The results of this study thus indicate that β-hydroxy esters pyrolyze to mixtures of the corresponding ester and aldehyde or ketone and that the reaction involves a cyclic transition state, which owing to the comparatively small substituent effects observed, most probably is concerted.

Experimental Section

β-Hydroxy Esters.—Ethyl 3-hydroxybutanoate was bought (Aldrich Chemical Co.); the other β-hydroxy esters were prepared by the Reformatsky reaction[12] between the appropriate aldehyde or ketone and α-bromo ester. All of the esters were distilled carefully before use and their purity checked by glc. The physical properties (boiling point and refractive index) of all the esters prepared agree closely with literature values.

Thermolysis of the β-Hydroxy Esters.—Thermolysis of the esters were carried out in carefully washed glass tubes, 2-mm i.d. and 40–50-mm length. The ester (20 μl) was placed in the tube, the contents were frozen in Dry Ice–acetone, and the tube was evacuated, flushed several times with nitrogen, and finally evacuated and sealed. The tubes were then placed in a heated aluminum block (see the kinetic measurements), and thermolyzed during 4 or 5 half-lives. At the end of the reaction, the tubes were cooled in Dry Ice–acetone, and a sample was withdrawn and analyzed by glc using a 5-ft SE-30 column. A further sample was withdrawn and added to a solution of 2,4-dinitrophenylhydrazine in phosphoric acid,[13] and the resulting 2,4-dinitrophenylhydrazone was filtered and crystallized and its melting point was determined.

Kinetic Procedures.—The kinetic methods used were those described previously.[4] ACS reagent grade toluene was used without further purification. *p*-Xylene (Aldrich Chemical Co.) was refluxed over sodium and then fractionated. Thermolyses were carried out in a heated aluminum block 14 in. long by 8 in. in diameter insulated by glass wool. The block was heated by a resistance coil and its temperature controlled to ±0.2° by a Fielden type TCB2 temperature controller. The absolute temperature was checked by a chromel–alumel thermocouple. Approximately 10–15 μl of a solution of the β-hydroxy ester (4% v/v) and *p*-xylene (2% v/v) in toluene was injected through a rubber septum into a nitrogen-filled capillary, 2-mm i.d. and 40–50-mm length. The capillary was then sealed. Five such capillaries were placed in holes drilled in the block, the holes being of such diameter that the tubes fitted precisely, and at determined intervals the tubes were withdrawn and the reaction was quenched by quickly plunging them into cold water. The contents of the tubes were analyzed by glc using a 5-ft SE-30 column at 180° for the phenyl ester and 100° for the other esters. Under these conditions retention times of 1–2 min were observed. The areas of the peaks due to the starting β-hydroxy ester and the standard *p*-xylene were compared using a Photovolt Model 49 integrator. In the case of ethyl 3-hydroxy-3-methyl butanoate, the reaction was also followed at various temperatures by comparing the areas of the peaks due to ethyl acetate and acetone (the products of the reaction) with that of the standard *p*-xylene. Identical rate constants were obtained as by the former method.

The validity of this method was established by a determination of the rates of pyrolysis of 2-methyl-4-penten-2-ol at 330 and 320°. Rates of 10.5 and 6.20 × 10^{-4} sec^{-1} were obtained compared to extrapolated literature values[3] of 11.1 and 6.31 × 10^{-4} sec^{-1}. In the case of ethyl 3-phenyl-3-hydroxypropionate, decalin (refluxed over sodium and fractionated) was used as an internal standard, the reaction was studied in the liquid phase. Sufficient solution (50–100 μl) of the ethyl 3-phenyl-3-hydroxypropionate in toluene was injected into the capillary so that the capillary was about half full. Under these conditions all of the sample remained in the liquid phase. A sample placed in the hot block showed no decrease in volume but rather an increase due to the thermal expansion of the sample.

Quantitative measurement of the yield of the products of reaction was carried out under the same conditions as for the kinetic measurements, but the reaction mixture was pyrolyzed during 4–5 half lives and then analyzed by glc using a 5-ft SE-30 column. The areas of the peaks obtained were compared to those obtained from a known mixture of the aldehyde or ketone, ester, and *p*-xylene in toluene using a Photovolt integrator Model 49 to compare the peak areas.

