cohol (methanol or ethanol) was heated in an ampule at 140 °C for 2 h. The mixture was then esterified with the appropriate diazoalkane (diazoethane in the case of methanol and diazomethane in the case of ethanol) and analyzed by VPC (conditions AZ-1). In both solvents about 33–34% of decarboxylation took place to give alkyl 2-*n*-butyl-hexanoate (7).

References and Notes

(1) Paper No. 71 in the Cyclic Peroxide Series.
(2) NIH Career Development Awardee (1977–1980).
(3) W. Adam and R. Rucktäschel, *J. Am. Chem. Soc.*, **93**, 557 (1971).
(4) O. L. Chapman, P. W. Wojtkowski, W. Adam, O. Rodriguez, and R. Rucktäschel, *J. Am. Chem. Soc.*, **94**, 1365 (1972).
(5) W. Adam, J.-C. Liu, and O. Rodriguez, *J. Org. Chem.*, **38**, 2269 (1973).
(6) M. M. Martin, F. T. Hammer, and E. Zador, *J Org. Chem.*, **38**, 3422 (1973).
(7) W. Adam and R. Rucktäschel, *J. Org. Chem.*, **37**, 4128 (1972).
(8) R. Ciegee, E. Hoger, G. Huber, P. Kruck, F. Marktscheffel, and H. Schellenberger, *Justus Liebig Ann. Chem.*, **599**, 81 (1956).
(9) E. S. Huyser, "Free Radical Chain Reactions", Wiley, New York, N.Y., 1970, pp 264, 274.
(10) R. Hiatt in "Acyl Peroxides", Vol. 2, D. Swern, Ed., Wiley-Interscience, New York, N.Y., 1971, Chapter 8, pp 856–859.
(11) B. J. Tighe, *Chem. Ind. (London)*, 1837 (1969).

Rearrangement of Allyl Alcohols to Aldehydes with Superacids[1]

George A. Olah,* David Meidar, and Gao Liang

Institute of Hydrocarbon Chemistry, Department of Chemistry, University of Southern California, Los Angeles, California 90007
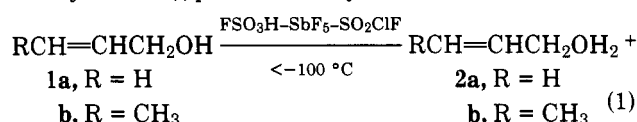
The superacid-catalyzed rearrangement of allyl alcohols into aldehydes was studied in superacid solutions under stable ion conditions followed by ^{1}H NMR spectroscopy, as well as in the gas phase over a solid perfluorinated resinsulfonic acid catalyst (Nafion-H).

The catalytic rearrangement of allyl alcohol to propionaldehyde, brought about by H$_2$SO$_4$,[2] Fe(CO)$_4$,[3] Fe(CO)$_5$,[4] Co$_2$(CO)$_8$,[5] and acid-catalyzed electrolysis,[6] as well as in the gas phase, over Al$_2$O$_3$, ZnO, or pumice at elevated temperatures[7] has been studied. We wish to report now a study of the mechanism of the superacid-catalyzed isomerization of allyl alcohols in superacid solutions under stable ion conditions using ^{1}H NMR spectroscopy and directly observing the intermediate(s) responsible for such transformations. We also report that similar superacid-catalyzed isomerization takes place by catalysis over Nafion-H, a solid perfluorinated resinsulfonic acid in the gas phase at relatively mild conditions. Allyl alcohol is effectively isomerized to propionaldehyde. 2-Methylallyl alcohol, crotyl alcohol, and 3-methyl-2-buten-2-ol are also isomerized, under the same condition, to isobutyraldehyde, butyraldehyde and methyl isopropyl ketone, respectively.

