crystalline at room temperature. Although specific measurements were not carried out, the behavior of the materials on drying suggests that only the hexahydrate might have a vapor pressure of water high enough to measure by manometric means at a temperature where the material was crystalline. The formation of strongly bound anion–molecule complexes without concurrent lattice stability has been observed before with the larger tetraalkylammonium ions; thus we found[7] that tetrapropyl- and tetrabutylammonium hydrogen dibromides are extremely tightly bound stoichiometric salts which are liquids at or just above room temperature.

The solid state infrared spectrum of the hexahydrate is typical of those of the clathrate hydrates[2] such as tetramethylammonium hydroxide pentahydrate[8a,9] or fluoride tetrahydrate,[8b,9] and shows, in addition to cation bands, a broad stretching band of hydrogen-bonded water centered at $3300\ \text{cm}^{-1}$ and a bending band at $1650\ \text{cm}^{-1}$; no rocking modes of strongly coordinated water are present. The infrared spectrum of the tetrapropylammonium fluoride dihydrate, on the other hand, shows a stretching region for unusually strongly hydrogen-bonded water centered at $2900\ \text{cm}^{-1}$, a bending band at $1630\ \text{cm}^{-1}$ which is now nearly as intense as the stretching band, and a broad, strong rocking band stretching from 600 to $1100\ \text{cm}^{-1}$[9]. Thus this dihydrate, like tetramethylammonium fluoride monohydrate and hydroxide monohydrate,[2,9] contains a water–anion moiety in which the water oxygen is apparently tricoordinate and involved in very strong hydrogen bonds.

The symmetrical hydrogen difluoride anion in potassium hydrogen difluoride shows $\nu_3$ (asymmetric stretch) as a broad band at $1450\ \text{cm}^{-1}$ and $\nu_2$ (bending) as a fairly sharp single band at $1222\ \text{cm}^{-1}$.[10] The $\nu_1$ (symmetic stretch) mode is not observed under $D_{\infty h}$ symmetry. We have reported [5]that the hydrogen difluoride anion in *p*-toluidinium hydrogen difluoride, which is known[11] to be a linear, unsymmetrical species of $C_{\infty v}$ symmetry, shows $\nu_3$ as a very broad, strong band centered at $1740\ \text{cm}^{-1}$, and $\nu_2$ appears as a pair of bands at 1080 and $1230\ \text{cm}^{-1}$ as a result of the lifting of the degeneracy of this band in the asymmetric crystal environment. Subsequently we have found that $\nu_1$ can be observed in this salt, as predicted by theory, as a broad and reasonably intense band centered at $450\ \text{cm}^{-1}$; there is no absorption in this area in the infrared spectrum of *p*-toluidinium hexachlorostannate.

In tetrapropylammonium hydrogen difluoride $\nu_3$ ($1900\ \text{cm}^{-1}$) and $\nu_2$ (1255 and $1315\ \text{cm}^{-1}$) resemble the corresponding bands in the *p*-toluidinium salt; however, $\nu_1$ does not appear in the spectrum. The ion thus is presumably still of $D_{\infty h}$ symmetry, since in either $C_{\infty v}$ or $C_{2v}$ $\nu_1$ would be infrared active; however, it lies in a crystal site that lifts the degeneracy of the $\Pi_u\nu_2$ bending mode. Low-temperature infrared studies of this and related hydrogen difluorides are under investigation.

Dehydration of solutions of tetramethylammonium fluoride in water yields a monohydrate; further removal of water can be effected by heating *in vacuo* at 140°.[12] Preparation of the anhydrous fluoride by this method is always accompanied by some decomposition to trimethylamine and methyl fluoride, and the decomposition is complete at higher temperatures.[13] With tetrapropylammonium fluoride it is clear that either there is no monohydrate, or it decomposes at the temperature necessary to remove water from the dihydrate to form it. The solid material which remains after the elimination reaction has been run partially to completion gives an infrared spectrum which is the composite of those of the dihydrate and the hydrogen difluoride, with no new absorptions attributable to a monohydrate, and the matter balance of the reaction shows that there are essentially 2 mol of water remaining for each mole of fluoride salt. Whether proton abstraction by fluoride occurs within the lattice of the dihydrate or in the anhydrous salt left after water is removed cannot be established at this time.