Acknowledgments.—The authors would like to thank the Fund for Overseas Grants and Education (FORGE) and the Comité de Investigaciones of the Universidad del Valle for support of this work.

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Stable Carbocations. CXXII.[1] Diprotonation of Allophanates and Their Cleavage Reactions to Alkylcarbenium Ions and Diprotonated Allophanic Acid in Fluorosulfuric Acid–Antimony Pentafluoride ("Magic Acid"®) Solution

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The behavior of alkyl allophanates has been investigated in FSO_3H–SbF_5–SO_2 solution. Carbonyl oxygen diprotonation was observed in all cases by means of low-temperature pmr spectroscopy. With some of the diprotonated allophanates, cleavage occurred in the extremely strong acid system at higher temperatures to give stable alkylcarbenium ions and diprotonated allophanic acid. The elusive allophanic acid thus was directly observed for the first time in its stable diprotonated form.

Protonated amides and alkyl carbamates have been investigated in superacid solutions.[3–6] The protonation of allophanates, their cleavage reactions, and the possibility of the existence of allophanic acid in its diprotonated form have not as yet been investigated. It was felt of interest to extend our studies to the behavior of allophanates in FSO_3H–SbF_5–SO_2 solution and to investigate, over a range of temperature, their cleavage reactions.

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Results and Discussion

Methyl, ethyl, *n*-propyl, isopropyl, *n*-butyl, isobutyl, and *tert*-butyl allophanates were studied in FSO_3H–

TABLE I

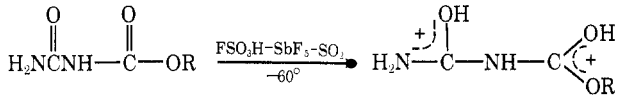
PMR CHEMICAL SHIFTS[a] AND COUPLING CONSTANTS[b] OF PROTONATED ALLOPHANATES IN FSO_3H–SbF_5–SO_2 SOLUTION

Compd	Registry no.	Temp, °C	—OH / —C—	NH	NH_2	H_1	H_2	H_3	H_4
$H_2NCONHCOCH_3$	761-89-7	−90	13.0	9.8	8.95	4.71			
	31585-11-2[c]		12.1		8.40	4.88			
$H_2NCONHCOCH_2CH_3$	626-36-8	−60	12.9	9.87	8.60	5.30	1.73		
	31585-12-3[c]		11.9		8.36	(q, 7.0)[b]	(t, 7.0)		
$H_2NCONHCOCH_2CH_2CH_3$	31598-83-1	−70	12.8	10.0	8.63	5.23	2.15	1.15	
	31585-13-4[c]		11.9		8.40	(t, 6.0)	(m)	(t, 6.0)	
$H_2NCONHCOCH_2CH_2CH_2CH_3$	3147-85-1	−80	13.0	10.1	8.78	5.36	2.16	1.77	1.20
	31585-14-5[c]		12.2		8.50		(m)	(m)	(t, 6.0)
$H_2NCONHCOH$	625-78-5	−80	13.4[d]	10.0	8.85				
	31585-15-6[c]		11.3		8.43				
			12.8						

[a] Chemical shifts are in δ, parts per million, referred to external TMS as standard. [b] Coupling constants, in hertz, are given in parentheses following the multiplicity of the peak. [c] Diprotonated derivative. [d] Observed only at temperatures below −90°.

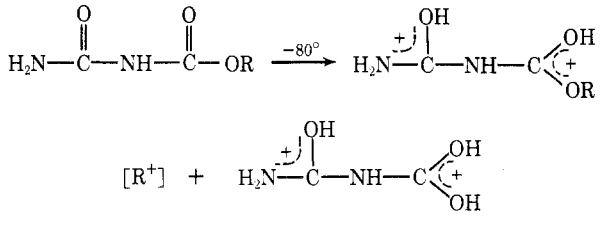
SbF_5–SO_2 solution at low temperature, generally at −78°.

