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Stereomutation of 1-Hydroxyallyl Cations. Thermal and Photochemical Isomerizations of Protonated Enones[1]

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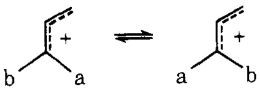
Abstract: Protonated *trans*-crotonaldehyde (**2**), *trans*-crotonic acid (**4**), *trans*-tiglaldehyde (**6**), *trans*-pent-3-en-2-one (**8**), and *trans*-3-methylpent-3-en-2-one (**10**), prepared by protonation of the analogous enones or acid in FSO_3H, isomerized to give the corresponding cis isomers **11, 12, 13, 14,** and **15**, respectively, when irradiated at low temperatures. A photostationary state was set up between the cis and trans isomers of these hydroxyallyl cations, which in the case of the **2**/**11** and **4**/**12** systems, could be approached by starting with either the cis or trans forms. The cis isomers were all thermally unstable and quantitatively reverted to the corresponding trans isomers on heating. The rate constants for these stereomutations have been obtained in FSO_3H and FSO_3H/SbF_5 (4:1) media at +50 °C. In particular it was found that the rate constants for the isomerization of **11** → **2** and **13** → **6** were decreased by a factor of 10^2 on the addition of SbF_5 to FSO_3H, while a comparable change in medium for the isomerizations of **14** → **8** and **15** → **10** enhanced their rates of isomerization by a small amount. No deuterium incorporation could be detected when these photochemical or thermal isomerizations were carried out in FSO_3D or FSO_3D/SbF_5 (4:1). It is suggested that in FSO_3H the thermal isomerizations of **11** and **13** take place by a mechanism involving addition of a nucleophile to C(3) of the allyl cations, rotation and subsequent reionization. However, it would appear that the thermal stereomutation of **12, 14,** and **15** in both FSO_3H and FSO_3H/SbF_5 and the stereomutation of **11** and **13** in FSO_3H/SbF_5 all proceed by formation and subsequent ring opening of a protonated oxete. Possible reasons for the operation of these two pathways and the implications of this work to the parent allyl cations are discussed.

Allyl cations were one of the first classes of carbonium ions to be characterized as long-lived entities, and it is not surprising, therefore, that many studies of their properties have been reported.[2] While the initial thrust of these reports has been largely directed toward their characterization, more recently there has been considerable experimental[3-8] and theoretical[9-11] interest in the stereomutation of allyl cations (eq 1).



(1)

These cis/trans isomerization reactions, which have been studied very largely with alkyl-substituted cations, typically take place with fairly low activation energies ($\Delta F^{\ddagger} \sim 12$-25 kcal/mol). Some four different mechanisms have been con-

Table I. ^1H Chemical Shifts of Hydroxyallyl Cations

	Chemical shifts (ppm)[a]						Coupling constants (Hz)		
Compd	H_1	$(CH_3)_1$	H_2	$(CH_3)_2$	H_3	$(CH_3)_3$	$J_{1,2}$	$J_{2,3}$	J_{3,CH_3}
2	9.59 d		7.07 m		8.61 dq	2.67 d	10	16	8
11	9.08 d		7.08 m		8.72 dq	2.59 d	10	11	7
6	8.97 d			2.07	8.45 q	2.52 d			7
13	9.57 d			2.12	8.42 q	2.55 d			8
8		2.94	6.88 m		8.55 dq	2.48 d		16	8
14		2.94	6.92 m		8.02 dq	2.62 d		11	7
10		3.04		2.12	8.49 q	2.52 d			7
15		3.04		2.26	7.94 q	2.57 d			8
4			6.30 m		8.06 dq	2.19 d		15	7
12			6.26 m		7.67 dq	2.43 d		11	7

[a] In ppm relative to CH_2Cl_2 (δ = 5.30 ppm) as internal standard; d = doublet, q = quartet, dq = doublet of quartets, m = multiplet.

Table II. ^{13}C Chemical Shifts of 1-Hydroxyallyl Cations[a]

		Chemical shift (ppm)					
Compd	Temp, °C	C_1	C_2	C_3	C_1Me	C_2Me	C_3Me
2	32	204.9	129.4	198.6			23.1
11	−30	201.8	126.6	192.8			19.4
6	−30	204.9	139.7	196.2		7.3[b]	20.3[b]
13	−30	199.5	135.9	191.9		13.8	18.3
8	−60	218.8	128.4	184.6	22.4		22.4
14	−60	218.0	124.0	180.4	21.6[c]		20.4[c]
10	32	216.7	136.4	176.6	22.1[c]	8.9	18.1[c]
4	32	181.3	114.5	172.0			19.8
12	32	181.7	112.6	173.2			18.3

[a] In FSO_3H using Me_2SO-d_6 as external (capillary) lock and reference (40.6 ppm) at 32 °C and acetone-d_6 as external (capillary),lock and reference (29.2 ppm) at low temperatures. [b] Assignment confirmed by selective decoupling. [c] Assignment may be reversed.

sidered for these isomerizations, and on the basis of results obtained with the dimethyl-[5] and tetramethylallyl[6] cations, it has been suggested that the stereomutation involves a "simple" bond rotation. This proposal seems to have been generally accepted for other systems although experimental evidence is lacking.

