

that perhaps the expected diamagnetic shift occurs for both kinds of nuclei. However, for the carbon resonances this would be overlaid by a downfield shift corresponding to the paramagnetic term in the Ramsey shielding expression which is larger when there are lower lying excited states for the electrons surrounding the nuclei. This idea does not receive experimental support from the absorption spectra of acetic acid and sodium acetate in aqueous solution, each of which has about the same absorption maximum, although acetate ion has the larger extinction coefficient.¹⁵

The rate of falloff of the chemical shift with distance along the chain as a function of substituent is of special interest. There are problems in making comparisons along these lines with aliphatic compounds carrying different substituent groups because of the possibilities of differences in conformations. We have chosen here to consider the changes in ¹³C chemical shifts which occur on ionization of valeric acid at the α , β , γ , and δ carbons. If we consider the negative charge of the carboxylate anion to be centered between the carboxylate oxygens and take the carbon chain to be in the staggered extended conformation, then the falloff of β , γ , and δ chemical shifts relative to the α chemical shift is reasonably close to what would be expected for a r^{-3}

(15) H. Ley and B. Arends, *Z. Physik. Chem.*, **B17**, 177 (1932).

dependence, in accord with the undocumented prediction of van Gorkom.¹³

Experimental Section

The 2 *M* solutions of the acids at the low pH values were made by dissolving reagent grade carboxylic acid, an equimolar amount of tetramethylammonium chloride, and a small amount of 6 *N* hydrochloric acid in the proper volume of water. The corresponding solutions at high pH values were prepared similarly using the acids, a corresponding amount of tetramethylammonium hydroxide, and water. The less concentrated solutions were prepared by appropriate dilutions. The pH's of the solutions all differed by at least 2.5 units from the p*K* values.

The ¹³C chemical shifts were measured on samples in 10-mm tubes in the external lock mode using the Varian DFS spectrometer previously described³ with a Hewlett-Packard 5200A frequency synthesizer driving a Boonton 230A power amplifier to provide appropriate proton decoupling frequencies. The ¹³C resonance of the tetramethylammonium ion was used as an internal standard. About 60 scans were averaged on a Varian C-1024 computer of average transients for the most dilute solutions. For correlation with carbon disulfide as reference, the chemical shifts were calibrated by making cross comparisons between a mixture of equal volumes of carbon disulfide, benzene, dioxane, methylene chloride, and tetramethylsilane and a solution of 5 mmol of tetramethylammonium chloride in 1 ml of dioxane and 4 ml of water.

Acknowledgment. We are much indebted to Dr. Frank J. Weigert for his help and suggestions with this research.

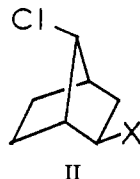
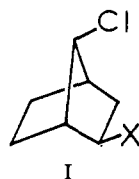
Ionic Reactions in Bicyclic Systems. VIII. Acetolysis of *syn*- and *anti*-7-Chloro-*exo*-norbornyl *p*-Toluenesulfonates¹

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Abstract: Acetolysis of *syn*- (I-OTs) and *anti*-7-chloro-*exo*-norbornyl *p*-toluenesulfonate (II-OTs) has been re-investigated. Ion-pair return associated with solvolysis results in isomerization of I-OTs to II-OTs; at 70% solvolysis of I-OTs the composition of the unsolvolyzed ester is about 70% I-OTs and 30% II-OTs. Isomerization in the opposite direction is unimportant. The I-OTs \rightarrow II-OTs isomerization involves a 6,2-hydride shift and migration of the anion from C₂ to C₆. This transformation is intramolecular (very little exchange with *p*-toluenesulfonate ion) and evidently involves internal return. Intermediates generated from I-OTs and II-OTs undergo 6,2-hydride shifts in competition with solvent capture.

In an earlier investigation² it was observed that 6,2-hydride shifts are involved in acetolysis of *syn*- (I-OTs) and *anti*-7-chloro-*exo*-norbornyl *p*-toluenesulfonate (II-OTs). Both esters give mixtures of *syn*- and *anti*-7-chloro-*exo*-norbornyl acetate (I-OAc and



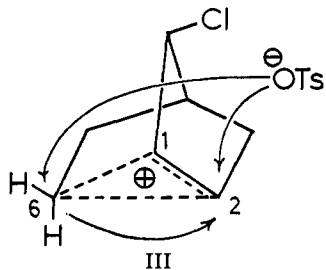
II-OAc). Formation of the *anti* product from the *syn* substrate, and *vice versa*, requires a 6,2-hydride shift and *exo* capture at C₆. It was also observed that 6,2 shifts are apparently associated with ion-pair return (presumably internal return³) as well as with solvent capture; infrared analysis of the unsolvolyzed ester indicated that I-OTs and II-OTs are interconverted during solvolysis. As illustrated by III, this isomerization involves migration of the anion from C₂ to C₆ as well as a 6,2-hydride shift. We were particularly interested in this isomerization in connection with our

(1) This research was supported by the National Science Foundation (GP-6555X) and the Air Force Office of Scientific Research (AFOSR-847-67).

(2) W. G. Woods, R. A. Carboni, and J. D. Roberts, *J. Am. Chem. Soc.*, **78**, 5653 (1956).

