to the lone pair on X, which would then shift it further downfield. This steric hindrance in an isopropyl (or other secondary) compound would be much greater and would therefore produce the enhanced increment in downfield shift. An effect of the lone pair H distance on δ is also reflected in the decreasing value for Δ for the first, second, and third period elements, corresponding to an increasing C–X bond length and thus increasing α H to X distance.

The rather remarkable success of the empirical postulate of a constant chemical shift for α H by an adjacent skew unshared electron pair for cases where conformational changes are not a factor lends strong support to the utility of this postulate as one useful empirical means of estimating conformational relationships for such hydrogens.

Ionic Addition Mechanism Investigation. Determination of Deuterated Nortricyclyl Alcohol Stereochemistry

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Ionic additions to norbornadiene[1] and related solvolyses[2] have historically been scrutinized by stereochemical investigation of the olefinic product; this represented incomplete investigation of the various attendant ionic processes in that nortricyclyl (nonolefinic) product often was the *major* product. Complete analysis of labeled nortricyclyl derivatives in previous studies has been omitted because the nmr spectrum is such a complicated band of absorptions that even 220 MHz plus 100-MHz nmr spectra combined with spin-decoupling analyses have not permitted complete proton assignments.[3] This paper describes the successful application of shift reagents,[4] combined (in part) with spin-decoupling techniques, to the precise determination of the position of deuterium in so-labeled nortricyclyl alcohol samples. Thus the stereochemistry of the processes described above can be determined whenever significant amounts of nortricyclyl derivatives are obtained that can be converted into nortricyclyl alcohol without skeletal rearrangements.

The addition of acetic acid-*O*-d_1, using 0.018 *M* sulfuric acid catalyst, to norbornadiene (**1**) was carried out to afford the labeled products shown in Scheme I; nomenclature, analysis, and structure determination of the **2a**/**2b** (55:45 in this work) and the **2**/**3** (20:80 in this work) ratios have been described before.[1d-g] The **3a**/**3b** ratio is the focus of much of the remaining discussion. Mass spectroscopic analysis[1g] of the total

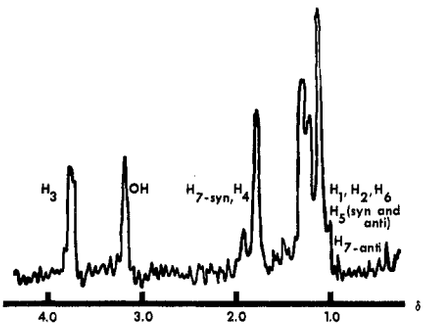
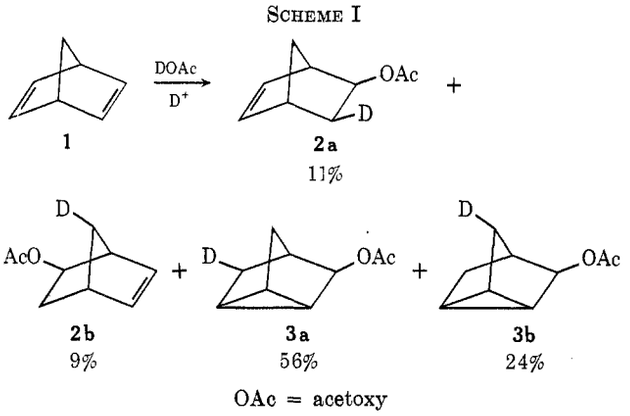


Figure 1.—60-MHz nmr spectrum of **4** in 0.5 ml of CCl_4.

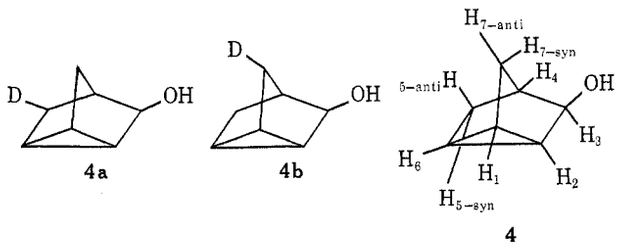
SCHEME I



OAc = acetoxy

deuterium content in the product **2a** plus **2b** acetates (77%) indicated that 77% of the sample was deuterated; this agreed within experimental error (*ca.* ±1%) with the deuterium content of the **3a**–**3b** sample measured mass spectroscopically, and both figures corresponded well to the total deuterium content in the product nortricyclyl acetate as determined by nmr (79%, see below). The data in Scheme I represent the spread of isomers within the *labeled* samples only (see below).

