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PMR SPECTRA OF HYDROXYALLYL CATIONS

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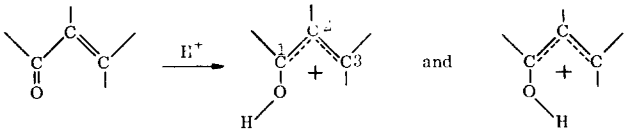
In this communication we report a pmr spectroscopic investigation of 1-hydroxyallyl cations formed by protonation of acrolein and some of its methyl and ethyl derivatives.



The cations were prepared by dissolving the corresponding carbonyl compounds in HF-SbF_5 or $HFSO_3$-SbF_5. The spectroscopic data are collected in Table I*.

The C-H part of the spectrum of the unsubstituted hydroxyallyl cation (I) is shown in Fig. 1. The peak assignments follow directly from the spin-spin couplings; the latter were checked by double-resonance measurements.

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* Pmr spectra of some hydroxycyclopentenyl cations and of protonated mesityl oxide(VIII) have been measured by Deno et al.(1) in H_2SO_4; in this solvent no OH resonances were observed because of fast proton exchange.

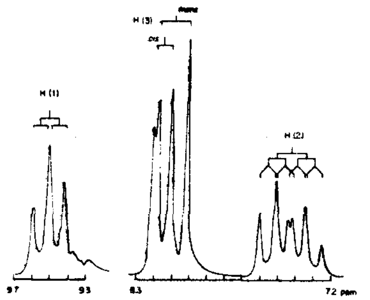

FIG. 1
C-H Region of the Spectrum
of Hydroxyallyl Cation (I)
(HF-SbF_5; -20 °C; 100 Mc/s)

The chemical shifts of the hydrogens bonded directly to the allyl group show the expected order of shieldings. The very low shielding of H(1) is due to anisotropy of the C-OH group and the shieldings of the hydrogens at C_2 and C_3 reflect the higher positive charge density at the terminal carbon C_3. The shieldings of the methyl hydrogens in the other cations follow the same pattern. The hydroxyl resonances occur at a much higher field than those of protonated saturated aldehydes and ketones(2,3,4,5), which is in keeping with the delocalization of the positive charge over the allylic group.

The coupling constants of 9-10 c/s and of 16-17 c/s in the spectra of I and the other cations are typical of cis and trans vicinal couplings, respectively *. We therefore conclude that the hydroxyl group is trans with respect to the hydrogen at C_2.

The same configuration about the C_1-C_2 bond is suggested for the other cations. Replacement of H(1) by methyl will increase the preference of the OH group to be trans with respect to H(2) for steric reasons, while the insensitivity of the OH shift towards replacement of H(2) by methyl strongly indicates that this substitution does not give rise to a change of configuration about the C_1-C_2 bond.

Pmr spectra of protonated aldehydes and dialkyl ketones have amply demonstrated that rotation about the partially double C-OH bond is highly restricted(2,3,4,5) thus giving rise to syn-anti isomerism. With ions I-IV only one isomer is found, which according to the H(1)-OH coupling has the aldehyde hydrogen H(1) syn and the "vinyl" group anti with respect to the OH hydrogen. The strong preference for this configuration about the C-OH bond is in keeping with that observed with protonated saturated aldehydes(3,5). With protonated methyl and ethyl vinyl ketones the co-existence of two isomeric cations was observed at -60 °C (Fig. 2). The differences in methyl shift between

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* In protonated 2-cyclohexen-1-one the cis coupling $J_{H(2)-H(3)}$ has the value of 9.5 c/s.

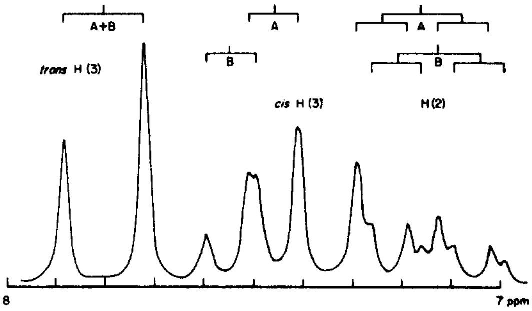

FIG. 2

Allyl-H Region of the Spectrum of the Co-existing Isomers of Protonated Methyl Vinyl Ketone ($HF-SbF_5$; -60 °C; 100 Mc/s)

the two isomers of V and in ethyl shifts between the two isomers of VI are the same as those observed for syn and anti methyl and ethyl groups in protonated saturated ketones(4). Since the latter assignments have been firmly established, the configurations about the C-OH bond of the isomers of V and VI can be inferred unambiguously. It turns out that the more stable isomer of V (A) and the less stable isomer of VI (B) have the methyl group and ethyl group, respectively, syn to the OH hydrogen. These assignments are confirmed by the fact that the OH shifts are the same for V-B and VI-A, and differ by about 0.4 ppm between V-A and VI-B. The above results show the "vinyl" group to be in between the methyl and ethyl groups as regards its preference for the syn position.

