Stable Carbocations. CLXXXII.[1a] The Acetoacetylium and Diacetoacetylium Ions

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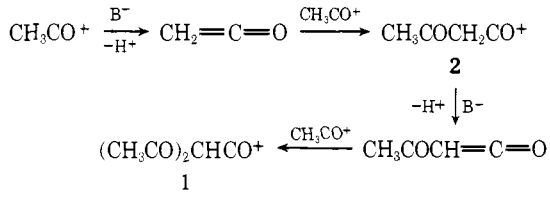
Abstract: The acetoacetylium ion was prepared both from acetoacetyl fluoride in SbF_5-SO_2 and from acetoacetic esters in HSO_3F-SbF_5 ("magic acid") solution. The keto form of the ion could be observed only at −70° as an unstable intermediate while, upon heating the solution to −30°, the enol tautomer is formed showing an equilibrium between its two cis-trans isomers. NMR and infrared data indicate a significant contribution of the "ketene-like" resonance forms, more important than in the case of the model crotonylium ion. The diacetoacetylium ion, as its hexafluoroantimate salt, was also prepared. The carbon-13 NMR data of this cation confirm the enol structure and the important contribution of the "ketene-like" resonance form. The significance of the acid catalyzed, electrophilic interconversion of acetyl, acetoacetyl, and diacetoacetyl systems is discussed.

Recently it was shown by Germain, Commeyras, and Casadevall[2] that the diacetoacetylium ion **1** is responsible for the absorption band around 2200 cm^{-1} observed in the infrared spectra of some acetylating systems.[2-5] Diacetoacetylium tetrachloroaluminate $[(CH_3CO)_2CHCO^+AlCl_4^-]$ was indeed subsequently isolated from the acetyl chloride-aluminum chloride system. The following mechanism was suggested for the trimerization of the acetylium ion, with the first step considered to be rate determining.



The acetoacetylium ion **2** was never observed previously. However, a recent calculation[6] predicted its existence, which was also indicated from retroacetoacetylation reactions.[7]

We report now the preparation and infrared, as well as proton and carbon-13 NMR, spectroscopic study of the acetoacetylium ion **2** as well as a novel, unequivocal preparation of the diacetoacetylium ion and its proton and carbon-13 NMR spectroscopic study.

Results and Discussion

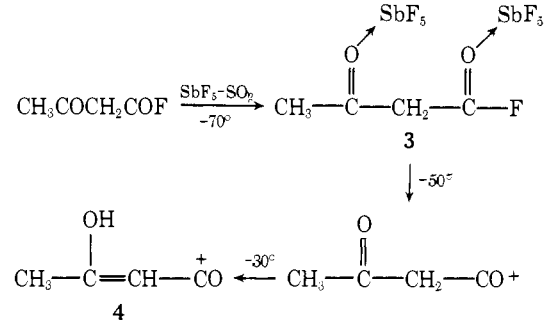
The Acetoacetylium Ion. Two procedures are generally used for obtaining acylium ions:[8] the ionization of the corresponding acyl halides by an appropriate Lewis acid halide (preferentially antimony pentafluoride) or the protolytic dehydration (cleavage) of the corresponding carboxylic acids or esters.

(a) Preparation from Acetoacetyl Fluoride. Acetoacetyl fluoride, the only stable acyl halide of acetoacetic acid (the chloride is rather unstable), gives in SO_2 solution with excess of SbF_5 in SO_2 at −70° the rather unstable complex **3**, which when the temperature of the solution is raised from −70 to −30° is successively converted into ions **2** and **4**. Proton NMR data of these species are given in Table I.

At −70°, the first observed species **3** shows the presence of maintained proton-fluorine coupling (J_{H-F} = 4.2 Hz) and thus must be considered as a donor-acceptor complex. The observed deshielding of both the CH_3 and CH_2 protons, from those of the keto form of the precursor (1.23 and 1.25 ppm, respectively), is particularly important, especially that for the methyl protons. The chemical shifts are comparable to those of diprotonated ethyl acetoacetate[9,10] (δ_{CH_3} = 3.63; δ_{CH_2} = 5.35) and are different from those of monoprotonated ethyl acetoacetate[10] (δ_{CH_3} = 2.73; δ_{CH_2} = 4.25). Thus, the first obtained species is certainly the acetoacetyl fluoride-bis(antimony pentafluoride) complex **3**.