Despite the large amount of work on alkyl-substituted allyl cations, relatively little is known about the effect of the introduction of more strongly electron-donating groups upon this stereomutation. Cis/trans isomerizations of the 1,1,3,3-tetramethoxyallyl cation[7] and certain halogen-substituted systems[4] have been reported. As a result of theoretical calculations, Radom, Pople, and Schleyer have predicted that electron-donating groups on C(2) of an allyl cation should profoundly alter the preferred isomerization pathway.[10] Very recently Brouwer[12a] has reported that protonated *cis*-pent-3-en-2-one rearranges to give the corresponding trans isomer at 30 °C.[12a]

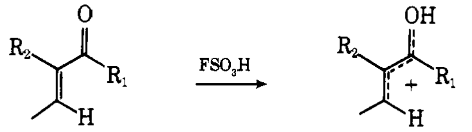
Two methods have been used to measure the rates of rotation of substituted allyl cations, both of which utilize NMR techniques. In the first of these, the slow isomerization of a thermodynamically less stable isomer to a more stable form is monitored over a period of time. For this method to work, the substituents a and b (eq 1) must be dissimilar and it must be possible to obtain the thermodynamically less stable isomer. Alternatively, the rate of stereomutation can be determined by a line shape analysis of the resonances attributable to the substituents on the termini of the allyl cation, under conditions where the two substituents are undergoing rapid exchange. This technique, which has been used solely with cations where a and b (eq 1) are the same, can only be applied when the rate of isomerization is fairly high. The rate of isomerization can be increased by raising the temperature of the sample; however, the onset of other reactions, e.g., sulfonation, fragmentation, etc., set a practical limit to the range of systems which can be studied by this method.

Of these two basic methods, only the former is readily amenable to use with the 1-hydroxyallyl cations,[6,12] albeit this must inevitably necessitate the preparation of the thermodynamically less stable isomers of these cations. The conventional route to such allyl cations would be to prepare, isolate, and protonate at low temperatures the appropriate cis enone. In view of the well-known photochemical cis/trans isomerizations of enones,[13] reactions which are thought to involve a π,π^* excited state, it seemed that a simple route to the desired protonated cis enones would be to irradiate a solution of the protonated trans enone. In this paper we show that such a photoisomerization does indeed occur and that the so formed protonated cis enones thermally rearrange back to the starting trans isomers by at least two different pathways.

Results

The cations **2**, **4**, **6**, **8**, and **10** were prepared by dissolving the corresponding enones in FSO_3H, FSO_3H/SbF_5, or 96% H_2SO_4 at low temperatures. The NMR spectra of these cations (Tables I and II) correspond fairly closely with those previously reported for **2**,[14,15] **4**,[16] and **6**.[15,17] The geometry of the C(2)C(3) bond of **2**, **4**, and **8** was clearly shown to be trans by the magnitude of the coupling constant between the two protons on this partial double bond, and in each case the geometry corresponds to that of the starting enone.[18] The stereochemistries of **6** and **10** are more difficult to deduce from their NMR spectra. The structures assigned are based upon the structures of the enone precursor, no stereomutation being expected upon protonation. The aldehyde **5** is commercially available and is known to have the trans configuration, while the structure of

9, prepared by the addition of methyllithium to tiglic acid, has been previously established.[19] Further evidence for these structural assignments will be presented later.



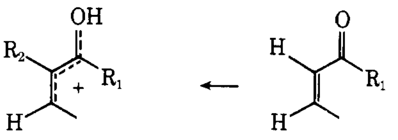
1, $R_1 = R_2 = H$
3, $R_1 = OH, R_2 = H$
5, $R_1 = H, R_2 = CH_3$
7, $R_1 = CH_3, R_2 = H$
9, $R_1 = R_2 = CH_3$

2, $R_1 = R_2 = H$
4, $R_1 = OH, R_2 = H$
6, $R_1 = H, R_2 = CH_3$
8, $R_1 = CH_3, R_2 = H$
10, $R_1 = R_2 = CH_3$

These hydroxyallyl cations were found to be thermally stable at fairly high temperatures. For example, at +80 °C, although a small amount of charring was evidenced by discoloration of the acid solutions, no change in their ^1H NMR spectra could be detected over considerable periods of time. No changes were observed in the ^1H NMR spectra of these cations as the samples were cooled. FSO_3H/SO_2ClF solutions of **6** and **8** were cooled to −90 °C and their ^1H NMR spectra carefully examined; however, no additional resonances over those given in Table I could be detected.

Compounds **1** and **7** were dissolved in FSO_3D and FSO_3D/SbF_5 to give **2D** and **8D**, respectively, in which a deuterium had been added to each carbonyl oxygen. No further deuterium incorporation could be detected when these acid solutions were kept at +50 °C for several hours.

Photoisomerization of 1-Hydroxyallyl Cations. The uv spectra of the protonated enones are given in Table III. As each cation exhibited a fairly intense absorption at ca. 250 nm, a low-pressure mercury lamp was used as a light source. FSO_3H solutions of cations **2, 4, 6, 8,** and **10** contained in quartz tubes were irradiated at low temperature, and the reactions were monitored by ^1H NMR. In each case, the formation of an isomer of the starting protonated enone was observed, and these photoproducts were identified as the corresponding cis isomers, **11–15**, on the basis of their NMR spectra (Tables I and II). The NMR spectra of the photoproducts are completely consistent with their assigned structures. In particular, the magnitude of the coupling constants between the two protons attached to the C(2)C(3) partial double bonds of **11, 12,** and **14** were indicative of the cis configuration of these two hydrogen atoms.