(3) The 7-chloronorbornyl *p*-toluenesulfonates, I-OTs and II-OTs, are considerably less reactive than the parent *exo*-norbornyl *p*-toluenesulfonate and consequently would not be expected to show a special salt effect. Thus, presumably only internal return is involved in these systems. See S. Winstein, *et al.*, *ibid.*, **78**, 2784 (1956); **80**, 169, 459 (1958); **83**, 885 (1961).

investigations of the chemistry of ion-pair intermediates⁴ and in the present work we have reinvestigated the acetolysis of I-OTs and II-OTs using more suitable analytical techniques (nmr spectroscopy and gas chromatography) than that available for the earlier work (infrared analysis).



The isomeric 7-chloro-*exo*-norbornanols (I-OH and II-OH) were prepared as described earlier⁵ and structural assignments were confirmed by nmr spectroscopy and the following transformations. Oxidation of the two isomers by the Brown-Garg method⁶ gave the corresponding 7-chloronorcamphors which were converted to 7-chloronorbornane by Wolf-Kishner reduction. This establishes that the chlorine and hydroxyl are at the 7 and 2 positions, respectively. It was also observed that I-OH and II-OH react much slower than *exo*- or *endo*-2-chloronorbornane with alcoholic silver nitrate as would be expected for the unreactive⁷ 7-norbornyl system. Hydroboration⁸ of *anti*-7-chloronorbornene followed by oxidation of the adduct gave II-OH. This establishes the stereochemistry at C₇ and C₂ for this compound.

Chemical shifts for the 2- and 7-protons in *syn*- and *anti*-7-chloro-*exo*-norbornyl derivatives (I and II) are presented in Table I together with the 7-proton shifts

Table I. Chemical Shifts (and Multiplicities) for the 2 and 7 Protons in 7-Chloro-2-norbornyl Derivatives^a

Compound	τ^b	
	2 proton	7 proton
I-OH	6.21 (dt)	6.05 (q)
I-OTs	5.53 (q)	6.19 (q)
I-OAc	5.21 (m)	5.97 (mp)
<i>syn</i> -7-Chloro-norcamphor		5.78 (qui)
II-OH	6.22 (q)	5.78 (bs) ^c
II-OTs	5.53 (t)	5.87 (bs) ^c
II-OAc	5.25 (q)	5.74 (bs) ^c
<i>anti</i> -7-Chloro-norcamphor		5.79 (bs) ^c

^a Chemical shift relative to tetramethylsilane in CDCl₃. ^b Multiplicities indicated as follows: bs, broad singlet; t, triplet; q, quartet; qui, quintet; dt, doublet of triplets; m, unresolved multiplet. ^c Width at half-height \sim 4 cps (60 MHz spectra).

for *syn*- and *anti*-7-chloronorcamphor. The signals for the 2-proton for corresponding *syn* and *anti* isomers

(4) For references see H. L. Goering and R. W. Thies, *J. Am. Chem. Soc.*, **90**, 2967, 2968 (1968).

(5) J. D. Roberts, F. O. Johnson, and R. A. Carboni, *ibid.*, **76**, 5692 (1954).

(6) H. C. Brown and C. P. Garg, *ibid.*, **83**, 2952 (1961).

(7) S. Winstein, M. Shatavsky, C. Norton, and R. B. Woodward, *ibid.*, **77**, 4183 (1955).

(8) H. C. Brown and G. Zweifel, *ibid.*, **83**, 2544 (1961); H. C. Brown, "Hydroboration," W. A. Benjamin, Inc., New York, N. Y., 1962.

differ by less than 0.05 ppm. In the norbornyl system *exo* protons are deshielded relative to *endo* protons⁹ and the difference for *exo*- α and *endo*- α protons would be expected to be 0.3 to 0.5 ppm.^{9a} The similar shifts for the 2-proton in the two series indicate that the stereochemistry at C₂ is the same and this is established as *exo* by the stereospecific synthesis of II-OH mentioned above.

The observed downfield shift for the *syn*-7 proton in II relative to the *anti*-7 proton in I is also in agreement with the configurational assignments. It has been observed that in systems of this type 7-protons *syn* to *exo*-hydroxyl, -tosyloxy, or -acetate substituents are deshielded relative to *anti*-7 protons by amounts comparable to those observed in the present case.¹⁰ It should also be noted that the multiplicities of the *endo*-2 hydrogen signals are larger for the *syn* (I) than for the *anti* (II) series as would be expected because of long-range coupling with the *anti*-7 proton.¹¹ The chemical shifts and multiplicities for I-OH, II-OH, II-OAc, and *anti*-7-chloronorcamphor are similar to those of the corresponding 7-bromo analogs.¹²

Rates, solvolysis products, and ion-pair return associated with solvolysis were investigated for acetolysis of I-OTs and II-OTs (\sim 0.025 *M*) in buffered acetic acid (KOAc = 0.0397 *M*) at 78.45°. The substrates used in these experiments were derived from homogeneous samples of the corresponding alcohol. The first-order rate constants were $6.9 \pm 0.15 \times 10^{-5} \text{ sec}^{-1}$ for I-OTs and $5.6 \pm 0.05 \times 10^{-5} \text{ sec}^{-1}$ for II-OTs. These constants are in good agreement with those reported earlier.² At 25° the rates for II-OTs, I-OTs, and the parent *exo*-norbornyl *p*-toluenesulfonate, relative to cyclohexyl *p*-toluenesulfonate, are: 1.3, 2.4, and 512, respectively.² Thus the β -chloro substituent has an appreciable retarding effect. However, the Foote¹³ correlation indicates that both I-OTs and II-OTs are accelerated about as much as the parent *exo*-norbornyl system (carbonyl frequencies for *syn*- and *anti*-7-chloronorcamphor are 1762 and 1758 cm⁻¹, respectively).