When the solution is allowed to warm to −50°, the proton-fluorine coupling disappears, indicating the cleavage of the carbon-fluorine bond (or rapid exchange). The more deshielded methylene proton absorption and the more shielded methyl proton absorption compared with those of complex **3** are consistent with the keto form of the acetoacetylium ion, i.e., **2**.

When the solution is further allowed to warm to −30°,



the more stable *enol* form of the acetoacetylium ion **4** is formed. The OH proton (δ 10.83 ppm) is coupled with the α proton (J = 3.0 Hz) and with the methyl protons (J = 0.7 Hz) (see Figure 1). In fact, two cis-trans isomers can be envisaged. The observation of a second methyl signal, the relative intensity of which is temperature dependent (20% at −30° and <10% at −70°), is consistent with an equilibrium between the two isomers. The OH proton and the α proton of the minor isomer could not be detected. The question of this equilibrium will be discussed subsequently.

(b) Preparation from Acetoacetyl Esters. We reported previously[9] the preparation and study of diprotonated acetoacetic acid as well as its diprotonated methyl and ethyl esters in HSO_3F-SbF_5-SO_2 solution. The diprotonated acid was obtained from the *tert*-butyl ester, which cleaves immediately even at −80°. It was noted that the solution of the diprotonated acid decomposes (cleaves) at 0°, without, however, identifiable products being observed. We report now our further observations concerning diprotonated acetoacetic acid and its esters.

As mentioned, *tert*-butyl acetoacetate cleaves at room temperature in neat HSO_3F-SbF_5 to give diprotonated acetoacetic acid and the *tert*-butyl cation. The ethyl ester

Table I. ^{1}H NMR Data of Ions Formed from Acetoacetyl Fluoride–Antimony Pentafluoride in SO_2

Temp, °C	Species	Chemical shifts, ppm[a]			
		CH_3	CH_2	=CH–	OH
−60	Parent	2.15[b]	3.75 (d = 7.0)[d]		
	In SO_2	1.90[c]		5.05 (d = 6.0)[d]	[e]
−70	**3**	3.38	5.00 (d = 4.2)[d]		
−50	**2**	2.72	6.33		
−30	**4a**[f]	2.85 (d = 0.7)		5.90 (d = 3.0)	10.83 (dq = 3.0, 0.7)
	4b[f]	2.91 (d = 0.6)		[e]	[e]

[a] Chemical shifts (δ) referred to external Me_4Si. Multiplicity and coupling constants (in hertz) are given in parentheses. d = doublet: dq = doublet of quartet. [b] Keto form (>95%). [c] Enol form (<5%). [d] Proton–fluorine coupling. [e] Not observable. [f] Ratio **4a**:**4b** = 80:20.

