hz), 5.89 (q, 1, J = 7 Hz, of d, J = 4 Hz); ir 3021, 2950, 2110, 1449, 1387, 1316, 1253, 1209, 1122, 1075, 1063, 1021, 1008, 962, and 883 cm^{-1}.

Anal. Calcd for $C_4H_8BrN_3$: C, 26.99; H, 4.52. Found: C, 27.09; H, 4.46.

trans-**3-Azido-2-butene (18a).** This compound was prepared from *threo*-2-azido-3-bromobutane (**17a**) similar to the formation of *cis*-3-azido-2-butene (**18b**): yield, 0.190 g (48%). The low yield was presumably due to the volatility of the vinyl azide. The nmr was identical with that reported.[3]

α-**Bromo-β-azido-β-deuterioethylbenzene (25).** To a solution of 0.52 g (5 mmol) of *cis*-β-deuteriostyrene (**6**) in 13 ml of pentane (purged with N_2) was added 13 ml of 0.5 *M* bromine azide solution (6.5 mmol), prepared as in procedure 2, with irradiation by a 100-W incandescent lamp. The solution was allowed to stand 30 min, then evaporation of the pentane under reduced pressure gave 1.17 g (100%) of crude α-bromo-β-azido-β-deuterioethylbenzene (**25**).

Treatment of α-Bromo-β-azido-β-deuterioethylbenzene (25) with Base. To a Dry Ice cooled solution of 1.7 g (5 mmol) of impure α-bromo-β-azido-β-deuterioethylbenzene in 20 ml of anhydrous ether was added 0.62 g (5.5 mmol) of potassium *t*-butoxide. The mixture was allowed to come to room temperature and let stand for 30 min with occasional stirring. The reaction was then extracted with two 25-ml portions of H_2O, dried ($MgSO_4$), and evaporated to give 0.69 g (95%) of crude vinyl azide. Nmr analysis, corrected for nondeuterated product, showed β-azidostyrene (**26**), with an H:D ratio of 1:1: nmr (β-deuterio-β-azidostyrene) τ 3.83 (t, J = 2 Hz; J = 7 Hz, of d, J = 5 Hz); ir 2985, 2941, 2110, 1449, 1385, 1252, 1160, 1054, 1010, 990, 970, and 883 cm^{-1}.

Anal. Calcd for $C_4H_8BrN_3$: C, 26.99; H, 4.52. Found: C, 27.13; H, 4.54.

Acknowledgment. Support of this investigation by Petroleum Research Fund Grant No. 2004A from the American Chemical Society and by the U. S. Public Health Service Grant No. CA-4474 from the National Cancer Institute is gratefully acknowledged.

Cyclopropane Participation and Degenerate Rearrangement in the Solvolysis of 9-Pentacyclo[4.3.0.0^{2,4}.0^{3,8}.0^{5,7}]nonyl *p*-Nitrobenzoate[1]

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Abstract: The synthesis of pentacyclo[4.3.0.0^{2,4}.0^{3,8}.0^{5,7}]nonan-9-ol (**4a**) has been accomplished by ultraviolet irradiation of 8-tetracyclo[4.3.0.0^{2,4}.0^{3,7}]nonen-5-ol (**5**). The latter is conveniently prepared by reaction of deltacyclene epoxide with hydrobromic acid followed by dehydrobromination of the resulting rearranged bromohydrin (**10a**). The rate of hydrolysis of the pentacyclic *p*-nitrobenzoate **4b** in 65% aqueous acetone (7.00×10^{-5} sec^{-1}, 125°) is enhanced by 10^{10}–10^{12} compared to 7-norbornyl derivatives. Hydrolysis of the deuterium-labeled analogs, **4b**-9-*d* and **4b**-*anti*-4-*d*, revealed a degenerate rearrangement which specifically interchanges the 9 with the *anti*-2,3 positions and the *anti*-4 with the 1,8 positions. These data demonstrate effective and exclusive participation by the *anti*-cyclopropane ring in the hydrolysis of **4b**. The formation of a relatively stable, threefold symmetric trishomocyclopropenyl-type cation (**24**), which reacts with water faster than it undergoes bridge inversion, best explains the reactivity and scrambling results.

The extent and consequences of remote cyclopropane participation in carbonium ion reactions have received considerable attention in the recent literature.[3–7] Although the analogy with remote double bond participation has provided a useful basis for comparison, it is now evident that the influence of these two groups

(1) Taken in part from the Ph.D. Thesis of J. L. K., University of Illinois, 1969.

(2) National Institutes of Health Trainee, 1968–1969.

(3) (a) G. E. Cartier and S. C. Bunce, *J. Amer. Chem. Soc.*, **85**, 932 (1963); (b) M. Hanack and H-M. Ensslin, *Tetrahedron Lett.*, 4445 (1965); *Justus Liebigs Ann. Chem.*, **713**, 49 (1968); (c) R. R. Sauers and R. W. Ubersax, *J. Org. Chem.*, **31**, 495 (1966); (d) M. J. S. Dewar and J. M. Harris, *J. Amer. Chem. Soc.*, **90**, 4468 (1968); (e) Y. E. Rhodes and T. Takino, *ibid.*, **90**, 4469 (1968); (f) G. D. Sargent, R. L. Taylor, and W. H. Demisch, *Tetrahedron Lett.*, 2275 (1968); (g) R. Muneyuki, T. Yano, and H. Tanida, *J. Amer. Chem. Soc.*, **91**, 2408 (1969).

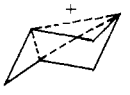
(4) (a) C. F. Wilcox, Jr., and R. G. Jesaitis, *Tetrahedron Lett.*, 2567 (1967); (b) M. A. Eakin, J. Martin, and W. Parker, *Chem. Commun.*, 955 (1967); (c) P. J. Kropp, *J. Amer. Chem. Soc.*, 88, 4926 (1966).

(5) (a) R. R. Sauers and J. A. Beisler, *Tetrahedron Lett.*, 2181 (1964); (b) K. B. Wiberg and G. R. Wenzinger, *J. Org.*

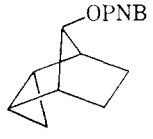
can be substantially different. While the usual steric requirement of back-side attack is common to both double bond and cyclopropane participation, the effect of a remote cyclopropane ring in freely rotating structures[3] is small compared to the appropriate unsaturated analogs.[8] In addition, the orientation of the three-membered ring is important. For rigid structures in which "face" participation by a three-membered ring is geometrically feasible, no kinetic assistance is observed.[7a,c,f,g] On the other hand, when the disposition of the cyclopropane ring will allow either "edge" or "corner" participation, substantial solvolytic rate enhancement and/or rearranged products are found.[4b,c,5-7]

The *cis*-3-bicyclo[3.1.0]hexyl and related ring systems appear to be particularly prone to homocyclopropyl participation.[6,7] The parent tosylate (**1**), for example, undergoes acetolysis with an enhanced rate, complete retention of the *cis* stereochemistry, and a statistical scrambling rearrangement. These results (and other data as well) have been interpreted in terms of a symmetrical trishomocyclopropenyl intermediate (**2**).[6a] The conformationally rigid *endo,anti*-8-tricyclo[3.2.1.$0^{2,4}$]-octyl *p*-nitrobenzoate (**3**) is hydrolyzed with an enormous kinetic acceleration (10^{12}–10^{14}) as compared to 7-norbornyl derivatives.[7b,c] This dramatic effect indicates that remote cyclopropane participation can provide a potent stabilizing influence when the orientation factors are optimal. However, the extent to which overall strain relief[9] might contribute to rate enhancement found in the solvolysis of **3** is difficult to assess.

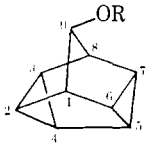
1



2

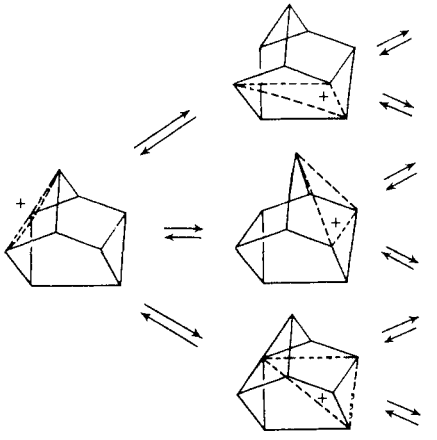


3



4a, R = H
b, R = PNB

The 9-pentacyclo[4.3.0.$0^{2,4}$.$0^{3,8}$.$0^{5,7}$]nonyl cage structure (**4**) presents an interesting three-dimensional molecular framework in which to examine remote cyclopropane participation. With three-membered rings situated both *syn* and *anti* to the leaving group, a direct intramolecular competition would exist between *syn* and *anti* participation. If **4** undergoes a homocyclopropylcarbinyl rearrangement during solvolysis, the rearranged structure is in fact identical with the original; thus, overall strain relief as a driving force cannot be involved. And finally, if both cyclopropane rings become involved in the rearrangement, all carbon atoms in the molecule could become equivalent. As illustrated below using the trishomocyclopropenyl formulation,[6a] each position can eventually exchange with every other as the three-center cation face migrates over the molecular surface; thus, all nine carbon atoms would eventually lose their original identity.



The study of such potentially degenerate cationic rearrangements has been of considerable recent interest,[10] especially those cases in which a complete three-dimensional scrambling is feasible. In the following, we present a synthesis of the functionalized pentacycle **4** and a detailed investigation into its solvolytic reactivity and the course of the ensuing cationic rearrangement.[11]

The key to the construction of the desired pentacyclo[4.3.0.$0^{2,4}$.$0^{3,8}$.$0^{5,7}$] nucleus appeared to be a photochemical valence isomerization of a tetracyclo[4.3.0.-$0^{2,4}$.$0^{3,7}$]nonene precursor substituted in the 5 position (*e.g.*, **5**). Such light-induced intramolecular cyclopropane–ene additions had been previously employed in the formation of the parent pentacyclononane[12,13] as well as other similar polycyclic compounds.[14]

Chem., **30**, 2278 (1965); (c) A. K. Coulter and R. C. Musso, *ibid.*, **30**, 2462 (1965); (d) R. R. Sauers, J. A. Beisler, and H. Feilich, *ibid.*, **32**, 569 (1967); (e) J. A. Berson, R. G. Bergman, G. M. Clarke, and D. Wege, *J. Amer. Chem. Soc.*, **90**, 3236 (1968); (f) J. A. Berson, D. Wege, G. M. Clarke, and R. G. Bergman, *ibid.*, **90**, 3240 (1968); (g) B. C. Henshaw, D. W. Rome, and B. L. Johnson, *Tetrahedron Lett.*, 6049 (1968); (h) G. D. Sargent, M. J. Harrison, and G. Khoury, *J. Amer. Chem. Soc.*, **91**, 4937 (1969); (i) P. K. Freeman and D. M. Balls, *Tetrahedron Lett.*, 437 (1967); P. K. Freeman and J. N. Blazevich, *Chem. Commun.*, 1357 (1969).