11, $R_1 = R_2 = H$
12, $R_1 = OH, R_2 = H$
13, $R_1 = H, R_2 = CH_3$
14, $R_1 = CH_3, R_2 = H$
15, $R_1 = R_2 = CH_3$

16, $R_1 = H$
17, $R_1 = OH$

Confirmation of these structural assignments was made by the synthesis of **11** and **12** by alternate, nonphotochemical routes. *cis*-Crotonic acid (**17**), prepared by the procedure of Hocking,[20] was protonated at low temperature to give **12**, which had an identical ^1H NMR spectrum with the material obtained photochemically. Similarly, *cis*-crotonaldehyde (**16**), prepared by CrO_3/pyridine oxidation of *cis*-but-2-en-1-ol, was protonated in FSO_3H at −78 °C to give predominantly **11**, with a small amount of **2** present.

On continued irradiation, a photostationary state was set up between the cis and trans isomers of these protonated enones, the composition of which is shown in Table IV. In the case of the **2,11**, and **4,12** cis/trans isomer pairs, a mixture of the same composition could be reached by starting the photoisomerization with either the cis or trans isomers. No other products or material loss could be detected by ^1H NMR during the course of these irradiations.

Table III. Uv Absorption Spectra of 1-Hydroxyallyl Cations

Compd	λ_{max}, nm	ϵ
2[a,b]	258	4.37×10^4
6	278	4.68×10^4
8	261	3.01×10^4
10[b]	276	1.62×10^4
4[a,b]	236	4.08×10^4
12	238	4.06×10^4

[a] Cf. M. W. Palmer and D. S. Urch, *J. Chem. Soc.*, 174 (1963). [b] Cf. R. I. Zalewski and G. E. Dunn, *Can. J. Chem.*, **46**, 2469 (1968).

Table IV. Composition of Photostationary States Obtained on Irradiation of 1-Hydroxyallyl Cations[a]

Cation pair		Composition	
Trans	Cis	Trans %	Cis %
2	**11**	46	54[b]
6	**13**	26	74
8	**14**	55	45
10	**15**	41	59
4	**12**	58	42[b,c]

[a] In FSO_3H at −78 °C using light λ 254 nm. Unless otherwise stated photostationary state only reached by irradiation of trans isomer. [b] Mixture of same composition reached by starting with either cis or trans isomers. [c] At 0 °C.

Solutions of **2D** and **8D** in FSO_3D gave **11D** and **14D**, respectively, on irradiation. No incorporation of deuterium, other than that on the carbonyl oxygen, could be detected in any of these cations.

Thermal Isomerizations. These protonated cis enones underwent a quantitative isomerization back to the corresponding trans isomers when the acid solutions were heated. No products other than the trans isomers could be detected by ^1H NMR at any time during these isomerizations. At completion of the reactions, it was not possible to detect any residual protonated cis enone.

The rate constants for these isomerizations were determined by heating the acid solutions of the appropriate cation in a constant temperature bath for known lengths of time, quenching the reaction by rapidly cooling the sample to −78 °C, and assaying the ratio of cis/trans isomers by ^1H NMR. The ^1H NMR spectra were obtained at a sufficiently low temperature such that further isomerization was not significant. In all cases, these rate determinations were carried out using the cis/trans mixtures obtained photochemically. However, with **11** and **12**, exactly the same results were obtained by starting with solutions of these cations obtained by direct protonation of **16** and **17**, respectively. The results of this study are given in Table V.

Antimony pentafluoride was added to FSO_3H solutions of **11, 13, 14,** or **15**, and the rate constants for isomerization of these cations to their corresponding trans isomers were determined as described above. It was found that in order to get reproducible rate constants, both the FSO_3H and SbF_5 had to be carefully purified. The results shown in Table V were all obtained in at least duplicate runs.

No deuterium incorporation could be detected by ^1H NMR

Table V. Rate Data for Isomerization of 1-Hydroxyallyl Cations

		FSO_3H		FSO_3H/SbF_5 (4:1)[b]	
Isomerization	Temp, °C	k, $s^{-1} \times 10^5$	$\Delta F^{\ddagger}$, kcal/mol	k, $s^{-1} \times 10^5$	$\Delta F^{\ddagger}$, kcal/mol
11 → 2	50	3960[a]	21.0	12.7	24.7
11 → 2	20	408			
11 → 2	0	68.1			
13 → 6	50	632	22.2	3.27	25.6
14 → 8	50	2.74	25.7	13.0	24.7
15 → 10	50	1.87	25.9	3.38	25.6
12 → 4	50	16.6[a]	24.5		
12 → 4	34	3.78			
12 → 4	48	14.2			
12 → 4	55	32.9			

[a] Rate constant obtained by extrapolation of data obtained at other temperatures. [b] Further increase in the ratio of SbF_5 to FSO_3H produced only very small changes in these rate constants.

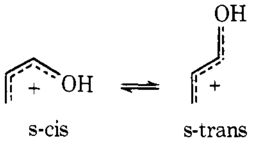
when **11D** and **14D** in FSO_3D or FSO_3D/SbF_5 underwent isomerization to give **2D** and **8D**, respectively.

Discussion

Structure of the 1-Hydroxyallyl Cations. There are three partial double bonds in these hydroxyallyl cations, the C–O, C(1)–C(2), and C(2)–C(3) bonds, and as rotation about each of these is expected to be restricted, these cations could potentially exist in some eight different conformations. The results described earlier completely define the stereochemistry about the C(2)C(3) bond of these systems. Not only is the ^1H NMR evidence compelling in those cases where the C(2)C(3) bond is disubstituted and the magnitude of the coupling constant between the protons on C(2) and C(3) can be observed, but with each cation pair the isomer assigned the cis geometry was found to be thermodynamically less stable than the corresponding trans isomer. Such a thermodynamic preference for a substituent to be on the "outside" of an allyl cation is well known.[5,11]

Assignment of the stereochemistry of the C(1)C(2) bond is much less secure. Almost certainly, rotation about this bond is rapid at room temperature. The absence of any changes in the ^1H NMR of these cations as their solutions were cooled to −90 °C would seem to indicate in each case that one conformation is preferred.