In the superacid solvent system, FSO_3H–SbF_5–SO_2 solution, methyl, ethyl, *n*-propyl, and *n*-butyl allophanates are diprotonated on the carbonyl oxygen atoms as observed by pmr spectroscopy. The pmr chemical shifts and coupling constants are summarized in Table I. The protons on oxygen occur at lower

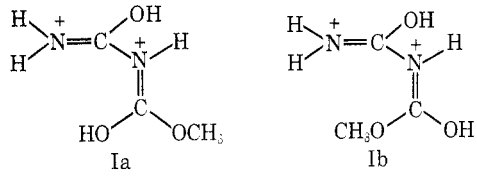


R = CH_3, CH_3CH_2, $CH_3CH_2CH_2$

field than those in protonated amides and carbamates, but is more shielded than those in diprotonated ketocarboxylic acids.[7] Isopropyl, isobutyl, and *tert*-butyl allophanates studied under the same conditions undergo alkyl oxygen cleavage to give diprotonated allophanic acid and alkyl carbenium ions.



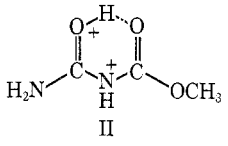
The pmr spectrum of methyl allophanate in FSO_3H–SbF_5 solution diluted with SO_2 at −90° consists of two methyl singlets at δ 4.88 and 4.71 with a relative area ratio of 3:2, two broad singlets for the NH_2 protons at δ 8.95 and 8.40, two singlets at δ 10.1 and 9.8 for the NH proton, and two OH resonances at δ 12.1 and 13.0 with the same peak area ratios (3:2). This indicates that methyl allophanate is diprotonated on the carbonyl oxygens, and two isomeric species (Ia and Ib) are observed due to restricted rotation at low temperatures around the C=N bonds.



Ia Ib

On raising the temperature to −40°, because of the low barrier of rotation around the C–N bond, the nmr spectrum showed only one singlet at δ 4.79 for the methyl group, a singlet for NH at δ 9.80, and a broad peak at δ 8.40 for the NH_2 protons. The OH protons are not observed at this temperature owing to fast proton exchange with the acid solvent system.

After keeping the sample at room temperature for about 1 hr and then cooling it back to −90°, the pmr spectrum showed only a singlet for the CH_3 group at δ 4.50 (0.38 ppm higher field than what is observed before heating the sample) and three resonances for the protons on nitrogen at δ 7.98, 7.80, and 9.90 with a relative area ratio of 1:1:2 and no absorptions in the OH region. The appearance of higher field chemical shifts for the CH_3 and NH_2 protons than those in ions Ia and Ib can probably be attributed to the nitrogen-protonated species II. The OH resonance is not observed due to rapid equilibration between the carbonyl oxygen atoms and rapid proton exchange with the acid–solvent system.

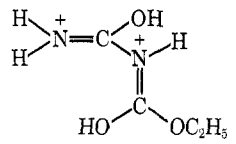


II

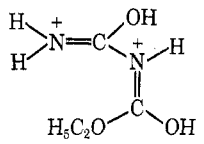
Ethyl allophanate in FSO_3H–SbF_5 diluted with SO_2 at −60° showed the NH proton at δ 9.87, the NH_2 protons

(7) G. A. Olah, A. T. Ku, and J. Sommer, *J. Org. Chem.*, **35**, 2159 (1970).

at δ 8.60 and 8.36, the CH_2 quartet at δ 5.30, the CH_3 triplet at δ 1.73, and an OH resonance at δ 12.9. On lowering the temperature to −90°, a new broad OH resonance at δ 11.9 and new resonances in the NH region are also observed, indicating that at this low temperature two protonated forms (IIIa and IIIb) are



IIIa



IIIb

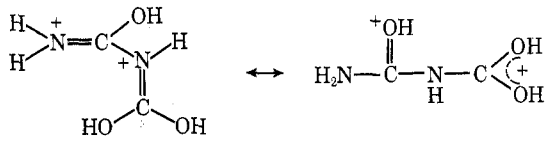
observed. On warming the solution, ion III decomposed to, so far, unidentified products.