In view of the fact that alcohols respond more to shift reagents' effects than do acetates,[5] the **3a**/**3b** mixture was converted (Na/CH_3OH) into the corresponding **4a**/**4b** mixture. The nmr spectrum of Figure 1 allows assignment of only H_3 (α to OH[6]) and the $H_4/H_{7\text{-syn}}$ pair (β to OH[6]). The signal for H_2 is expected to be further upfield since it is a cyclopropyl proton[7] and is least proximate to the OH group of the three β protons. The remaining protons are assigned



(1) (a) S. Winstein and M. Shatavsky, *Chem. Ind. (London)*, 56 (1956); (b) S. J. Cristol, *et al.*, *J. Amer. Chem. Soc.*, **84**, 3918 (1962); (c) E. Vogelfanger, Ph.D. Thesis, UCLA, 1963; (d) S. J. Cristol, *et al.*, *J. Org. Chem.*, **31**, 2719 (1966); (e) *ibid.*, **31**, 2722 (1966); (f) *ibid.*, **31**, 2733 (1966); (g) *ibid.*, **31**, 2738 (1966); (h) T. C. Morrill and B. E. Greenwald, *ibid.*, **36**, 2769 (1971).

(2) S. J. Cristol, *et al.*, *J. Amer. Chem. Soc.*, **88**, 3087 (1966).

(3) G. Gray and W. Jackson, *ibid.*, **91**, 6205 (1969).

(4) R. Rondeau and R. Sievers, *ibid.*, **93**, 1522 (1971).

(5) J. K. M. Sanders and D. H. Williams, *ibid.*, **93**, 641 (1971).

(6) R. Silverstein and S. Bassler, "Spectrometric Identification of Organic Compounds," Wiley, New York, N. Y., 1967, p 137.

(7) L. M. Jackman and S. Sternhell, "Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press, Elmsford, N. Y., 1969, p 98.

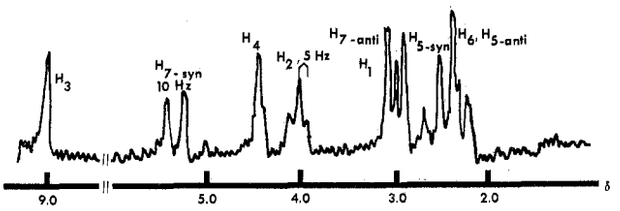


Figure 2.—60-MHz nmr spectrum of 70 mg of **4** in 0.5 ml CCl_4 containing 58 mg of Eu(fod)$_3$.

to the upfield band. Structure **4** is numbered by the method of Paasivirta.[8,9]

Treatment of the preceding **4** sample with Eu(fod)$_3$[4] resulted in the spectrum of Figure 2.[8] Only vicinal cyclopropyl (*ca.* 5 Hz) and geminal (*ca.* 10 Hz) coupling are considered significant herein.[8] Thus the δ 5.3 signal of Figure 2 is assumed to be $H_{7\text{-syn}}$ and $H_{7\text{-syn}}$ is geminally coupled to $H_{7\text{-anti}}$ which gives rise to outer pair of lines at *ca.* δ 2.8.[8] This is confirmed by the spin-decoupling experiment of Figure 3; irradiation at $H_{7\text{-syn}}$ collapses the doublet of $H_{7\text{-anti}}$ onto the center line of the H_1 triplet. All assignments in Figure 2 are consistent with very similar work on **4** using Eu(DPM)$_3$[9] which have been described in detail.[8,10]