In the earlier work² infrared analysis indicated that I-OTs and II-OTs give almost the same mixture of *syn*- and *anti*-7-chloronorbornyl acetates (I-OAc and II-OAc). In the present work, compositions were determined by gc and components were identified by infrared and nmr spectroscopy. Acetolysis of I-OTs gives 33.4% I-OAc, 49.4% II-OAc, and 17.2% of three unidentified components. The products derived from II-OTs are 71.0% II-OAc, 14.3% I-OAc, and 14.7% of the same three unidentified components. These results show that I-OTs and II-OTs give different capturable intermediates; however, there is substantial *syn* \rightleftharpoons *anti* crossover which involves a 6,2-hydride shift.

The results suggest that I-OTs and II-OTs give isomeric bridged ions which are interconverted in com-

(9) (a) E. W. C. Wong and C. C. Lee, *Can. J. Chem.*, **42**, 1245 (1964); (b) J. I. Musher, *Mol. Phys.*, **6**, 93 (1963); P. Laszlo and P. von R. Schleyer, *J. Am. Chem. Soc.*, **86**, 1171 (1964); P. M. Subramanian, M. T. Emerson, and N. A. LeBel, *J. Org. Chem.*, **30**, 2624 (1965).

(10) S. J. Cristol and G. W. Nachtigall, *ibid.*, **32**, 3738 (1967); D. C. Kleinfelter, *ibid.*, **32**, 3526 (1967); E. I. Snyder and B. Franzus, *J. Am. Chem. Soc.*, **86**, 1166 (1964); J. C. Davis, Jr., and T. V. Van Auker, *ibid.*, **87**, 3900 (1965).

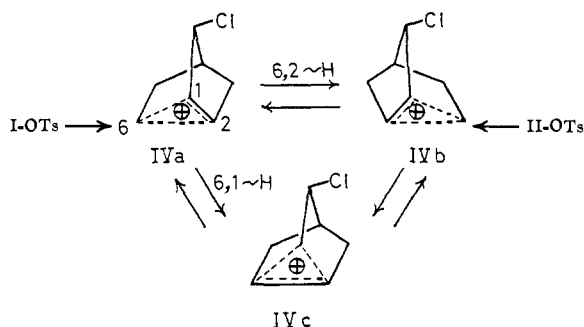
(11) J. Meinwald and Y. C. Meinwald, *ibid.*, **85**, 2514 (1963).

(12) A. C. Oehlschlager, C. D. Kennedy, and L. H. Zalkow, *J. Org. Chem.*, **31**, 1682 (1966); A. C. Oehlschlager and L. H. Zalkow, *Tetrahedron Letters*, 2663 (1964).

(13) C. S. Foote, *J. Am. Chem. Soc.*, **86**, 1853 (1964).

petition with solvent capture. According to this interpretation (Scheme I), I-OTs gives mainly IVa (as shown below some *syn* → *anti* crossover occurs prior to generation of capturable intermediates) and II-OTs gives mainly IVb. Only product-forming intermediates are included in Scheme I. Most of the product results from *exo* capture of IVa and IVb to give I-OAc and II-OAc, respectively. Presumably, at least one of the three minor components results from *exo* capture at C₁ to give 3-chloro-*exo*-2-norbornyl acetate. However, in any case capture of IVa or IVb at C₁ is minor relative to capture at C₂ and C₆. As noted earlier,² this is probably due to the low cationic character at C₁ because of the inductive effect of the adjacent chlorine atom.

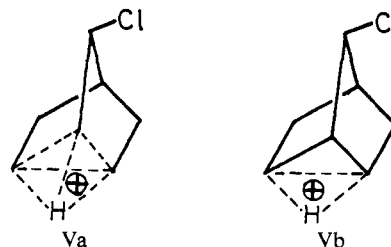
Scheme I



In the parent norbornyl system, 6,2- and 6,1-hydride shifts are necessarily equal because C₁ and C₂ are equivalent. However, this is not the case in the present system and it is apparent that the 6,1 shift to give IVc is less important than the 6,2 shift that interconverts IVa and IVb. Presumably one or two of the three minor components are derived from IVc. The two minor unidentified components present in the largest amounts are formed in the same ratio from I-OTs and II-OTs. For this reason, these isomers, which total 15.2% of the product from I-OTs and 12.5% of the product from II-OTs, are thought to be the isomeric 5-chloro-*exo*-2-norbornyl acetates derived from IVc. If this analysis is correct, the isomer formed in smallest amount (2% from I-OTs and 2.2% from II-OTs) is 3-chloro-*exo*-norbornyl acetate resulting from *exo* attack at C₁.

