Table III. SCF Ab Initio Calculation on the (Cl^- + Cation 1) System, with Cl^- at Position A or C

	Energy, hartree		A − C difference, kcal mol^{-1}
	Position A	Position C	
Potential energy (−eV)	−0.187	−0.180	− 4.4
Coulomb + exchange energy[a]	−0.072	−0.028	−27.6
Exchange energy[b]	0.115	0.152	
SCF interaction energy[c]	−0.230	−0.169	−38.3
Polarization and charge-transfer effects[d]	−0.158	−0.141	

[a] First-order interaction energy defined as E (first iteration) $- E_{cation} - E_{Cl^-}$, with $E_{cation\ 1} = -153.606\ 838$ hartrees and $E_{Cl^-} = -458.922\ 869$ hartrees.[19] [b] Difference between (coulomb + exchange energy) and potential energy. [c] Defined as $E_{R+Cl^-}{}^{SCF} - E_{cation} - E_{Cl^-}$. In addition to the first-order energy, this includes polarization and charge-transfer effects. [d] Difference between SCF interaction energy and (coulomb + exchange energy).

We are left with the question of why in sulfolane our HCl addition occurs in equal amounts at the α and β positions, instead of predominantly at C_α. To answer this question we first remark that our calculations are "gas phase calculations." For solutions their predictive value is restricted at best to weakly solvating solvents. Furthermore, the predictive value of electrostatic arguments such as we use is restricted to reactions with an early transition state.

To a certain extent both conditions are met in our chloride ion addition reaction in 95% aqueous ethanol. Water and alcohol are relatively hard solvents.[20] These hard solvents have only a minor solvating effect on our cations.[21] An early transition state is plausible because the chloride addition is a fast step, subsequent to the slow proton transfer.

Sulfolane will have an appreciably stronger solvating effect on the cation,[22] and our quantum chemical predictions are less applicable. For example, the propargylic position (C_α) could be the more strongly solvated position and therefore more screened for attack by chloride; the ratio of propargylic to allenylic attack will be lower than predicted. Moreover, the chloride attack might be slower in sulfolane than in aqueous alcohol and correspondingly the transition state somewhat more product-like. Probably, the energies of our propargylic and allenylic products are approximately equal. For example, from calculations on $H_2C{=}C{=}CHCl$ and $HC{\equiv}C{-}CH_2Cl$,[23] we find an energy difference of only 0.2 kcal/mol, the former molecule in fact being the slightly more stable one. Thus, if the transition state is more product-like, the product ratio will shift to 1:1.

Finally, we return to the literature data on solvolysis reactions of allenylic and propargylic halides and tosylates. These reactions are of the S_N1 type; their slow step can be considered to be the reverse of our Cl^--addition step. Since, as we just mentioned, the halides have approximately equal energies, our theoretical predictions are in line with a more rapid solvolysis of propargylic than of allenylic halides. As for Cl^- addition, the condition is that the solvent must have a low solvating power for cations. All these solvolysis reactions were performed in relatively hard aqueous solutions, and indeed all follow the predicted behavior of a faster rate for the propargylic compared with the allenylic isomer.[6] In the second step of these solvolysis reactions, a solvent molecule attacks either the α or the β position. Our calculations predict preferred attack at the α position, and indeed, experimentally, propargylic products are preferentially formed, except when attack at C_α is sterically highly hindered. Actually, in these systems, the ratio of propargylic to allenylic products is even higher than in our pentatriene system because of the presence of different substituents and the use of more aqueous solvents.