Study of Allyl Alcohols in Superacid Solutions

When a solution of allyl alcohol 1 in SO$_2$ClF at −78 °C (dry ice–acetone bath) is slowly introduced into a well-stirred solution of FSO$_3$H–SbF$_5$–SO$_2$ClF kept below −100 °C (ethanol–dry ice bath), protonated allyl alcohol 2 is observed.

$$\text{RCH=CHCH}_2\text{OH} \xrightarrow[<-100\ °C]{\text{FSO}_3\text{H–SbF}_5\text{–SO}_2\text{ClF}} \text{RCH=CHCH}_2\text{OH}_2{}^+ \quad (1)$$

1a, R = H   **2a**, R = H
b, R = CH$_3$ **b**, R = CH$_3$

The structure of **2** is identified by its 60-MHz ^{1}H NMR spectrum (Figure 1) obtained at −90 °C, which shows four proton resonances (Table I). The two-proton signal at δ 9.75 assigned to the protonated hydroxyl group confirms the formation of **2**. Protonated alcohols are known to show strong absorptions at about δ 10–11 in superacids.[8]

When raising the temperature of protonated allyl alcohol **2** in FSO$_3$H–SbF$_5$–SO$_2$ClF above −80 °C, **2** slowly undergoes addition of FSO$_3$H to the double bond, giving protonated 2-fluorosulfonyl-1-propanol (**3**). The structure of **3** is confirmed by its proton and fluorine-19 NMR spectra (Table I). The process of slow transformation from **2** (−90 °C) to **3** (−40 °C) is clearly seen in Figure 1. When the solution of **2** is allowed to stand at −40 °C, the original ^{1}H NMR spectrum of

Table I. Proton and Fluorine-19 NMR Parameters of Protonated Allyl Alcohol and Its FSO$_3$H and HF Addition Products

ion	registry no.	acid (temp, °C)^b	CH$_3$	CH$_2$–OH$_2{}^+$	CH	=CH	=CH$_2$	–CH$_2$–	OH$_2{}^+$	ϕ_{19F}	J_{H-F}, Hz
2	67315-77-9	A, B, (−90)		5.28 (d, 6.0)		6.58 (m)	6.17 (m)		9.75 (b)		
3a	67315-78-0	A (−50)	185 (d, 6.6)	5.12 (b)	5.78 (m)				11.05 (b)	−40.0 (s)	
3b	67315-79-1	A (−50)	1.94 (t)	5.24 (b)	5.75 (b)			3.88 (m)	10.3		
4	67315-80-4	B (−50)	1.60 (dd, 6.6)	5.10 (dt)	5.75 (dqm)				11.0 (t, 4.0)	+185.3 (dq)	J_{CH_3-F} = 24.0; J_{CH_2-F} = 22.0; J_{CH-F} = 50.0

^{a} Proton and fluorine-19 chemical shifts are in ppm from external Me$_4$Si and CCl$_3$F, respectively. Multiplicities and coupling constants (in Hz) are given in parentheses: b = broad, d = doublet, m = multiplet, s = singlet, t = triplet, q = quartet, dd = doublet of doublets, dt = doublet of triplets, dq = doublet of quartets, dqm = doublet of quartet of multiplets, tt = triplet of triplets, td = triplet of doublets, qt = quartet of triplets. ^{b} A = FSO$_3$H–SbF$_5$–SO$_2$ClF; B = HF–SbF$_5$–SO$_2$ClF.
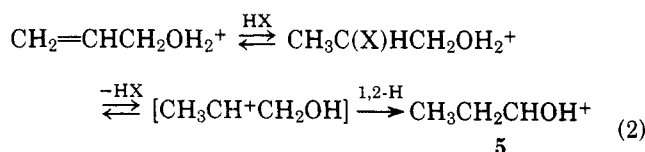
2 is completely replaced by that of **3**. In order to further establish the reaction of **2a** in $FSO_3HSbF_5SO_2ClF$, we have also treated allyl alcohol with $HFSbF_5SO_2ClF$ under the same conditions.

$$RCH_2C(X)HCH_2OH_2^+$$

3a, X = OSO_2F; R = H

b, X = OSO_2F; R = CH_3

4, X = F; R = H
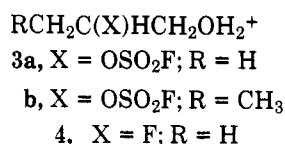
According to the ^1H NMR spectra of the solution of **1** in this acid system, both the protonation of the hydroxy group (**2**) and the addition of HF to the double bond (to give protonated 2-fluoro-1-propanol (**4**)) take place at −90 and −78 °C, respectively. The structure of **4** is characterized inter alia by the large J_{H-F} coupling and fluorine-19 resonance (Table I). Brouwer et al.[9] reported that addition products of the acid solvent ($HF:SbF_5$ or $HSO_3F:SbF_5$) to 3-penten-2-one and analogues are serving as intermediates in the cyclization process of these compounds to tetrahydrofuran derivatives via a multistep reaction.