It has been suggested on the basis of the magnitude of the coupling constant between the protons on C(1) and C(2) of the protonated unsaturated aldehydes that these cations exist in the s-cis conformation (eq 2).[14,15] However, as the bond order of the C(1)C(2) bond is not known and in the absence of suitable models, it is by no means certain what the difference in this coupling constant might be for these two conformations.



(2)

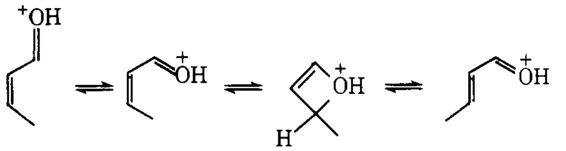
On the basis of the expected steric size of the substitutents (Me > OH > H)[21,22] and the known conformational preferences of the parent allyl cations,[5,11] it is likely that the s-trans conformation would predominate with these protonated aldehydes. This would be particularly true for those cations such as **11** where a C(3) methyl group is in the "inside" position and in which there would be a severe steric interaction between this methyl group and the hydroxy function in the s-cis conformation. It is interesting that the magnitude of the coupling constants between the protons on C(1) and C(2) of **11** and **2** are nearly the same, suggesting that both of these cations exist predominantly in the same conformation. With the protonated unsaturated ketones it is likely that the two conformations are much closer in energy, and it is possible that the s-cis conformations predominate.[23]

The configuration about the C(1)O bond has been discussed by Olah[15] and Brouwer.[14] Exchange of the oxygen proton was rapid under the conditions that most of these cations were studied.

Thermal Isomerization Pathways. There are some six different mechanisms which can be considered to account for the thermal stereomutation of these hydroxyallyl cations. These are: A, simple rotation about the C(2)C(3) bond; B, addition of a nucleophile to C(3), rotation, and reionization; C, disrotatory formation and opening of a cyclopropyl cation; D, proton loss from C(4), rotation of the so formed dienol, and reprotonation; E, protonation at C(2) to form a dication, rotation, and deprotonation; F, formation and ring opening of a protonated oxete.

The first four of these mechanisms have been considered previously for the stereomutation of the alkyl-substituted allyl cations.[5,6] Path E, although applicable to these alkyl-substituted systems, has not been considered before. Reason to include consideration of such a process with these hydroxyallyl cations stems from the suggested intermediacy of such a cation in the ring contractions of protonated cyclohexenones.[25]

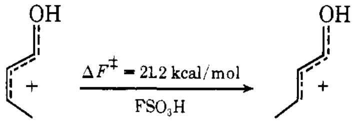
Path F (eq 3), which is not applicable to the parent allyl cations, could be considered to be a concerted, four-electron electrocyclic closure and subsequent opening of a four-membered ring.[26] In such a reaction, the stereochemistry about the C(1)O bond would be also expected to change; however, this could not be examined as the steric integrity of this bond would not be maintained in these media at +50 °C.



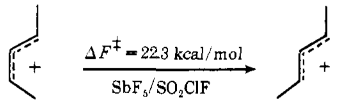
(3)

The preparation of several substituted oxetes has been reported.[27,28] As might be expected, oxetes are not particularly stable entities, and they have been found readily to undergo a facile acid-catalyzed isomerization to give α,β-unsaturated carbonyl compounds.[28] In FSO_3H or FSO_3H/SbF_5, a protonated oxete would likely be a very short-lived species and rearrange rapidly to give a protonated enone.

As has already been pointed out, it is generally accepted that the stereomutation of alkyl-substituted allyl cations takes place by the direct rotation mechanism, path A. It has also been found that an electron-donating group on C(1) of an allyl cation raises the barrier to rotation of the C(2)C(3) bond,[4,10,11] indicating that the positive charge becomes localized on C(3) during this isomerization. As a hydroxy group is a more powerful electron-donating substituent than is a methyl group,[29] the barriers to stereomutation about the C(2)C(3) bond of these hydroxyallyl cations by path A would be expected to be substantially higher than those encountered for comparable alkyl-substituted systems. This is not the case, however, as is evidenced by a comparison of eq 4 and 5,[5] and this would suggest that in FSO_3H, these 1-hydroxyallyl cations undergo cis/trans isomerization by a route other than direct rotation (path A).



(4)



(5)

No deuterium incorporation was detected when cations **11** and **14** rearranged to give **2** and **8**, respectively, in either FSO_3D/SbF_5 or FSO_3D. Thus mechanisms D and E can be eliminated from further consideration as possible pathways for these stereomutations. Pathway D would lead to deuterium incorporation at the C(3) methyl and at C(2),[30] while path E should give deuterium exchange only at the latter site.

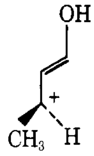
The disrotatory formation of a cyclopropyl cation, mechanism C, would involve the localization of the positive charge at C(2). As such, the introduction of a methyl group on this carbon should increase the relative rates of these isomerizations.[10] However, the results in Table V indicate the reverse to be the case. The rates of isomerization of **13** and **15** are both slower by about a factor of 10 than those of the comparable systems, cations **11** and **14**, respectively. It is worth noting that the introduction of a methyl group at C(2) would be expected to reduce the relative basicity of this site toward protonation, and this should result in a net rate retardation if pathway E were operative.[31] Such a mechanism has, of course, been eliminated on the basis of the lack of deuterium incorporation.