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The Spiropentyl to 3-Methylenecyclobutyl Cation Rearrangement Avoids CH⁺–Trimethylenemethane or the 1-Bicyclo[1.1.1]pentyl Cation

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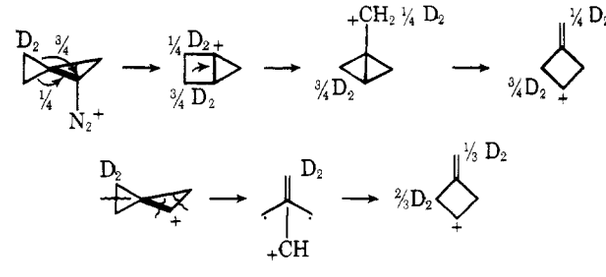
In view of successful efforts to characterize CH^+ complexes of $4n$ cyclic π systems and homologues,[1] the reported deuterium distribution in the 3-methylenecyclobutanol product from deamination of *anti*-4,4-dideuteriospiropentylamine[2] occasioned speculation in our laboratory that CH^+–trimethylenemethane (CH^+–TMM) might be involved. Applequist



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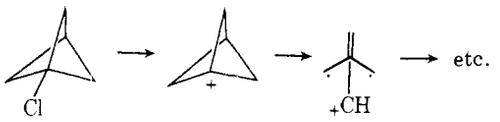
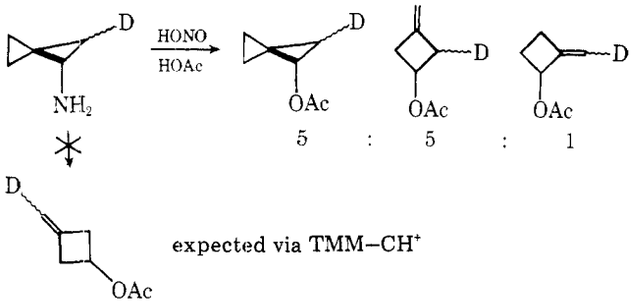
suggested that preferential migration of the anti carbon was involved to give sequentially the 1-bicyclo[2.1.0]pentyl cation, the 1-bicyclo[1.1.0]butylcarbinyl cation, and the 3-methylenecyclobutyl cation, but this was prior to Hoffmann's prediction of stabilization of CH^+–$4n$ π systems.[3] Moreover, Wiberg's[4] observations that 1-bicyclo[1.1.1]pentyl chloride has enormous solvolytic reactivity to 3-methylenecyclobutyl product might also be interpreted in terms of high stability of CH^+–TMM, although relief of ring strain was suggested as



the important factor as well as the possibility of cross-ring interaction with the opposite bridgehead.

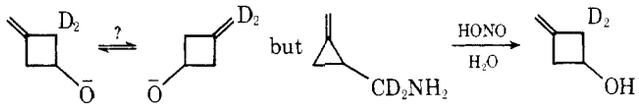
Results and Discussion

In order to distinguish between the Applequist suggestion and the more interesting CH^+–TMM complex, 2-deuteriospiropentylamine was prepared and deaminated in acetic acid. Three products were obtained; these were spiropentyl acetate, 3-methylcyclobutyl acetate, and 2-methylcyclobutyl acetate in ratio 5:5:1. The latter two products (as alcohols) were observed by Applequist in the aqueous deamination; presumably, spiropentanol does not survive the aqueous conditions. The ^2H NMR of the VPC purified reaction mixture revealed the presence of 2-deuteriospiropentyl acetate, 2-deuterio-3-methylenecyclobutyl acetate, and 2-deuteriomethylenecyclobutyl acetate in a 5:5:1 ratio with little, if any, 3-deuteriomethylenecyclobutyl acetate being formed. Thus, substantial incursion of CH^+–TMM (or the 1-bicyclo[1.1.1]pentyl cation) as an intermediate is ruled out, verifying the Applequist proposal of unsymmetrical involvement of C_4 and C_5 in the spiropentylamine deamination.



In view of the large number of isomers that have been sources of the 3-methylenecyclobutyl cation, we here summarize these pathways (Scheme I) indicating those that are ruled out by labeling studies or product distributions. Classical structures are drawn where no experimental distinction between classical or nonclassical behavior has been made.

