The *p*-**nitrobenzoate** had mp 56.5–57.0° (from absolute methanol).

Anal. Calcd for $C_{15}H_{17}NO_4$: C, 65.44; H, 6.22. Found: C, 65.22; H, 6.17.

The *p*-**toluenesulfonate** of this alcohol remained a liquid in our hands. The *p*-bromobenzenesulfonate, **19**-OBs, decomposed in a similar manner to that of **20**.

5-*endo*-Methyl-2-norbornanone. A small sample of alcohol **19** was converted to the ketone with Jones reagent in acetone and the product purified on column G to yield a clear liquid which crystallized just below room temperature.

Anal. Calcd for $C_8H_{12}O$: C, 77.38; H, 9.74. Found: C, 77.20; H, 9.92.

The **2,4-dinitrophenylhydrazone** of the ketone was obtained as orange platelets, mp 151.0–151.5° (absolute methanol).

Anal. Calcd for $C_{14}H_{16}N_4O_4$: C, 55.26; H, 5.30; N, 18.41. Found: C, 55.22; H, 5.36; N, 18.25.

5- and 6-*exo*-Methyl-2-*exo*-norbornyl acetates (acetates of 21 and 22) were obtained from pure 5-norbornene-2-*exo*-carboxylic acid by the same procedure used for the 5- and 6-*endo*-methyl compounds. Analysis with capillary column L showed two main peaks to be present in a ratio of 1:1 and two smaller peaks, each of intensity about 3% of the total. Presumably the latter peaks represent a small amount of *endo*-hydroboration product. The first emerging of the two major peaks, the 6-*exo*-methyl-2-*exo* isomer (acetate of **22**), was completely absent from the acetolysis products of **19**-OBs or the arenesulfonates of **1a**. Its retention time was identical with that of one of the two products from acetolysis of **20**-OBs, the second product being the acetate of **20**.[18]

The other major peak (acetate of **21**) had a retention time identical with that of one of the products from the acetolysis of **19**-OBs and **1a**.[18]

1-Methyl-3-*exo*-norbornanol (31) was formed by alkaline hydrogen peroxide oxidation of the residues from partial asymmetric hydroboration[8b] of 1-methyl-2-norbornene,[9] a reaction that had been carried out in another study.[28] The resulting mixture of 1-methyl-2-*exo*- and 1-methyl-3-*exo*-norbornanols (**29** and **31**) was separated by vpc on column D (**31** emerged second) and then on column F. Alcohol **31** was obtained as a waxy solid.

Anal. Calcd for $C_8H_{14}O$: C, 76.14; H, 11.18. Found: C, 75.97; H, 11.29.

The *p*-**nitrobenzoate** was recrystallized from methanol and had mp 93–94°.

Anal. Calcd for $C_{15}H_{17}O_4N$: C, 65.44; H, 6.22; N, 5.09. Found: C, 65.35; H, 6.12; N, 5.06.

The **acetate** was a liquid.

Anal. Calcd for $C_{10}H_{16}O_2$: C, 71.39; H, 9.59. Found: C, 71.53; H, 9.62.

The *p*-**toluenesulfonate** was a liquid that could not be induced to crystallize at −65° in pentane. It was homogeneous by thin layer chromatography.

Jones oxidation of **31** followed by lithium aluminum hydride reduction of the resulting ketone gave a two-component mixture of **31** and a much larger amount of another alcohol, presumably 1-methyl-3-*endo*-norbornanol (**32**), which emerged just before **31** on column L.

(28) S. Fanega, unpublished work.

The Chemistry of Methylnorbornyl Cations. III. Configurational Correlation of 2,3- and 2,7-Substituted Norbornyl Derivatives by Way of 3-Substituted Nortricyclenes[1]

Jerome A. Berson and Robert G. Bergman[2]

Contribution from the Department of Chemistry, University of Wisconsin, Madison, Wisconsin. *Received October 31, 1966*

Abstract: The relative configurations and optical rotations of *anti*-7-methyl-2-*exo*- and -3-*endo*-methyl-2-*exo*-norbornyl acetates are established by two independent correlations. Both correlations involve 3-nortricyclene derivatives as relay compounds, and the transformations provide absolute configurations and rotations of these substances also.

Although a network of absolute and relative configurational correlations among 1- and 2-substituted bridged bicycloheptane and bicyclooctane derivatives has been constructed,[3] only a few correlations between 2- and 7-substituted norbornanes are available. In studying one aspect of the mechanism of carbonium ion rearrangements of methyl-labeled norbornyl cations,[4] we found the need to establish such correlations. Since the methods adopted to achieve this involve nortricyclenic relay compounds, the present results also provide the first determinations of absolute configuration of nortricyclenes.