When the (labeled) **4a**/**4b** alcohol mixture was subjected to shift reagent nmr analysis, Figure 4 was obtained. The intensity of the $H_{7\text{-anti}}$–H_4 signal decreases by 24% of one proton (referenced internally to, *e.g.*, H_4 as a one proton absorption). That this is due to deuterium incorporation at $H_{7\text{-anti}}$ is consistent with (a) the decrease in intensity being associated with the outer lines (compare Figure 4 to Figure 2), (b) the $H_{7\text{-syn}}$ signal (Figure 4) has lost much of its doublet character (loss of substantial geminal coupling constant magnitude), and (c) expectations consistent with addition mechanisms involving diene **1**.[1]

A decrease in intensity of the H_5 (syn and anti)–H_6 proton region is also noted in comparing Figures 4 and 2. The more downfield pair of lines has been assigned to $H_{5\text{-syn}}$.[8,10] That the decrease in intensity here is due to deuterium incorporation at $H_{5\text{-anti}}$ is substantiated by (1) a decrease in the H_6–$H_{5\text{-anti}}$ to $H_{5\text{-syn}}$ intensity from *ca* 2:1 to *ca.* 1.5:1 in going from Figure 2 to 4, (2) the substantial loss of geminal coupling in the same Figure sequence for $H_{5\text{-syn}}$, and (3) mechanistic expectations.[1] Thus of the total nortricyclyl acetates (as determined by alcohols), 55% are labeled as in **3a** and 24% as in **3b** with 21% unlabeled; *i.e.*, the **3a**/**3b** ratio is 70:30, and, since the percentage of product that is nortricyclyl skeleton is 80, 80% of 70 or 56% of all deuterated product is **3a** and (30)(80) = 24% is **3b** (see Scheme I).

A similar study utilizing Pr(fod)$_3$[4] was carried out; this study indicated a labeled **4** isomer partition of 55/29 but was less conclusive regarding the structural identity of the isomers than was the Eu study.

Observation of a nonunity **3a**/**3b** ratio precludes any discrete, symmetrical (or virtually symmetrical) cations, *e.g.*, **5** or **6**, as being the sole product determining

(8) A very similar nmr spectrum for **4** in the presence of Eu(DPM)$_3$[5] has been reported;[6] their results and ours for Eu(fod)$_3$ (Figure 2) are essentially identical. In addition, the same work[9] yields the relative sensitivities of the protons in **4** to shift reagent as $H_3 > H_{7\text{-syn}} > H_2 \sim H_4 > H_{7\text{-anti}} \sim H_1 > H_6 \sim H_{5\text{-syn}} \sim H_{5\text{-anti}}$.

(9) J. Paasivirta, *Suom. Kemistilehti B*, **44**, 135 (1971).

(10) J. Paasivirta, *ibid.*, **42**, 37 (1969).

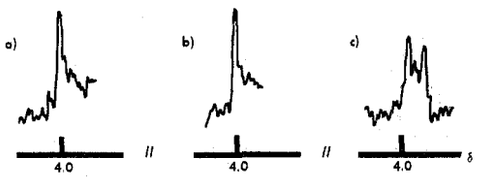


Figure 3.—Spin-decoupling study: 60-MHz nmr spectra of the δ 3.9 signal of **4** (δ 2.9 in Figure 2), signal (H_1 and $H_{7\text{-anti}}$) in 0.5 ml of CCl_4 containing 47 mg of Eu(fod)$_3$. (a) Irradiated at δ 7.0 ($H_{7\text{-syn}}$ signal); (b) repeat of a; (c) nonirradiated.

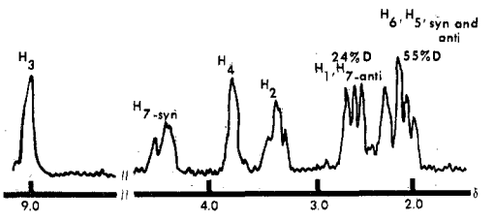
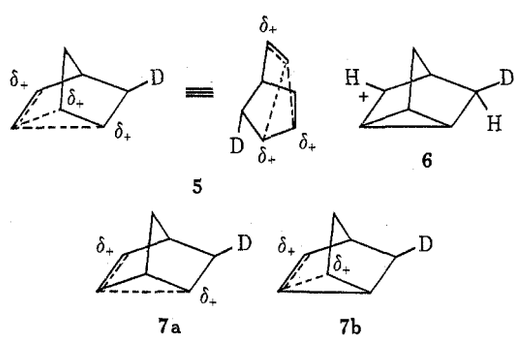