The addition of SbF_5 to FSO_3H is known to increase the acidity of the acid medium.[32] While the acidity function of these acid mixtures is initially very dependent upon SbF_5 concentration, after 4 mol % of the Lewis acid is reached, the function levels off and shows little further dependence upon SbF_5 concentration. The concentrations of SbF_5 used in this work were well in excess of 4 mol % so that small variations in the concentration of SbF_5 and also the enone would not significantly alter the acidity of the medium. Concomitant with an increase of acidity, the addition of SbF_5 to FSO_3H will reduce the basicity of the medium.

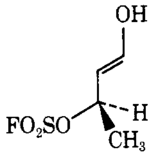
The effect of the addition of SbF_5 to the FSO_3H upon the rate of stereomutation of these hydroxyallyl cations would seem to depend on the structure of the starting enone. As is shown in Table V, both the protonated aldehydes **11** and **13** exhibit a very large decrease in the rate of their isomerization as the acidity of the medium is increased. For example, the rate constant for the rearrangement of **11** to **2** is decreased by a factor of some 300. In contrast, the protonated ketones show little change in the rates of their isomerization as SbF_5 is added to the medium. The rate constant for the rearrangement of **14** to **8** increases by about a factor of 5, while that for the rearrangement of **15** to **10** increases by about a factor of 2 on the addition of SbF_5. It would seem apparent that *at least two different stereomutation pathways are operative with these systems.*

Bearing in mind that mechanisms C, D, and E have been ruled out, the marked retardation in the rate of isomerization of hydroxyallyl cations **11** and **13** as the acidity of the medium is increased would suggest that this reaction proceeds by path B. In other words, at least *in FSO_3H, the stereomutation of 11 and 13 involves the interaction of the organic cation with a base.*[33] Conversely, the very small changes in rate observed for the rearrangement of the protonated ketones **14** and **15** as the acidity of the medium is increased would seemingly rule out a mechanism such as B and suggest that either pathways A or F might be involved.

The structure of the transition state for stereomutation of any of these protonated enones by path A would be a perpendicular allyl cation in which the positive charge is localized on C(3), e.g., **18**. The π electrons of the enol double bond cannot conjugate with the positive center in such a structure and, indeed, the enol can be expected to behave as an electron-withdrawing group.[8,34] Thus, a cation such as **18** would be somewhat less stable than a simple secondary carbonium ion.



18



19

While stable solutions of certain secondary carbonium ions can be prepared in FSO_3H/SbF_5 media, in FSO_3H itself these cations are not stable, and covalent alkyl sulfates are the predominant species present.[35] On this basis, it would seem reasonable that a cation such as **18** would be less stable in FSO_3H than the covalent addition product **19**. Thus, during the stereomutation of the 1-hydroxyallyl cations in FSO_3H, a pathway which involved the formation of a covalent adduct such as **19** would be expected to have a lower activation energy than a pathway involving a perpendicular allyl cation. In FSO_3H/SbF_5 media, however, **18** would likely be more stable than **19**, and thus stereomutation by direct rotation would now become a lower energy process than the base addition route (Figures 1A and B).

Such an analysis, which in essence consists of a consideration *of the position of a hypothetical equilibrium* between **18** and **19**, should hold irrespective of the nature of any substituents on the enol position of these cations. For example, the replacement of the C(1) hydrogen in **18** and **19** by a methyl or a hydroxy group should have little effect in determining the relative difference in the energy between **18** and **19**. However, one expected consequence of the introduction of a substituent on C(1) would be to raise the activation energy for isomerization by both path A and path B. In both of these isomerization routes, the positive charge is removed from C(1) and the replacement of a hydrogen atom at C(1) by an electron-donating substituent would make this electron redistribution more difficult.[36] If paths A and B were the only options left open for the stereomutation of these hydroxyallyl cations in FSO_3H, then the introduction of a charge stabilizing substituent on C(1) would be expected to raise the barrier to isomerization by both of these routes and yet, overall, still maintain a preference for path B.

The results obtained for the rearrangement of protonated ketones **14** and **15** (Table V) indicate that the base addition pathway is not operative with these isomerizations. This would suggest for these systems that an additional pathway now has a lower activation energy than that of path B. The only alternative route remaining is path F, the formation of a protonated oxete. Such a suggestion is consistent with the very small rate changes observed with **14** and **15** as the acidity of the medium was increased by the addition of SbF_5. Although the barrier

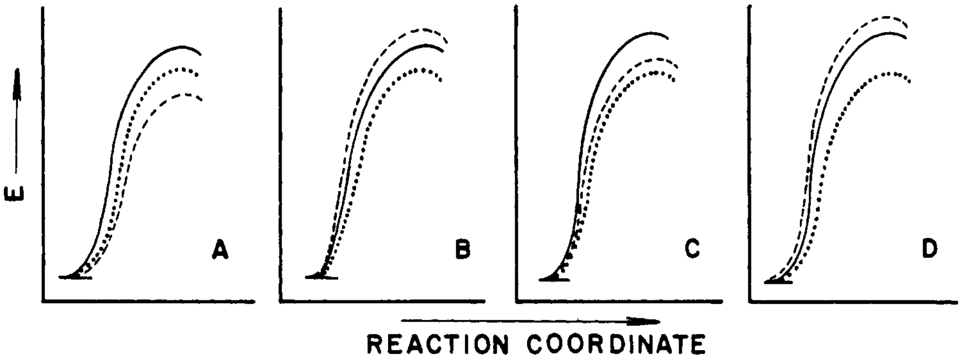


Figure 1. Schematic representation of the activation energies for the stereomutation of various 1-hydroxyallyl cations by direct rotation (—), addition of a nucleophile (- - - - - -), and via a protonated oxete (• • •). Isomerization of aldehydes **11** or **13** in FSO_3H (A) and FSO_3H/SbF_5 (B); isomerization of ketones **14** or **15** in FSO_3H (C) or FSO_3H/SbF_5 (D).

to rearrangement of path B should increase as the acidity is enhanced, the rate of isomerization by path F should show little change and it should still remain the lowest energy route (Figures 1C and D).