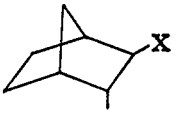
(1) The support of part of this work by the National Institutes of Arthritis and Metabolic Diseases through Grant No. AM-07505 is gratefully acknowledged.

(2) National Institutes of Health Predoctoral Fellow, 1964–1966.

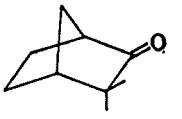
(3) (a) *Cf.*, *inter alia*, J. A. Berson, J. S. Walia, A. Remanick, S. Suzuki, P. Reynolds-Warnhoff, and D. Willner, *J. Am. Chem. Soc.*, **83**, 3986 (1961), and references cited therein; (b) K. Mislow and J. G. Berger, *ibid.*, **84**, 1956 (1962); (c) J. A. Berson and A. Remanick, *ibid.*, **86**, 1749 (1964).

(4) Paper V of this series: J. A. Berson, R. G. Bergman, J. H. Hammons, and A. W. McRowe, *ibid.*, **89**, 2581 (1967).

Acetolysis of the *p*-bromobenzenesulfonate (**1b**) of optically active 3-*endo*-methyl-2-*exo*-norborneol (**1a**) gives a mixture of products[4] from which are isolated (−)-3-*endo*-methyl-2-*exo*-norbornyl acetate (**1c**), identical in sign and magnitude of rotation with **1c** obtained by direct acetylation of **1a**, and (−)-7-*anti*-methyl-2-*exo*-norbornyl acetate (**2b**). (The rotatons refer to the sodium D line.) The absolute configuration of (−)-**1c** is established by oxidation and methylation to (+)-camphenilone (**3**).[4] For reasons discussed elsewhere,[4] a correlation of **1b** and **2b** is mechanistically significant but cannot be based on the assumption that (−)-**1c** and (−)-**2b** are related as simple Wagner–Meerwein

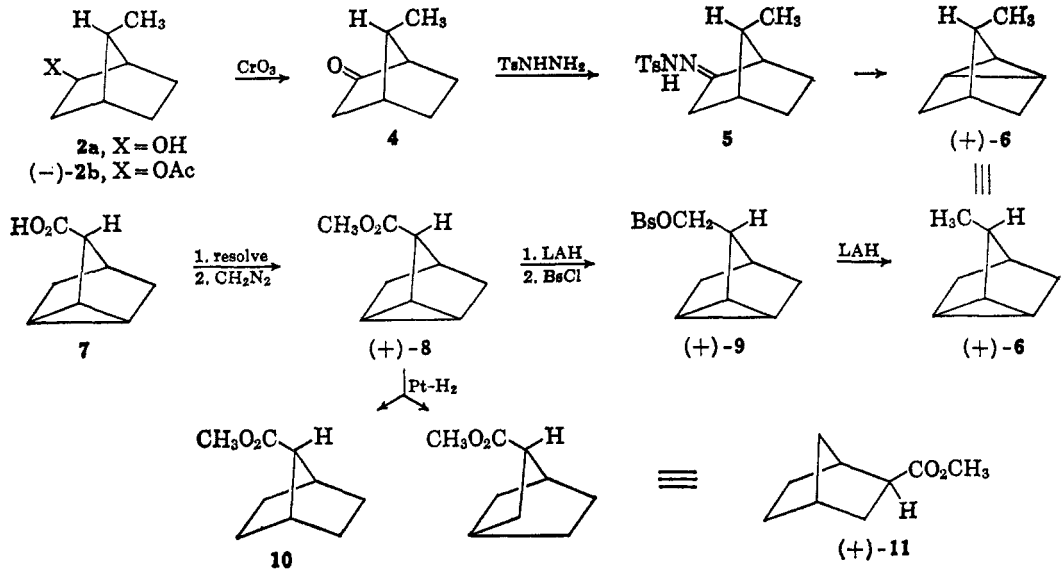


1a, X = OH
b, X = OBs
(−)-**c**, X = OAc



(+)-**3**

Scheme I



isomers. The configuration of **2b** must accordingly be established by independent means. In the following reaction diagrams, which illustrate two such correlations, the indicated configurations are absolute.