The elimination reaction of quaternary ammonium fluorides would at first appear to have limited synthetic application when compared to that of the hydroxides, since one-half of the starting amine salt is retained as the hydrogen difluoride.[14,15] However, since the fluoride salts could be prepared in neutral solution, such as by reaction of sulfates with barium fluoride or halides with silver fluoride, this process affords a means to achieve, if desirable, the results of a Hofmann elimination reaction without the need to expose a molecule to solution in aqueous base.

**Acknowledgments.** We wish to acknowledge the donors of the Petroleum Research Fund, administered by the American Chemical Society, the National Science Foundation, and the Biomedical Support Committee of Oakland University for support of this work. Two of us (I. A. G. and S. L. M.) held NSF–URP summer fellowships.

**Registry No.**—Tetrapropylammonium fluoride hexahydrate, 51934-09-9; tetrapropylammonium fluoride dihydrate, 51934-10-2; tetrapropylammonium fluoride trihydrate, 51934-11-3; tetrapropylammonium fluoride, 7217-93-8; tetrapropylammonium hydrogen difluoride, 52003-47-1.

## References and Notes

(1) Reported in part: K. M. Harmon, R. W. Carling, D. L. Duffy, and S. L. Madeira, Abstracts, 165th National Meeting of the American Chemical Society, Dallas, Tex., April 13, 1973, No. INORG-163.
(2) K. M. Harmon, I. Gennick, and S. L. Madeira, Abstracts, 167th National Meeting of the American Chemical Society, Los Angeles, Calif., April 5, 1974, No. INORG-228.
(3) W. T. Miller, J. H. Fried, and H Goldwhite, *J. Amer. Chem. Soc.*, **82**, 3091 (1960).
(4) D. V. Banthrope, "Elimination Reactions," American Elsevier, New York, N. Y., 1963, p 35.
(5) K. M. Harmon, S. L. Madeira, and R. W. Carling, *Inorg. Chem.*, **13**, 1260 (1974).
(6) Yield corrected for weight of ir sample; all yields based on stoichiometry of eq 1.
(7) K. M. Harmon, S. D. Alderman, K. E. Benker, D. J. Diestler, and P. A. Gebauer, *J. Amer. Chem. Soc.*, **87**, 1700 (1965).
(8) (a) R. K. McMullan, T. C. W. Mak, and G. A. Jeffrey, *J. Chem. Phys.*, **44**, 2338 (1966); (b) W. J. McLean and G. A. Jeffrey, *ibid.*, **47**, 414 (1967).
(9) Infrared spectra of these compounds will be reproduced and discussed: K. M. Harmon and I. Gennick, *Inorg. Chem.*, in preparation.
(10) J. A. A. Ketelaar and W. Vedder, *J. Chem. Phys.*, **19**, 654 (1951).
(11) J. M. Williams and L. F. Schneemeyer, *J. Amer. Chem. Soc.*, **95**, 5790 (1973).
(12) W. K. Musker, *J. Org. Chem.*, **32**, 3189 (1967).
(13) T. A. Lawson and J. N. Collie, *J. Chem. Soc.*, **53**, 624 (1888).
(14) The quaternary salt could be recovered fairly easily as the fluoride by half-neutralization with aqueous base, or as the chloride by treatment with calcium chloride in aqueous solution.
(15) It is possible that addition of an equimolar amount of fluoride ion, say as sodium fluoride, to absorb hydrogen fluoride would increase the yield; Hayami, *et al.*, reports[16] quantitative yields of styrenes by treatment of 2-arylethyl derivatives with a large excess of fluoride ion.
(16) J. Hayami, N. Ono, and A. Kaji, *Bull. Chem. Soc. Jap.*, **44**, 1628 (1971).