***n*-Propyl allophanate,** again in FSO_3H–SbF_5–SO_2 solution, is diprotonated. At −70°, the nmr spectrum showed the NH singlet at δ 10.1, NH_2 singlets at δ 8.63 and 8.40, the α-CH_2 at δ 5.32 (t, 6.0), β-CH_2 at δ 2.15, and methyl triplet at δ 1.15. As the temperature was lowered to −90°, two broad peaks at δ 12.8 and 11.9 appeared which are assigned to protons on oxygen. Obviously only one isomer of diprotonated *n*-propyl allophanate was observed. As, however, no coupling was observed, no structural assignment could be made. On raising the temperature to −20°, alkyl–oxygen cleavage occurred to give diprotonated allophanic acid and *tert*-hexyl cations.

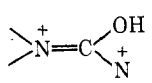
***n*-Butyl allophanate** in FSO_3H–SbF_5 is also diprotonated on the carbonyl oxygens. The derived chemical shifts are shown in Table I. Even at −90°, the nmr spectrum also showed a small singlet at δ 4.0 which is assigned to the *tert*-butyl cation and is probably due to cleavage because of local overheating during sample preparation. The intensity of this peak did not increase with time at −80°. At −60°, the δ 4.0 singlet increased with time, indicating that alkyl–oxygen cleavage occurred to give *tert*-butyl cation and diprotonated allophanic acid. At −20°, the cleavage was completed within a few minutes.

Protonated **isopropyl, isobutyl,** and ***tert*-butyl allophanates** could not be observed. Cleavage reactions occurred even at a temperature as low as −90°, to give diprotonated allophanic acid and the corresponding stable alkyl carbenium ions (*tert*-butyl and *tert*-hexyl cations).

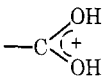
Diprotonated allophanic acid was thus generated with ease by cleavage of isopropyl, isobutyl, and *tert*-butyl allophanates in FSO_3H–SbF_5 solution containing an equal volume of SO_2 as diluent. The nmr spectrum at −80° showed OH absorptions at δ 11.3 and 12.8, NH at δ 10.0, and NH_2 at δ 8.85 and δ 8.43. At −90°, the nmr spectrum showed another broad peak in the OH region at δ 13.4. This indicates that allophanic acid is diprotonated. The resonance at δ 13.4 is



assigned to the OH proton in i; the two OH resonances at higher field are assigned to the OH protons of ii.



i



ii

These resonances are broadened, but no resolvable coupling was observable. Hence no differentiation or assignment could be made between the two OH protons. The nmr spectrum also showed a singlet at δ 9.40 which is not understood at the present time.

Experimental Section

Materials.—Methyl, ethyl, and isopropyl allophanates were prepared by the method of Dains and Wertheim[8] by the reaction of urea and the corresponding alkyl chloroformates. *n*-Propyl and *n*-butyl allophanates were prepared by the reaction of the corresponding alcohols in glacial acetic acid with potassium cyanate.[9] Isobutyl allophanate was prepared by treating isobutyl alcohol with cyanic acid generated from cyanuric acid.[10] Fluorosulfuric acid and antimony pentafluoride were distilled prior to their use.

Preparation of Solutions.—Samples of protonated allophanates were prepared by dissolving approximately 2 ml of FSO_3H–SbF_5 in an equal volume of SO_2 and cooling to −78°, Dry Ice–acetone temperature. The allophanate (~0.5 g) was slowly added to the acid solution with vigorous agitation. The acid was always in large excess as indicated by the large acid peak at δ 10.4–11.0.

Nmr Spectra.—A Varian Associates Model A-56/60A nmr spectrometer equipped with low-temperature probe was used for all spectra. Chemical shifts are reported in parts per million (δ) from external (capillary) tetramethylsilane.

Registry No.—Isobutyl allophanate, 31598-85-3; *tert*-butyl allophanate, 31598-86-4; isopropyl allophanate, 763-58-6.

Acknowledgment.—Support of this work by a grant from the National Institutes of Health is gratefully acknowledged.

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