Scheme I. The general objective of Scheme I is the correlation of *anti*-7-methyl-2-*exo*-norbornyl acetate (**2b**)[4] with *exo*-norbornanecarboxylic ester (**11**). Oxidation of alcohol **2a**, configurationally related to (−)-acetate **2b**, gives a ketone **4**, which is converted to the *p*-toluenesulfonylhydrazone. Pyrolysis of the *dry* sodium salt *in vacuo* smoothly converts it to (+)-3-methylnortricyclene (**6**).[5] The same hydrocarbon is obtained by a reduction–arenesulfonylation–reduction sequence from (+)-methyl 3-nortricyclenecarboxylate (**8**), the corresponding active acid **7** being available by resolution *via* the cinchonidine salt. The ester (+)-**8** serves as a relay for the entire series. Catalytic hydrogenation (40 psi, acetic acid solvent, platinum oxide catalyst) breaks the cyclopropane ring of (+)-**8** to give a mixture of about equal parts of methyl 7-norbornanecarboxylate (**10**) and (+)-methyl 2-*exo*-norbornanecarboxylate (**11**). Very little of the epimeric methyl 2-*endo*-norbornanecarboxylate, the product of the third possible mode of ring cleavage, is formed under these conditions. A small amount of unreacted tricyclic ester **7** of undiminished rotation can be recovered; this gives assurance that partial epimerization (that is, racemization) of **7** does not accompany hydrogenation. From the known[3a] configuration of (+)-**11**, the configurations of the substances of Scheme I follow.

This correlation, although straightforward in establishing configurational relationships, leaves something to be desired when quantitative comparisons of optical purities of solvolysis substrate **1b** and product **2b** are to be made. Thus, Scheme I correlates the magnitudes of rotation of **2b** and **11**, without reliance on an outside standard of optical purity, from the product of the three rotation ratios **2b**:**6**, **6**:**8**, and **8**:**11**. However, the maximum rotation of **1b** is correlated with that of camphenilone **3**,[4] a substance not included in Scheme I.

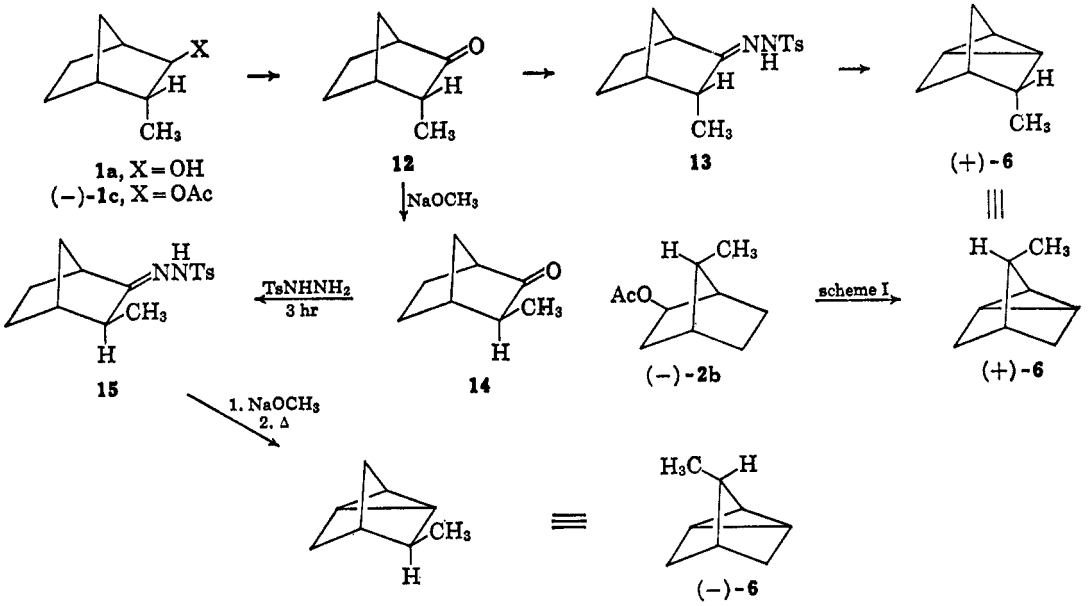
(5) (a) *Cf.* W. R. Bamford and T. S. Stevens, *J. Chem. Soc.*, 4735 (1952); (b) L. Friedman and H. Shechter, *J. Am. Chem. Soc.*, **81**, 5512 (1959); (c) J. W. Powell and M. C. Whiting, *Tetrahedron*, 7, 305 (1959); (d) see, especially, G. M. Kaufman, J. A. Smith, G. G. Vander Stouw, and H. Shechter, *J. Am. Chem. Soc.*, **87**, 935 (1965).

