positive chromotropic acid test for methanol. In preliminary experiments, the reaction mixture (after removal of CO_2) was again made alkaline and extracted continuously with ether. The neutral residue obtained on evaporation of the ether amounted to only 2.0 mg; by gas chromatography it was shown that no dimethyl oxalate was present.

When the acidified reaction mixture was steam distilled, the distillate gave a weak reaction for formic acid in the chromotropic acid test and a strong positive test for acetic acid.[12]

After removal of the steam-volatile acids, the acid solution was extracted continuously with ether for 24 hr. The dried ether extract was evaporated to a semicrystalline residue (74 mg). The residue was transferred to a Celite column (18 g) moistened with 0.5 *N* H_2SO_4,[3] which was eluted with 1-butanol–chloroform (35:65); fractions were collected every 30 min. The combination of fractions 16–21 yielded 11.7 mg of a solid, mp 125–130°, which was identified as slightly impure malonic acid on the basis of paper chromatography. On recrystallization from acetone–benzene, 5.8 mg of pure malonic acid was obtained, showing no melting point depression (135–137°) on admixture with authentic material. A second acid was obtained in larger amount (25.8 mg) from fractions 27–35; after crystallization from ether–pentane (1:3) the melting point was 155–156°. On paper chromatography, the acid, **4**, behaved as a tricarboxylic acid, and the R_f value was actually close to that of citric acid.

Anal. Calcd for $C_7H_8O_7$: C, 41.18; H, 3.95; equiv wt, 74.0. Found: C, 41.41; H, 4.00; equiv wt, 73.0.

The trisodium salt of **4** was prepared by the method of Habicht and Schneeberger.[13]

Anal. Calcd for $C_7H_5O_7Na_3$: Na, 25.5. Found: Na, 25.3.

The trimethyl ester of **4** was obtained as an oil by treatment of the acid, either with diazomethane in ether or with methanolic HCl. The infrared spectrum showed $\lambda_{max}^{CCl_4}$ 5.7 μ (ester C=O); no bands in the 3-μ region (OH) or in the 5.5-μ region (γ-lactone C=O); nmr spectrum τ 6.27, 6.30, 6.31 (OCH_3), two doublets at 6.86 (J = 17 cps) and 7.25 (J = 18 cps) (CH_2), 8.4 (CCH_3).

Anal. Calcd for $C_{10}H_{14}O_7$: C, 48.75; H, 5.73; OCH_3, 37.81. Found: C, 48.37; H, 5.88; OCH_3, 37.51.

γ-Lactone of α-Methyl-α,β-dihydroxytricarballylic Acid (5, R = H). A solution of γ-methyl-*cis*-aconitic anhydride[14] (3.0 g), $KClO_3$ (2.4 g), K_2CO_3 (0.6 g), and OsO_4 (0.09 g) in water (60 ml) was heated at 45° for 5 hr. After the addition of concentrated HCl (2.0 ml), the solution was extracted with ten 150-ml portions of ethyl acetate. The residue (1.53 g) obtained after drying the solution over Na_2SO_4 and vacuum evaporation, was dissolved in 10 ml of ethyl acetate and decolorized with Norit A. A 500-mg portion of the yellow oil obtained on evaporation was chromatographed on a column of Celite (60 g) mixed with 0.5 *N* H_2SO_4 (42 ml). The column was eluted first with 1-butanol–chloroform (10:90), then with 1-butanol–chloroform (35:65), and fractions were collected at 30-min intervals (about 8 ml initially). Fractions 48–58 were combined, and on evaporation yielded 230 mg of a colorless oil. A white, crystalline solid was obtained by dissolving the oil in ether and adding petroleum ether (bp 30–60°). The γ-lactone of α-methyl-α,β-dihydroxytricarballylic acid (**5**, R = H) had mp 185–187°; infrared spectrum λ_{max}^{KBr} 2.85 (OH), 5.63 (γ-lactone C=O), and 5.80 μ (acid C=O).

Anal. Calcd for $C_7H_8O_7$: C, 41.18; H, 3.95. Found: C, 41.75; H, 4.33.

The dimethyl ester (**5**, R = CH_3) was prepared with diazomethane in ether and had mp 153–155°; infrared spectrum λ_{max}^{KBr} 2.95 (OH), 5.65 (γ-lactone C=O), and 5.83 μ (ester C=O); nmr spectrum τ 6.10, 6.19 (OCH_3), 6.97, 6.99 (CH_2), 8.50 (CCH_3), 6.25 (OH).

Anal. Calcd for $C_9H_{12}O_7$: C, 46.55; H, 5.21; OCH_3, 26.73. Found: C, 46.62; H, 5.32; OCH_3, 26.48.