In the presently discussed cases, the addition products between the acid (HF or HSO_3F) and the protonated allyl alcohols **3** and **4** cannot play a role in the reaction mechanism as they would prevent further reaction, i.e., the 1,2-hydride shift to give the protonated carbonyl compound. Hence, the reaction rate at this stage is controlled by the elimination of the acid from **3** or **4**.

The thermal stability of **3** and **4** is different. The solution of **4** in $HF-SbF_5-SO_2ClF$ undergoes no further change when the temperature is raised from −78 to 0 °C (pressure NMR tube). In contrast, a slow transformation yielding protonated propionaldehyde (**5**)[10] takes place when the solution of **3** in $FSO_3H-SbF_5-SO_2ClF$ is allowed above − 40 °C (Figure 1, eq 2).

$$CH_2{=}CHCH_2OH_2^+ \underset{-HX}{\overset{HX}{\rightleftarrows}} CH_3C(X)HCH_2OH_2^+$$

$$\overset{-HX}{\rightleftarrows} [CH_3CH^+CH_2OH] \overset{1,2-H}{\longrightarrow} CH_3CH_2CHOH^+ \quad (2)$$

$$\mathbf{5}$$

The ^1H NMR spectrum of **5** (recorded after the solution has been cooled back to −80 °C) is identical to that previously reported for protonated propionaldehyde.[10] The proton spectrum of **5** displayed in Figure 1 at 0 °C indicates fast exchange between the proton on oxygen and the acid (FSO_3H). The difference in reactivity between **3** and **4** reflects the difference in C–X bonds, i.e., the C–O(SO_2F) bond is weaker than the C–F bond.

2-Methylallyl alcohol (**6**), crotyl alcohol (**7**), and 2,3-dimethylallyl alcohol (**8**) also undergo similar isomerization in $FSO_3H-SbF_5-SO_2ClF$ solution yielding protonated isobutyraldehyde (**9**)[10] (eq 3a), protonated butyraldehyde (**10**) (eq
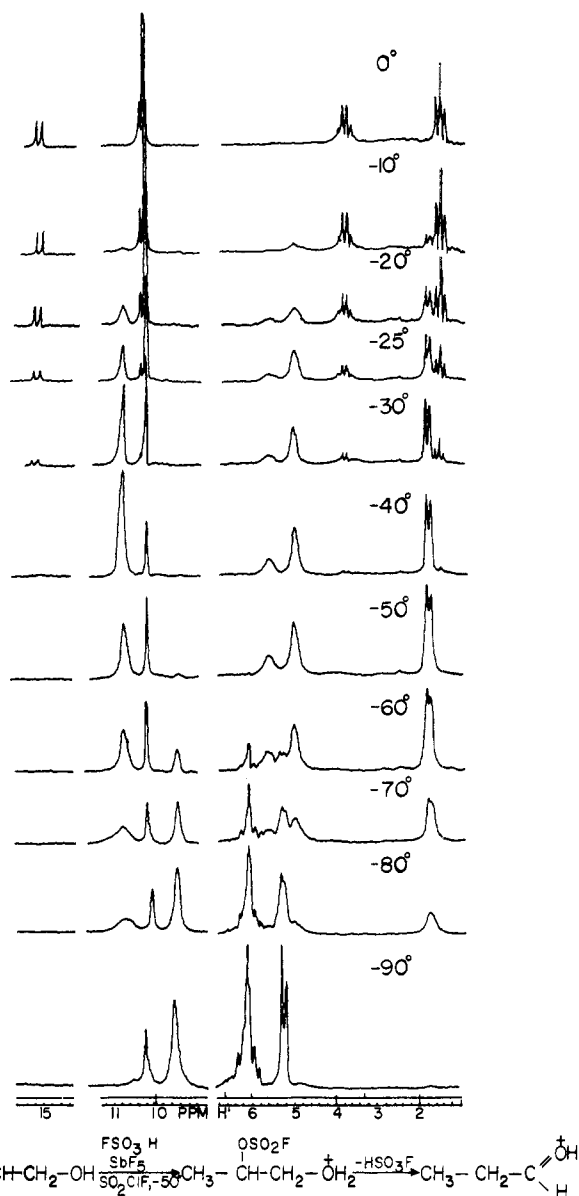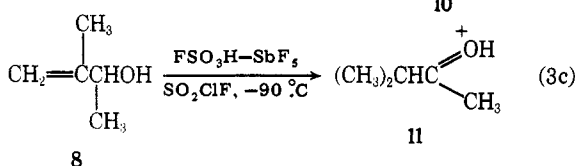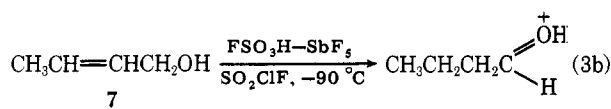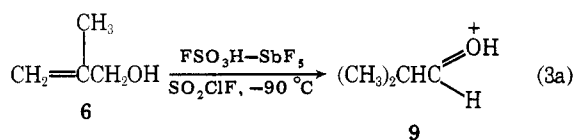