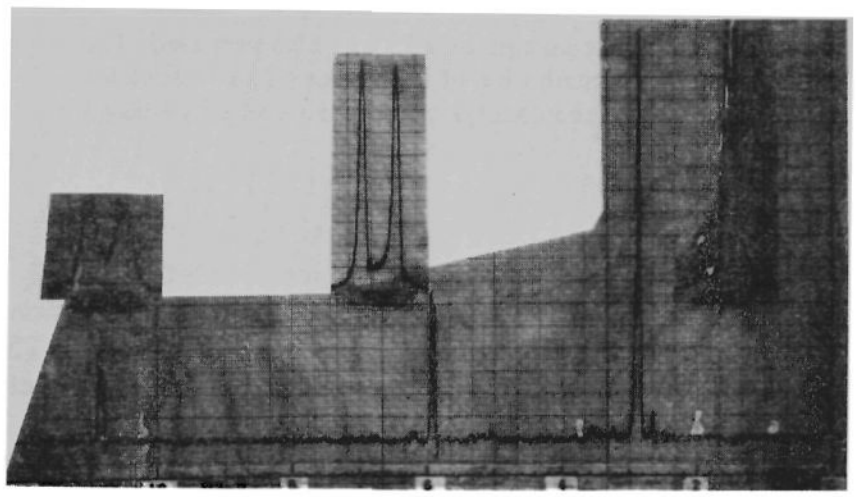
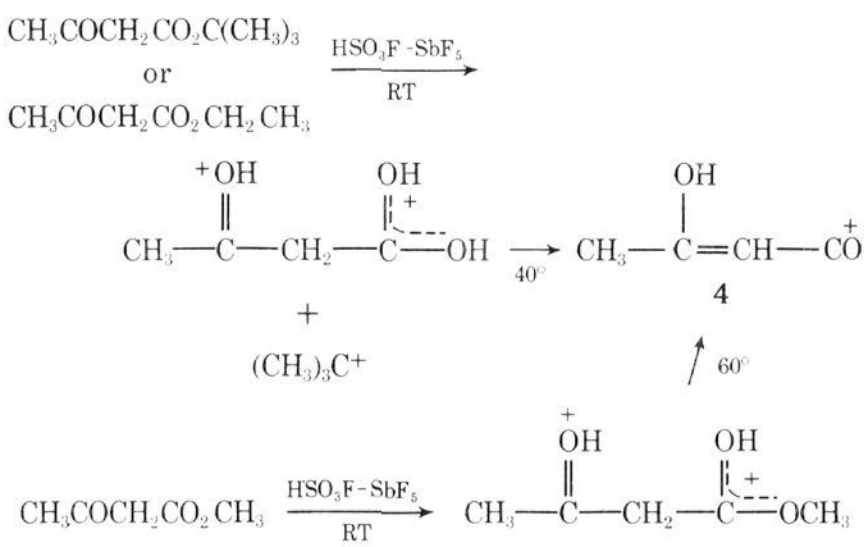
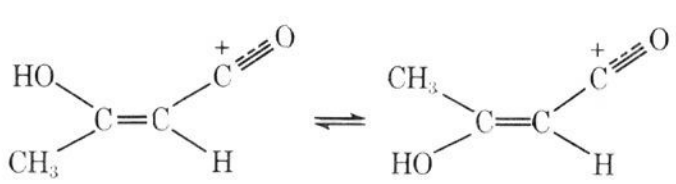


Figure 1. Proton NMR spectrum at 60 MHz of the acetoacetylium ion in SO_2 (−30°).

shows the same behavior, while the diprotonated methyl ester is stable under these conditions. The dehydration of diprotonated acetoacetic acid occurs around 40° to give the same proton NMR (Table II) spectrum as that which is obtained by the cleavage, at 60°, of the diprotonated methyl ester. In addition to the methyl absorption of the *tert*-butyl cation (δ 4.44), two methyl peaks (δ 3.31 and 3.37) and a singlet at δ 6.22 are observed. The intensity of this later peak is ⅓ of the intensity of the two combined methyl peaks. The strong, broad solvent signal at ≃11 ppm does not permit one to observe any OH proton, but the spectrum obtained at −30°, after addition of SO_2, is identical with that obtained for the acetoacetyl fluoride–SbF_5 system, proving the formation of the enol forms of the acetoacetylium ion **4**.



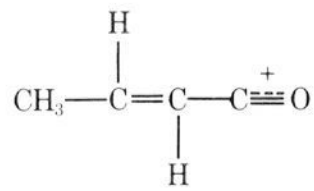
The two methyl peaks are attributed to the two cis–trans isomers (with relative intensities at 40°: **4a**:**4b** = 60:40).



4a **4b**

The absence of coalescence of these peaks separated by only 3 Hz, even at 60°, signifies that the cis–trans equilibrium is slow on the NMR time scale. However, fast exchange occurs between the OH proton and the solvent, as evidenced by lack of coupling to the α proton and the methyl protons.