The same lactone (**5**, R = H) was also prepared from the epoxytricarboxylic acid (**4**, 5 mg) by heating for 1 hr at 80–85° with 1 ml of 1% aqueous $HClO_4$. After cooling in ice and saturating the solution with SO_2, the excess SO_2 was removed by a stream of nitrogen. The solution was evaporated to dryness in a stream of nitrogen at 80° and the residue was dried under vacuum. This material had the same R_f as **5** (R = H) on chromatography in the ethyl acetate–5 *M* formic acid solvent system. The residue was converted to the ester by reaction with diazomethane in ether. After removal of the ether, the residue was sublimed at 0.1 mm and 80–85°, and the sublimate was then crystallized from ether–pentane. The white crystals had mp 154–156°, and this melting point was unchanged in admixture with the synthetic ester (**5**, R = CH_3).

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(12) F. Feigl, "Spot Tests in Organic Analysis," Elsevier Publishing Co., Amsterdam, 1960, pp 357, 515.

(13) E. Habicht and P. Schneeberger, *Helv. Chim. Acta*, **39**, 1316 (1956).

(14) O. Gawron and K. P. Mahajan, *Federation Proc.*, **24**, 228 (1965). We are very much indebted to Professor O. Gawron for details of this synthesis in advance of publication.

Communications to the Editor

Stereospecific 6,1 Migration of Deuterium during Rearrangement of 2-Phenylnorbornane-2,3-*cis*-*exo*-diol-5,6-d_2[1]

Sir:

In 1961 Kleinfelter and Schleyer[2] reported that diol I (without deuterium) rearranges, in sulfuric acid, to produce 3-*endo*-phenylnorbornanone-2 (II, without deuterium). We showed[3] later that this rearrangement proceeds: (1) with inversion of configuration, (2) with intramolecular migration of the original 3-*endo*-hydrogen, and (3) without migration of phenyl (the asterisks denote appropriate labels with tritium and carbon-14). These results are compatible with the presence of the bridged ion intermediates A and B. In the rearrangement A → B an intramolecular 6,1-hydride shift must take place.[3] We were curious as to whether this shift occurs (1) by a discrete shift of the *exo*-6-hydrogen, (2) through a "face-protonated" cyclopropane intermediate,[4,5] or (3) through some

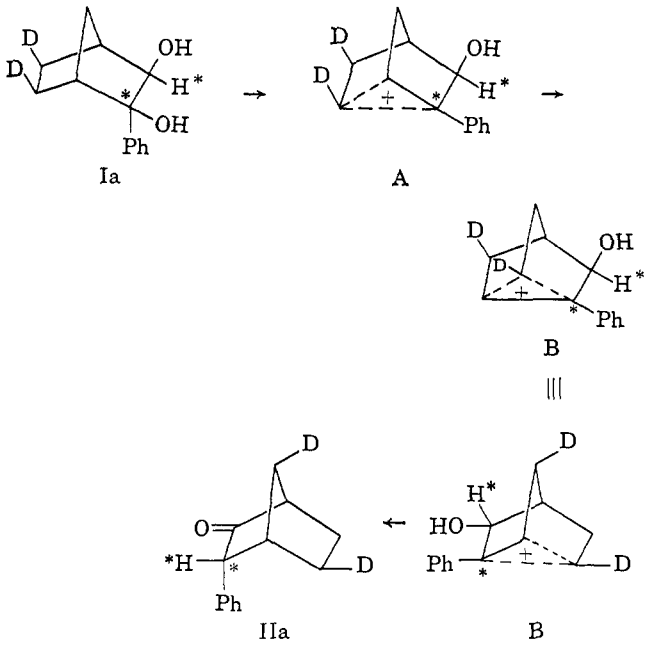
(1) Research sponsored by the U. S. Atomic Energy Commission under contract with the Union Carbide Corporation.

(2) D. C. Kleinfelter and P. von R. Schleyer, *J. Am. Chem. Soc.*, **83**, 2329 (1961).

(3) C. J. Collins, Z. K. Cheema, R. G. Werth, and B. M. Benjamin, *ibid.*, **86**, 4913 (1964).