A comparison of maximum rotations of **11** and **3** is not now available by direct correlation. The maximum rotation of **11** rests on isotopic dilution analysis,[6] whereas that of **3** has an entirely separate basis.[3a] Therefore, since there is no common relay, the **11**:**3** rotation ratio and hence the crucial **2b**:**1b** ratio is subject to a pyramiding of the errors inherent in each separate rotation. This is probably the cause of the somewhat low apparent value (92% retention) found[4] when the data of Scheme I are used to calculate the stereochemical result of the **1b** → **2b** reaction. Furthermore, the exact magnitude of the absolute rotation of the *exo* ester **11** is subject to some question, since it was originally prepared[6] from a sample of 2-*exo*-5-norbornenecarboxylic ester which was subsequently shown[3a] to contain a small amount of impurity. It seems desirable therefore to provide a correlation free of these disadvantages. This is given in Scheme II, where the rotations of **1b** and **2b** are related through that of a common reference, the tricyclic hydrocarbon **6**.

Scheme II. A sample of optically active **1a** (at the same level of optical purity as the sulfonate **1b** used for the solvolysis from which (−)-**2b** is isolated) is oxidized to the ketone **12** with Jones reagent (chromic acid–acetone). Although the oxidation proceeds in good yield, it is accompanied by epimerization, the product being a 90:10 mixture of the *endo*- and *exo*-methyl ketones, **12** and **14**. The small amount of **14** is removed by vapor chromatography and the pure *endo* ketone **12** is transformed into the *p*-toluenesulfonylhydrazone (**13**). Hydrazone formation is slow, and if allowed to proceed too long in an effort to force complete conversion, is accompanied by partial epimerization. This becomes evident when the corresponding sodium salt is pyrolyzed to the tricyclic hydrocarbon (+)-**6**. The structural change converts epimerism to enantiomerism, and the rotation of the (+)-**6** obtained in this way (+14.7°) is significantly lower than that (+16.3°) obtained from (−)-**2b** in Scheme I. This is a particularly awkward result because it is not obvious which of the two epimeric hydrazones the hydrocarbon product is derived from, and hence the correlation of (−)-**1c**

(6) J. A. Berson and D. A. Ben-Efraim, *ibid.*, **81**, 4083 (1959).

Scheme II



with (+)-**6**, already seen to be unreliable in magnitude of rotation, actually might be reversed in sign. (In fact, this reversal of sign would be not inconceivable even if the rotation were identical in magnitude.) A conversion of the epimeric *exo* ketone **14** to tricyclic hydrocarbon enantiomeric with that obtained from the *endo* ketone **12** is therefore needed to make a firm correlation. Deliberate epimerization of the above mixture of optically active ketones enriches the **14** content to about 40%. Isolation of pure **14** by vapor chromatography, conversion to the *p*-toluenesulfonylhydrazone (under milder conditions than before), and pyrolysis of the sodium salt give (−)-**6** with an optical rotation (−16.4°) opposite in sign but essentially equal in magnitude to that obtained from (−)-**2b**. This eliminates any possibility of a sign inversion in the correlation of (−)-**1c** and (+)-**6**. Since no obvious mechanism for racemization is available in the (−)-**2b**–(+)**6** conversion of Scheme I, the production of (−)-**6** with the same magnitude of rotation as (+)-**6** from the same ultimate source, (−)-**1c**, must mean that the (−)-**1c**, (−)-**2b**, and (−)-**6** samples all have the same optical purity. The data show that **2b** (in 95% ethanol) has 1.72 times the specific rotation of **1c** (in absolute ethanol) at the same level of optical purity.

This shows that acetolysis of **1b** gives **2b** by simple Wagner–Meerwein change and with complete retention of optical purity. The mechanistic significance of this observation is discussed in an accompanying paper.[4]

Experimental Section

For details of vapor chromatographic and other standard techniques, see paper II.[7]