(6) (a) S. Winstein, E. C. Friederich, R. Baker, and Y. Lin, *Tetrahedron, Suppl.*, **No. 8** (Part II), 621 (1966); S. Winstein, *Quart. Rev. Chem. Soc.*, **23**, 141 (1969), and pertinent references therein; (b) W. J. le Nobel, B. L. Yates, and A. W. Scaplehorn, *J. Amer. Chem. Soc.*, **89**, 3751 (1967); (c) H. Kuczynski, M. Walkowicz, and C. Walkowicz, *Rocz. Chem.*, **42**, 1277 (1968).

(7) (a) J. Haywood-Farmer, R. E. Pincock, and J. I. Wells, *Tetrahedron*, **22**, 2007 (1966); (b) H. Tanida, T. Tsuji, and T. Irie, *J. Amer. Chem. Soc.*, **89**, 1953 (1967); (c) M. A. Battiste, C. L. Deyrup, R. E. Pincock, and J. Haywood-Farmer, *ibid.*, **89**, 1954 (1967); (d) H. Tanida, *Accounts Chem. Res.*, **1**, 239 (1968); (e) J. S. Haywood-Farmer and R. E. Pincock, *J. Amer. Chem. Soc.*, **91**, 3020 (1969); (f) S. A. Sherrod, R. G. Bergman, G. S. Gleicher, and D. G. Morris, *ibid.*, **92**, 3469 (1970); (g) R. C. Bingham, W. F. Sliwinski, and P. von R. Schleyer, *ibid.*, **92**, 3471 (1970).

(8) (a) For data concerning homoallylic participation, *cf.* M. Hanack and H. J. Schneider, *Angew. Chem., Int. Ed. Engl.*, **6**, 666 (1967); (b) R. S. Bly, R. K. Bly, A. O. Bedenbaugh, and O. R. Vail, *J. Amer. Chem. Soc.*, **89**, 880 (1967).

(9) W. G. Dauben, J. L. Chitwood, and K. V. Scherer, *ibid.*, **90**, 1014 (1968).

(10) (a) P. von R. Schleyer, J. J. Harper, G. L. Dunn, V. J. DiPasquo, and J. R. E. Hoover, *J. Amer. Chem. Soc.*, **89**, 698 (1967); (b) J. C. Barborak and R. Petit, *ibid.*, **89**, 3080 (1967); (c) M. J. Goldstein and B. J. Odell, *ibid.*, **89**, 6356 (1967); (d) P. von R. Schleyer and R. E. Leone, *ibid.*, **90**, 4164 (1968); (e) G. W. Klumpp, *Recl. Trav. Chim. Pays-Bas*, **87**, 1053 (1968); (f) J. C. Barborak, J. Daub, D. M. Follweiler, and P. von R. Schleyer, *J. Amer. Chem. Soc.*, **91**, 7760 (1969); (g) for a more complete listing, see J. E. Nordlander, F. Y.-H. Wu, S. P. Jindal, and J. B. Hamilton, *ibid.*, **91**, 3962 (1969); (h) J. C. Barborak and P. von R. Schleyer, *ibid.*, **92**, 3184 (1970); (i) J. B. Grutzner and S. Winstein, *ibid.*, **92**, 3186 (1970).

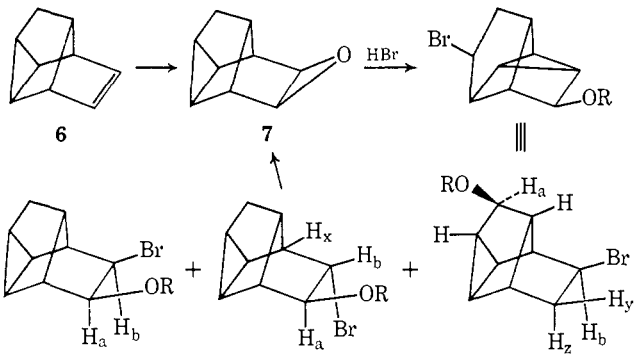
(11) (a) A brief account of a portion of this research has been published: R. M. Coates and J. L. Kirpatrick, *ibid.*, **90**, 4162 (1968); (b) for the synthesis of the *t*-butyl ether of **4a** see ref 10d.

(12) (a) H. Prinzbach and D. Hunkler, *Angew. Chem., Int. Ed. Engl.*, **6**, 247 (1967); (b) P. K. Freeman and D. M. Balls, *J. Org. Chem.*, **32**, 2354 (1967); (c) E. Wiskott and P. von R. Schleyer, *Angew. Chem., Int. Ed. Engl.*, **6**, 694 (1967).

(13) See also C. F. Huebner, E. Donoghue, L. Dorfman, E. Wenkert, W. E. Streth, and S. W. Donelly, *Chem. Commun.*, 419 (1966).

The more efficient of two synthetic routes to alcohol **5** was based upon a variation of an approach which has proven particularly useful in the synthesis of 7-substituted norbornenes.[15] Addition of the elements of HOX to the appropriate norbornene is usually accompanied by predominant Wagner–Meerwein rearrangement; subsequent elimination of HX then affords the *syn*-7-norbornenyl derivative.[15] A similar sequence of events originating from deltacyclene (8-tetracyclo[4.3.0.0^{2,4}.0^{3,7}]nonene (**6**)) and involving instead a homocyclopropyl carbinyl rearrangement[5] leads ultimately to the required tetracyclic alcohol **5**. This plan was realized in the reaction of deltacyclene epoxide with hydrobromic or acetic acids (Charts I and II).[16]

Chart I



Pyrolysis[17a] of the norbornadiene dimers[18] served as a source of relatively large quantities of deltacyclene. The corresponding epoxide upon reaction with aqueous hydrobromic acid gave rise to a mixture of three isomeric bromohydrins which could be separated by column chromatography. The structure of each isomer was readily established by inspection of the nmr spectra of the *p*-nitrobenzoates. The derivative of the least polar bromohydrin (12%) shows an AB doublet for the protons on carbon-bearing oxygen (H_a, τ 4.64) and bromine (H_b, τ 5.44) with J_{ab} = 6.0 Hz, a coupling constant consistent only with the *exo,exo* stereochemistry (**8b**).[19]

These same protons in the ester of the second bromohydrin (8%) appeared as a doublet (H_a, τ 4.60) and a pair of doublets (H_b, τ 5.70), respectively, with J_{ab} = 2.0 Hz and J_{bx} = 4.0 Hz. This coupling pattern requires the *exo,endo* stereochemistry of isomer **9**.[19] These assignments were confirmed by the facile reconversion of the *exo,endo*-bromohydrin to the epoxide with potassium carbonate in methanol, conditions which left the *exo,exo* isomer unchanged.

The major and most polar bromohydrin (35–50%)[20] clearly possesses a rearranged structure since the two carbinyl protons are no longer coupled. The hydrogen on carbon-bearing bromine appears as a pair of doublets (H_b, τ 5.78, J_{by} = 3.0 Hz and J_{bz} = 7.0 Hz), indicating an *exo* orientation for the halogen and the presence of an adjacent methylene group.[19] The proton on carbon-bearing oxygen now appears as a triplet (H_a, τ 4.68) with J = 1.5 Hz. These data are consistent with the desired rearranged substitution pattern of **10**.

The double bond was then reintroduced by elimination of hydrobromic acid with potassium *t*-butoxide in dimethyl sulfoxide, producing the hydroxylated delta-

Chart II

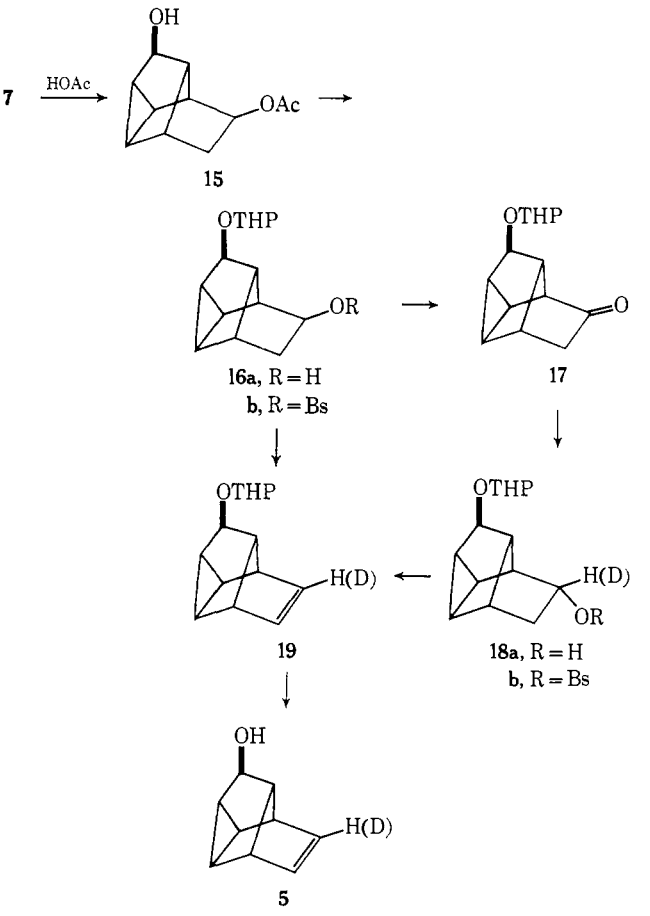
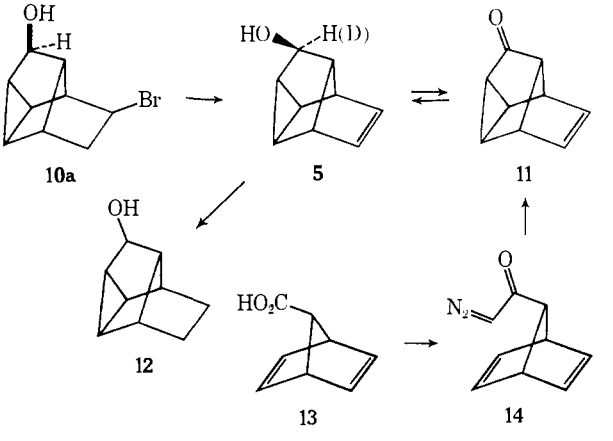


Chart III



(14) H. Prinzbach, W. Eberbach, and G. von Veh, *Angew. Chem.*, 77, 454 (1965); P. K. Freeman, D. G. Kuper, and V. N. M. Rao, *Tetrahedron Lett.*, 3301 (1965); H. Prinzbach, *Chimia*, 21, 194 (1967).

(15) (a) S. Winstein and E. T. Stafford, *J. Amer. Chem. Soc.*, 79, 505 (1957); (b) P. D. Bartlett and W. P. Giddings, *ibid.*, 82, 1240 (1960); (c) S. Winstein and C. Ordonneau, *ibid.*, 82, 2084 (1960); (d) H. Tanida and T. Tsuji, *J. Org. Chem.*, 29, 849 (1964); (e) P. R. Story, *J. Org. Chem.*, 26, 287 (1961); (f) W. C. Baird, Jr., *ibid.*, 31, 2411 (1966).