The carbon-13 NMR spectra in SO_2 solution, like those in neat HSO_3F–SbF_5, confirm the enol form of the ion and the existence of the equilibrium between the two isomers (see Table III). The chemical shifts and ^{13}C–H coupling constants can be compared with those of the crotonylium ion **5**.[11] For both isomers, a deshielding of the carbonyl carbons and a shielding of the α carbons is observed compared with the corresponding shifts of the crotonylium ion. The carbonyl carbons and the α-carbons shifts resemble more those of ketene **7** and diphenyl ketene **8**,[12] respectively.



26.5 202.6 84.3 151.5

(J_{CH} = 131.3, 168.3, 197.6)

5

CH_2=C=O

2.8 194.7

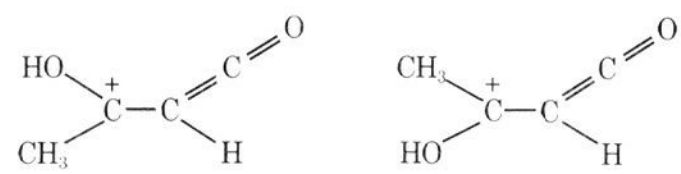
7

$(C_6H_5)_2$C=C=C=O

48.7 201.5

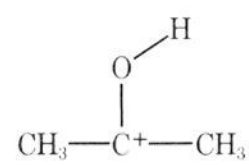
8

Thus a significant contribution of the "ketene-like" mesomeric forms **6a** and **6b** to ions **4a** and **4b** is indicated. The more deshielded β carbons also agree with this assumption, although it is difficult to estimate the effect of the hydroxyl substituent.



6a **6b**

Although the carbon-13 NMR data signify a substantial contribution of the "ketene-like" resonance forms, these are not the predominant ones. If this would be the case, the rotation around the C_α–C bond (i.e., cis–trans isomerization) would be fast. In limiting case, only one methyl peak would be observed. Furthermore, the ^{1}H NMR shifts for the OH proton and the methyl protons would be more deshielded. The observed data are also very different from those for protonated acetone **9** (δ_{CH_3} = 3.45; δ_{OH} =



9

Table II. ^1H NMR Data of the Ions Formed from Acetoacetic Esters in HSO_3F–SbF_5 Solution

Species	Temp, °C	Chemical shifts, ppm[a] CH_3–	$-CH_2-$	=CH–	COH	$CO_2HR(H)$
$CH_3C(=^+OH)CH_2CO_2H_2^+$	−80[b]	3.67	5.53		16.8	14.1
						14.3
	30	3.88	5.66		*c*	*c*
$CH_3C(=^+OH)CH_2CO_2MeH^+$	−60[b]	3.66	5.43		16.7	14.2
	30	3.45	5.42		*c*	*c*
4a[d]		3.31				
	50			6.22	*c*	
4b[d]		3.37				

[a] Chemical shifts (δ) referred to external Me_4Si. [b] In SO_2 solution, from ref 9. [c] Not discernible from the solvent signal. [d] Ratio **4a**:**4b** = 60:40.

Table III. Carbon-13 NMR Data of Acetoacetylium Ions

Solvent	Ion	Temp, °C	Chemical shifts, ppm[a] ^+CO	COH	CH	CH_3
	4a[b]		161.4	212.5	52.4 (d = 195.3)	25.9 (q = 132.8)
SO_2		−60				
	4b[b]		*d*	*d*	55.6 (d = 187.0)	25.1 (q = 136.0)
HSO_3F	**4a**[c]		161.2	213.2	51.8	25.9
		40				
SbF_5	**4b**[c]		164.8	209.9	54.6	24.4

[a] Chemical shifts referred to external Me_4Si. Multiplicity and carbon–proton coupling constant (in hertz), when determined from undecoupled spectrum, are given in parentheses. d = doublet; q = quartet. [b] Ratio **4a**:**4b** = 88:12. [c] Ratio **4a**:**4b** = 57.43. [d] Not observable.