Figure 1.

3b), and protonated methyl isopropyl ketone (**11**)[11] (eq 3c), respectively. The ^1H NMR spectra of **9–11** are identical to those previously reported.[10,11]

We have previously[12] reported our results on the formation of allyl cations from the corresponding allylic alcohol in superacidic media. Ionization of 2,4-dimethyl-1-penten-3-ol gave a 1:1 mixture of **12** and **13** (eq 4). In treating alcohols **1** and
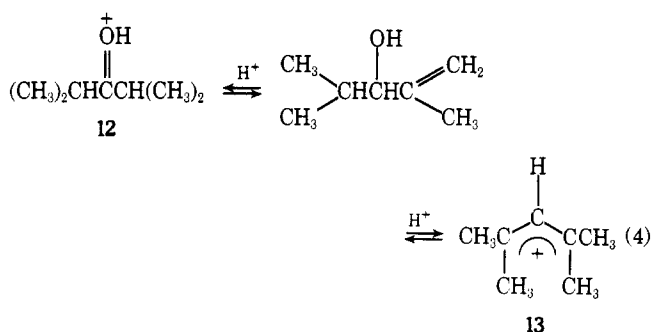

6–8 in superacids under similar conditions, no ionization of the OH_2^+ group takes place to give the corresponding allyl cations **14–16**. The results are in agreement with the findings

### Table II. Isomerization of Allylic Alcohols to Aldehydes in the Gas Phase over Nafion-H Catalyst[a]

| alcohol	registry no.	reaction temp, °C	liquid feed rate, mL/min	contact time, s	product (aldehyde yield, %)	registry no.
Allyl	107-18-6	195	0.06	3	propionaldehyde (40)	123-38-6
		195	0.02	8	(60)	
		170	0.02	8	(45)	
		140	0.02	8	(0)	
2-Methylallyl	513-42-8	195	0.06	3	isobutyraldehyde (88)	78-84-2
		180	0.06	3	(80)	
Crotyl	6117-91-5	195	0.02	8	butyraldehyde (55)	123-72-8
		195	0.06	3	(40)	

[a] Carrier gas, nitrogen at 30 mL/min.
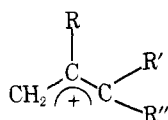
14, R = R' = R'' = H
15, R = R'' = H; R' = CH₃
16, R = R' = CH₃; R'' = H
17, R = R' = R'' = CH₃

indicating that the stabilities of allylic cations are in the order:
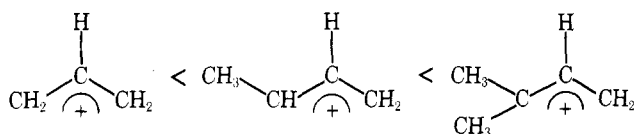
The same order was observed in solvolytic rate studies of the corresponding allyl chlorides[13] indicating that the addition of a methyl group to a terminal carbon in the allylic ion stabilizes it by ~5 kcal/mol. Addition of the tertiary 2,3,3-trimethylallyl alcohol 18 into FSO_3H–SbF_5–SO_2ClF solution at −90 °C gave only the isomerized product, i.e., methyl *tert*-butyl ketone 19 (protonated) (eq 5), and the allylic ion 17 was not detected.
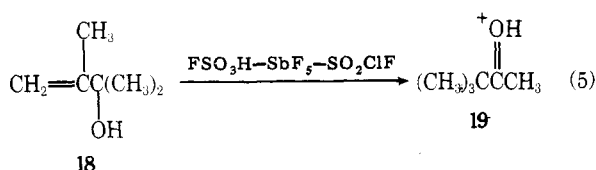
The Rearrangement of Allyl Alcohols over Nafion-H Catalyst in the Gas Phase