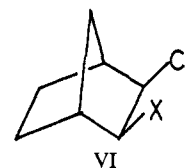
The spread in product compositions for I-OTs and II-OTs shows that the face-protonated^{2,14} (Va) or edge-protonated (Vb)¹⁵ nortricylonium ion cannot be the sole product-forming intermediate because both of these are common to the two substrates. It should also be noted that ¹⁴C-tracer experiments have established¹⁶ that nortricylonium ions are unimportant product-forming intermediates in the parent norbornyl system. Because of the evidence that Va and Vb are unimportant product-forming intermediates and the absence of evidence that such species are involved at all, we prefer the bridged structures IV.

It is apparent that the transition state relating the carbonium ion system (IV) to the *anti* isomer (II) is of lower free energy than the *syn* transition state leading to



I because capture gives more II than I. This, and the slightly higher reactivity of I-OTs than of II-OTs, shows that the ground-state free energy of the *syn* isomer is a little higher than that of the *anti* isomer. Or to put it another way, I-OTs is accelerated somewhat, relative to II-OTs, by relief of steric strain.¹⁷

The Wagner-Meerwein isomer of I-OTs, *cis*-*exo*-3-chloronorbornyl *p*-toluenesulfonate (VI-OTs), was prepared from a homogeneous sample of the corresponding chlorohydrin.¹⁸ The rate of acetolysis of this isomer is at least 239 times slower than that for I-OTs. This means that any VI-OTs formed from I-OTs by ion-pair return would accumulate—ten solvolytic half-lives for I-OTs corresponds to <3% reaction for VI-OTs. The Wagner-Meerwein isomer of II-OTs, *endo*-3-chloro-*exo*-norbornyl *p*-toluenesulfonate, would be expected to be about as unreactive as VI-OTs¹⁹ and also would accumulate if formed by ion-pair return. Acetolysis of pure I-OTs and II-OTs for ten half-lives gave 0.97 and 0.96 equiv of toluenesulfonic acid, respectively. This shows that, at most, there is only a few per cent return to the Wagner-Meerwein isomer in either case. Infrared spectra of unsolvolyzed ester isolated at 70% reaction for acetolysis of I-OTs and II-OTs did not show any evidence for the presence of VI-OTs; the latter has a characteristic band at 950 cm⁻¹.



The reported² interconversion of I-OTs and II-OTs during acetolysis was investigated as follows. The unsolvolyzed esters were isolated in such a way as to minimize fractionation and examined by infrared and nmr spectroscopy—attempts to convert the chloronorbornyl *p*-toluenesulfonates to the corresponding chlorohydrins (which can be analyzed by gc) were unsuccessful.

After 10% acetolysis of the *syn*-*p*-toluenesulfonate (I-OTs) the isolated unsolvolyzed ester contained 6% II-OTs and after 70% reaction 29% of II-OTs was detected. In each case, the nmr and infrared spectra corresponded to binary mixtures of I-OTs and II-OTs. Compositions of the unsolvolyzed ester were determined by multiple integrations of expanded sweep-width scans of the 7-proton absorptions. Analysis of

(17) H. C. Brown and R. S. Fletcher, *ibid.*, 71, 1845 (1949).

(18) E. Tobler, D. E. Battin, and D. J. Foster, *J. Org. Chem.*, 29, 2834 (1964).

(19) The difference in acetolysis rates for the *cis* and *trans* isomers in the norbornyl system would probably be less than the factor of 4 for the 2-chlorocyclohexyl system: E. Grunwald, *J. Am. Chem. Soc.*, 73, 5458 (1951).

(14) J. D. Roberts and C. C. Lee, *J. Am. Chem. Soc.*, 73, 5009 (1951).

(15) G. A. Olah, A. Commeyras, and C. Y. Lui, *ibid.*, 90, 3882 (1968); G. Klopman, *ibid.*, 91, 89 (1969).

(16) J. D. Roberts, C. C. Lee, and W. H. Saunders, Jr., *ibid.*, 76, 4501 (1954).

synthetic binary mixtures of I-OTs and II-OTs gave values within one percentage unit of the known compositions.

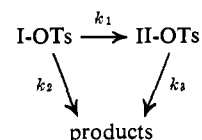
In similar experiments, acetolyses of the *anti-p*-toluenesulfonate (II-OTs) were interrupted after 13.8, 50, and 70% completion. In each case the infrared and nmr spectra of the unsolvolyzed ester were indistinguishable from those of pure II-OTs. Thus in this case isomerization of the ester could not be detected. The earlier work² indicated that this isomer is isomerized to I-OTs.

Acetolysis of I-OTs in the presence of ¹⁴C-labeled sodium *p*-toluenesulfonate was investigated to determine if the I-OTs → II-OTs isomerization is intramolecular. In these experiments the conditions were the same as for the product studies except for the presence of 0.0209 M sodium *p*-toluenesulfonate-¹⁴C. After one half-life the composition of the unsolvolyzed ester was 19% II-OTs and 81% I-OTs and this material had undergone 2.1% exchange. The *syn-p*-toluenesulfonate (I-OTs) was separated from this mixture and the amount of exchange for this isomer was 0.7%. From this, the total exchange (2.1%), and the composition of the unsolvolyzed ester (19% II-OTs), it can be determined that 8% exchange had occurred in the *anti* isomer. Thus isomerization is primarily (*i.e.*, >90%) intramolecular. Presumably the small amount of exchange in the *syn* isomer as well as that in the *anti* isomer results from external return. Most of the *syn* isomer has not reacted at the time of isolation and for this reason less exchange would be expected in this isomer than in the *anti* isomer.