(16) Attempts to effect direct bridge oxygenation with either benzoyl peroxide[15d] or *t*-butyl perbenzoate[15e] in the presence of cuprous bromide were unsuccessful.

(17) (a) L. G. Cannell, *Tetrahedron Lett.*, 5967 (1966); (b) T. J. Katz, J. C. Cornahan, and R. Boecke, *J. Org. Chem.*, 32, 1301 (1967).

(18) J. J. Mrowca and T. J. Katz, *J. Amer. Chem. Soc.*, 88, 4012 (1966).

(19) J. I. Musher, *Mol. Phys.*, 6, 93 (1963).

(20) The relative proportion of this isomer was reduced considerably when the epoxide was treated with anhydrous hydrogen bromide in various solvents (see Experimental Section).

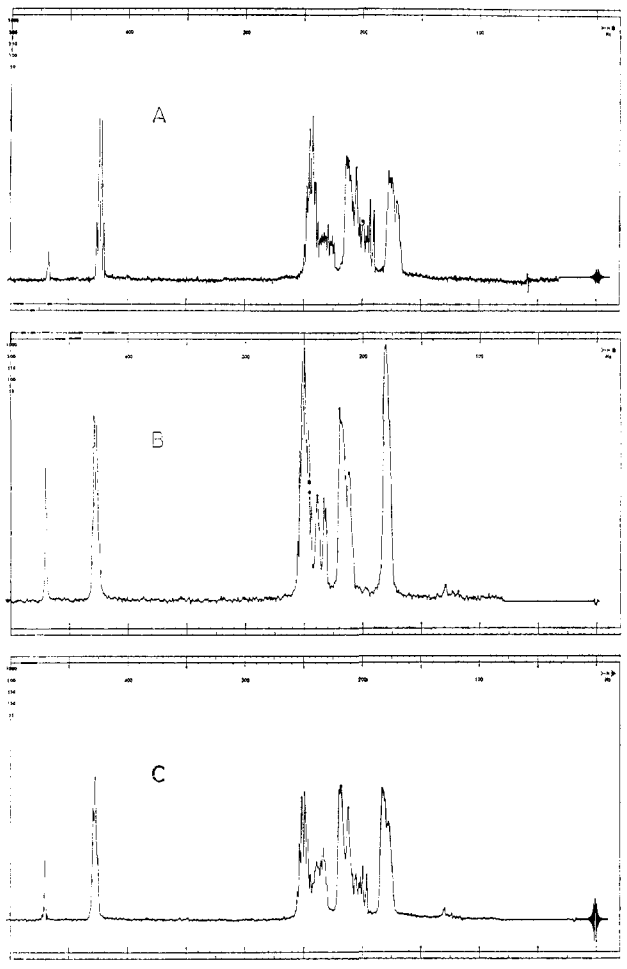


Figure 1. 100-MHz nmr spectra of **4a** (A), **4a**-*anti*-4-*d* (B), and scrambled product (C) from hydrolysis of **4b**-*anti*-4-*d*. In all spectra the hydroxyl proton has been eliminated by exchange with deuterium oxide.

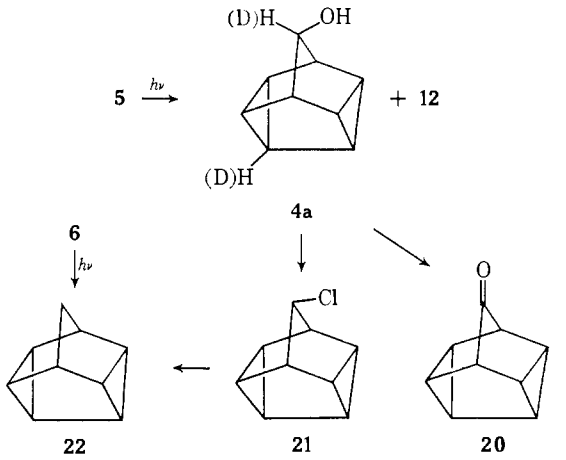
cyclene **5** in 83% yield. Reduction of the corresponding ketone **11** with lithium aluminum deuteride served as a means to label the carbinyl position of **5** and eventually the pentacyclic alcohol as well (Chart III).

A different synthetic pathway to ketone **11**, though not practical for the preparation of large quantities, provided confirmation for the tetracyclic structure indicated.[21] 7-Norbornadienyl carboxylic acid (**13**), prepared by hydrolysis of the corresponding nitrile,[22,23] was converted to the diazo ketone **14**. The latter upon catalytic decomposition with copper powder in tetrahydrofuran gave rise to the expected cyclopropyl ketone, identical with that obtained from deltacyclene.

In order to introduce deuterium into a different position of **5**, we developed the alternate synthetic route outlined in Chart II, again making use of the homocyclopropyl carbinyl rearrangement. In this case the reaction of epoxide **7** with acetic acid gave entirely rearranged product. Although the subsequent reactions require no special comment, it should be noted that, as a consequence of the *exo* configuration of the original epoxide, the deuterated vinyl position in **5** must be *anti* to the bridge hydroxyl function.

The photochemical rearrangement of **5** to the pentacyclic alcohol caused considerable difficulty. One side reaction, saturation of the double bond giving dihydro alcohol **12**,[24] was kept to a minimum by using 50% aqueous *t*-butyl alcohol as solvent, a relatively poor hydrogen-donating medium. Nevertheless, the direct photolysis of **5** afforded at best a 5:1 mixture of **4a** and **12** from which the pure, crystalline pentacyclic alcohol could be obtained in 6–8.5% yield by preparative glpc.[26] Apparently the majority of **5** is diverted into nonvolatile materials (Chart IV).

Chart IV



That the photoisomer has the pentacyclic cage structure designated in **4a** is based upon its spectral characteristics, reduction to the known parent hydrocarbon, and the photochemical analogy.[12–14] One novel feature in the nmr spectrum of **4a** (see Figure 1A) is the clean quartet (τ 5.75, J = 2.0 Hz) for the proton on the hydroxyl-bearing carbon. The extra multiplicity beyond that from coupling with the two bridgehead protons must be due to coupling with the unique *syn* (*i.e.*, *syn* to the hydroxyl group) cyclopropyl hydrogen through five σ bonds, since a quartet is also observed in the 4-*anti*-deuterio compound (see Figure 1B).[27] The two-proton sextet at τ 7.55 (J = 2 Hz) is clearly from the two bridgehead protons and as expected becomes a quintet in the 9-deuterio analog. The two one-proton multiplets at τ 7.57 and 8.05 may be assigned to the individual *syn*- and *anti*-cyclopropane hydrogens, respectively, since the latter disappears in the spectrum of **4a**-*anti*-4-*d* (Figure 1B). The higher field multiplet of the two two-proton bands (τ 7.90

(21) For other syntheses in this tetracyclic series see ref 10d and 10e. The nmr spectra of **5** and **11** proved to be identical with the spectra of the same compounds reported by Schleyer and Leone.[10d]

(22) (a) G. W. Klumpp and F. W. Bickelhanpt, *Tetrahedron Lett.*, 865 (1966); (b) H. Tanida and Y. Hata, *J. Org. Chem.*, **30**, 977 (1965).

(23) Several attempts to improve upon the reported syntheses[22a] of **13** were fruitless. 7-Norbornadienyl bromide (prepared readily by the action of phosphorus tribromide upon the alcohol in pentane at 0°) could not be induced to form a Grignard reagent. Quadracyclyl bromide (obtained by benzophenone-sensitized irradiation of the bromodiene) reacted readily with magnesium but evidently gave only coupling products [see also H. Tanida, Y. Hata, Y. Matsui, and I. Tanaka, *J. Org. Chem.*, **30**, 2259 (1965)]. Pyrolysis of 7-norbornadienylisonitrile[22a] in dimethylformamide did not give the nitrile according to glpc analysis.

(24) Photochemically induced double bond reduction of norbornenes has been previously encountered.[12b,25]

(25) R. R. Sauers, W. Schinski, and M. M. Mason, *Tetrahedron Lett.*, 4763 (1967).

(26) Irradiation of **5** in ether or hexane gave higher proportions of **12**. Trial irradiations with the corresponding acetate (in hexane, ether, acetonitrile, and *t*-butyl alcohol), methyl ether (in ether and aqueous *t*-butyl alcohol), and tetrahydropyranyl ether (**19**, in aqueous *t*-butyl alcohol) gave in each case less satisfactory results according to glpc analysis.

(27) For a similar long-range coupling, see K. Tori and M. Ohtsuro, *Chem. Commun.*, 886 (1966).

and 8.23) must be due to the pair of *anti*-cyclopropane hydrogens since this broad band sharpens considerably in the spectrum of **4a**-*anti*-4-*d*.

Oxidation of **4a** with Collins reagent[28] furnished the pentacyclic ketone **20** (ν_{max} 1770 cm^{-1}), the nmr spectrum of which displays two complex multiplets of four protons each at τ 7.50 and 8.00. Chloride **21** was obtained from **4a** by reaction with thionyl chloride. Reduction of **21** with lithium aluminum hydride in tetrahydrofuran provided the hydrocarbon **22** (72%) spectrally indistinguishable from a sample prepared by direct photolysis[12b,c] of deltacyclene.

The *p*-nitrobenzoyl derivative (**4b**) proved to be a suitable substrate for kinetic studies. The hydrolysis of **4b** in 65% aqueous acetone was followed by titration and gave good first-order plots. The rate constants at various temperatures are compiled in Table I ($\Delta H^{\pm}$ = 26.8 ± 0.3 kcal/mol, $\Delta S^{\pm}$ = −11.5 ± 0.4 eu at 125°). The hydrolysis of 7-norbornadienyl *p*-nitrobenzoate (**23**)[7c,15c] was also determined in order to have a direct reference point. The hydrolysis reaction regenerated the original alcohol **4a** in 50–70% yield. A minor, more polar by-product was eliminated when the hydrolysis was carried out in the presence of 2,6-lutidine.

Table I. Titrimetric First-Order Rate Constants[a] in 65% Aqueous Acetone[b]

Substrate[c]	Temp, °C[d]	Rate constant, sec^{-1}
4b	100.0	$6.94 \pm 0.9 \times 10^{-6}$
	113.8	$25.40 \pm 0.9 \times 10^{-6}$
	125.0	$7.00 \pm 0.2 \times 10^{-5}$
7-Norbornadienyl *p*-Nitrobenzoate (**23**)	125.0	$5.80 \pm 0.1 \times 10^{-4}$

[a] Determined from three runs at each temperature. [b] 65% acetone–35% water by volume. [c] Substrate concentration approximately 0.0065 *M*. [d] ±0.1°.

The two deuterium-labeled substrates (**4b**-9-*d* and **4b**-*anti*-4-*d*) were hydrolyzed in 65% aqueous acetone at 125° in order to examine the extent of rearrangement. That a scrambling process had occurred was immediately clear from the reappearance of the carbinyl quartet in the nmr spectrum of the product from **4b** labeled in the 9 position. Quantitative integration of this band using **23** as a weighed internal standard indicated the presence of 0.67 ± 0.02 H. In addition, the high-field multiplet for the pair of *anti*-cyclopropane protons was reduced to about two-thirds (*i.e.*, 1.3 H) of its original intensity.[29] Thus, a rearrangement involving evidently limited scrambling has occurred, in which the 9 and *anti*-2,3 positions have become equivalent.