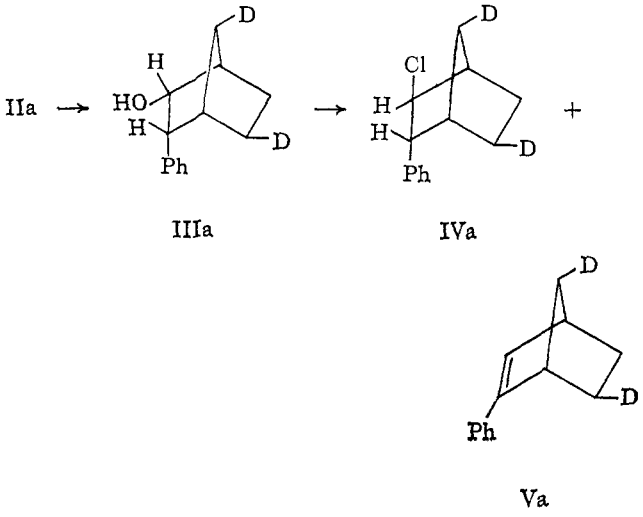
(4) J. D. Roberts and C. C. Lee, *ibid.*, **73**, 5009 (1951).

(5) J. A. Berson and P. W. Grubb, *ibid.*, **87**, 4016 (1965), give a brief discussion of the stereochemistry of hydride shift in norbornyl compounds.



mechanism in which the three hydrogens in the 6 and 1 positions (of I) become involved in reversible migrations. We have now shown that it is the *exo*-6-hydrogen which undergoes a discrete 6,1 shift, and becomes the *exo*-5-hydrogen in II.

Glycol Ia, containing *exo*-5- and *exo*-6-deuterium, was obtained[2,3] starting with a mixture of deuterated 2-norbornanols which was prepared by catalytic deuteration of the mixed 2-norbornen-5-ols.[6] Ketone IIa, obtained upon rearrangement[2,3] of Ia, contained deuterium in the *exo*-5 and *anti*-7 positions. This was demonstrated through the arguments presented herein after reduction of IIa with lithium aluminum hydride to 3-*endo*-phenyl-2-*endo*-norbornanol (IIIa, mp 71°),[7]



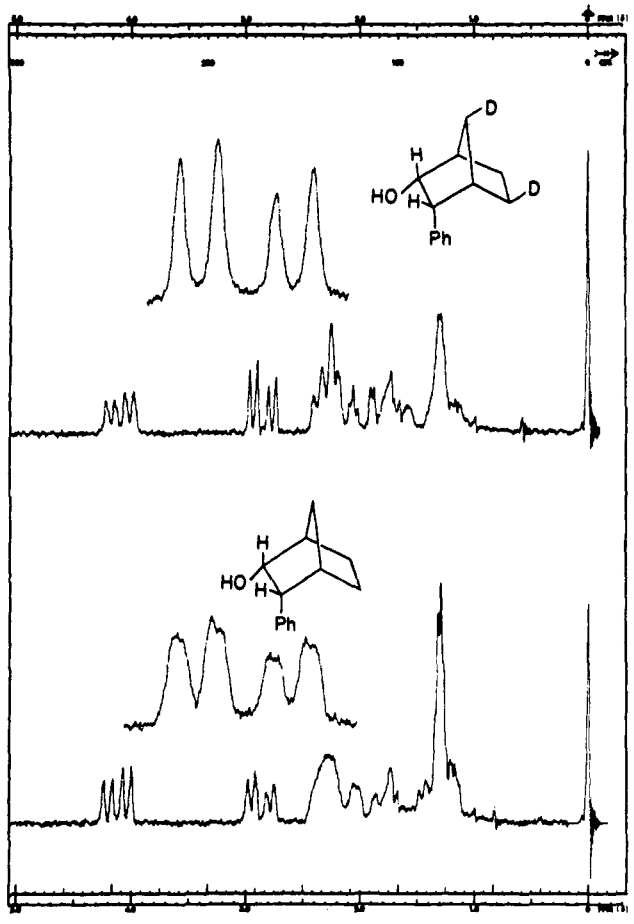


Figure 1.

which was converted under SN2 conditions to the chloride IVa, and 2-phenyl-2-norbornene-*exo*-6-*anti*-7-d_2 (Va). Confirmation of the structure of III is obtained from its nmr spectrum (Figure 1). The signal for the *exo*-2-hydrogen is a quartet (δ = 4.12 ppm, $J_{1,2}$ = 4.6 cps, $J_{2,3}$ = 10.0 cps). The signal assigned to the *exo*-3-hydrogen is also a quartet (δ = 2.87 ppm, $J_{3,4}$ = 4.0 cps, $J_{2,3}$ = 10.0 cps).[8] This signal shows an additional splitting in each component of 0.9 cps (inset, Figure 1) which is attributed to long-range coupling with the *exo*-5-hydrogen.[8,9] The corresponding signal for IIIa is a sharp quartet; the width of each component at half-height is 1.5 cps (inset, Figure 1). Compound IIIa therefore contains deuterium in the *exo*-5 position. The two bridgehead protons (1 and 4) of III exhibit signals centered at δ = 2.25 ppm. The integrals of these signals compared with integrals of corresponding signals from IIIa show that not more than 3% deuterium could be in the two bridgehead positions. The bridgehead protons of ketones II and IIa also exhibit isolated signals centered at δ = 2.65 ppm. Comparison of the pertinent integrals further indicated less than 3% deuterium at the bridgeheads. Thus at least 94%