Figure 4.—Deuterium-labeled (see text) **4** (*ca.* 70 mg) plus 96 mg of Eu(fod)$_3$ in 0.5 ml of CCl_4.

intermediates. Proposing reaction pathways involving symmetrical cations and cis-concerted reactions[11] does not have direct application here. The results cannot be totally rationalized in terms of an equilibration between ions **7a** and **7b**; in either very rapid equilibration



or equilibration at a rate comparable to cation capture (steady state applied to **7b** in **1** → **7a** ⇌ **7b**, with **7a** giving **2a** and **3a** only and **7b** giving **2b** and **3b** only), the ratio of **2a**/**3a** would be predicted to be equal to the **2b**/**3b** ratio. This is expected since the rate of formation of **2a** from **7a** should be equal to the rate of formation of **2b** from **7b** by symmetry and the rate of formation of **3a** from **7a** should be equal to the rate of formation of **3b** from **7b**. Thus, the **2a**/**3a** and **2b**/**3b** ratios should also be identical (unity, if the **7a**,**7b** equilibrium is *rapidly* established) and governed by the rapid or moderate **7a**/**7b** partition. Concerted 1,5 addition must be discounted since this would be expected to give rise to labeled acetate **8** and there is no evidence for such a product.

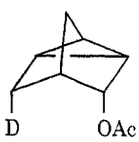
The importance of ion pairing in acetic acid solvent cationic reactions is clear; the existence of two ion-pair intermediates has been required to explain acetolysis results.[12] An important ion pair might be expected to be represented by **9**. The proximity of the gegen ion is expected[12,13] to cause the product ratios (**2a**/**2b**, **3a**/**3b**) to be other than 50:50. Ion **9**, how-

(11) S. J. Cristol and J. M. Sullivan, *J. Amer. Chem. Soc.*, **93**, 1967 (1971).

(12) E. L. Allred and S. Winstein, *ibid.*, **89**, 4012 (1967).

(13) J. R. Hazen, *Tetrahedron Lett.*, 1897 (1969).

ever, would be expected to cause the **2a/2b** ratio to depart from 50:50 to a greater degree than would the **3a/3b** ratio. Since this is not observed, ion pair **9** (or



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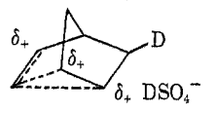

9

the ion pairs corresponding to rapidly equilibrating **7a** and **7b**) cannot be the predominant product determining intermediate(s).

Since no single one of the preceding limiting cases applies, the reaction must involve a complex set of ionic intermediates with different, ion paired, unsymmetrical precursors to each of the **2a/2b** and **3a/3b** pairs. In addition, the precursor (or precursors) to the **3a/3b** pair must cause less symmetrical product labeling than caused by the precursor(s) to **2a/2b**.

Experimental Section

Nuclear magnetic resonance spectra were determined on a Hitachi Perkin-Elmer R-20 (60 MHz) spectrometer with tetramethylsilane as a reference standard (δ 0.00 ppm). Mass spectral analyses were determined on a CEC-104 mass spectrometer under conditions previously reported.[1g] Shift reagents were obtained commercially from Norell Chemical Co., Inc. The addition of labeled acetic acid to diene **1** was carried out, and the products (**2a**, **2b**, **3**) were analyzed using conditions previously reported.[1e]

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A Facile Rearrangement of a Carbohydrate Cyclic Carbonate