The 100-MHz nmr spectrum of the product obtained from the hydrolysis of **4b**-*anti*-4-*d* (Figure 1C) shows the reappearance of absorption at τ 8.05 (*ca.* 0.7 H) for a single *anti*-cyclopropane hydrogen and an obvious intensity decrease in the region of the bridgehead hydrogens (*ca.* 1.3 H). Only approximate integration was possible owing to the overlap with other bands. In this case, therefore, the *anti*-4 position has interchanged with the two equivalent bridgehead positions.

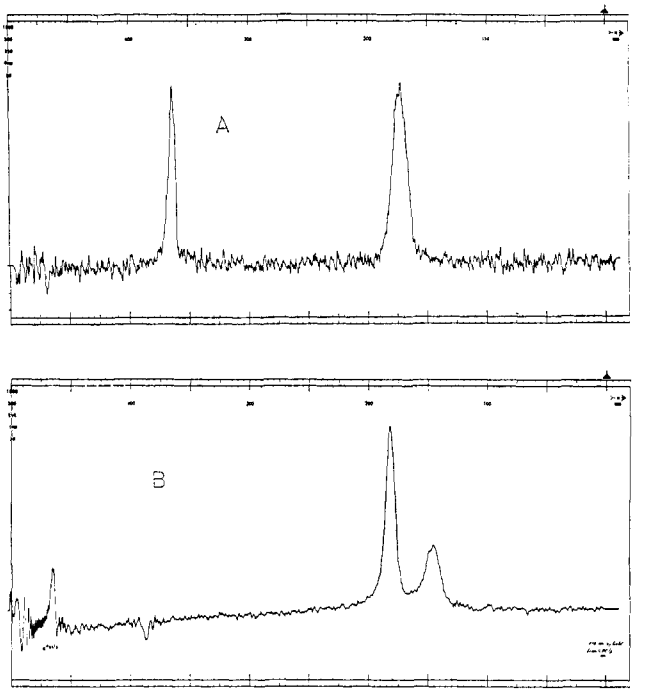


Figure 2. Dmr spectra (15.35 MHz) of labeled **4a** recovered from the hydrolysis of **4b**-9-*d* (A) and **4b**-*anti*-4-*d* (B) in 65% aqueous acetone at 125°

The specificity of this rearrangement is more clearly demonstrated in the deuterium nmr (dmr) spectra of the scrambled products (Figure 2). This method has the advantage of directly detecting the label itself, rather than its absence as in the proton nmr spectra. Although the sensitivity with which deuterium may be detected is low (~1% of the hydrogen isotope), computerized accumulation of repeated scans enables good quality spectra to be obtained even with modest sample sizes (*e.g.*, Figure 2A, 100 scans with 28 mg).

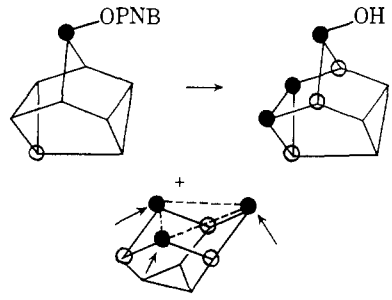
The dmr spectrum of **4a** labeled in the 9 position exhibits a single resonance at τ 5.75 for the carbinyl deuterium atom. The alcohol recovered from hydrolysis of **4b**-9-*d* gives a dmr spectrum (Figure 2A) with two bands (τ 5.75 and 8.23) in a ratio of 1:2.05 ± 0.08. The deuterium label, therefore, has been cleanly distributed into two equivalent locations which on the basis of the chemical shift must be the *anti*-2,3 positions.

The dmr spectrum of the product from **4b**-*anti*-4-*d* (Figure 2B) displays two bands at τ 7.55 and 8.0 in an approximate intensity ratio of 2:1, in place of the single resonance (τ 8.0) for the 4-*anti* deuteron in the original alcohol. The chemical shift of the new signal corresponds to that of the bridgehead position, indicating again equilibration between the 4-*anti* and 1,8 sites.

The specific label scrambling results ean be simply interpreted in terms of the threefold symmetric trishomocyclopropenyl cation intermediate **24**. Stereo-

(28) J. C. Collins, W. W. Hess, and F. J. Frank, *Tetrahedron Lett.*, 3363 (1968).

(29) The same scrambling result was obtained whether the hydrolysis of **4b**-9-*d* was performed in the presence or absence of 1.4–1.5 equiv of 2,6-lutidine; however, the recovery of **4a** increased from 46 to 66% with the amine present. Exposure of **4a**-9-*d* to the solvolytic conditions (1 equiv of *p*-nitrobenzoic acid, 125°, four to five half-lives) gave appreciable scrambling (32 ± 2% of that observed in the solvolysis); in the presence of 2,6-lutidine, however, only a slight amount (4 ± 2%) of scrambling was found. Recovery of unreacted **4b**-9-*d* after partial reaction indicated only a minor amount (4 ± 2%) of rearrangement prior to the actual hydrolysis.



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specific reaction of **24** with water from the three equivalent directions affords **4a** with the observed positional degeneracy. The overall substitution reaction proceeds with retention of configuration at C-9 but inversion at the original *anti*-2,3 positions.

It is also clear that only the *anti*-cyclopropane ring becomes involved in the bond rearrangements. Although secondary involvement of the *syn*-cyclopropane ring bonds in **24** is stereochemically feasible, it is evidently unable to compete with the attack of water. Such a bridge-inversion process must result in further deuterium scrambling, a possibility which is excluded to the extent of 90–95% in these hydrolysis experiments.[30] The absence of bridge inversion may be attributed to a combination of the loss of the resonance stabilization and the severely compressed bond angle in the trigonal transition state for inversion. A high barrier to inversion ($\Delta F^{\ddagger} \geq 19.6$ kcal/mol) has been found for the similarly structured norbornadienyl cation in fluorosulfonic acid.[31]

The rate of hydrolysis of **4b** is obviously highly accelerated in comparison to simple 7-norbornyl sulfonates, the usual reference point.[7] Since $k_{4b}/k_{23} = 0.12$ (Table I), the kinetic enhancement is in the range of 10^{10}–10^{12}.[32,33] The tricyclic ester **3** is accordingly about 80 times more reactive than **4b**, the former also having been directly compared with **23** ($k_3/k_{23} = 10$, 70% aqueous acetone, 90.2°).[7c]

The greater reactivity of **3** may be a consequence of a certain amount of extra strain relief in the solvolytic transition state,[9] since it does in fact rearrange to an apparently less strained structure.[7d,e] Another factor may be the somewhat different orientation of the *anti*-cyclopropane ring in the cage structure of **4b**. The 4,5 bond connecting the two three-membered rings tends to direct the electrons of the participating bent bond somewhat less favorably with respect to the carbinyl carbon.

Nevertheless, the difference in reactivity between **3** and **4b** is small compared to the total rate enhancement. Anchimeric assistance from participation of the *anti*-cyclopropane ring in the solvolytic transition state clearly provides most of the extra driving force. The increased reactivity of the polycyclic esters compared to the simple bicyclic compound (**1**) is reasonably attributed to bending enforced upon the five-membered rings by the rigid carbon bridges within **3** and **4b**, as has been previously suggested.[7c] This distortion appears to improve the alignment for cyclopropane participation as well as to decrease the distance to the carbon bearing the leaving group.

The intervention of the symmetrical trishomocyclopropenyl ion **24** with a relatively stable two-electron, three-center bond affords the simplest explanation for both the high reactivity and stereospecific rearrangement observed in the hydrolysis of **4b**. A classical carbonium ion is unequivocally excluded by the stereospecificity. While an alternative representation having the *anti*-cyclopropane ring weakly interacting with the p orbital of a trigonal carbon at position 9 and equilibrating with the two equivalent forms will also explain the data at hand,[34,35] this picture seems inappropriate to the high reactivity of **4b**. This conclusion is also in line with theoretical calculations which indicate that symmetrization of the 3-bicyclo[3.1.0]hexyl cation is energetically favored.[36]

Experimental Section[37]

Tetracyclo[4.3.0.0^{2,4}.0^{3,7}]non-8-ene (Deltacyclene, 6).[17] The norbornadiene dimer was prepared by the general method of Mrowca and Katz.[18] In our hands, a ratio of 120 g of freshly distilled norbornadiene (from calcium hydride) to 4 g of 5% rhodium on carbon gave the most consistent results. An increase in either the scale or the ratio usually resulted in an undesirable dimerization or in no reaction: bp 58–60° (0.25 mm) (lit.[18] bp 76–77° (0.8 mm)); yield about 55%. The dimer (331 g, 1.8 mol) was allowed to drip into a Pyrex tube packed with glass helices, heated to a temperature of 488–495°, at a rate between 10 and 15 drops/min using a nitrogen flow of 100 ml/min. The volatile components were trapped using a Dry Ice–isopropyl alcohol bath. The cyclopentadiene was removed at reduced pressure (rotary evaporator) at 25°. Distillation of the residue afforded 103.5 g (56%) of deltacyclene (**6**) as a slightly

(30) An experiment was also performed in which once-scrambled pentacyclic alcohol from **4b**-9-*d* was reconverted to the *p*-nitrobenzoate and submitted to a second scrambling cycle. The dmr spectrum of the product again showed no evidence for further rearrangement. This result reduces the maximum amount of leakage *via* bridge inversion to less than about 3–5%.

(31) M. Brookhart, R. K. Lustgarten, and S. Winstein, *J. Amer. Chem. Soc.*, **89**, 6352 (1967).

(32) This estimated range is derived from the rate enhancement attributed to *anti*-7-norbornenyl *p*-nitrobenzoate (10^{9}, 10^{11})[7b,c,e] and the observation that 7-norbornadienyl *p*-nitrobenzoate (**23**) is about 100 times more reactive.[7c] The anchimeric assistance for 4-OTs is calculated to be 11.7–11.9 according to the Foote–Schleyer correlation [C. S. Foote, *J. Amer. Chem. Soc.*, 86, 1853 (1964); P. von R. Schleyer, *ibid.*, 86, 1854, 1856 (1964)] using $\nu_{C=O}$ 1770 cm^{-1} and assuming that $k_{4\text{-OTs}}$ is ten times greater than *anti*-7-norbornenyl tosylate (the approximate reactivity factor for the *p*-nitrobenzoates), *i.e.*, log $k_{rel} \sim 5.1$.

(33) There is, of course, no proof that the measured titrimetric rates in Table I actually correspond to the true rates of ionization [see, for example, V. J. Shiner and W. Dowd, *J. Amer. Chem. Soc.*, **91**, 6528 (1969); V. J. Shiner, Jr., R. D. Fisher, and W. Dowd, *ibid.*, 91, 7748 (1969)]. However, if there is rapid ion pair return in the hydrolysis of **4b**, it must proceed without significant rearrangement since little scrambling in the starting material is found (see ref 29).