Scheme I. Correlation of 7-*anti*-Methyl-2-*exo*-norbornyl Acetate [(−)-2b] with 3-Methylnortricyclene [(+)-6]. Acetate **2b** (0.58 g) of rotation $[\alpha]^{22.9}D$ −3.19° (95% ethanol)[4] was reduced to the corresponding alcohol and oxidized with Jones reagent to 7-*anti*-methyl-2-norbornanone (**4**). The procedure used was identical with that employed in the oxidation of 3-*endo*-methyl-2-*exo*-norbornanol below. An infrared spectrum of the ketone obtained in this way showed a strong C=O band at 5.72 μ and no O–H absorption. This material was chromatographed on column B at 120° and obtained 99.5% pure by capillary vpc. It was distilled bulb to bulb and used without further characterization. The ketone (0.156 g) was dissolved in 3 ml of absolute ethanol and 0.234 g of *p*-toluenesulfonylhydrazine was added. The resulting mixture was heated at reflux on a steam bath for 1.5 hr, after which it was cooled and allowed to stand overnight at room temperature. Addition of water caused precipitation of a white solid; this was removed by extracting three times with $CHCl_3$. The combined chloroform extracts were washed with 5% HCl and saturated NaCl and dried over magnesium sulfate. Filtration and evaporation at the aspirator left 0.354 g of white solid (96% yield), presumed to be 7-*anti*-methyl-2-norbornyl *p*-toluenesulfonylhydrazone. An infrared spectrum of the material, showing bands at 3.1 (N–H), 6.01 (C=N), and 6.29 μ (aromatic), was consistent with the proposed structure. The lack of C=O absorption indicated that the ketone had reacted completely. An nmr spectrum in $CDCl_3$ showed absorption from δ 7.2 to 8.0 (4 H) assigned to the aromatic protons, and a singlet at δ 2.4 (3 H) due to the aromatic methyl group. A doublet assigned to the 7-methyl group (J = 7 cps) was centered at δ 0.9, superimposed on complex absorption, arising from the nitrogen proton and the remaining protons of the norbornyl skeleton, running from δ 0.9 to 2.3 (total 13 H).

The sodium salt of the *p*-toluenesulfonylhydrazone was prepared by the following procedure. (It is extremely important that the sodium salt formation be carried out under scrupulously anhydrous conditions, since the salt is quite hygroscopic and the presence of water prevents the formation of tricyclic hydrocarbon in the subsequent pyrolysis.) The entire sample of *p*-toluenesulfonylhydrazone (0.354 g) was placed in a 25-ml, round-bottomed flask, which had been swept with dry nitrogen. A 15-ml portion of tetrahydrofuran, freshly distilled from lithium aluminum hydride, was added quickly to the flask, along with 0.143 g of sodium methoxide. The resulting mixture was stirred overnight at room temperature, protected by a blanket of dry nitrogen. Evaporation of the solvent and drying *in vacuo* overnight (0.2 mm) left a white solid caked to the walls of the flask. The vacuum was broken with dry nitrogen and the salt loosened from the sides of the flask with a spatula in a dry atmosphere.

The flask was then attached, *via* a Pyrex tube, to a receiver cooled in a Dry Ice–acetone bath, the system evacuated to a pressure of 18 mm (normal vacuum pump pressures, of the order of 0.2 mm, prevent efficient trapping of the volatile hydrocarbon), and the flask was heated with an air gun. At the reaction temperature (estimated to be about 110°), the salt decomposed completely in about 10 sec, evolving gas and bubbling off hydrocarbon. A slightly tan solid was left in the flask, and about 0.080 g of volatile product had collected in the trap. A vpc analysis of this material on column O indicated it to be almost completely (*ca.* 97%) 3-methylnortricyclene contaminated with a small amount of a second material. No diazo compound was detectable[5] (infrared spectrum), but vpc analysis on column L at 125° indicated the presence of a small amount (*ca.* 1%) of 7-*anti*-methyl-2-norbornanone (**4**).

(7) J. A. Berson, A. W. McRowe, R. G. Bergman, and D. Houston, *J. Am. Chem. Soc.*, **89**, 2563 (1967).

The tricyclic hydrocarbon (+)-**6** was collected vpc pure from chromatography on column H-1 at 80°. Its specific rotation was found to be $[\alpha]^{23.7}D$ +16.3° (95% ethanol), and its infrared spectrum was identical with that of the hydrocarbon obtained from nortricyclene-3-carbinyl *p*-bromobenzenesulfonate (**9**).

Scheme I. Optical Activation of Nortricyclene-3-carboxylic Acid (7). The cinchonidine salt was prepared in methanol, 95% ethanol, and acetone, but crystals were obtained only from the latter solvent. A solution of 79.0 g of the acid[8] in 250 ml of acetone was heated to boiling on a steam bath, and 189 g of solid cinchonidine was added. After having been heated at reflux for 0.5 hr, the mixture was filtered, concentrated on the steam bath, and cooled to room temperature. The solution was allowed to stand for 8 days at room temperature, and the crystals were collected on a Büchner funnel. Four recrystallizations from boiling acetone gave a total of 110 g (wet) of salt in the head crop. A 50.0-g portion of this material was reconverted to carboxylic acid in the manner described for the ephedrine salt of 3-*endo*-methyl-2-*exo*-norbornyl acid phthalate,[4] yielding 14.6 g of optically active material as a greenish oil. Reaction with diazomethane in ether solution and evaporation of the solvent gave **methyl 3-nortricyclenecarboxylate (8)** which distilled as a clear oil shown to be 98.5% pure by capillary vpc. The nmr and infrared spectra were identical with those of the racemic compound. A sample was chromatographed on column E at 175° to give material of greater than 99.9% purity which was redistilled bulb to bulb. This material had $[\alpha]^{24.1}D$ +15.3° (95% ethanol).