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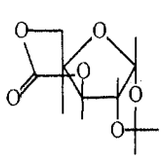
Five-membered ring carbonates are well known in the carbohydrate series and are readily prepared by treating sugars containing cis vicinal hydroxyl groups with difunctional carbonyl derivatives such as phosgene, diphenyl carbonate, and alkyl chloroformates.[1] In marked contrast to the large number of known sugar-derived ethylene carbonates, little has been reported on corresponding six-membered cyclic carbonates. In instances where alternate paths exist for five- and six-membered ring formation in the same molecule, the ethylene carbonate is formed exclusively; *e.g.*, with methyl α-D-galactopyranoside and benzyl chloroformate the only product obtained was methyl 2,6-di-*O*-benzyloxycarbonyl-α-D-galactoside-3,4-carbonate.[2] In the absence of cis vicinal hydroxyl groups an acyclic derivative usually results; *e.g.*, methyl α-D-glucopyranoside on similar treatment yields its tetra-*O*-benzyloxycarbonyl derivative.[2] Presumably the formation of a trimethylene carbonate is precluded because of additional bond strain required for forming a six-membered ring containing an sp^2 hybridized carbon atom.[3] The first six-membered ring carbonate known in the sugar series is 1,2-*O*-isopropylidene-α-D-xylofuranose-3,5-carbonate (**1**) prepared by Haworth, *et al.*, by treating



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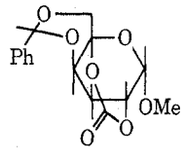

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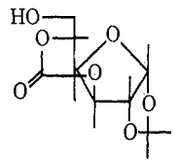

3

D-xylose with phosgene in acetone.[4] Compound **1** exhibited unusual reactivity for a sugar carbonate in that it underwent facile methanolysis at room temperature. The ease of ring opening suggested that cis-fused **1** might contain at least as much ring strain as the recently prepared trans-fused five-membered ring glucose carbonate **2**.[5,6] In support of our supposition, methyl 2,3-di-*O*-methyl-α-D-glucopyranoside-4,6-carbonate was recently prepared and shown to undergo ring opening at twice the rate of **2**.[7]

In accord with the seeming instability of six-membered ring sugar carbonates we were not able to prepare the desired 4,6-carbonate derivatives of methyl α-D-gluco- or galactopyranosides by direct reaction with phosgene in CH_2Cl_2–pyridine at −70°. In both cases only polymeric carbonates were obtained. The formation of polymer was surprising to us, since similar reaction conditions led to high yield of monomeric cyclic carbonates from 1,3-propanediol and both *cis*- and *trans*-2-hydroxymethylcyclohexanols. The possibility that a sugar 4,6-carbonate may have been first formed and then reacted intermolecularly to form polymer seemed unlikely because no reaction could be observed between methyl α-D-glucopyranoside and *cis*-2-hydroxymethylcyclohexanol carbonate in pyridine at 25° after 16 hr.

In view of the unusual behavior of the methyl glycosides toward phosgene, we decided to investigate the stability and fate of an intact, preformed six-membered carbonate ring in a sugar molecule also containing a free hydroxyl group. The compound chosen for study was 1,2-*O*-isopropylidene-α-D-glucofuranose-3,5-carbonate (**3**).

Results and Discussion

To achieve the synthesis of **3** we sought a function which could (1) be unequivocally attached to C-3 of a

(1) L. Hough, J. E. Priddle, and R. S. Theobald, *Advan. Carbohyd. Chem.*, **15**, 91 (1960).

(2) L. Hough and J. E. Priddle, *Chem. Ind. (London)*, 1600 (1959).

(3) H. C. Brown, J. H. Brewster, and H. Shechter, *J. Amer. Chem. Soc.*, **76**, 467 (1954).

(4) W. N. Haworth, C. R. Porter, and A. C. Waine, *Recl. Trav. Chim. Pays-Bas*, **57**, 541 (1938).

(5) W. M. Doane, B. S. Shasha, E. I. Stout, C. R. Russell, and C. E. Rist, *Carbohyd. Res.*, **4**, 445 (1967).

(6) W. M. Doane, B. S. Shasha, E. I. Stout, and C. R. Russell, *ibid.*, **11**, 321 (1969).

(7) D. Trimnell, W. M. Doane, C. R. Russell, and C. E. Rist, *ibid.*, **18**, 301 (1970).