Table IV. ^1H NMR Data of Diacetoacetylium Ion and Related Derivatives

Compd	Solvent	Temp, °C	Chemical shift, ppm[a] CH_3	CH	OH
$[(CH_3CO)_2CHCO]_2O, 3BF_3$	SO_2	−50	2.77	*b*	
$(CH_3CO)_2CHCO_2H_2^+SbF_6^-$	SO_2	−60	3.06	*b*	11.48
$(CH_3CO)_2CHCO^+SbF_6^-$	SO_2	−60	3.25	*b*	12.24
$(CH_3CO)_2CHCO^+AlCl_4^-$	SO_2	−30	3.03[c]	*b*	
$(CH_3CO)_2CHCO^+AlCl_4^-$	$SbCl_5$	20	3.64	*b*	

[a] Chemical shifts (δ) referred to external Me_4Si. [b] Not observable. [c] From ref 2.

14.93)[13] that can be considered as a suitable model compound for ions **6**.

From the NMR data, it is not possible presently to unequivocally assign which isomer is **4a** or **4b**. The observation of the long range coupling (J = 3.0 Hz) between the OH proton and the α proton for the major isomer in SO_2 at low temperature (**4a**) can indicate a "W" structure, i.e., the isomer where the OH and CO substituents are in cis position. However, this coupling cannot be considered as decisive proof.

In the infrared spectrum of the ion, at room temperature, only one carbonyl stretching vibration is observed at 2210 ± 5 cm^{-1}. It is probable that the frequencies of the two isomers are identical or very close. This frequency is lower than the one of the crotonylium ion (2240 cm^{-1}),[14] probably due to the contribution of the "ketene-like" resonance forms. However, it is higher than that of the diacetoacetylium ion (2180 cm^{-1}),[15] as anticipated by theoretical calculations.[6]

In our studies there was no evidence that the acetoacetylium ion would undergo cyclodimerization to give dehydroacetic acid or form an open chain dimer or trimer.

The Diacetoacetylium Ion. Attempts to obtain the diacetoacetylium ion by cleavage of diacetoacetyl ester (methyl and ethyl esters) in superacids were unsuccessful. Diacetoacetyl fluoride is not known and could not yet be obtained. Subsequently preparation of the ion was undertaken from the known boron trifluoride complex of diacetoacetic anhydride.

According to Meerwein,[16] acetic anhydride treated with boron trifluoride forms an adduct of diacetoacetic anhydride **10**.

$$5(CH_3CO)_2O + 7BF_3 \longrightarrow [(CH_3CO)CHCO]_2O, 3BF_3 + 4CH_3CO_2H, BF_3$$

10

The diacetoacetic anhydride–boron trifluoride adduct was isolated and subsequently treated with at least 3 mol excess of HF–SbF_5 (1:1) in SO_2 solution at −60°. As generally observed for the protolysis of anhydrides in superacid systems,[17,18] acylium ion **1** and protonated acid **11** are first formed. When warming the solution to room temperature (in the previously described pressure NMR tube),[18] dehydration of the protonated acid **11** takes place with formation of the diacetoacetylium ion **1**.

$$[(CH_3CO)_2CHCO]_2O, 3BF_3 + 2HF\text{-}SbF_5 \xrightarrow[-80^\circ]{SO_2}$$

$$\underset{\mathbf{1}}{(CH_3CO)_2CHCO^+SbF_6^-} + 3BF_3 + \underset{\mathbf{11}}{(CH_3CO)_2CHCO_2H_2^+SbF_6^-}$$

$$(CH_3CO)_2CHCO_2H_2^+SbF_6^- + HF\text{-}SbF_5 \xrightarrow{\Delta}$$

$$\underset{\mathbf{1}}{(CH_3CO)_2CHCO^+SbF_6^-} + H_3O^+SbF_6^-$$

Proton NMR data of the observed diacetoacetyl species are summarized in Table IV. It must be noted that the methine proton never was discernible, obviously due to the enolization process. The infrared spectra of isolated diacetoacetylium ion salts show, however, the dominant strong $\nu_{C=O}$ absorption around 2200 cm^{-1}.

The diacetoacetylium ion **1** was also obtained by treating 3 mol of acetyl chloride with 1 mol of SbF_5 in SO_2 solution at room temperature [when treating 1 mol of SbF_5 with 1 mol of acetyl chloride, however, only the acetylium ion (ν_{CO} = 2300 cm^{-1}) is formed].