Concern that Applequist's label distribution could be due to a reversible 1,3-sigmatropic shift in the conjugate base of 3-methylenecyclobutanol, a reaction which may be quite facile by comparison with Evans' Cope rearrangements,[6] does not appear to be the case since Kato isolated unscrambled 2,2-dideuterio-3-methylenecyclobutanol from the deamination of α,α-dideuterio-α-methylenecyclopropylcarbinylamine[5] using workup conditions comparable in acidity to those utilized by Applequist.



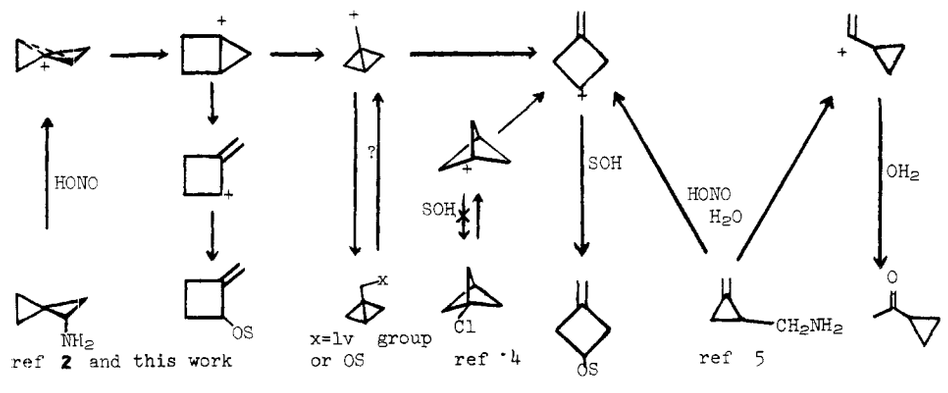
Finally, the isolation of spiropentyl acetate in the spiropentylamine deamination represents one of the few examples of nucleophilic trapping of a cyclopropyl cation which is electronically stabilized but not sterically prevented from ring opening. In the foremost example the 1-cyclopropylcyclopropyl cation is generated by solvolysis[7] or rearrangement;[8] the spiropentyl cation as studied here is generated by acidic deamination.

Experimental Section[10]

2-Deuteriospiropentanecarboxylic acid was prepared from methyl *cis*-β-deuterioacrylate and cyclopropyldiphenylsulfonium fluoroborate by Trost's method.[11] Methyl *cis*-β-deuterioacrylate was prepared by Hill's procedure[12] from methyl 3-deuteriopropiolate, which was prepared from decarboxylation of acetylenedicarboxylic acid monopotassium salt in deuterium oxide, containing 88% of one deuterium as determined by ^1H NMR: ^1H NMR of acid, δ 0.96 (s, 4 H), 1.3 (dd, 1 H, J = 4, 8 Hz), 1.5 (t, 1 H, J = 4 Hz), 1.89 (dd, 1 H, J = 4, 8 Hz), 10 (br s, 1 H). The 2-deuterio material showed a diminution in both upfield single proton resonances.

2-Deuteriospiropentylamine Hydrochloride. 2-Deuteriospiropentanecarboxylic acid azide was prepared by Weinstock's procedure.[13] Thus, rearrangement of 2-deuteriospiropentanecarboxylic acid azide to the isocyanate was effected by heating it in tetrahydrofuran to 110 °C in a sealed tube. After 3 h at that temperature, the tube was cooled and opened, and its contents poured into 20% hydrochloric acid. After stirring under nitrogen, the organic solvent was removed under aspirator vacuum. The acidic aqueous solution was then washed with ether, made basic with aqueous potassium hydroxide, and extracted with pentane. The pentane solution was dried over magnesium sulfate; then gaseous hydrogen chloride was passed over the dry pentane solution, and a white cloud formed immediately. Removal of pentane in vacuo gave 2-deuteriospiropentylamine hydrochloride as a white powder (45% yield from the acid). Spiropentylamine and its acid chloride prepared by this method have the following NMR characteristics: spiropentylamine hydrochloride (in D_2O), δ (relative to H_2O) −1.91 (dd, 1 H, J = 6, 3 Hz), −3.46 (t, 1 H, J = 6 Hz), −3.64 (dd, 1 H, J = 6, 3 Hz), −3.82 (s, 4 H); spiropentylamine (in CCl_4), δ (relative to Me_4Si) 0.55 (t, 1 H, J = 4 Hz), 0.73 (d,