In a similar experiment, II-OTs was solvolyzed in the presence of sodium *p*-toluenesulfonate-¹⁴C and the unsolvolyzed ester was isolated after one half-life. Infrared and nmr spectra indicated this material was pure II-OTs and the amount of exchange was 1.7%. Since exchange is first order in *p*-toluenesulfonate ion, more will occur under the conditions of the exchange experiments (because of the added *p*-toluenesulfonate ion) than during acetolysis where the only *p*-toluenesulfonate ion present is that produced by solvolysis. As outlined earlier,²⁰ the amounts of exchange with the toluenesulfonate ion produced by solvolysis can be determined for any stage of the reaction from the second-order exchange constant, 0.24 l. mol⁻¹ hr⁻¹ and 0.15 l. mol⁻¹ hr⁻¹ for I-OTs and II-OTs, respectively, and the average toluenesulfonate ion concentration. In this way it can be shown that for 70% acetolysis of I-OTs, the unsolvolyzed ester (29% II-OTs; 71% I-OTs) undergoes 2% exchange with the *p*-toluenesulfonate ion produced by solvolysis. Similarly, at 70% acetolysis of II-OTs, the unsolvolyzed ester is 1.5% exchanged.

These present experiments confirm that acetolysis of I-OTs is accompanied by isomerization to the *anti* isomer, II-OTs, and show that this transformation is intramolecular. Isomerization in the opposite direction could not be detected. Acetolysis of I-OTs and II-OTs and the accompanying I-OTs → II-OTs isomerization are summarized by Scheme II. The rate constants for acetolysis of I-OTs (k_2) and II-OTs (k_3) reported above were determined directly—the first-order acetolysis of I-OTs is not disturbed detectably during the first 50% reaction because isomerization is rela-

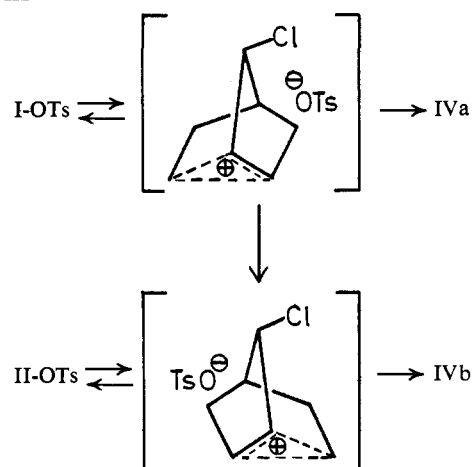
Scheme II



tively slow and the isomers are of comparable reactivity. The rate constant for isomerization (k_1) can be determined from the integrated rate equation which relates the composition of the unsolvolyzed ester with time.²¹ In this way it was determined that the solvolysis to isomerization ratio for I-OTs (k_2/k_1) is about 4.1.

Evidently this remarkable *syn* → *anti* intramolecular isomerization (III) occurs at the intimate ion-pair stage as illustrated in Scheme III, or, in other words, this

Scheme III



isomerization is associated with internal return.³ This shows that internal return can result in rearrangements in which the anion migrates a considerable distance—in this case from the *exo* face of C₂ to the *exo* face of C₆.

Experimental Section

***syn*-7-Chloro-*exo*-2-norbornyl Derivatives (I).** Norbornene was treated with an equivalent amount of hypochlorous acid according to the procedure of Roberts and coworkers.⁵ Distillation of the product at 1 mm gave a 45% yield of a colorless waxy solid. Capillary gc (cyanosilicone) indicated three components with relative peak areas of 6.4:2.4:1.0. This mixture was separated by preparative gc (cyanosilicone on Chromosorb W). Sublimation of the major component (first peak) gave pure *syn*-7-chloro-*exo*-2-norbornanol (I-OH), mp 91.5–92.5° (lit.⁵ mp 90–91.5°). The infrared spectrum (CCl₄) showed strong absorption at 3590 cm⁻¹ (intramolecular hydrogen bonding). The two minor components (second and third peaks) were identified as *syn*-*exo*-2,7-dichloronorbornane (I-Cl)⁵ and *anti*-7-chloro-*exo*-2-norbornanol (II-OH), respectively. These identifications involved comparison of retention times and infrared and nmr spectra with those of authentic samples.

Pure I-OH was converted² to *syn*-7-chloro-*exo*-2-norbornyl *p*-toluenesulfonate (I-OTs) which after purification by recrystallization from an ether-pentane mixture had mp 61.0–61.5° (lit.² 51–52°). The infrared and nmr spectra indicated this product to be homogeneous, *i.e.*, the *anti* isomer could not be detected.

syn-7-Chloro-*exo*-2-norbornyl acetate (I-OAc) was prepared by acylation of I-OH with acetic anhydride and sodium acetate. This colorless oil had bp 101–102° (6 mm), *n*_D²⁰ 1.4836. Capillary gc (Ucon Polar) indicated that the acetate was 99% pure and infrared and nmr spectral properties were in agreement with the structural assignment.