---

# On the Products of Hydroboration of 1-Chloronorbornene

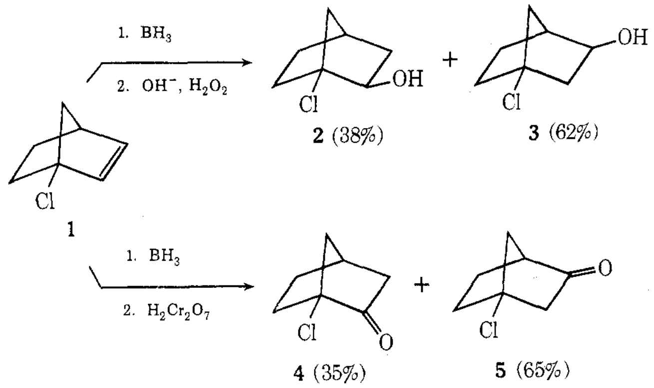
René J. Muller and B. L. Murr*

*Department of Chemistry, The Johns Hopkins University,*
*Baltimore, Maryland 21218*

*Received January 22, 1974*

For the penultimate step in a synthesis of 1-deuterio-*exo*-norborneol, we repeated a procedure by Fry and Farnham for the preparation of 1-chloro-2-*exo*-norbornanol from the hydroboration of 1-chloronorbornene.[1] Fry and Farnham reported that reaction of 1-chloronorbornene (1) with diborane in THF gave a mixture of 38% 1-chloro-2-*exo*-norbornanol (2) and 62% 1-chloro-3-*exo*-norbornanol (3) when the borane intermediates were oxidized with alkaline hydrogen peroxide and a mixture of 35% 1-chloro-2-norbornanone (4) and 65% 1-chloro-3-norbornanone (5) when the borane intermediates were oxidized with chromic acid (Scheme I).

**Scheme I**



Structural assignments for chloro ketones 4 and 5 were based on the facts that 5 had ir and nmr spectra identical with those of 1-chloro-3-norbornanone prepared according to Wiberg[2] and that 4 had ir and nmr spectra compatible with those expected for the isomeric chloro ketone.

Structural assignments for 2 and 3 were based mainly on the fact that the ratio of chloro alcohols 2 and 3 from the hydroboration were the same, within experimental error, as the ratio of chloro ketones 4 and 5. This similarity of product composition seemed reasonable, since the diborane addition step must determine the orientation for formation of the borane intermediates in both reactions. Exo configurations for the previously unknown 2 and 3 were assigned by analogy with products of hydroboration of other norbornenes[3] and from the characteristic $\alpha$-hydroxy proton absorption in the nmr spectra of both chloro alcohols.[4]

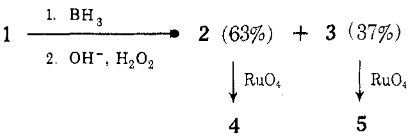
We repeated the hydroboration of 1-chloronorbornene as described by Fry and Farnham except that the solvent was removed by distillation through a Vigreux column rather than with a rotary evaporator. The concentrated ether solution was examined by glpc and found to contain, in order of increasing retention time, 8% starting material, a peak of 57% (hereafter referred to as the major chloro alcohol), an unidentified peak of 1%, and a peak of 34% (hereafter referred to as the minor chloro alcohol).[5]

Because we had on hand a small amount of 1-chloro-2-*exo*-norbornanol[6] we injected a sample into the chromatograph expecting the peak to have the same retention time as that of the minor chloro alcohol of the hydroboration mixture. Instead, the retention time was identical with that of the major chloro alcohol, the two peaks being well separated under the conditions used.