Scheme I



4 H, J = 7 Hz), 0.91 (dd, 1 H, J = 4, 6 Hz), 1.1 (br s, 2 H), 2.41 (dd, 1 H, J = 4, 6 Hz).

Deamination of 2-Deuteriospiropentylamine Hydrochloride. 2-Deuteriospiropentylamine hydrochloride (0.3 g, 5.2 mmol) was dissolved in 10 mL of glacial acetic acid and solid sodium nitrite (0.36 g, 5.2 mmol) was added in small portions over a 3-h period. After standing overnight, an additional 0.36 g of sodium nitrite was added over a 6-h period. The reaction mixture was allowed to stand 2 h after addition of sodium nitrite was complete; then 45 mL of a 10% sodium hydroxide solution was added cautiously. The still acidic reaction mixture was extracted four times with a total of 75 mL of pentane. The combined organic extracts were washed with a 10% sodium bicarbonate solution until the washings were basic. The solution was then washed once with saturated brine and dried over magnesium sulfate. Pentane was removed through a Vigreux column till approximately 1 mL of solution was left. The residue was analyzed by an SE-30 column, revealing a single peak which was collected: ^{2}H NMR (in $CDCl_3$) δ (relative to Me_4Si) 1.25 (two peaks of equal intensity, 5 D), 3.05 (two peaks of equal intensity, 5 D), 5.10 (two peaks of equal intensity, 1 D). In a separate run, spiropentylamine hydrochloride was deaminated in glacial acetic acid. The ^{1}H NMR spectrum [δ (CCl_4) 0.75 (s), 1.0 (m), 1.13 (t), 1.95 (3 s), 2.2~2.5 (br m), 2.75 (br m), 2.95 (br m), 4.1 (dd), 4.82 (p), 4.90 (m), 5.35 (m)] of the single peak on the SE-30 column indicated three acetates. On a 200 °C DBTCP capillary column a 5:5:1 mixture of three compounds was observed. On a UCON preparative column two peaks in a ~1:1 ratio were observed and collected. One peak was spiropentyl acetate; δ 0.79 (m, 3 H), 1.0 (m, 2 H), 1.14 (t, 1 H, J = 6 Hz), 1.96 (s, 3 H), 4.1 (d of d, 1 H, J = 6, 2 Hz).

The second peak was a mixture of 2- and 3-methylenecyclobutyl acetate in a 1:5 ratio: ^{1}H NMR of mixture, δ 1.97 (s, 3 H), 2.0 (s, 0.6 H), 2.40 (v br m, 0.8 H), 2.75 (br m, 2 H), 2.95 (br m, 2H), 4.80 (p, 2 H, J = Hz), 4.9 (m, 1.4 H), 5.35 (m, 0.2 H).

Acknowledgment. We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the National Science Foundation for partial support of this work.

Registry No.—2-Deuteriospiropentanecarboxylic acid, 64345-60-4; 2-deuteriospiropentanecarboxylic acid azide, 64345-61-5; 2-deuteriospiropentane isocyanate, 64345-62-6; 2-deuteriospiropentylamine hydrochloride, 64345-63-7; 2-deuteriospiropentylamine, 64345-64-8; 2-deuteriospiropentyl acetate, 64345-65-9; 2-deuteriomethylenecyclobutyl acetate, 64345-66-0; 2-deuterio-3-methylenecyclobutyl acetate, 64345-67-1.