(20) H. L. Goering, and J. F. Levy, *J. Am. Chem. Soc.*, **84**, 3853 (1962).

(21) S. Winstein and K. C. Schreiber, *ibid.*, **74**, 2171 (1952); R. A. Alberty and W. G. Miller, *J. Chem. Phys.*, **26**, 1231 (1956).

anti-7-Chloro-*exo*-2-norbornyl Derivatives (II). Hydrogenation of the Diels-Alder adduct of cyclopentadiene and *trans*-dichloroethylene by a previously described procedure⁵ gave a product which had bp 88–90° (18–19 mm). Capillary gc (Ucon Polar) gave two peaks with an area ratio of 4:1. This mixture was separated by preparative gc (cyanosilicone on Chromosorb W) and the major component was identified as *trans*-2,3-dichloronorbornane by the nmr spectrum²² (m , τ 5.82, *exo* proton; t , τ 6.35, *endo* proton). The minor component was apparently the Wagner-Meerwein isomer, *anti-*exo*-2,7-dichloronorbornane* (II-Cl), n_D^{20} 1.5085 (lit.²³ n_D^{20} 1.5086). The nmr spectrum (CCl₄) was consistent with this assignment and had a broad peak at τ 5.69, a quartet at 6.18, and a broad peak at 7.65.

Hydrolysis of the above 4:1 mixture of *trans*-2,3-dichloronorbornane and *anti-*exo*-2,7-dichloronorbornane* (II-Cl) by the method described earlier⁵ gave a mixture of chlorohydrins. The highest boiling fraction, 129–130° (24 mm), contained about 95% *anti-7-chloro-*exo*-2-norbornanol* (II-OH). Preparatory gc (cyanosilicone on Chromosorb W) gave pure II-OH, mp 75–77° (lit.⁵ mp 79–83°). The nmr and infrared spectra were indistinguishable from spectra of II-OH prepared by hydroboration of *anti-7-chloronorbornene* (see below). The hydrolysis mixture also contained *syn-7-chloro-*exo*-2-norbornanol* (I-OH) and an unidentified component.

*anti-7-Chloro-*exo*-2-norbornanol* (II-OH) was also derived from *anti-7-chloronorbornene* as follows. *anti-7-Chloronorbornene* was obtained from *anti-7-norbornanol*²⁴ (shown to be homogeneous by gc) in 37% yield by reaction with thionyl chloride according to the procedure of Tanida and Hata.²⁵ The yield was increased to 66% by a catalytic amount of pyridine.²⁶ The product had bp 71–72° (60 mm), n_D^{20} 1.4930 (lit.²⁵ bp 70.5–71.5° (60 mm); n_D^{20} 1.4937) and was shown to be homogeneous by gc. The infrared and nmr spectra²⁷ were in agreement with published spectral data for *anti-7-chloronorbornene*. Hydroboration⁸ of the above *anti-7-chloronorbornene* followed by oxidation of the adduct gave a 95% yield of *anti-7-chloro-*exo*-2-norbornanol* (II-OH) which after purification by sublimation had mp 69–71° (lit.⁵ 79–83°). This product was shown to be homogeneous by gc and the infrared and nmr spectral properties were the same as those of II-OH obtained by hydrolysis of *trans*-1,2-dichloronorbornane.

*anti-7-Chloro-*exo*-2-norbornyl *p*-toluenesulfonate* (II-OTs) was prepared⁵ from pure II-OH and had 65–65.5° (lit.² 64–65.4°). The infrared and nmr spectra indicated that this material did not contain any of the *syn* isomer.

*anti-7-Chloro-*exo*-2-norbornyl acetate* (II-OAc) was prepared from II-OH containing 6% I-OAc by the method used to prepare the *syn* isomer (I-OAc). The *anti* acetate (II-OAc) had bp 94–95° (6 mm), n_D^{20} 1.4811, and was shown to contain 5% I-OAc by gc. The infrared and nmr spectra were consistent with the structural assignment.

***syn*- and *anti-7-Chloronorcamphors*.** Oxidation of *syn-7-chloro-*exo*-2-norbornanol* (I-OH) by the procedure of Brown and Garg⁶ gave a 70% yield of a colorless solid, bp 113–117° (19 mm). Capillary gc (Ucon Polar) gave four peaks with relative areas of 1:20:4:1. Pure *syn-7-chloronorcamphor* (the major component) was separated by preparative gc (cyanosilicone on Chromosorb W) and had mp 64–65° (lit.²⁸ mp 69–70°). The 2,4-dinitrophenylhydrazone derivative had mp 190–190.5° (lit.⁵ 192.5–193.5°).

In a similar manner *anti-7-chloro-*exo*-2-norbornanol* (II-OH) was converted to *anti-7-chloronorcamphor* which was isolated by preparative gc (the *anti* isomer has a shorter retention time than the *syn* isomer) and had mp 77–80° (lit.²⁸ mp 68–70.5°). The 2,4-dinitrophenylhydrazone derivative had mp 174–175° (lit.⁵ mp 143.5–145°). Contamination with the *syn* isomer lowered the melting point to ca. 140°.