(34) (a) E. J. Corey and R. L. Dawson, *ibid.*, 85, 1782 (1963); E. J. Corey and H. Uda, *ibid.*, **85**, 1788 (1963); (b) see also discussion and references in ref 6a, 7d, and 7e.

(35) This explanation would also require that solvation (or some other factor) prevent the *syn*-cyclopropane ring from interacting similarly with the other lobe of the p orbital.

(36) R. Hoffmann, *Tetrahedron Lett.*, 3819 (1965).

(37) Melting points were taken in open capillary tubes on a Thomas–Hoover melting point apparatus and are uncorrected. Infrared spectra were determined on a Perkin-Elmer Infracord, Model 132 or Model 337, spectrophotometer. The nmr spectra were obtained with tetramethylsilane as internal standard on a Varian Associates Model A-60-A, A-56-60, or HA-100 spectrophotometer. The dmr spectra were obtained with deuteriochloroform [$\tau(CDCl_3) = \tau(CHCl_3) = 2.73$] as internal standard on a Varian Associates HA-100 spectrometer at a frequency of 15.35 MHz using a Varian Associates C-1024 time-averaging computer. Mass spectra were determined by Mr. J. Wrona on an Atlas CH_4 mass spectrometer. Microanalyses were performed by Mr. J. Nemeth and associates at the University of Illinois Microanalytical Laboratory. Gas chromatography was performed on a Wilkens Aerograph Model A-90-P3 using either a 6 ft × 0.25 in. copper tube packed with 15% Carbowax 20M on 60–80 mesh chromosorb W and a 5 ft × 0.25 in. copper tube packed with 20% SE-30 silicone rubber on 60–80 mesh Chromosorb W or on a HY-FI Model 600-D using a 5 ft × ⅛ in. copper tube packed with 5% SE-30 silicone rubber on 60–80 mesh DMCS Chromosorb W and 5 ft × ⅛ in. copper tube packed with 5% Carbowax 20M on 60–80 mesh Chromosorb W.

yellow liquid (95% pure by glpc): bp 55–58° (25 mm) (lit.[17b] bp 140°); ν_{max}^{film} 1550, 695 cm^{-1}; nmr ($CDCl_3$) τ 4.0 (t, 2, olefinic protons), 7.48 (br s, 2, bridgehead protons), 8.10 (br s, 1), 8.38 (m, 3), and 8.80 (d, 2, J = 5.0 Hz). Further fractionation resulted in the recovery of 40.5 g of the dimer.

Tetracyclo[4.3.0.0^{2,4}.0^{3,7}]nonane *exo*-8,9-Epoxide (7). To a chloroform (750 ml) solution of *m*-chloroperbenzoic acid (about 0.4 *N*)[38] cooled to 0° was added 25 g (0.21 mol) of tetracyclo[4.3.0.0^{2,4}.0^{3,7}]non-8-ene (**6**). The solution was allowed to stand at 0° for 30 min, then extracted with a 10% sodium hydroxide solution, washed with water, and dried over anhydrous sodium sulfate. After removal of the chloroform on a rotary evaporator, the residue was added to that from three other identical runs and distilled at reduced pressure: 96 g (84%, generally 78–85%); bp 59–60°; ν_{max}^{film} 852, 695 cm^{-1}; nmr ($CDCl_3$) τ 6.72 (s, 2, protons on carbons bearing epoxide), 7.70 (br s, 2, bridgehead protons), 8.38 (br s, 1), 8.54 (br s, 3), and 8.90 (d, 2, J = 5.0 Hz).

Anal. Calcd for $C_9H_{10}O$: C, 80.56; H, 7.51. Found: C, 80.29; H, 7.74.

Caution: Using *m*-chloroperbenzoic acid that had been prepared by the method described by Ogata and Sowaki,[38] a rapid decomposition of the distillation pot residue occurred near the end of the distillation of **7**. A modification which involved the extraction of the aqueous solution of sodium *m*-chloroperbenzoate with chloroform prior to acidification, to remove any *m*-chlorobenzoyl peroxide that was formed, eliminated the hazard.

Reaction of Tetracyclo[4.3.0.0^{2,4}.0^{3,7}]nonane *exo*-8,9-Epoxide (7) with Hydrogen Bromide. A. Treatment with 48% Aqueous Hydrobromic Acid. To a solution of 28 g (0.21 mol) of **7** in 100 ml of chloroform in a 100-ml separatory funnel was added 500 ml of 48% aqueous hydrobromic acid and the mixture was shaken for about 30 sec. After the addition of about 200 ml of saturated sodium chloride, the reaction mixture was extracted with three portions of ether. The combined extracts were washed with 5% sodium bicarbonate solution, water, and dried over anhydrous sodium sulfate. After removal of the solvent *in vacuo*, the crude reaction product was shown to be a mixture of at least three volatile products by glpc. Separation was effected by elution from a silica gel (500 g, 0.05–0.20 mm) column using mixtures of petroleum ether–ether.

The first compound eluted was *exo*-8-hydroxy-*exo*-9-bromotetracyclo[4.3.0.0^{2,4}.0^{3,7}]nonane (**8a**): 5.5 g (12.2%); mp 48–50°. Recrystallization from pentane afforded an analytical sample: mp 50–51°; ν_{max}^{Nujol} 3380 cm^{-1}; nmr ($CDCl_3$) τ 5.4 (d, 1, J = 6.0 Hz), 5.9 (d, 1, J = 6.0 Hz), 7.64 (br s, 2), 7.82 (br s, 3), 8.38 (br s, 2), and 9.07 (d, 2, J = 5.0 Hz).

Anal. Calcd for $C_9H_{11}BrO$: C, 50.25; H, 5.18. Found: C, 50.01; H, 5.13.

The *p*-nitrobenzoate derivative (**8b**) was prepared by the standard method and recrystallized from chloroform–methyl alcohol: mp 128–129°. The nmr spectrum ($CDCl_3$) shows an AB doublet for the protons on carbon bearing bromine (τ 5.44) and oxygen (τ 4.64) with J = 6.0 Hz.

Anal. Calcd for $C_{16}H_{14}BrNO_4$: C, 52.76; H, 3.87; N, 3.84. Found: C, 52.45; H, 4.01; N, 3.84.

The second compound eluted was *exo*-8-hydroxy-*endo*-9-bromotetracyclo[4.3.0.0^{2,4}.0^{3,7}]nonane (**9a**): 3.9 g (8.5%). The analytical sample, from pentane, had mp 82–83°; ν_{max}^{Nujol} 3220 cm^{-1}; nmr ($CDCl_3$) τ 5.70 (d, 1, J = 2.0 Hz), 5.90 (2 d, 1, J = 4.0 Hz, J = 2.0 Hz), 7.75 (m, 5), 8.26 (m, 2), and 8.86 (d, 2, J = 5.0 Hz).

Anal. Calcd for $C_9H_{11}BrO$: C, 50.25; H, 5.18. Found: C, 50.45; H, 5.16.

The *p*-nitrobenzoate (**9b**) was prepared by the standard method and recrystallized from chloroform–methyl alcohol, mp 170–171°. The nmr spectrum ($CDCl_3$) showed a downfield shift of the doublet assigned to the proton on carbon bearing the hydroxyl to τ 4.60 (J = 2.0 Hz). The two doublets for the proton on carbon bearing bromine shifted to τ 5.70 (J = 4.0 and 2.0 Hz).

Anal. Calcd for $C_{16}H_{14}BrO_4$: C, 52.76; H, 3.87; N, 3.84. Found: C, 52.69; H, 4.11; N, 4.04.

The third component eluted was *anti*-5-hydroxy-*exo*-8-bromotetracyclo[4.3.0.0^{2,4}.0^{3,7}]nonane (**10a**): 22 g (49%, generally 35–50%). Recrystallization from ether–pentane afforded the analytical sample: mp 73–74°; ν_{max}^{Nujol} 3250 cm^{-1}; nmr ($CDCl_3$) τ 5.75 (br s, 1), 5.82 (2 d, 1, J = 3.0 Hz, J = 7.0 Hz), 7.60 (m, 5), 7.94 (s, 1), and 8.84 (m, 3).

Anal. Calcd for $C_9H_{11}BrO$: C, 50.25; H, 5.18. Found: C, 50.38; H, 5.27.

(38) Y. Ogata and Y. Sowaki, *Tetrahedron*, **23**, 3327 (1967).

The *p*-nitrobenzoate derivative (**10b**) was prepared by the standard method and recrystallized from chloroform–methyl alcohol, mp 164–166°. The nmr spectrum ($CDCl_3$) shows a triplet at τ 4.68 (J = 1.5 Hz) for the C-5 proton and a pair of doublets at τ 5.78 (J = 3.0 and 7.0 Hz) for the proton on carbon bearing bromine.

Anal. Calcd for $C_{16}H_{14}BrO_4$: C, 52.76; H, 3.87; N, 3.84. Found: C, 52.78; H, 3.90; N, 4.06.

A fourth component (by tlc) was not identified.

B. Treatment with Anhydrous Hydrogen Bromide. When **7** was treated with anhydrous bromide in a variety of solvents, the yield of **10a** relative to the combination of **8a** and **8b** was very low, with one exception. The general procedure was as follows. Dry hydrogen bromide gas was bubbled into a solution of **7** in a separatory funnel for about 1 min, then shaken for an additional minute. The reaction mixture was washed with saturated sodium chloride, 5% sodium bicarbonate, and water, and then dried over anhydrous sodium sulfate. Removal of the solvent gave the crude reaction mixture which was analyzed by glpc. The results are given as the proportion **8a**:**9a**:**10a** for various solvents (± ~0.5): pentane, 2:4:1; benzene, 5:2:3; ether, 2:7:1; chloroform, 5:1:3; 1,2-dimethoxyethane, 8:1:1; hexamethylphosphoramide, 1:1:8. In the last two cases, saturated sodium chloride solution was added, the mixture extracted with ether, and the work-up continued as above. The absolute yield of bromohydrins in hexamethylphosphoramide was very low.

***exo*-8-Bromotetracyclo[4.3.0.0^{2,4}.0^{3,7}]nonan-5-one.** The procedure employed for the preparation of **11** was employed. From 0.7 g (3.2 mmol) of **10a** dissolved in 35 ml of acetone and 8 mmol of chromic acid solution, 0.6 g of crude ketone was obtained. Recrystallization from pentane gave 0.41 g (59%) of product: mp 59–60°; $\nu_{max}^{CCl_4}$ 1755 cm^{-1}; nmr ($CDCl_3$) τ 5.72 (2 d, 1, J = 3.0 Hz, J = 7.0 Hz).

Anal. Calcd for C_9H_9BrO: C, 50.73; H, 4.26. Found: C, 50.90; H, 4.37.