The aluminum chloride salt of **1** when hydrolyzed at room temperature gives acetylacetone. The enol form of protonated acetylacetone **12** (δ_{CH_3} = 2.56; δ_{CH} = 6.29)[19] is

$$(CH_3CO)_2CHCO^+SbF_6^- + H_2O \longrightarrow [(CH_3CO)_2CHCO_2H] + HF\text{-}SbF_5$$

$$\downarrow -CO_2$$

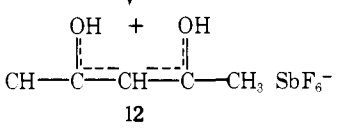


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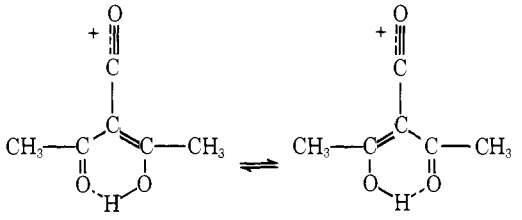
Table V. Carbon-13 NMR Data of the Diacetoacetylium Ion in SO_2 Solution (−40°)

Chemical shifts, ppm[a]			
^+CO	CO	C_α	CH_3
168.3	207.3	76.8	30.5 (q = 132.5)

[a] Chemical shifts referred to external Me_4Si. Multiplicity and carbon–proton coupling constant (in hertz) obtained, from undecoupled spectrum, are given between parentheses. q = quartet.

observed when water is added to the solution of the antimony fluoride salt in SO_2 solution. **12** can also be obtained by reaction of aluminum chloride salt with $NF-SbF_5-H_2O$.

The carbon-13 NMR spectrum (see Table V) of the diacetoacetylium ion confirms the predominant enol form **13**



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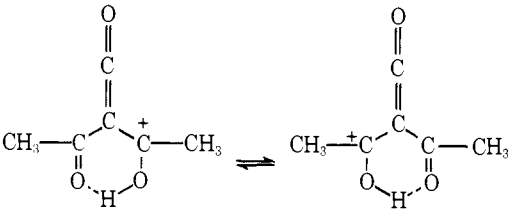
of the ion by the absence of coupling between the α carbon with any proton. The equivalence of the two β-carbonyl carbons, like that of the two methyl carbons and protons, indicates a fast equilibrium between the two equivalent positions of the enolic proton. A recent analysis of the infrared spectra of the $AlCl_4^-$ salt of the ion and its deuteriated analog[20] shows, effectively, the existence of a strong hydrogen bond with a symmetrical double minimum potential.

The more deshielded CO^+ carbon in **1**, as compared with that of the acetoacetylium ion **3**, signifies, like the lower $\nu_{C=O}$ frequency, the more important participation of the "ketene-like" forms **14.**



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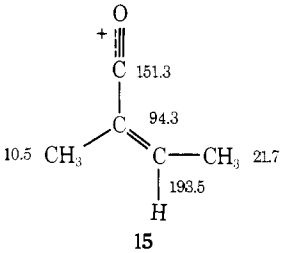
Due to its substitution, the C_α carbon chemical shift cannot be directly compared with that of the acetoacetylium ion. However, by comparison with the tigloylium ion **15,**[11]



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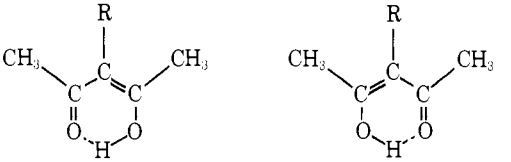
the shielding effect is compatible with a more important participation of the "ketene-like" form.

The chemical shift of the β-carbonyl carbons, more shielded than the β carbon of the acetoacetylium ion, must be, in fact, the average of the enol and keto forms. Comparison with the enol tautomer of acetylacetone and its monoethyl substituted derivative, **16a–b,**[21] shows a substantial



16a, R = H (δ_{CO} 189.4)
b, R = CH_3 (δ_{CO} 198.0, in SO_2)

deshielding effect of these carbons, according to the augmentation of the charge due to the participation of "ketene-like" mesomeric form.