In a protonated oxete, all the positive charge formally resides on the oxygen atom. However, as it has been shown that a substantial fraction of the positive charge in a protonated enone also resides on this heteroatom,[15,37] the change in charge distribution on going from the protonated enone to the transition state for rearrangement to the protonated oxete would likely be small. If this is indeed the case, then the rate of stereomutation by path F would be less sensitive to changes in the substitution pattern of the starting protonated enone than isomerization by paths A and B. As is shown in Table V, in FSO_3H/SbF_5 the rates of isomerization of both the protonated aldehydes **11** and **13** and ketones **14** and **15** are almost the same, suggesting that in this more strongly acid medium, all the hydroxyallyl cations isomerize by way of a protonated oxete (path F, Figures 1B and D).

The activation energy associated with the base addition route, path B, would be expected to be less in FSO_3H as compared with FSO_3H/SbF_5 media for all the hydroxyallyl cations. The difference in behavior of the protonated aldehydes and ketones in FSO_3H could be that the barrier to isomerization by path B for the protonated aldehydes drops below that of path F, Figure 1A. In the case of the protonated ketones, the presence of the C(1) methyl group would raise the barrier to isomerization by path B, relative to the aldehyde systems, and this route must still remain about the same or somewhat higher in energy than path F, Figure 1C.[38]

The rate constant for the stereomutation of the protonated acid **12** in FSO_3H is almost the same as those found for the protonated ketones **14** and **15** in FSO_3H. As a C(1) hydroxy function would be expected to retard isomerization by both paths A and B even more than would a C(1) methyl group, this would again indicate that the isomerization does not proceed by either of these two pathways but rather involves a protonated oxete.

Photochemical Isomerizations. Considerable interest has been shown in the photochemical cis/trans isomerization of enones.[13] It has been suggested that these isomerizations about the C(2)C(3) bond involve π,π^* states which, on the basis of calculated potential energy diagrams, would appear to have a potential minimum when this bond is rotated through 90°.[39] As the protonation of the oxygen of a carbonyl compound is known to raise the energy of the n,π^* states and lower that of the π,π^* states,[40] it is probable that the latter type of excited state is involved in the stereomutations of these protonated enones. While it may be attractive to suggest that the photostereomutation of these protonated enones takes place by such an excited state rotation, this is not the only possibility. Further detailed discussion of the possible mechanisms involved in these photoisomerizations is premature at this stage of our investigation, as further evidence is required to delineate the process or processes involved.

Conclusion

The results of this study, particularly regarding the mechanism of the thermal isomerization of the 1-hydroxyallyl cation, raise certain interesting questions concerning the stereomutation of alkyl-substituted allyl cations. The evidence for the noninvolvement of base in the cis/trans isomerizations of these latter systems very largely rests on the results obtained with a single cation, the 1,1,3,3-tetramethylallyl cation.[6] On the basis of the analysis which was set forward earlier to decide upon the relative activation energies for the rotation versus base addition routes, it would seem perfectly reasonable that this highly substituted system should stereomutate via a simple rotation mechanism in FSO_3H. Thus, in this case, the perpendicular allyl cation transition state would be comparable with a tertiary carbonium ion, and such cations are known to be stable in FSO_3H.[35] However, the extension of this result to other systems should be treated with caution, for if the medium were to be made less acidic, or more importantly, if the allyl cation were to become less highly substituted, then the base addition route could become of lower energy.

This decreased stability of a less highly substituted perpendicular allyl transition state could potentially be offset by a significant increase in the acidity of the medium employed and probably the simple rotation mechanism is still the lowest energy pathway for secondary systems such as the 1,3-dimethylallyl cations in media such as SbF_5/SO_2ClF. However, it would seem unlikely on the basis of what is known about primary carbonium ions[41] that the barrier to rotation of an unsubstituted allyl cation could ever be measured directly in these super acid media.

Experimental Section

General. ^1H NMR spectra were recorded on a Varian HA-100 spectrometer equipped with a variable-temperature probe controlled by a Varian A-6040 temperature controller. ^{13}C spectra were obtained with a Bruker WH 90 Pulse Fourier Transform spectrometer equipped with a Bruker B-ST 100/700 variable-temperature controller. Proton noise decoupling and selective decoupling were achieved using standard methods. The probe temperatures of both instruments were measured with a copper-constantan thermocouple and a Leeds and Northrup 8692 potentiometer. Uv spectra were recorded on a Cary 14 spectrophotometer using 96% H_2SO_4 as solvent. Preparative gas chromatography was performed on an Aerograph A-90-P3 instrument using a 10 ft × ¼ in. column packed with 15% Carbowax 20 M on Chromosorb W.