8-Tetracyclo[4.3.0.0^{2,4}.0^{3,7}]nonen-5-ol (5). To a solution of 18.5 g (0.086 mol) of **10a** dissolved in 100 ml of dimethyl sulfoxide was added 20.8 g (0.185 mol) of potassium *t*-butoxide (MSA Research Corp.) dissolved in 75 ml of dimethyl sulfoxide and stirred at room temperature for 3 hr. After the addition of 300 ml of water, the reaction mixture was extracted with four portions of ether. The combined ethereal extracts were washed with water, dried over anhydrous sodium sulfate, and evaporated *in vacuo*. Distillation of the crude product (11.5 g) yielded the unsaturated alcohol (9.7 g), bp 74–78° (2.0 mm), which was shown, by nmr and ir, to contain approximately 5% **7**. Column chromatography on silica gel with pentane–ether mixtures effected separation to give 9.0 g (78%) of **5** as a clear colorless liquid: ν_{max}^{film} 3300, 3030, 2950, 1562, and 700 cm^{-1}; nmr ($CDCl_3$) τ 3.95 (m, 2, olefinic protons), 5.92 (t, 1, J = 2.0 Hz, carbinyl proton), 6.90 (br s, 1, bridgehead proton), 7.30 (br s, 1, bridgehead proton), 8.00 (s, 1, hydroxyl proton), 8.10 (br s, 1), 8.28 (m, 1), and 8.58 (d, 2, J = 5.0 Hz).

Anal. Calcd for $C_9H_{10}O$: C, 80.56; H, 7.51. Found: C, 80.25; H, 7.56.

The *p*-nitrobenzoate derivative was prepared by the standard method and recrystallized from chloroform–methyl alcohol, mp 81–83°.

Anal. Calcd for $C_{16}H_{13}NO_4$: C, 67.84; H, 4.63; N, 4.94. Found: C, 67.89; H, 4.67; N, 5.04.

Pentacyclo[4.3.0.0^{2,4}.0^{3,8}.0^{5,7}]nonan-9-ol (4a). A solution of 2.2 g (0.0165 mol) of 8-tetracyclo[4.3.0.0^{2,4}.0^{3,7}]nonen-5-ol (**5**) in 50% aqueous *t*-butyl alcohol (220 ml) was irradiated for about 20 hr with a 450-W medium-pressure Hanovia mercury lamp in a quartz immersion well. At approximately 3-hr intervals, the reaction was stopped and the immersion well cleaned due to the formation of an insoluble yellow material. When **5** could no longer be detected by glpc, the irradiation was stopped and most of the *t*-butyl alcohol was removed on a rotary evaporator at reduced pressure. The aqueous mixture (an insoluble material precipitated) was extracted with several portions of ethyl ether which were combined, washed with water, and dried over anhydrous sodium sulfate. After the ether was removed by evaporation, the residue was dissolved in benzene (with difficulty), and placed on a silica gel column. Elution with 25% ether–75% pentane separated the volatile components from a nonvolatile, very polar impurity. Gas chromatographic analysis of the material isolated from the column (0.3 g) showed three peaks whose relative retention times and areas were (Carbowax 20M, 150°) 1.0 (15%), 1.17 (3%), and 1.45 (82%). The components were separated by collection from a 5 ft × $^3/_8$ in. copper tube packed with Carbowax 20M on 60–80 mesh Chromosorb W at 140°.

The first peak was shown to be **12** by comparison of its infrared and nmr spectra, melting point, mixture melting point, and glpc behavior with an authentic sample (see below). The *p*-nitrobenzoate derivatives from both samples were also shown to be identical. The second peak was shown to be unreacted starting material (**5**) by spectral comparisons.

The third peak was pentacyclo[4.3.0.0^{2,4}.0^{3,8}.0^{5,7}]nonan-9-ol (**4a**): 150 mg (6.8%; generally 6–8.5%; absolute yield determined to be 10 ± 0.5% by glpc with a calibrated internal standard). Recrystallization from pentane afforded an analytical sample: mp 132–133°; mass spectrum, *m/e* 134, base peak 92; $\nu_{max}^{CCl_4}$ 3640, 3400, 1375, and 1060 cm^{-1}; nmr ($CDCl_3$) (Figure 1A) τ 5.75 (q, 1, J = 2.0 Hz, carbinyl proton), 7.55 (sextet, 2, J = 2.0 Hz, bridgehead protons), 7.57 (m, 1), 7.90 (m, 2), 8.05 (m, 1), and 8.23 (m, 2).

Anal. Calcd for $C_9H_{10}O$: C, 80.56; H, 7.51. Found: C, 80.40; H, 7.48.

The *p*-nitrobenzoate derivative was prepared by standard methods and recrystallized from chloroform–methyl alcohol, mp 153.5–154.5°.

Anal. Calcd for $C_{16}H_{13}NO_4$: C, 67.84; H, 4.63; N, 4.94. Found: C, 68.02; H, 4.74; N, 4.80.

Tetracyclo[4.3.0.0^{2,4}.0^{3,7}]nonan-5-ol (12). A mixture of 0.5 g (3.7 mmol) of 8-tetracyclo[4.3.0.0^{2,4}.0^{3,7}]nonen-5-ol (**5**) and 0.1 g of 30% palladium on carbon in 60 ml of ethyl alcohol was shaken on a Paar hydrogenation apparatus under 35 psi of hydrogen for 40 min. After filtration, the ethyl alcohol was removed by evaporation at reduced pressure. The residue was dissolved in ether, washed with water, and dried over anhydrous sodium sulfate. After evaporation of the ether, the crude product was crystallized from pentane at 0°. Upon collection by filtration, the resulting crystals softened at room temperature. After purification by filtration over a short silica gel column using mixtures of ether–pentane, 0.22 g (44%) of stable crystalline material was isolated from cold pentane: mp 38–39°; nmr ($CDCl_3$) τ 5.83 (poorly resolved triplet, 1), 7.50 (bs, 1), 7.75 (s, 1), 7.95 (bs, 1), 8.54 (m, 5), and 8.92 (broad singlet superimposed on a multiplet, 3). The spectral properties of the filtrate were identical with those of the crystalline material.

Anal. Calcd for $C_9H_{12}O$: C, 79.37; H, 8.88. Found: C, 79.29; H, 8.82.

The *p*-nitrobenzoate derivative was prepared using the standard method and recrystallized from chloroform–methyl alcohol, mp 78–79°.

Anal. Calcd for $C_{16}H_{15}NO_4$: C, 67.36; H, 5.36; N, 4.91. Found: C, 67.47; H, 5.47; N, 4.94.

Conversion of Pentacyclo[4.3.0.0^{2,4}.0^{3,8}.0^{5,7}]nonan-9-ol (4a) to Pentacyclo[4.3.0.0^{2,4}.0^{3,8}.0^{5,7}]nonane (22). A solution of 0.11 g (0.83 mmol) of **4a** and 0.3 g (2.5 mmol) of freshly distilled thionyl chloride in 10 ml of ether was stirred at room temperature. After the reaction was complete, as determined by the disappearance of **4a** by tlc analysis, the ether and excess thionyl chloride were removed *in vacuo*. A few milliliters of benzene was added and evaporated to ensure complete removal of the thionyl chloride. The crude chloride **21** was dissolved in tetrahydrofuran (10 ml) and added to a suspension of 0.1 g of lithium aluminum hydride in tetrahydrofuran (20 ml) and heated at reflux for 14 hr. The excess lithium aluminum hydride was destroyed with water, ethyl ether was added, and, after washing with water and drying over anhydrous sodium sulfate, the solvent was removed on a rotary evaporator. The hydrocarbon was collected using preparative glpc (5 ft × $^3/_8$ in. copper tube packed with Carbowax 20M on 60–80 mesh Chromosorb W) to give 22 mg (23%) of material which was found to be identical with the known hydrocarbon, prepared by the method of Freeman and Balls,[12b] by comparison of nmr and infrared spectrum. The isolated yield was low due to the volatility of **22**. The reaction was repeated and the absolute yield determined to be 72% by glpc using a calibrated internal standard.

8-Tetracyclo[4.3.0.0^{2,4}.0^{3,7}]nonen-5-one (11) from Tetracyclic Alcohol (5). To a solution of 6.6 g (0.049 mol) of 8-tetracyclo[4.3.0.0^{2,4}.0^{3,7}]nonen-5-ol (**5**) in 200 ml of acetone stirred at room temperature was added about 50 ml of a chromic acid solution (prepared by dissolving 5.3 g of CrO_3 and 4.5 ml of H_2SO_4 in 20 ml of water, then diluting to 50 ml with acetone) slowly until a reddish color persisted. The resulting mixture was stirred an additional 5 min and 3 ml of isopropyl alcohol was added. After filtration, water was added and most of the acetone was removed at reduced pressure on a rotary evaporator. The aqueous solution was extracted four times with ether which was washed with 5% sodium bicarbonate and water, and dried over anhydrous sodium sulfate. Removal of the solvent gave 6.0 g of crude product which, by tlc analysis, was shown to be a mixture of unreacted **5** and product **11**. Separation was effected by column chromatography on silica gel using pentane–ether yielding **11** as a colorless clear liquid: 4.9 g (75%; generally 70–80%); ν_{max}^{film} 3055, 2975, 1764, 1750, and 702 cm^{-1}; nmr ($CDCl_3$) τ 3.84 (t, 2, J = 2.0 Hz, olefinic protons), 6.78 (br s, 2, bridgehead protons), 7.78 (d, 2, J = 5.0 Hz), and 8.16 (m, 2).

Anal. Calcd for C_9H_8O: C, 81.79; H, 6.10. Found: C, 81.60; H, 6.14.

Ketone 11 from 7-Norbornadienecarboxylic Acid (13). 7-Norbornadienecarboxylic acid (**13**) was prepared from 7-chlorobornadiene *via* the corresponding nitrile essentially as reported by Klumpp and Bickelhaupt.[22a] The crystalline acid (1.64 g) was treated with 7.2 ml of oxalyl chloride in 60 ml of benzene and the resulting solution allowed to stand at room temperature for 1.5 hr. Evaporation of the solvent and excess reagent under reduced pressure (20 mm) afforded 1.80 g of an orange liquid (ν_{max} 1810 cm^{-1}, no OH absorption). A 1.21-g portion of the crude acid chloride in 20 ml of benzene was added to a solution of excess diazomethane (prepared from 5 g of N-nitroso-N-methylurea, codistilled with ether, and dried over sodium wire)[39] in 40 ml of ether over a 5–10-min period with stirring at 0°. The solution was allowed to stand at room temperature. The crude product, after evaporation of the solvent, was purified by chromatography on 60 g of silica gel. Elution with 300 ml of 30% ether–pentane gave three fractions containing the yellow liquid diazo ketone **14** (0.87 g, 67%, ν_{max} 1730 and 2010 cm^{-1}).

A solution of the diazo ketone in 10 ml of dry tetrahydrofuran was added slowly to a stirred suspension of copper powder in 20 ml of refluxing tetrahydrofuran. The mixture was allowed to heat at reflux for 1.8 hr and then set aside at room temperature overnight.