The isomeric 7-chloronorcamphors were converted to 7-chloronorbornane as follows. A solution of 2.5 g (16.8 mmol) of *syn-7-chloronorcamphor*, 3.4 g of 85% potassium hydroxide, and 7 ml of 99% hydrazine hydrate in 25 ml of diethylene glycol was refluxed for 1 hr. Excess hydrazine and water were removed by distillation and the solution was refluxed for 2 hr. The cooled reaction mixture

was diluted with water and extracted with ether. Distillation of the dried extract gave 7-chloronorbornane, bp 79–83° (60 mm), mp 40–41° (lit.²⁹ bp 73° (41 mm), mp 41–42°). The infrared spectrum agreed with the published spectrum and the nmr spectrum had a broad peak (width at half-height, 4 cps) with fine splitting at τ 6.09 (C₇ proton). *anti-7-Chloronorcamphor* was also converted to 7-chloronorbornane (identical with product derived from *syn* isomer) by this method.

***cis-*exo*-3-Chloronorbornyl *p*-Toluenesulfonate* (VI-OTs).** This ester was prepared from the corresponding chlorohydrin¹⁸ and after purification by recrystallization from ether-pentane had mp 62.5–63.0°; nmr (CCl₄): dd (one proton) centered at τ 5.61, J = 6.2 and 1.6 Hz (C₂-*endo* proton); and dd (one proton) at 6.20, J = 6.0 and 1.6 Hz (C₃-*endo* proton).

Anal. Calcd for C₁₄H₁₇ClO₃S: C, 55.90; H, 5.70; Cl, 11.79. Found: C, 55.93; H, 5.77; Cl, 11.96.

Acetolysis of *syn*- and *anti-7-Chloro-*exo*-2-norbornyl *p*-Toluenesulfonates* (I-OTs and II-OTs). A solution of 0.03 *M* I-OTs in anhydrous acetic acid containing 0.039 *M* sodium acetate was heated at 100° for 24 hr (more than ten solvolytic half-lives). After cooling, the acetic acid was neutralized with aqueous sodium bicarbonate. The aqueous solution was extracted with several portions of ether which were combined and dried (Na₂SO₄). Most of the ether was removed by fractionation and the concentrated residue was analyzed by capillary gc (Ucon Polar). Independent experiments showed the presence of five components with the following retention times in minutes (per cent of total peak areas): 72.4 (2), 73.8 (49.4), 95.2 (6.4), 101.0 (33.4), and 102.6 (8.8%). The major components with retention times of 73.8 and 101.0 min were identified as *anti*- and *syn-7-chloro-*exo*-2-norbornyl acetates* (I-OAc and II-OAc), respectively, by comparison with authentic samples. The other three components were not identified.

Two independent experiments showed that under these conditions the *anti-p*-toluenesulfonate (II-OTs) gives the same five compounds with the following percentages of total peak areas: 72.4 (2.2), 73.8 (71), 95.2 (5.5), 101.0 (14.3), and 102.6 (7.0). Thus product distributions differ for *syn*- and *anti-7-chloro-*exo*-2-norbornyl *p*-toluenesulfonates* (I-OTs and II-OTs) and the difference is reproducible.

Isomerization of *syn-7-Chloro-*exo*-2-norbornyl *p*-Toluenesulfonate* during Solvolysis. *syn*- and *anti-7-chloro-*exo*-2-norbornyl *p*-toluenesulfonates* (I-OTs and II-OTs) and the Wagner-Meerwein isomer of I-OTs, *cis-*exo*-2,3-chloronorbornyl *p*-toluenesulfonate* (VI-OTs), have characteristic bands in the infrared region at 1073, 1063, and 950 cm⁻¹, respectively, which can be used to detect the presence of these isomers in a ternary mixture.

The 60-MHz nmr signals for the C₇-*anti* proton in I-OTs and the C₂-*endo* proton in IV-OTs are centered at 229 Hz and these signals cannot be used for distinguishing between these isomers. The signal for the C₇-*syn* proton in II-OTs is centered at 248 Hz. Thus the C₇ proton signals can be used for quantitative analysis of binary mixtures of I-OTs and II-OTs.

A 0.043 *M* solution of *syn-p*-toluenesulfonate (I-OTs) in dry acetic acid containing 0.397 *M* potassium acetate was heated at 78.4° for 6 hr (78% acetolysis). From the rate of exchange of I-OTs with sodium *p*-toluenesulfonate-¹⁴C under these conditions (see below) it can be determined²⁰ that at this point <3% of the unsolvolyzed ester has exchanged with the *p*-toluenesulfonate ion produced by solvolysis. The cooled reaction mixture was diluted with water and neutralized with sodium carbonate. Extraction with several portions of ether followed by drying (Na₂SO₄) and evaporation of the combined extracts gave a yellow oil. Trituration of this residue with cold pentane removed the chloronorbornyl acetates. After complete removal of the acetates (no carbonyl absorption) the infrared spectrum corresponded to a binary mixture of I-OTs and II-OTs. The absence of absorption at 950 cm⁻¹ showed that IV-OTs (the Wagner-Meerwein isomer of I-OTs) was not present in detectable amounts. The nmr spectrum also corresponded to a binary mixture of I-OTs and II-OTs. Multiple integrations of 50-c sweep width scans of the signals at 248 Hz (II-OTs) and 229 Hz (I-OTs) corresponded to a composition of 27% *anti* isomer (II-OTs) and 63% *syn* isomer (I-OTs). Analysis of synthetic binary mixtures of I-OTs and II-OTs by this method gave compositions within one percentage unit of the known values.