Normally, replacement of hydrogen at a positively charged carbon by an electron-donating methyl group causes the shielding of the other protons of the cation to increase [cf., for example, the effect of methyl substitution in benzenium ions(6)]. Replacement of the cis-H at C_3 by methyl, however, has quite the opposite effect, leading to a considerable (0.9 ppm) downfield shift of the trans-H(3); also, the effect of this substitution on the OH shift (1.2 ppm to higher field) seems quite out of proportion. We suggest that the abnormal behaviour is caused by changes in the anisotropy of the allyl ion. The somewhat irregular way in which replacement of H(2) by methyl affects the shielding of H(3) may have the same cause. The importance of the magnetic anisotropy of the charged allyl group in relation to the shieldings of atoms bonded to it has recently been demonstrated in the case of allylic carbonions(7).

In the [illegible] of the present investigation we noted that hydroxyallyl cations deprotonate much more readily than dialkylhydroxycarbonium ions. This might indicate that α,β-unsaturated carbonyl compounds are weaker bases than saturated carbonyl compounds.

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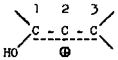
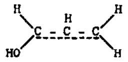
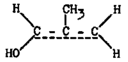
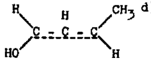
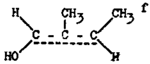
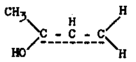
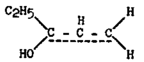
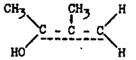
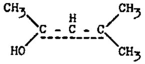
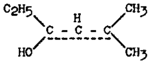
TABLE I

PMR SPECTRA[a] OF HYDROXYALLYL CATIONS 

Code	Cation	°C	Chemical shifts (ppm downfield from TMS)[b]							Coupling constants, c/s				
			OH	H(1)	H(2)	H(3)	CH_3(1)	CH_3(2)	CH_3(3)	H(1)-OH	H(1)-H(2)	H(2)-H(3)		others
												cis	trans	
I		-20	14.42 d	9.53 t	7.36 m	8.00 d (tr.) 8.05 d (cis)				8.0	9	10	16.5	
		-60	14.46 d											
		-20[c]	13.95 d	9.50 t	7.41 m	8.11 d (tr.) 8.16 d (cis)								
II		-20	14.40 d	9.53 d		7.72; 7.90		2.26		8				
		-60	14.50 d											
		-20[c]	13.82 d	9.46 d		7.76; 7.93		2.28						
III	 d)	-20	e)	9.23 d	7.20 m	8.87 m			2.67 d		10		15	H(3)-CH_3 6.75
		-20[c]	12.77 d	9.23 t	7.23 m	8.90 m			2.71 d	7				
IV	 f)	-20	13.15 d	9.18 d		8.60 q		2.16	2.62 d	8.0				6.75
V	 A g)	-60	14.07		7.15 m	7.80 d (tr.) 7.46 d (cis)	3.15					10	16.5	
	B g)	-60	13.75		7.12 m	7.80 d (tr.) 7.55 d (cis)	3.11					10	16.5	
VI	 A g)	-60	13.70		7.08 m	7.70 d (tr.) 7.30 d (cis)	CH_3 1.53 t CH_2 3.40 q					10.5	16.5	CH_2-CH_3 7.5
	B g)	-60	13.75		6.77 m	7.64 d (tr.) 7.34 d (cis)	CH_3 1.44 t CH_2 3.54 q							6.5
VII		-60	14.07			7.25; 7.57	3.17	2.24						
VIII		-60	12.63		6.91		2.85		2.71 2.56					
IX		-60	12.41		6.95		CH_3 1.50 t CH_2 3.09 q		2.73 2.59					7.0

a) In HF-SbF_5 unless indicated otherwise.

b) Based on δ = -3.20 for tetramethylammonium ion.
d = doublet, t = triplet, q = quartet, m = multiplet.

c) In $HFSO_3$-SbF_5.

d) Protonated crotonaldehyde.

e) Broad peak near 13.3 ppm at -60 °C.

f) Protonated tiglic aldehyde.

g) Two isomeric cations (60% A, 40% B for V, and 40% A, 60% B for VI). A with $CH_3(C_2H_5)$ syn, B with $CH_3(C_2H_5)$ anti; see text. Spectra of A and B coalesce at temperatures above -20 °C when OH exchanges with solvent.