Materials. Compounds **1**, **3**, **7**, and **9** were all commercial samples. The purity of each compound was checked by ^1H NMR and GLC before use. FSO_3H was distilled twice under N_2 before use and showed only end absorption in its uv spectrum. SbF_5 was purified in a similar manner to that described by Gillespie.[32]

***cis*-But-2-en-1-ol.** *cis*-Crotonic acid[20] (10.0 g) was treated with CH_2N_2 to yield the corresponding methyl ester (9 g). To this ester dissolved in ether (100 ml) was added sodium bis(-2-methoxyethoxy)aluminum hydride (45 ml of 70% solution in benzene), the reaction being kept under N_2 at 15-20 °C. The mixture was stirred for 1 h, excess hydride quenched with H_2O (10 ml), and the organic layer washed with dilute H_2SO_4 (5%, 100 ml), aqueous $NaHCO_3$ (10%, 2 × 50 ml), and water (2 × 50 ml). The organic layer was dried ($MgSO_4$) and the solvent evaporated to give a liquid which was purified by preparative GLC to give *cis*-but-2-en-1-ol: ^1H NMR (CCl_4) δ 1.55 (d, $J = 7$ Hz, CH_3, 3 H), 2.56 (s, OH, 1 H), 4.00 (m, CH_2, 2 H), 5.40 (m, vinyl H, 2 H).

***cis*-Crotonaldehyde (16).** A mixture of CrO_3 (1.66 g) and pyridine (2.62 g) in CH_2Cl_2 (40 ml) was stirred for 15 min at 20 °C before *cis*-but-2-en-1-ol (200 mg) was added to it. The resulting mixture was stirred for a further 5 min, filtered through Celite, and the filtrate washed with ice-cold aqueous HCl (5%, 50 ml), aqueous $NaHCO_3$ (10%, 2 × 50 ml), and H_2O (2 × 50 ml). The organic layer was dried ($MgSO_4$) and the solvent carefully removed through a short fractionating column to yield **16** together with 5% of **1** (^1H NMR). ^1H NMR of **16:** (CCl_4) δ 2.30 (d, $J = 7$ Hz, CH_3, 3 H), 5.91 (m, C_2H, 1 H), 6.70 (m, C_3H, 1 H), 10.07 (d, $J = 8$ Hz, aldehyde H, 1 H).

***trans*-3-Methylpent-3-en-2-one (9).** Tiglic acid (1.7 g) in ether (25 ml) at −50 °C was treated with a solution of CH_3Li in ether (15 ml, 1.7 M) and the reaction stirred for a further hour at −50 °C. The mixture was warmed to room temperature and dilute aqueous NaOH (5%, 10 ml) added. The organic layer was washed with water (2 × 15 ml), dried ($MgSO_4$), and the solvent evaporated to give 1.8 g of a 1:1 mixture of **11** and 2,3-dimethylpent-3-en-2-ol. These were separated by preparative GLC to give a pure sample of **9:** ^1H NMR (CCl_4) δ 1.83 (s, CH_3 3 H), 1.90 (d, $J = 8$ Hz, CH_3, 3 H), 2.35 (s, CH_3, 3H), 6.82 (q, $J = 8$ Hz, vinyl H, 1 H).

Preparation of Cations. The appropriate carbonyl compound (60-70 mg) was distilled under high vacuum into stirred FSO_3H (3 ml) kept at −78 °C. The resulting solution was transferred into a quartz tube for the photoisomerization or into an appropriate NMR tube for spectral studies. All transfers were made using dry ice cooled jacketed pipettes under a blanket of dry N_2. For those isomerizations which involve SbF_5, the SbF_5 was weighed into a NMR tube using a N_2 filled glovebox and the FSO_3H solution of the mixture of cis and trans isomers subsequently added.

Irradiations. All photoisomerizations were carried out using a "home made" photoreactor which consisted of ten low-pressure mercury lamps (Southern New England Ultraviolet Co., RPR 2537A) arranged in a circle around an unsilvered quartz dewar. The samples in quartz tubes were placed inside the dewar and cooled with a mixture of dry ice and methanol. The photoisomerizations were monitored by ^1H NMR.

Rate Measurements. The isomerization rates of the protonated enones were determined by placing sealed NMR tubes containing the appropriate cation pair and solvent mixture in a constant temperature bath. After a given time interval, the reaction was quenched by rapidly cooling the sample to −78 °C and the composition of the mixtures assayed by ^1H NMR at −30 °C. Each spectrum was scanned some six to eight times and the composition determined by an average of the peak heights of an appropriate resonance of each of the cis and trans isomers. The isomerization of $\mathbf{5} \rightarrow \mathbf{10}$ was monitored with the C(2) methyl resonances; $\mathbf{11} \rightarrow \mathbf{2}$, and $\mathbf{13} \rightarrow \mathbf{4}$ by the C(1) proton resonances; $\mathbf{12} \rightarrow \mathbf{3}$ and $\mathbf{14} \rightarrow \mathbf{7}$ by the C(3) methyl resonances. (The isomerization of $\mathbf{12} \rightarrow \mathbf{3}$ was determined at various temperatures directly in the NMR probe.) Each reaction was followed over at least 2 half-lives, some seven to ten different points were taken, and first-order kinetics were observed in every case. Each rate constant was determined in duplicate using independent samples. The errors in the rate constants are $\mp 5\%$ or better.

References and Notes

(1) This work was supported by the National Research Council of Canada.

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(17) Olah and co-workers have reported[15] that the protonation of tiglaldehyde gives cation **13.** However, the spectral properties quoted for **13** resemble very closely those given here for **6.** In view of the alternate preparation of **13** described here, the expected relative thermodynamic stabilities of **6** and **13,** and the known geometry of the precursor **5,** such an assignment would seem to be incorrect. The NMR spectra reported[15] for the cation resulting from protonation of 3-methylpent-3-en-2-one do not seem to agree with those quoted here for either **10** or **15.** We are not certain of the reason for this discrepency.