Scheme I. (+)-Nortricyclene-3-carbinyl *p*-Bromobenzenesulfonate [(+)-9]. This derivative (13.5 g) was prepared from 6.4 g of optically active methyl 3-nortricyclenecarboxylate [(+)-**8**] as described by Gajewski[9] and others[10] for the racemic series. Spectral properties of the sulfonate, as well as of its carbinol precursor, were identical with those of the racemic compounds.

The carbinol was also converted to (+)-nortricyclene-3-carbinyl acetate (also shown to be identical with the racemic compound), which was distilled, chromatographed on column E at 180° to give material completely pure by capillary vpc on column N-1, and redistilled bulb to bulb to give material of $[\alpha]^{22.2}D$ +17.9° (methanol).

Scheme I. (+)-3-Methylnortricyclene [(+)-6]. A small sample of nortricyclene-3-carbinyl *p*-bromobenzenesulfonate [(+)-**9**], prepared as above, was dissolved in dry ether and treated with 0.15 g of lithium aluminum hydride in a dry atmosphere. The solution bubbled vigorously for about 15 min and was heated at reflux overnight. The flask was cooled and the mixture worked up with sodium sulfate in the standard way, except that the pentane extracts were washed thoroughly with 20% sodium hydroxide solution before drying. Careful removal of the pentane through a Vigreux column left 0.30 g of greenish oil which was chromatographed on column H-1 at 80°. This gave capillary vpc pure (column O) material; the infrared spectrum showed readings at: 3.25, 3.4, 3.45, 6.9, 7.3, 7.4, 7.7, 7.8, 8.0, 10.34, and 11.1 μ (CCl_4). An nmr spectrum showed complex absorption from δ 1.3 to 3.3; no other signals were observed.

Anal. Calcd for C_8H_{12}: C, 88.82; H, 11.18. Found: C, 88.79; H, 11.23.

A rotation was taken on the vpc pure material. It exhibited $[\alpha]^{24.3}D$ +28.0° (95% ethanol).

Scheme I. Correlation of (+)-Methyl 3-Nortricyclenecarboxylate (8) with (+)-Methyl 2-*exo*-Norbornanecarboxylate (11). A 1.0-g portion of the above sample of (+)-**8**, $[\alpha]D$ +15.3° (95% ethanol), was hydrogenated over 1.5 g of platinum oxide in 50 ml of dry acetic acid at 40 psi until uptake ceased. The resulting mixture was passed through diatomaceous earth, diluted with water, and extracted with pentane. The combined pentane fractions were washed with water and then with saturated sodium bicarbonate solution until the washings were basic. After washing with saturated brine and drying over magnesium sulfate, the pentane was carefully removed through a Vigreux column, leaving about 0.9 g of clear oil which contained (by capillary vpc) 5% unreacted methyl 3-nortricyclenecarboxylate (**8**), 47% methyl 2-*exo*-norbornanecarboxylate (**11**), and 48% methyl 7-norbornanecarboxylate (**10**). The bicyclic esters were separated from the starting material on column E at 178°. The tricyclic ester **8** obtained was 99.0% pure by capillary vpc, and its rotation was unchanged compared with that taken before the hydrogenation, proving that it had not epimerized during the reaction. The active ester **11** was separated from its necessarily inactive isomer **10** by chromatography on column B at 120°. In this way **11** could be obtained 99.0% pure (contaminated with 1.0% of the 7-substituted isomer **10**). After redistillation it had $[\alpha]^{22.7}D$ +11.5° (95% ethanol).

The relative amounts of each of the two norbornanecarboxylic esters produced were estimated by capillary vpc peak areas (column N-1), after calibration with mixtures of authentic samples of known composition. A mixture containing 49.3% of methyl 2-*exo*-norbornanecarboxylate **11** and 50.7% of its 7-substituted isomer **10** had a specific rotation of $[\alpha]^{22.3}D$ +5.58°. Using the value of +11.5° (*vide infra*) for the specific rotation of **11** obtained on the 99.0% pure isomer as described above, the rotation of the 7-carbomethoxynorbornane could be calculated to be 0° within experimental error.