The chloro alcohol mixture was separated by preparative glpc and each chloro alcohol[7] was oxidized with ruthenium tetroxide[8] to the corresponding ketone. The major chloro alcohol on oxidation gave a ketone whose ir and nmr spectra were identical with those of 1-chloro-2-norbornanone prepared by ozonolysis of 1-chloro-2-methylenenorbornane.[9] The minor chloro alcohol on oxidation gave a ketone whose ir and nmr spectra were identical with those for 1-chloro-3-norbornanone prepared by the method of Wiberg.[2,10]

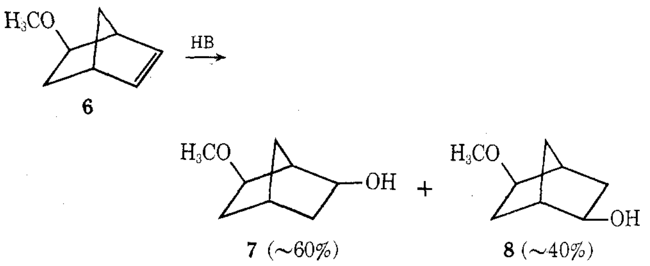
Hydroboration of 1-chloronorbornene (1) followed by oxidation with alkaline hydrogen peroxide thus gives 1-chloro-2-*exo*-norbornanol (2) as the predominant alcohol (Scheme II).[11,12] This observation is in agreement with the results of a number of hydroboration reactions, which show a marked tendency for boron to add nearer to chlorine in allylic chlorides, owing to the stabilizing −I effect on that position in the four-centered transition state.[13,14]

**Scheme II**



Another apposite example of the −I effect of a substituent on orientation is seen in the hydroboration of 5-*exo*-methoxy-2-norbornene (6), which gives ~60% 7 and ~40% 8 (Scheme III).[3] Here again, the boron becomes attached preferentially to the carbon closer to the substituent. Oxymercuration of 6 gives the opposite orientation as expected, a predominance (~92%) of 8 and ~8% of 7.[3]

**Scheme III**



There remains the unanswered question of why hydroboration of 1-chloronorbornene (1) gives a predominance (65%) of 1-chloro-3-norbornanone (5) when the borane intermediates are oxidized with chromic acid.[15] In hydroboration of an unsymmetrical chloroallylic system, orientation of the borane intermediates is determined at the stage of addition of diborane to the double bond. While it has been demonstrated that oxidation of organoborane intermediates with alkaline hydrogen peroxide is quantitative and that the resulting alcohols reflect the initial orientation of addition,[16] the yields of ketones derived from oxidation of organoboranes with chromic acid are less than quantitative (65–85%).[17] Considering that hydroboration of 1 followed by alkaline hydrogen peroxide oxidation leads to a predominance of 2 (Scheme II) and that oxymercuration (which gives orientation opposite to that of hydroboration) of 1 followed by oxidation with Jones reagent gives 5 solely,[15] the unexpected *observed* predominance of 5 in the hydroboration of 1 followed by oxidation with chromic acid (Scheme I) must be due to some factor unique to the chloroborane intermediates and/or the chromic acid medium.

One possible explanation for the observed predominance of 5 is that the rate of chromic acid oxidation for the borane precursor of 4 was slower than that for 5, resulting in a lesser degree of conversion (and a lower yield) to the chloro ketone. This hypothesis receives some support from the observation that 2 is converted to the chloro ketone more slowly than 3 by ruthenium tetroxide.[9] Furthermore, it is well known that ketones are not stable to strong oxidizing acids and that the contact time must be controlled carefully to maximize the yield of ketone. It may be that **4** is more labile to the acid medium than **5**.

Unfortunately, experimental verification for both hypotheses is lacking since no mass balance was reported for the reaction.

## Experimental Section

**Hydroboration of 1-Chloronorbornene (1).**[1] Aldrich 1 *M* diborane in THF (13.8 ml) was added to a stirred solution of 6.9 g (0.0537 mol) of **1** in 13.8 ml of freshly distilled THF under nitrogen. After 20 min, 5.7 ml of 3 *N* sodium hydroxide was added dropwise (caution, frothing) to the stirred solution followed by 4.2 ml of 50% hydrogen peroxide (slowly, reaction exothermic). The reaction mixture was stirred for 2 hr.

Water (20 ml) and some sodium chloride were added and the mixture was extracted three times with ether (30 ml, 2 × 20 ml). The combined ether extracts were washed with water (3 × 50 ml) and dried over magnesium sulfate. The ether solution was concentrated to about 30 ml by slow distillation through a small Vigreux column and examined by glpc (Perkin-Elmer Column K, 15% Carbowax 20M, 170°, 40 psi). The analysis showed, in order of increasing retention time, 8% **1**, 57% **2**, 1% of an unidentified substance, and 34% **3**.