The catalyst was filtered and *ca.* 1 ml of water was added. After a few minutes, the solution was diluted with ether, extracted with water and saturated sodium bicarbonate, and then dried ($MgSO_4$) and evaporated [this procedure removed two impurities (ketene?) observed in the glpc of the original product]. Further purification was effected by passage over a column of 15 g of silica gel, eluting with 25% ether–pentane. The liquid so obtained (577 mg, 54% from **13**) was identical with ketone **11** (see above) according to ir and nmr comparison.

Pentacyclo[4.3.0.0^{2,4}.0^{3,6}.0^{5,7}]nonan-9-one (20). A solution (some suspended material) of the dipyridine–chromium trioxide complex (1.5 g) in 50 ml of methylene chloride[28] was added with swirling to a solution of alcohol **4a** (0.1 g, 0.75 mmol) in 20 ml of methylene chloride over a 3-min period. After 5 min at room temperature with occasional swirling, the suspension was poured onto a column of silica gel. The first two fractions afforded ketone **20** (82 mg) pure according to tlc analysis. Recrystallization from pentane furnished 40 mg (40%) of the pure ketone: mp 87–89°; $\nu_{max}^{CCl_4}$ 3017, 3055, and 1170 cm^{-1}; nmr ($CDCl_3$) τ 7.50 (m, 4) and 8.00 (m, 4).

Anal. Calcd for C_9H_8O: C, 81.79; H, 6.10. Found: C, 81.50; H, 6.22.

8-Tetracyclo[4.3.0.0^{2,4}.0^{3,7}]nonen-5-deuterio-5-ol (5-5-*d*). To a suspension of 0.72 g (0.017 mol) of lithium aluminum deuteride (E. Merck A. G. Darmstadt) in 100 ml of anhydrous ether was added 4.9 g (0.037 mol) of **11** at room temperature during a 30-min period. Stirring was continued for 1 hr. The excess lithium aluminum deuteride was decomposed with water, the ether solution decanted, and the solid washed with 100 ml of ether in portions. After drying the combined ether washings over anhydrous sodium sulfate, the solvent was removed *in vacuo* giving a near quantitative yield of deuterated alcohol **5-5-*d***. Thin layer chromatographic and infrared spectral analysis showed no ketone to be present. No signal for the carbinyl proton (τ 5.92) could be seen in the nmr spectrum.

Pentacyclo[4.3.0.0^{2,4}.0^{3,8}.0^{5,7}]nonan-9-deuterio-9-ol (4a-9-*d*). The procedure previously described for the preparation of **4a** gave the labeled alcohol in the same yield. The nmr spectrum shows no signal at τ 5.75 for the carbinyl proton and the sextet at τ 7.55 of **4a** has been reduced to a quintet, with the remainder of the spectrum essentially unchanged. The dmr spectrum showed only one signal at τ 5.8.

The *p*-nitrobenzoate derivative, **4b-9-*d***, was prepared by standard methods and recrystallized from chloroform–methyl alcohol: mp 153.5–154.5° (80%); greater than 99% deuterium by nmr. The nmr spectrum showed no detectable carbinyl absorption.

(39) F. Arndt, "Organic Syntheses," Coll. Vol. II, John Wiley & Sons, Inc., New York, N. Y., 1943, p 165.

Anal. Calcd for $C_{16}H_{12}DNO_4$: D, 7.69 atom %. Found: D, 7.55 atom %.

anti-5-Hydroxy-*exo*-8-acetoxytetracyclo[4.3.0.0^{2,4}.0^{3,7}]nonane (15). To 22 g (0.164 mol) of tetracyclo[4.3.0.0^{2,4}.0^{3,7}]nonane *exo*-8,9-epoxide (**7**) was added 75 ml of glacial acetic acid cooled to 10°, and the mixture was stirred for 3–4 hr while warming to room temperature. Water (600 ml) was added and the reaction extracted with several portions of chloroform which was washed with 5% sodium bicarbonate and water, and then dried over anhydrous sodium sulfate. The chloroform was removed at reduced pressure on a rotary evaporator giving 29 g of crude product which was used without further purification. In earlier runs **15** was purified by distillation at reduced pressure but extensive decomposition reduced the yield to only 40%: bp 104–108° (0.3 mm); ν_{max}^{film} 3425, 1740 cm^{-1}; nmr ($CDCl_3$) τ 5.17 (2 d, 1, J = 2.5 Hz, J = 7.0 Hz), 5.80 (br s, 1), and 8.02 (s, 3).

Anal. Calcd for $C_{11}H_{14}O_3$: C, 68.02, H, 7.27. Found: C, 68.00; H, 7.30.

anti-5-(2′-Tetrahydropyranyloxy)-*exo*-8-hydroxytetracyclo[4.3.0.-0^{2,4}.0^{3,7}]nonane (16a). A solution of 29 g (0.15 mol) of crude **15** was dissolved in 32 g (0.38 mol) of dihydropyran, freshly distilled from potassium hydroxide, and two drops of concentrated sulfuric acid was added. The reaction, externally cooled to maintain the temperature at *ca.* 25°, was stirred for 1 hr, then dissolved in ethyl ether, which was washed with 5% sodium bicarbonate and water, and dried over anhydrous sodium sulfate. The ether was evaporated at reduced pressure to yield 43 g of crude *anti*-5-(2′-tetrahydropyranyloxy)-*exo*-8-acetoxytetracyclo[4.3.0.0^{2,4}.0^{3,7}]nonane. The crude tetrahydropyranyl derivative was dissolved in a solution of potassium hydroxide (25 g, 0.45 mol) in methyl alcohol (300 ml) and stirred at room temperature for 2 hr. After the removal of most of the methyl alcohol *in vacuo*, 400 ml of water was added to the residue which was extracted with several portions of ether. The ethereal extracts were combined, washed with water and saturated sodium chloride, and dried over anhydrous sodium sulfate. Evaporation of the ether on a rotary evaporator afforded 31.5 g of crude **16a**, which, by tlc, was shown to contain at least four components. Purification was effected by placing the material on a silica gel (600 g) column in benzene, followed by elution with petroleum ether–ether mixtures. The first three constituents eluted (2.2 g) showed no hydroxyl absorption in the infrared. Further elution gave **16a**: 24.9 g (64% based on epoxide **7**; generally 55–65%). Attempted purification of this substance or the acetoxy intermediate by distillation at reduced pressure resulted in the loss of the tetrahydropyranyl group. An analytical sample was prepared by careful chromatography on silica gel: ν_{max}^{film} 3450 cm^{-1}; the nmr spectrum was very complex.

Anal. Calcd for $C_{14}H_{20}O_3$ (236.3): C, 71.16; H, 8.53. Found: C, 71.39; H, 8.56.

5-(2′-Tetrahydropyranyloxy)tetracyclo[4.3.0.0^{2,4}.0^{3,7}]-non-8-ene (Unlabeled 19). A solution of 10 g (0.043 mol) of **16a** and 15 g (0.06 mol) of *p*-bromobenzenesulfonyl chloride in anhydrous pyridine (50 ml) was stirred at room temperature for 15 hr, then poured over ice. The aqueous solution was extracted with several portions of petroleum ether and the combined extracts were washed with water, 5% hydrochloric acid, and saturated sodium chloride, and dried over anhydrous sodium sulfate.

After removal of the solvent, 6.2 g (0.013 mol) of the crude brosylate **16b** (total weight of crude brosylate, 19.5 g) (no hydroxyl absorption in the infrared spectrum) was dissolved in xylene (50 ml) and added to a suspension of 2.1 g (0.018 mol) of potassium *t*-butoxide in xylene (120 ml). The reaction mixture was heated at reflux for 1 hr, cooled, and, after the addition of water, extracted with ether. The organic layer was washed with water and saturated sodium chloride and dried over anhydrou ssodium sulfate. After removal of the solvents *in vacuo*, the crude product was distilled at reduced pressure yielding unlabeled **19**: 1.3 g (45%); bp 105–110° (0.6 mm). A sample was purified for analysis by preparative glpc: ν_{max}^{film} 1565, 696 cm^{-1}; nmr ($CDCl_3$) τ 3.95 (m, 2, olefinic protons).

Anal. Calcd for $C_{14}H_{18}O_2$: C, 77.03; H, 8.31. Found: C, 77.17; H, 8.22.

Hydrolysis of Unlabeled 19 to 5. To a solution of 0.31 g (1.4 mmol) of unlabeled **19** in anhydrous methyl alcohol (7 ml) was added 3 drops of concentrated hydrochloric acid. After standing at room temperature for 20 min, the reaction mixture was poured into water and extracted with ether. The ether solution was washed with water and dried over anhydrous sodium sulfate. Removal of the ether *in vacuo* gave 0.17 g of crude product. Preparative glpc afforded material identical (infrared, glpc, tlc) with a previously characterized sample of 8-tetracyclo[4.3.0.0^{2,4}.0^{3,7}]nonen-5-ol (**5**).

anti-5-(2′-Tetrahydropyranyloxy)tetracyclo[4.3.0.0^{2,4}.0^{3,7}]nonan-8-one (17). To a solution of 5.0 g (0.021 mol) of **16a** dissolved in methylene chloride (150 ml) was added 33.5 g (0.13 mol) of solid dipyridine–chromium trioxide dissolved (some insoluble material was present) in methylene chloride[28] (300 ml) over a 10-min period with rapid stirring. Stirring was continued for 10 min after which the entire reaction mixture was filtered through a short silica gel column (250 g). Elution with methylene chloride was continued until only a trace of ketone was present in each fraction. The fractions were combined and, after removal of all traces of pyridine at reduced pressure, chromatographed on silica gel (110 g) using mixtures of petroleum ether–ether which afforded **17** as a pale yellow oil, 4.6 g (92%). An analytical sample was prepared by careful chromatography on silica gel: ν_{max}^{film} 1740 cm^{-1}; the nmr spectrum ($CDCl_3$) showed very complex patterns.

Anal. Calcd for $C_{14}H_{18}O_3$: C, 71.77; H, 7.74. Found: C, 71.75; H, 7.70.

anti-5-(2′-Tetrahydropyranyloxy)-*endo*-8-hydroxytetracyclo-[4.3.0.0^{2,4}.0^{3,7}]nonane (Unlabeled 18a). A solution of 1.5 g (6.4 mmol) of *anti*-5-(2′-tetrahydropyranyloxy)tetracyclo[4.3.0.0^{2,4}.0^{3,7}]-nonan-8-one (**17**) in 20 ml of ethyl ether was added dropwise with stirring to a suspension of 0.5 g (1.3 mmol) of lithium aluminum hydride in 50 ml of ether. The resulting mixture was stirred for 1 hr at room temperature. The excess lithium aluminum hydride was decomposed with water, under a blanket of nitrogen, and the ether solution was decanted from the resulting solid which was subsequently washed with additional ether. The combined ethereal layers were washed with water, dried over anhydrous sodium sulfate, and then concentrated to dryness *in vacuo*. Purification by chromatography on silica gel using mixtures of pentane–ether gave unlabeled **18a** as a colorless oil: 1.4 g (93%); ν_{max}^{film} 3410 cm^{-1}; the nmr spectrum ($CDCl_3$) was very complicated.