(6) The high preference for *exo* deuteration was demonstrated by an analysis of the nmr spectrum of *exo*-5,6-dideuterio-2-phenylnorbornene-2,[3] an intermediate in the synthesis of Ia. Comparison of pertinent integration areas showed that not more than 3% *endo* deuteration took place.

(7) Satisfactory carbon and hydrogen analyses were obtained for III and IV. Dr. D. C. Kleinfelter (University of Tennessee) has independently synthesized and characterized III (3-*endo*-phenyl-2-*exo*-norbornanol has been previously prepared[3] through hydroboration of V). The *cis* character of the phenyl and hydroxyl of III is confirmed by demonstrating hydrogen[3] bonding of the OH···Ph type; $\Delta\nu$ 12 cm^{-1} relative to the frequency of the OH band of *endo*-2-norbornanol (also measured and communicated to us by Dr. Kleinfelter, who informs us he has, in addition, synthesized and characterized the three other (2,3) isomers of III by nmr: Master's thesis, J. E. Mallory, 1966).

(8) These signals were further shown to be mutually coupled by double resonance. A range of 8.9–11.4 cps is expected for *exo–exo* couplings while 5.8–7.7 cps is usually found for *endo–endo* couplings [P. Laszlo and P. von R. Schleyer, *J. Am. Chem. Soc.*, **86**, 1171 (1964)]. Coupling between *endo* and bridgehead hydrogens is ordinarily not observed.

(9) F. A. L. Anet, *Can. J. Chem.*, **39**, 789 (1961).

of the original *exo*-6-deuterium of Ia migrated during the rearrangement Ia → IIa.

The structure of compound IV was confirmed by its nmr spectrum. A signal at 4.00 ppm is due to the *endo*-2-hydrogen. Splittings of 4.2 and 1.9 cps result from couplings with the *exo*-3 and *anti*-7-hydrogens,[10] respectively. The *anti*-7-hydrogen gives a doublet of components at 1.38 ppm, and double irradiation at this position removes the splitting of 1.9 cps exhibited by the *endo*-2-hydrogen (4.00 ppm). A broadened doublet, J_{gem} = 10.1 cps, for the *syn*-7-hydrogen appears at 2.06 ppm. The downfield shift of this signal is attributed to the anisotropic effect of the *exo*-2-chlorine. The appearance of the *exo*-3-hydrogen at 3.44 ppm as a triplet is expected from the almost equal $J_{4,exo\text{-}3}$ and $J_{endo\text{-}2,\,exo\text{-}3}$.[11] In the spectrum of IVa the signal for the *endo*-2-hydrogen is a simple doublet, $J_{2,3}$ = 4.2 cps, the signal for the *syn*-7-hydrogen is collapsed to a single line, and the doublet at 1.38 ppm for the *anti*-7-hydrogen is absent.

Finally, additional quantitative evidence for the *exo*-5-deuterium in IIa is found in the nmr spectrum of Va (see also ref 5). The *syn*-7 proton of V gives a multiplet centered at δ = 1.51 ppm, whereas the signals for the *exo*-5 and *exo*-6 protons are centered at 1.71 ppm. Comparison of pertinent integration areas of V and Va confirms that at least 95–96% of the deuterium originally in the *exo*-6 position of Ia resides in the *exo*-6 position of Va.

(10) J. Meinwald and Y. C. Meinwald, *J. Am. Chem. Soc.*, **85**, 2514 (1963).

(11) If a Wagner–Meerwein rearrangement had taken place during treatment of III with PCl_5, the formation of 7-*anti*-phenyl-2-*exo*-norbornyl chloride might be expected. Its nmr spectrum should be considerably different from that observed for IV.