The chloro alcohol mixture was separated by preparative glpc (column: 20 ft × 0.375 in. 20% SE-30 on Chromosorb P 45/60, 185°, 29 psi): 1-chloro-2-*exo*-norbornanol (**2**), mp 84.5–85.5°, ir ($CCl_4$) hydroxyl 3550 cm$^{-1}$, the nmr ($CDCl_3$) consisted of a multiplet centered at $\tau$ 6.36 ($\alpha$-hydroxy proton) and a multiplet between $\tau$ 7.65 and 9.0, in the ratio of 1:10; 1-chloro-3-*exo*-norbornanol (**3**), mp 76.5–77.5°, ir ($CCl_4$) hydroxyl 3590 cm$^{-1}$, the nmr ($CDCl_3$) consisted of a multiplet at $\tau$ 6.1 ($\alpha$-hydroxy proton) and a very complex multiplet between $\tau$ 7.7 and 8.95, in the ratio of 1:10.

**Oxidation of 1-Chloro-3-*exo*-Norbornanol (3).**[8] Ruthenium tetroxide [2.9 ml of *ca* 0.137 *M* solution in Freon 11 (Matheson)] was added with a chilled syringe to a stirred solution of 50 mg (0.00034 mol) of **3** in 2 ml of Freon 11 and 2 ml of pentane at 5–10°. It was necessary to add an equal volume of pentane to bring the chloro alcohol into solution; at 0° the chloro alcohol was only partially soluble. The reaction mixture was stirred at 0° for 20 min.

The excess oxidant was consumed by addition of 2 ml of anhydrous ether and the black ruthenium dioxide was removed by filtration. The solvent was removed by careful evaporation with nitrogen and sublimation of the residue afforded 25 mg of **5**, ir ($CCl_4$) carbonyl 1775 cm$^{-1}$, the nmr ($CDCl_3$) showed three multiplets centered at $\tau$ 7.3, 7.47, and 7.87.

**Oxidation of 1-Chloro-2-*exo*-norbornanol (2).**[8] Alcohol **2** (30 mg) in 2 ml of Freon 11 (**2** was completely soluble in Freon 11 at 0°) was oxidized with 1.9 ml (0.00026 mol) of 0.137 *M* ruthenium tetroxide solution at 0° as in the procedure above except that the reaction mixture was stirred at room temperature for 18 hr.[9] Work-up identical with that given above afforded 17 mg of **4**, ir ($CCl_4$) carbonyl 1780 cm$^{-1}$, the nmr ($CDCl_3$) showed two multiplets, one centered at $\tau$ 7.33 and the other between $\tau$ 7.5 and 8.8, with the relative areas of 1:9.4.

**Acknowledgment.** We wish to thank the National Science Foundation for financial support. We are grateful to Professor A. J. Fry for sending us copies of private correspondence and a number of spectra which were helpful in making this clarification. Gratitude is also expressed to Dr. Raymond Weglein for consultation on several aspects of this work.

**Registry No.**—**1**, 15019-71-3; **2**, 19916-70-2; **3**, 19916-71-3; **4**, 51417-65-3; **5**, 51417-66-4.

## References and Notes

(1) A. J. Fry and W. B. Farnham, *J. Org. Chem.*, **34**, 2314 (1969).

(2) K. B. Wiberg, B. R. Lowry, and T. H. Colby, *J. Amer. Chem. Soc.*, **83**, 3998 (1961).

(3) P. v. R. Schleyer, P. J. Stang, and D. J. Raber, *J. Amer. Chem. Soc.*, **92**, 4725 (1970).

(4) W. C. Baird, *J. Org. Chem.*, **31**, 2411 (1966).

(5) If only the chloro alcohol peaks are considered in the calculation, the major chloro alcohol accounts for 63% and the minor chloro alcohol for 37% of the mixture. Fry and Farnham observed starting material in the reaction mixture, although this was not reported in their paper. Private communication from Professor A. J. Fry.