Anal. Calcd for $C_{14}H_{20}O_3$: C, 71.16; H, 8.53. Found: C, 71.24; H, 8.46.

anti-5-(2′-Tetrahydropyranyloxy)-8-deuteriotetracyclo[4.3.0.0^{2,4}.-0^{3,7}]non-8-ene (19-*anti*-8-*d*). Using the same procedure as previously described for unlabeled **18a**, 17 g (0.073 mol) of **17** was treated with 2.0 g (0.048 mol) of lithium aluminum deuteride (E. Merck A. G. Darmstadt) to give 17.4 g of crude hydroxy ether. Without purification, this material was converted to the *p*-bromobenzenesulfonate derivative (**18b**-*anti*-8-*d*) by the previously described method, yielding 26.3 g of impure brosylate. This was dissolved in xylene (225 ml), 7.3 g (0.065 mol) of potassium *t*-butoxide was added, and the slurry was heated under reflux for 2.5 hr. After cooling, the reaction mixture was poured over ice and extracted with ether. The ether solution was washed with water and saturated sodium chloride and dried over anhydrous sodium sulfate. The solvent was removed *in vacuo* and the residue distilled at reduced pressure yielding **19**-*anti*-8-*d* as a clear colorless liquid: 4.26 g (27%); bp 108–112° (0.75 mm); nmr ($CDCl_3$) τ 3.86 (d, 1, J = 3.0 Hz, olefinic proton).

anti-5-Hydroxy-8-deuteriotetracyclo[4.3.0.0^{2,4}.0^{3,7}]non-8-ene (5-anti-8-*d*). The procedure for the conversion of unlabeled **19** to **5** was used essentially as described previously: 4.2 g (0.019 mol) of labeled **19** afforded 2.02 g (76%) of **5**-*anti*-8-*d*: bp 68–70° (1.0 mm); nmr ($CDCl_3$) τ 3.86 (d, 1, J = 3.0 Hz, olefinic proton), 5.92 (t, 1, J = 2.0 Hz, carbinyl proton), 6.88 (br s, 1, bridgehead proton), 7.30 (br s, 1, bridgehead proton), 7.95 (s, 1, hydroxyl proton), 8.10 (br s, 1), 8.28 (m, 1), and 8.55 (d, 2, J = 5.0 Hz).

4-*anti*-Deuteriopentacyclo[4.3.0.0^{2,4}.0^{3,8}.0^{5,7}]nonan-9-ol (4a-anti-4-*d*). The procedure previously described for the preparation of **4a** gave **4a**-*anti*-4-*d* in identical yield. The nmr spectrum (Figure 1B) shows no signal at τ 8.05. The multiplets at τ 8.23 and 7.67 have been reduced to a broad singlet and two doublets (J = 1.5 Hz, J = 5.5 Hz), respectively, with the remainder of the spectrum essentially unchanged. The dmr spectrum showed a single peak at τ 8.00.

The *p*-nitrobenzoate derivative, **4b**-*anti*-4-*d*, was prepared by the standard method and recrystallized from chloroform–methyl alcohol: mp 153.5–154.5° (81%); greater than 97% deuterium by nmr.

Anal. Calcd for $C_{16}H_{12}DNO_4$: D, 7.69 atom %. Found: D, 7.15 atom %.

General Methods and Materials for Solvolytic and Rearrangement Studies. The pentacyclo[4.3.0.0^{2,4}.0^{3,8}.0^{5,7}]nonan-9-ol (**4a**) was collected by glpc and the *p*-nitrobenzoate derivative, **4b**, was prepared and recrystallized to a constant melting point of 153.5–154.5°. The solvent was prepared as follows. Reagent grade

acetone was refluxed over calcium chloride for 2 hr and then distilled through a 40-cm Vigreux column, taking a center cut. Water was distilled through a 25-cm Vigreux column before use. The ratio of acetone to water was 65:35 by volume. Reagent grade 2,6-lutidine was used where specified without further purification. After each tube was filled with the measured amounts of solution, it was sealed under a nitrogen atmosphere. Tubes were taken out of the bath at the solvolysis temperature at measured intervals, and cooled rapidly in an ice bath. At the completion of the run, the tubes were opened and 5 ml of solution (taken with a 5-ml automatic delivery pipet) was removed and added to 15 ml of distilled water with 5 drops of 0.1% bromothymol blue indicator (in 50% ethyl alcohol). This mixture was titrated with approximately 0.03 *M* sodium hydroxide solution (prepared by diluting a 0.1 *N* sodium hydroxide Acculute to 500 ml with absolute methyl alcohol, then taking a 7.5-ml portion and diluting this to 500 ml with absolute methyl alcohol) under a blanket of nitrogen using magnetic stirring. All titrations were carried out using a 5-ml automatic reloading microburet which could be read to 0.01 ml. Two or three tubes containing solvent only and two tubes containing approximately 0.005 *M* *p*-nitrobenzoic acid were placed in the 125° bath and titrated at various intervals to check the base concentration. Infinity values were taken from tubes run at 125° for nine to eleven half-lives.

Solvolysis of Pentacyclo[4.3.0.0^{2,4}.0^{3,8}.0^{5,7}]non-9-yl *p*-Nitrobenzoate (4b). For each run approximately 85 mg (0.3 mmol) of **4b** was weighed into a 50-ml volumetric flask and 65% aqueous acetone was added to the mark. The solution had to be warmed to dissolve the ester completely. Eight tubes were prepared containing 6 ml of the above solution which had to be transferred to the tubes under pressure while still warm. Three independent runs were made at each temperature: 100.0, 113.8, and 125.0°. 7-Norbornadienyl *p*-nitrobenzoate (**23**)[7c,15c] was run at 125.0° The observed rates are listed in Table I.

The recovery of **4b** from the solvolysis reactions was carried out as follows. Most of the methyl alcohol and acetone from the titrated solutions was removed on a rotary evaporator. The aqueous solution was extracted with several portions of ether which was washed with 5% sodium bicarbonate and water, and dried over anhydrous sodium sulfate. The solvent was removed and the residue subjected to thin layer and gas chromatographic analyses which showed **4a** and **4b** to be free of major impurities. This mixture was converted to **4b** using the standard procedures to give, after recrystallization from chloroform–methyl alcohol, between 50 and 70% of the desired product, mp 153.5–154.5°.

Rearrangement of 9-Deuteriopentacyclo[4.3.0.0^{2,4}.0^{3,8}.0^{5,7}]non-9-yl *p*-Nitrobenzoate (4b-*anti*-9-*d*) and 4-Deuteriopentacyclo[4.3.0.0^{2,4}.0^{3,8}.0^{5,7}]non-9-yl *p*-Nitrobenzoate (4b-*anti*-4-*d*). The procedure described is for a typical rearrangement run. A 30-mg (1.05 mmol) sample of **4b**-9-*d* was weighed into each of six 18 × 150 mm Pyrex tubes, 10 ml of 65% aqueous acetone was added, and the tubes were sealed under nitrogen. After heating in a 125° bath for about 12 hr (four to five half-lives), the tubes were cooled, opened, and combined. Most of the acetone was removed on a rotary evaporator and the aqueous solution was extracted with four portions of ether which were combined, washed with 5% sodium bicarbonate and water, and dried over anhydrous sodium sulfate. Removal of the ether *in vacuo* gave a residue of 70 mg of crude product. Thin layer chromatographic analysis showed unreacted *p*-nitrobenzoate, a spot corresponding to the alcohol and a new spot at a lower R_f value which was not identified. Glpc (Carbowax 20M on Chromosorb W) showed only the alcohol and about 2% of an unidentified compound with a very short retention time, probably an olefin. Preparative glpc gave 28 mg (33%) of the rearranged alcohol **4a**, mp 130–132°. Using a calibrated internal standard, the absolute yield (glpc) was shown to be 46%. When the rearrangement was performed as described but with the addition of 15 mg (1.4 mmol) of 2,6-lutidine to each tube, tlc showed the absence of the lower R_f spot. The yield of collected rearranged alcohol increased to 49 mg (57%) and the absolute yield increased to 66%.

The nmr spectrum showed that a signal has appeared at τ 5.75 for the carbinyl proton. The signal at τ 8.23 has the same splitting but is decreased in intensity. Integration of these two positions against 7-norbornadienyl *p*-nitrobenzoate (**23**) shows an area of 0.67 ± 0.02 proton at τ 5.75 and 1.3 ± 0.1 protons at τ 8.23. The dmr spectrum (Figure 2A) shows only two signals at τ 5.75 and 8.23 in a ratio of 1:2.05 ± 0.08. This indicates one-third of the deuterium label remains at the carbinyl position and the remaining two-thirds is distributed between two other equivalent positions. Both the nmr and dmr data are the average of two separate runs. The *p*-nitrobenzoate of this once-scrambled alcohol was prepared and submitted to the rearrangement conditions for a second scrambling cycle. The dmr spectrum of the product was identical with the spectrum after the first scrambling cycle.

For the rearrangement of **4b**-*anti*-4-*d*, smaller samples were used and a slightly lower recovery (50%) was observed, even with the addition of 2,6-lutidine. The nmr spectrum (Figure 1C) shows that a signal has appeared at τ 8.05 with the same splitting as that for the unlabeled compound **4a**. The signals at τ 8.23 and 7.67 also show more complex splitting but not identical with those in **4a**, and the signal at τ 7.67 also shows more complex splitting but not identical with those in **4a**, and the signal at τ 7.55 (bridgehead protons) has the same splitting but is reduced in intensity. The signal for the carbinyl proton at τ 5.75 is now a triplet. No internal standard was used to obtain the exact ratio of the protons at τ 8.05 and 7.55, but they appeared to be approximately 2/3:4/3 by comparison to the other absorptions. The dmr spectrum (Figure 2B) shows only two signals at τ 7.55 and 8.0 in a ratio of essentially 2:1. This indicates that one-third of the label remains at the *anti*-4 position and the remaining two-thirds is distributed between the two equivalent bridgehead positions. The dmr data were identical in two separate runs.

Treatment of 4a-9-*d* with *p*-Nitrobenzoic Acid. When 86 mg (0.635 mmol) of **4a**-9-*d* and 106 mg (0.635 mmol) of *p*-nitrobenzoic acid were dissolved in 65% aqueous acetone and treated under rearrangement conditions, 22 mg (25%) of alcohol was recovered by preparative glpc after the usual isolation procedure. The nmr spectrum showed some rearrangement, about 32 ± 2% of the recovered material. Under the same conditions with 1.5 equiv of 2,6-lutidine, 60% of the alcohol was recovered which only showed 4 ± 2% scrambling had occurred.

Recovery of 4b-9-*d* after Partial Hydrolysis. A 30-mg (1.05 mmol) sample of **4b**-9-*d* was weighed into four tubes and 10 ml of 65% aqueous acetone added. After sealing, the tubes were heated at 125° for 170 min and worked up as previously described. The crude product was recrystallized from chloroform–methyl alcohol to give 44 mg of recovered **4b**-9-*d*, mp 153–154°. The nmr spectrum showed a very small signal at τ 4.82 which indicates about 4 ± 2% of rearrangement prior to product formation.

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