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(23) α,β-Unsaturated aldehydes have been shown to exist predominantly in the s-trans conformation.[24a] On the other hand, the *s-cis* and *s-trans* conformations of α,β-unsaturated ketones are much closer in energy, and both conformations are frequently detected.[24b] Thus **7** has been shown to exist largely in the *s-trans* form with a small amount of the *s-cis* conformation being present. A ketone such as mesityl oxide, with a bulky group on the β position, exists predominantly in the s-cis conformation with some departure from coplanarity.

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Radical Ions in Photochemistry. 3. Photosensitized (Electron Transfer) Cleavage of β-Phenethyl Ethers[1]

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Abstract: The photosensitized (electron transfer) irradiation of some β-phenethyl ethers led to cleavage of the α-carbon-carbon bond. For example, the photosensitized irradiation of 2,2-diphenylethyl isopropyl ether (IIb) in acetonitrile-methanol solution gave diphenylmethane (III) and the methyl isopropyl acetal of formaldehyde (IVb). Photosensitizers which were effective include methyl *p*-cyanobenzoate (V), *p*-dicyanobenzene (VI), and 1,4-dicyanonaphthalene (VIII); 1-cyanonaphthalene (VII) was not effective. Electrochemical and photophysical evidence was obtained which supports the proposed mechanism. The primary process is an electron transfer which gives the sensitizer radical anion and the ether radical cation. Fluorescence studies indicated that the singlet states of the sensitizers V, VI, and VIII were quenched by IIb. The singlet state of VII was not quenched by IIb. Triplet-triplet transfer photosensitized experiments indicate that the triplet of VI does not bring about reaction. The relationship involving the reduction potential of the sensitizer, the oxidation potential of the ether, the available electronic-excitation energy, and the energy associated with the electron-transfer process has been used to correlate the results.

Introduction

In part 1 of this series we described the photosensitized (electron transfer) additions of alcohols to 1,1-diphenylethylene (I) (reaction 1 (eq 1)).[3a] This reaction, which yields the

$$\underset{\text{I}}{(C_6H_5)_2C{=}CH_2} + ROH \xrightarrow[CH_3CN]{h\nu,\,\text{sens}} \underset{\text{II}}{(C_6H_5)_2CHCH_2OR} \qquad (1)$$

ethers IIa–c expected from anti-Markownikoff addition, has been studied in detail and, when the minor products were isolated and characterized, diphenylmethane (III) was found among them. In fact, under some conditions, III was formed in quite significant amounts (>15%). Diphenylmethane was not an expected product, the mechanism of its formation under these conditions was not obvious, and, since this reaction could represent an important limitation of the synthesis of ethers by reaction 1, we decided to focus some attention on it.

	R	% yield
IIa	$-CH_3$	36
b	$-CH(CH_3)_2$	49
c	$-C(CH_3)_3$	17

Sens: methyl *p*-cyanobenzoate (V)
p-dicyanobenzene (VI)
1-cyanonaphthalene (VII)

We found that diphenylmethane (III) was a secondary photolysis product which results from the photosensitized (electron transfer) decomposition of the initially formed ether (reaction 2 (eq 2)). The other product of this reaction was the acetal of formaldehyde (IV). In fact, by either prolonged irradiation starting with the olefin (I) or by starting with the ether (II), yields between 40 and 60% of III and IV can be realized under some conditions.

$$\underset{\text{IIa–c}}{(C_6H_5)_2CHCH_2OR} + R'OH \xrightarrow[CH_3CN]{h\nu,\text{sens}} \underset{\text{III}}{(C_6H_5)_2CH_2} + \underset{\text{IV}}{R'OCH_2OR} \qquad (2)$$

IVa, $R = R' = CH_3$
b, $R = CH(CH_3)_2$; $R' = CH_3$
c, $R = R' = CH(CH_3)_2$
d, $R = R' = C(CH_3)_3$

Sens: V, VI, 1,4-dicyanonaphthalene (VIII)
(VII was *not* effective)

The mechanism we propose for reaction 2 is summarized in Scheme I. The first step involves excitation of the sensitizer, which is potentially an electron acceptor (A). Step 2 may occur in several stages, but leads ultimately to the solvent-separated

Scheme I

(1) $A \xrightarrow{h\nu} A^*$

(2) (a) $A^* + II \longrightarrow II \ldots A^*$ (encounter complex)

(b) $II \ldots A^*$ (encounter complex) $\longrightarrow II^{\cdot +} \ldots A^{\cdot -}$ (radical ion pair or exciplex)

(c) $II^{\cdot +} \ldots A^{\cdot -}$ (radical ion pair or exciplex) $\longrightarrow II^{\cdot +}_{(s)} + A^{\cdot -}_{(s)}$

(3) $II^{\cdot +}_{(s)} \longrightarrow [(C_6H_5)_2CH]\cdot + [CH_2OR]^+_{(s)}$

(4) $[(C_6H_5)_2CH]\cdot + A^{\cdot -}_{(s)} \longrightarrow [(C_6H_5)_2CH]^-_{(s)} + A$

(5) $[(C_6H_5)_2CH]^-_{(s)} + H^+_{(s)} \longrightarrow (C_6H_5)_2CH_2$

(6) $[CH_2OR]^+_{(s)} + R'OH \longrightarrow R'OCH_2OR + H^+_{(s)}$