In an independent experiment the composition of the unsolvolyzed ester for 70% acetolysis of I-OTs was determined in the same way and found to be 29% II-OTs and 71% I-OTs.

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In similar experiments the *anti-p*-toluenesulfonate (II-OTs) was partially solvolyzed; 14% solvolysis in one case and 70% in another. The unsolvolyzed ester was isolated as described above for the *syn* isomer and in each case the infrared and nmr spectra corresponded to pure II-OTs. Thus II-OTs does not undergo detectable isomerization during acetolysis.

Exchange Associated with Acetolysis of *syn*- and *anti*-7-Chloro-*exo*-2-norbornyl *p*-Toluenesulfonates. A 0.0408 *M* solution of the *syn-p*-toluenesulfonate (I-OTs) in anhydrous acetic acid containing 0.05 *M* potassium acetate and 0.0209 *M* sodium *p*-toluenesulfonate-¹⁴C (8.02 μ Ci/mmol) was heated at 78.4° for one solvolytic half-life (2.8 hr). The radioactive salt was prepared by sulfonation of toluene-1-¹⁴C. The unreacted ester was isolated as described in the preceding section. Infrared and nmr spectra corresponded to a binary mixture of I-OTs and II-OTs and nmr analysis indicated the composition to be 19% II-OTs and 81% I-OTs.

In a similar experiment a 0.0405 *M* solution of *anti-p*-toluenesulfonate (II-OTs) containing 0.05 *M* potassium acetate and 0.0206 *M* sodium *p*-toluenesulfonate-¹⁴C was heated at 78.4° for one half-life (3.5 hr). The infrared and nmr spectra of the recovered ester corresponded to pure II-OTs.

The ¹⁴C contents of the above samples of unsolvolyzed ester, α^{ROT_s} (microcuries per millimole corrected for background and efficiency of counting), were determined with a scintillation spectrometer (toluene-2,5-diphenyloxazole solution). The average *p*-toluenesulfonate salt concentration $[\text{NaOTs}]_{\text{av}}$ during the partial solvolysis can be determined from the rate constant for acetolysis (k_a) as²⁰

$$[\text{NaOTs}]_{\text{av}} = [\text{NaOTs}]_0 + [\text{ROT}_s]_0 [1 + (1/k_s t)(e^{-k_s t} - 1)] \quad (1)$$

where $[\text{NaOTs}]_0$ is the concentration of ¹⁴C-labeled salt present at the outset.

The average activity of the salt during the solvolysis, $\alpha_{\text{av}}^{\text{NaOT}_s}$, is

$$\alpha_{\text{av}}^{\text{NaOT}_s} = \alpha_0^{\text{NaOT}_s} [\text{NaOTs}]_0 / [\text{NaOTs}]_{\text{av}} \quad (2)$$

and the per cent exchange in the unsolvolyzed ester is given by

$$\% \text{ exchange} = 100 \alpha^{\text{ROT}_s} / \alpha_{\text{av}}^{\text{NaOT}_s} \quad (3)$$

Exchange data are presented in Table II. The second column

Table II. Data for Exchange between *syn*- and *anti*-7-Chloro-*exo*-2-norbornyl *p*-Toluenesulfonates and Sodium *p*-Toluenesulfonate-¹⁴C during Acetolysis at 78.4°

Compd	$[\text{NaOTs}]_{\text{av}}$, <i>M</i>	$\alpha_{\text{av}}^{\text{NaOT}_s}$, $\mu\text{Ci}/\text{mmol}$	α^{ROT_s} , $\mu\text{Ci}/\text{mmol}$	% exc	k_{exc} , 1/(mol hr)
I-OTs	0.0323	5.19	0.109	2.1	0.24
II-OTs	0.0319	5.18	0.087	1.7	0.15

shows the average salt concentration (eq 1) for the above reaction periods and the fifth column shows the observed amount of exchange for the unsolvolyzed ester. The last column shows the second-order rate constant (k_{exc}) determined²⁰ from

$$\% \text{ exchange} = 100(1 - e^{-k_{\text{exc}}[\text{NaOTs}]_{\text{av}} t}) \quad (4)$$

The rate of exchange between the unsolvolyzed ester and *p*-toluenesulfonate ion produced by solvolysis can be determined from these constants and the average *p*-toluenesulfonate ion concentration.²⁰

Recrystallization of the unsolvolyzed ester for the above exchange experiment starting with I-OTs (19% II-OTs and 81% I-OTs; $\alpha^{\text{ROT}_s} = 0.109 \mu\text{Ci}/\text{mmol}$) gave I-OTs which had $\alpha = 0.0350 \mu\text{Ci}/\text{mmol}$. From this it can be determined that $\alpha = 0.424 \mu\text{Ci}/\text{mmol}$ for the II-OTs in the unsolvolyzed ester. This corresponds to 8% exchange for this isomer. An activity of 0.035 $\mu\text{Ci}/\text{mmol}$ for the *syn* isomer (I-OTs) in the unsolvolyzed ester corresponds to 0.7% exchange.