Scheme II. The 3-Methyl-2-norbornanones. Optically active 3-*endo*-methyl-2-*exo*-norbornyl acetate (**1c**) of specific rotation $[\alpha]^{25.6}D$ −1.85° (absolute ethanol)[4] was reconverted to the corresponding alcohol **1a** with lithium aluminum hydride. The alcohol obtained in this way (about 3.1 g), dissolved in 50 ml of acetone, was cooled to 0° in an ice bath, and 8 ml of Jones reagent[11] was added slowly with rapid stirring of the cold solution. The mixture was stirred for 2 min after the addition, poured onto cracked ice, salted heavily, and extracted four times with pentane. After combination, the organic extracts were washed with water and saturated sodium chloride and dried over sodium sulfate. Decantation of the liquid and careful removal of the pentane left 2.2 g (69% yield) of material which had a decidedly camphoraceous odor. The product was identified as a mixture of 90% 3-*endo*-methyl-2-norbornanone (**12**) and 10% of its 3-*exo*-methyl epimer **14**,[12] along with minor amounts of other unidentified products.

Scheme II. Epimerization of 3-Methyl-2-norbornanones. A 0.70-g sample of the above ketone mixture was dissolved in 20 ml of dry methanol. Sodium was cut freshly under heptane and 0.115 g added to the solution; the resulting mixture was heated at reflux for 2.5 hr in a nitrogen atmosphere (it was found by trials with racemic samples of this mixture that longer reflux times produced only disappearance of product due to condensation, and no further equilibration of the monomeric ketones). The reaction mixture was quenched with water, salted heavily, and extracted four times with pentane. After the combined pentane fractions had been washed with water and brine, they were dried over magnesium sulfate and concentrated under a Vigreux column on the steam bath. Vpc analysis of the residue indicated the presence of about 40% 3-*exo*-methyl-2-norbornanone (**14**) and 60% of its 3-*endo*-methyl epimer **12**. These were separated on column B at 130°; each was obtained pure by capillary vpc.

Scheme II. Optical Correlation of 3-*endo*-Methyl-2-*exo*-norbornyl Acetate [(−)-1c] with 3-Methylnortricyclene [(+)-6]. A sample of acetate (−)-**1c** of rotation $[\alpha]^{25.6}D$ −1.85° (absolute ethanol) was converted to the ketones **12** and **14** as described directly above. The *p*-toluenesulfonylhydrazone of 3-*endo*-methyl-2-norbornanone (**12**) was prepared from the ketone (purified by vpc) by the same procedure used for 7-*anti*-methyl-2-norbornanone (**4**), except that 1.5 hr of reflux time was insufficient to completely convert the ketone to its derivative. The reflux was, therefore, continued overnight, and the product worked up and converted to the hydrocarbon as described for **4**. The pyrolysis reaction mixture from the sodium salt of 3-*endo*-methyl-2-norbornyl *p*-toluenesulfonylhydrazone consisted of 6% of an unidentified compound, 3.2% of a material whose retention time was identical with that of 2-methyl-2-norbornene, 1% 3-*endo*-methyl-2-norbornanone (**12**), and the remainder 3-methylnortricyclene [(+)-**6**]. The tricyclic hydrocarbon was separated on column G-1 at 95°. It was pure by vpc and had $[\alpha]^{23}D$ +14.7° (95% ethanol).

Pure 3-*exo*-methyl-2-norbornanone obtained from the same optically active source was converted to a *p*-toluenesulfonylhydrazone derivative in the same way as **12** except that the reaction mixture was heated at reflux only 3 hr; the infrared spectrum of the white solid obtained indicated contamination from about 5% of

(8) Racemic material was prepared according to J. D. Roberts, E. R. Trumbull, Jr., W. Bennett, and R. Armstrong, *J. Am. Chem. Soc.*, **72**, 3116 (1950).

(9) J. J. Gajewski, Ph.D. Dissertation, University of Wisconsin, 1966.

(10) (a) R. R. Sauers and J. A. Beisler, *Tetrahedron Letters*, 2181 (1964); (b) K. B. Wiberg and G. R. Wenzinger, *J. Org. Chem.*, **30**, 2278 (1965).

(11) T. G. Halsall, R. Hodges, and E. R. H. Jones, *J. Chem. Soc.*, 3019 (1953).

(12) The racemates have been reported by S. Beckmann and R. Mezger, *Chem. Ber.*, **90**, 1559 (1957).

ketone. This mixture was carried through to the hydrocarbon as before. The pyrolysis product in this case, despite scrupulous vacuum drying of the sodium salt, was contaminated with about 30% of tetrahydrofuran. The other products consisted of about 6% 3-*endo*-methyl-2-norbornanone (**12**), 1.5% 2-methyl-2-norbornene, 1.5% of an unidentified compound, and the remainder 3-methylnortricyclene. The tricyclic hydrocarbon was again separated by preparative vpc on column G-1 at 130°, shown by infrared to be identical with material obtained from previous preparations, and its purity checked by capillary vpc. It had $[\alpha]^{23.2}D$ −16.4° (95% ethanol), a value essentially identical in magnitude and opposite in sign with that of hydrocarbon obtained above in Scheme I directly from 7-*anti*-methyl-2-*exo*-norbornyl acetate (**2b**).