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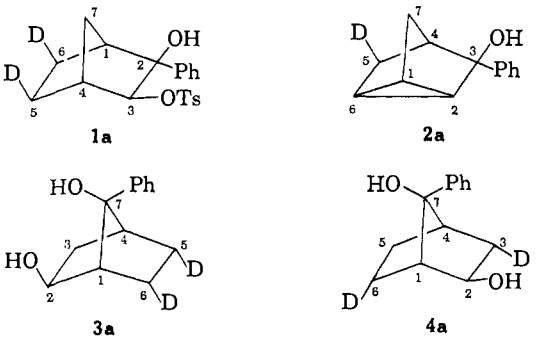
Stereospecific Elimination and Migration of Deuterium during Hydrolysis of a Substituted Norbornyl Tosylate[1]

Sir:

Hydride shifts (6,1 and 6,2)[2] occur during solvolyses of 2-*exo*-norbornyl derivatives. We recently established the intramolecularity and stereochemistry of one of these shifts.[3,4] During hydrolysis of the dideuterated[5] tosylate **1a** we now report (1) a stereospecific elimination and (2) a stereospecific 5,4 migration, respectively, of the 5-*exo* deuterium. Hydrolysis of **1a** in aqueous acetone (containing sodium carbonate), led to the quantitative production of compounds **2a**, **3a**, and **4a** with deuterium in the positions shown. The three products were easily separated by chromatography on alumina in yields of 25, 60, and 15%, respectively. Traces of another diol have been detected.

The structures of compounds **2**, **3**, and **4** (without deuterium) were established through their nmr and infrared spectra and by their chemical reactions.[6] In addition, **2** was independently synthesized by reaction of nortricyclenone with phenylmagnesium bromide. Compounds **3** and **4** were also prepared by solvolysis of **1** which contained a deuterium in the *endo*-3 position, and each, as expected, contained one atom of deuterium per mole in the 1 (bridgehead) position. Deuterium contents in all cases were determined by integration of the appropriate signals of the nmr spectra.



Most of the signals in the nmr spectrum of **2** are well separated, and can be assigned on the basis of expected inductive and anisotropic effects. In addition to five aromatic hydrogens and one exchangeable hydrogen (OH), the following are observed: (1) a one-proton doublet, J = 10.1 cps at 2.13 ppm, due to the *syn*-7-hydrogen. It is deshielded by the hydroxyl and therefore appears at lowest field. The latter doublet is reciprocated by a doublet at 1.29 ppm (7-*anti*-H); (2) a one-proton (4 H) broadened signal at 1.73 ppm; and (3) signals for the remaining five hydrogens in two bands at 1.23 ppm (3 H) and at 1.07 ppm (2 H).

In the spectrum of **2a** the band at 1.07 ppm had an intensity of only one hydrogen. The relative intensities of all other lines were the same. Thus at least 95–96% of a deuterium atom was lost during the reactions **1a** → **2a**. In addition, the signal for the C-4 hydrogen of **2a** exhibits a width at half-height of 4.6 cps, whereas the same signal for **2** has a width of 5.2 cps, and the deuterium atom in **2a** results in the removal of one coupling constant. Double irradiation shows that the C-4 hydrogen of **2** is weakly spin coupled to hydrogens, contributing to the signals at 1.23 and 1.07 ppm. The latter are assigned to the methylene hydrogens at C-5. Double irradiation of the one-proton signal at 1.07 ppm had no effect upon the signal for the C-4 hydrogen of **2a**. The deuterium atom in **2a** is thus located at C-5 and *anti* to the phenyl substituent at C-3.

The spectra of **3** and **4** both exhibit one-proton signals appearing as X parts of ABX systems. The pattern is characteristic for an *endo*-hydrogen of an H–C–O group.[7] The signal is centered at 3.64 ppm for compound **3** and at 3.56 ppm for compound **4**. In the upfield region of the spectrum of **3** there are two bands at 1.39 and at 1.21 ppm, assigned to the *exo*-5- and -6-hydrogens and confirmed through spin decoupling from the 1- and 4-hydrogens at 2.24 and 2.47 ppm. Two bands at 0.99 and at 0.82 ppm are assigned to the 5- and 6-*endo*-hydrogens. The *exo* and *endo* protons at C-3 appear at 1.89 ppm, and these were spin decoupled

(1) Research sponsored by the U. S. Atomic Energy Commission under contract with the Union Carbide Corporation.

(2) J. Berson, "Molecular Rearrangements," Vol. 1, P. de Mayo, Ed., Interscience Publishers, Inc., New York, N. Y., 1963, pp 138–155.

(3) B. M. Benjamin and C. J. Collins, *J. Am. Chem. Soc.*, **87**, 1556 (1965).

(4) See also J. A. Berson and P. W. Grubb, *ibid.*, **87**, 4016 (1965).

(5) Not more than 3% *endo* deuteration took place (see ref 3).

(6) All gave satisfactory carbon and hydrogen analyses, performed by Huffman Microanalytical Laboratories, Wheatridge, Colo.

(7) T. J. Flautt and W. F. Erman, *J. Am. Chem. Soc.*, **85**, 3212 (1963).