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(10) ^{1}H NMR spectra were determined on a Varian HR-220 MHz spectrometer operated in the CW mode; ^{2}H NMR spectra were determined on the same spectrometer operated in the FT mode at 33.77 MHz—a 0.2-ppm downfield shift of deuterium resonances relative to proton resonances were observed. ^{2}H NMR line widths were on the order of 0.06 ppm. Gas chromatography was performed on Varian aerograph A-90 P and 1220-2 series chromatographs using the following columns: $^3/_8$ in. × 20 ft SE-30; $^1/_4$ in. × 20 ft UCON 50-HB-2000; and a 200 in. × 0.01 in. i.d. di-*n*-butyl tetrachlorophthalate (DBTCP) capillary column.
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Mass Spectrometry of Pyrimidine Anhydronucleosides

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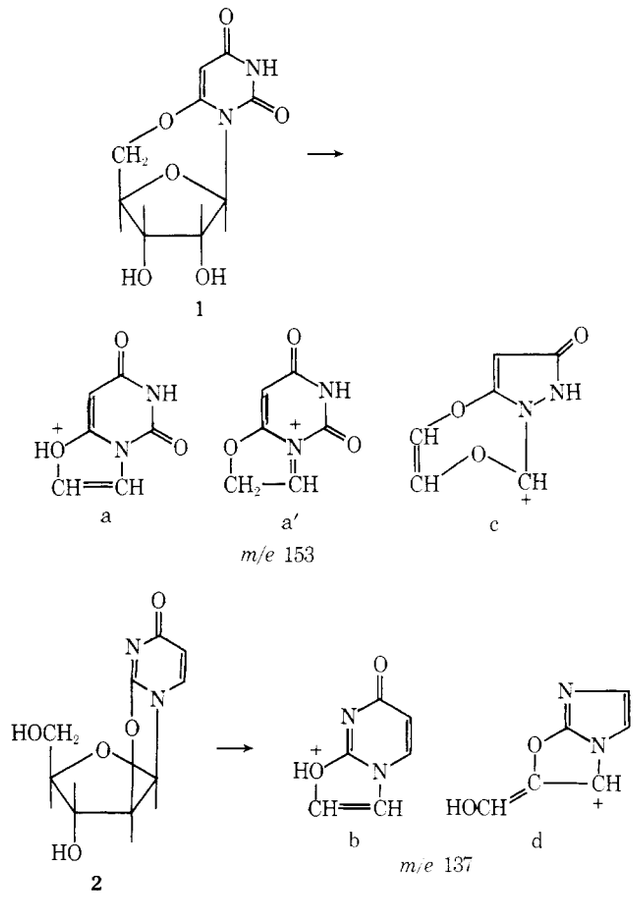
Anhydronucleosides often play an important role in the synthesis of nucleosides,[2,3] and their mass spectra have been shown to be useful for structural characterization (e.g., ref 4–10). The fragmentation reactions of anhydronucleosides are somewhat different from those of conventional nucleosides[11,12] in that conformational rigidity prevents base–sugar hydroxyl interactions that usually generate the primary reaction paths[13] and because of increased complexity of the system due to the anhydro linkage. In the mass spectra of O^6,5′-anhydropyrimidine nucleosides, a decomposition sequence has been proposed in which CO is first eliminated from the molecular ion and in which additional fragmentation of the base proceeds during subsequent reaction steps.[5] The latter rationale contrasts with the general behavior of normal nucleosides in which the heterocyclic base remains intact in initial reaction steps and decomposes only at the stage at which the free base has been generated. However, because initial reaction steps involve loss of neutral species which contain C, H and O but not N, the interpretation of both low- and high-resolution mass spectra is ambiguous, and fragmentation could proceed from either the base or sugar moieties.

The leading examples which clearly demonstrate the principle involved are the intermediate fragment ions m/e 153 ($C_6H_5N_2O_3$) from O^6,5′-anhydrouridine (**1**) and m/e 137 ($C_6H_5N_2O_2$) from O^2,2′-anhydrouridine (**2**). Originally de-



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