When gaseous allyl alcohols were passed over Nafion-H, a polyfluorinated resinsulfonic acid, at 170–190 °C, rearrangement occurred giving the corresponding aldehydes. Table II summarizes the data obtained from the rearrangement of allyl and substituted allyl alcohols in the gas phase over the solid superacidic catalyst. The reactions are substantially influenced by the temperature as well as by the contact time. The data suggest that reaction occurs faster with 2-methylallyl alcohol than with allyl or crotyl alcohols. This is in agreement with the mechanism, discussed earlier herein.

Experimental Section

Materials. Allyl alcohols used are commercially available.

NMR Spectra. A Varian Associates Model A-56/60A spectrometer with variable temperature probe was used for all spectra. Chemical shifts are recorded in ppm (δ) from external (capillary) Me_4Si for ^1H NMR spectra and from external (capillary) CCl_3F for ^{19}F NMR spectra.

Study of the Rearrangement of Allyl Alcohols in Superacid Solution. The procedure used for the preparation of FSO_3H–SbF_5–SO_2ClF and HF–SbF_5–SO_2ClF solutions of the protonated alcohols was the same with that described earlier.[11]

Solutions of the protonated alcohols were prepared by dissolving the appropriate precursors (approximately 0.1 mL) in 0.5 mL of SO_2ClF at the desired temperature and slowly adding the mixture to a well-stirred solution of 1 mL of FSO_3HSbF_5 or HF–SbF_5 solutions (1:1 molar solutions) in 1 mL of SO_2ClF maintained at dry ice–acetone bath temperature. (Dry ice ether slug was used for protonation at temperatures lower than −90 °C.) The resulting solution was transferred immediately with cooling into an NMR tube precooled at dry ice–acetone temperature.

Rearrangement of Allyl Alcohols in the Gas Phase over Nafion-H Catalyst. The reactor, experimental procedure, and activation of Nafion-H catalyst were those previously reported.[14] Reactions were carried out at temperatures between 140 and 195 °C, using 1 g of the catalyst. Products were collected in a trap immersed in a −60 °C bath. Products were identified using IR and NMR spectroscopies.

References and Notes

(1) Synthetic Methods and Reactions. Part 50. For part 49 see G. A. Olah and S. C. Narang, *Synthesis* (in press).
(2) (a) *Methoden Org. Chem. (Houben-Weyl), 4th Ed.*, **7**, 227 (1954); (b) G. W. Hearne, M. Tamele, and W. Converse, *Ind. Eng. Chem.*, **33**, 805 (1941).
(3) G. F. Emerson and R. Pettit, *J. Am. Chem. Soc.*, **83**, 4591 (1961).
(4) W. T. Hendrix, F. G. Cowherd, and J. L. von Rosenberg, *Chem. Commun.*, 97 (1968).
(5) V. Macho, M. Polievka, and L. Komora, *Chem. Zvesti*, **21**, 170 (1967).
(6) Ah. Il Bobanova, G. A. Bogdanovskii, and G. D. Vovehenko, *Vestri. Mosk. Univ. Khim.*, **24** (4), 88 (1969).
(7) "Kirk-Othmer Encyclopedia of Chemical Technology," Vol. 1, p 920.
(8) (a) G. A. Olah and E. Namanworth, *J. Am. Chem. Soc.*, **88**, 5327 (1966); (b) G. A. Olah, J. Sommer, and E. Namanworth, *ibid.*, **89**, 3576 (1967).
(9) D. M. Brouwer, J. A. Van Doorn, and A. A. Kiffer, *Recl. Trav. Chim. Pays-Bas*, **94**, 198 (1975).
(10) G. A. Olah, D. H. O'Brien, and M. Calin, *J. Am. Chem. Soc.*, **89**, 3582 (1967).
(11) G. A. Olah, M. Calin, and D. H. O'Brien, *J. Am. Chem. Soc.*, **89**, 3586 (1967).
(12) H. Mayr and G. A. Olah, *J. Am. Chem. Soc.*, **99**, 510 (1977).
(13) C. A. Vernon, *J. Chem. Soc.*, 425 (1954).
(14) G. A. Olah, J. Kaspi, and J. Bukala, *J. Org. Chem.*, **42**, 4187 (1977).