(6) The reduction of 1-chloronorcamphor with sodium borohydride gave a 3:1 mixture of 1-chloro-2-*endo*-norbornanol and 1-chloro-2-*exo*-norbornanol. Satisfactory analyses were obtained for both chloro alcohols. R. J. Muller and B. L. Murr, unpublished results.

(7) The ir spectra of the major and minor chloro alcohols were identical with those of the first and second chloro alcohol peaks, respectively, from the preparative glpc carried out by Fry and Farnham. We are grateful to Professor Fry for sending copies of these *spectra*.

(8) E. J. Corey, J. Casanova, Jr., P. A. Vatakencherry, and R. Winter, *J. Amer. Chem. Soc.*, **85**, 169 (1963).

(9) The instantaneous appearance of black ruthenium dioxide on addition of the oxidizing solution to the alcohol solution characteristic of all the ruthenium tetroxide oxidations of norborneols—including 1-chloro-3-*exo*-norbornanol—carried out in this study was not observed with 1-chloro-2-*exo*-norbornanol. The black precipitate appeared approximately 1 min after the addition and formed slowly thereafter, indicating a retarding influence of bridgehead chlorine on the oxidation. A similar retarding influence was noted in the ozonolysis of 1-chloro-2-methylenenorbornane, which required about 36 hr for completion as compared to several hours for the unsubstituted olefin under the same conditions. R. J. Muller and B. L. Murr, unpublished results.

(10) We are grateful to Professor R. Sauers for sending copies of these spectra.

(11) The ir spectra of **4** and **5** (prepared from **1** by hydroboration and chromic acid oxidation) sent to us by Professor Fry were identical with the ir spectra of the chloro ketones prepared from the oxidation of **2** and **3**, respectively.

(12) Reduction of **2** with sodium and ethanol afforded *exo*-norborneol.

(13) H. C. Brown and E. F. Knights, *J. Amer. Chem. Soc.*, **90**, 4439 (1968).

(14) D. J. Pasto and J. Hickman, *J. Amer. Chem. Soc.*, **90**, 4445 (1968).

(15) Schleyer and Raber carried out the same reaction and observed 65% **5** and 21% **4**. They also found that oxymercuration of **1** gave **5** as the sole product. Private communication from D. Raber to H. C. Brown. We are grateful to Professor Fry for sending us a copy of this correspondence.

(16) H. C. Brown, "Hydroboration," W. A. Benjamin, New York, N. Y., 1962, pp 5, 6.

(17) Reference 16, p 73.

---

# Conformation of Acyloxy Groups in *I,I*-Diacyloxyiodobenzenes. A Dipole Moment Study

Otto Exner*

*Institute of Organic Chemistry and Biochemistry, Czechoslovak Academy of Sciences, 166 10 Prague 6, Czechoslovakia*

Božo Plesničar

*Department of Chemistry, University of Ljubljana, 61000 Ljubljana, Yugoslavia*

*Received December 27, 1973*

In the compounds of general formula R–X–Y–X–R, where X and Y stand for any divalent group, the two bonds Y–X are equivalent and *a priori* the same conformation on both may be expected. Summarizing the results of our dipole moment studies and those obtained from other methods, we reached the conclusion[1] that the actual conformation can be predicted from the conformation of the simpler model compound R–Y–X–R. If it is planar, the electronic configuration on the central atom Y is usually sp$^2$ and the bonds Y–X acquire partial double bond character. The whole molecule R–X–Y–X–R is then also planar, or nearly planar (carbonates and their analogs, anhydrides,[2] diacyl sulfides,[1] boronic esters[3]). When the central atom Y has a tetrahedral sp$^3$ configuration, the model molecule R–Y–X–R as well as the bifunctional molecules R–X–Y–X–R are nonplanar. The latter has more frequently $C_2$ than $C_s$ symmetry (acetals,[4] *gem*-disulfones,[4] sulfonic acid anhydrides,[1] dialkylphosphinic esters,[5] trisulfides).