The Chemistry of Methylnorbornyl Cations. IV. Ratios of Rates of Nucleophilic Capture of the Cations at Wagner–Meerwein-Related Sites[1]

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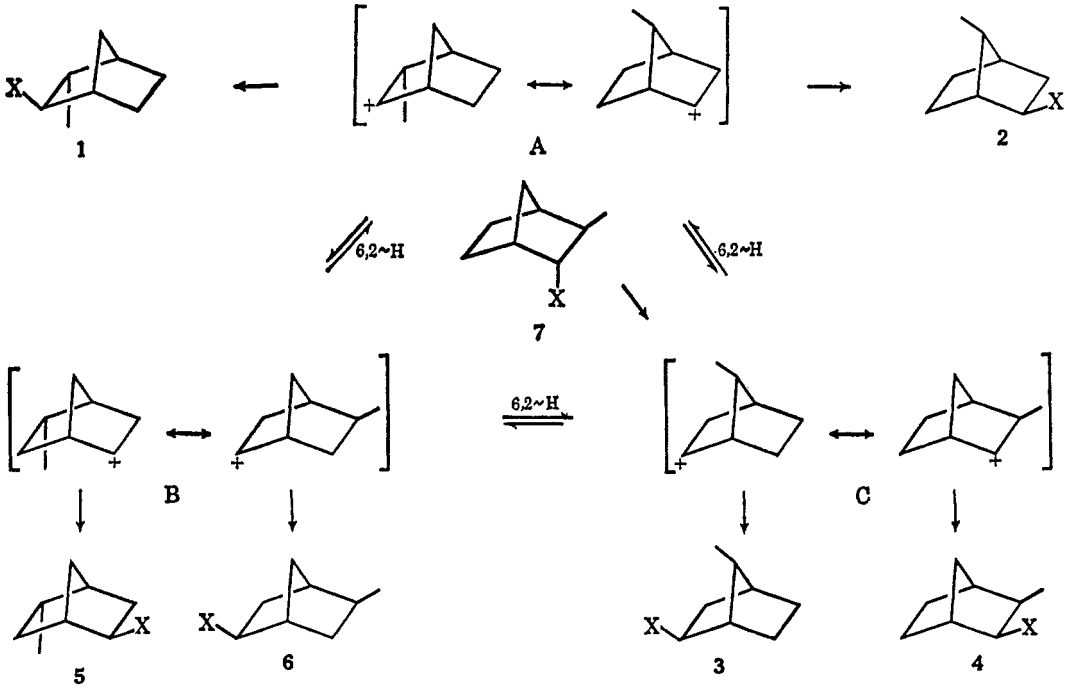
Abstract: A detailed study of the product distributions from solvolyses and deaminations of a number of precursors of methylnorbornyl cations permits the evaluation of the relative rates of capture of these species at each of the two Wagner–Meerwein-related sites. A direct steric effect on nucleophilic approach and another effect which opposes developing hydrogen–methyl repulsions in the transition state are noted. The characteristic capture ratios observed in the solvolytically produced ions apply also to the deaminatively produced ones, the major difference between the two processes being the excess of "direct substitution" observed in deamination. A comparison of the deamination results with those obtained earlier in the unsubstituted norbornyl case reveals that the "direct substitution" is very sensitive to a β-methyl steric effect, which causes a complete reversal of the stereochemistry of the process.

The summarizing rearrangement scheme given in paper I[3] of this series outlines the interconversions of a set of "core" methylnorbornyl cations A, B, and C by 6,2-hydride shifts (Chart I) and their escape to "periphery" cations A_1, B_1 (≡B_2), and C_1 by 3,2-hydride shifts. The present paper provides evidence for this scheme from studies of the products derived from solvolyses of various methylnorbornyl derivatives.

Chart I. "Core" System



a, X = OPhth; b, X = O_2CH; c, X = OAc; d, X = OH; e, X = OBs; f, X = NH_2

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(3) J. A. Berson, J. H. Hammons, A. W. McRowe, R. G. Bergman, A. Remanick, and D. Houston, *J. Am. Chem. Soc.*, **89**, 2561 (1967).