Conclusions

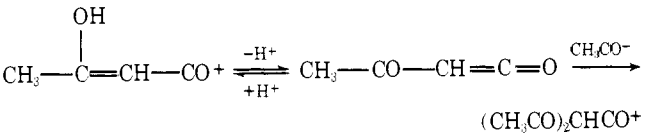
Acetoacetylations play an important role in synthetic organic chemistry, as well in biological processes. The observation of the acetoacetylium ion provides a significant insight in the mechanistic understanding of electrophilic acetoacetylations.

The formation of acetoacetates generally takes place through base catalyzed Claisen condensations of the corresponding acetates. The biochemical counterpart of this reaction is the self-condensation of acetyl coenzyme A in the presence of the enzyme acetyl CoA transacetylase to form acetoacetyl-CoA.

Observation of the formation of the diacetoacetylium ion via trimerization of the acetylium ion suggested an electrophilic mechanism, in which the acetoacetylium ion is intermediately formed, via acetylation of ketene, the deprotonation product of the acetylium ion.

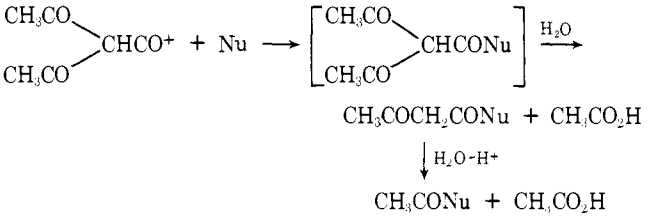
Having prepared and studied by spectroscopic methods the stable acetoacetylium ion, this mechanism now could be directly proved.

The fast hydrogen exchange of the enolic proton of the acetoacetylium ion in superacidic media implies the intermediate formation of the corresponding ketene, which then, can react with the electrophilic acetylium ion giving the di-



acetoacetylium ion. Indeed, it was possible to carry out this reaction when acetylium ion was added to a solution of the acetoacetylium ion.

The possible involvement of the diacetoacetylium ion in acylating systems is not yet fully understood. It can give, however, with nucleophiles (Nu) both acetoacetylated as well as acetylated products, through ready, acid catalyzed cleavage reactions.



These aspects will be reported separately.

It is not unreasonable to suggest therefore that, in biological systems too, acetoacetylated derivatives can be formed not only under base but also acid catalyzed conditions.

Experimental Section

Materials. Acetoacetyl fluoride was prepared according to Olah and Kuhn by treating freshly distilled diketone with anhydrous hydrogen fluoride.[7]

Methyl and ethyl diacetoacetate were prepared by acetylation of the corresponding acetoacetates.[22]

All other starting materials were commercially available.

Spectra. Infrared spectra were obtained on a Beckman IR 10 spectrophotometer, using IRTRAN or AgCl plates.

Proton NMR spectra were obtained on a Varian Associates Model A56/60A equipped with variable temperature probes. External Me_4Si (capillary) was used as reference.

Carbon-13 NMR spectra were obtained on Varian Associates Model HA-100 and XL-100 spectrometers both equipped with a broad-band decoupler, Fourier transform accessory, and a variable temperature probe. External ^{13}C-enriched Me_4Si (capillary) was used as reference.

Preparation of Ions. Acetoacetylium Ion. (a) A cold solution of acetoacetyl fluoride (2 mmol) in 1 ml of liquid SO_2 was added, with vigorous stirring, to a solution of SbF_5 (6 mmol) in 1 ml of SO_2 at −78°. For NMR studies, an aliquot of the about 10% solution was used after transfer to an NMR tube. For ir studies, the solvent was removed under vacuum to give a somewhat viscous semicrystalline product.

(b) Acetoacetic esters were added to a 1:1 *M* HSO_3F-SbF_5 mixture at −20°, using the general reaction conditions described previously.[9]

Diacetoacetylium Ion. Crystalline diacetoacetylium tetrachloroaluminate was prepared as described.[2]

Diacetoacetic anhydride-$3BF_3$ was prepared according to Meerwein.[16]

Diacetoacetylium hexafluoroantimonate was prepared by adding the anhydride-$3BF_3$ adduct (2 mmol) in SO_2 (2 ml) to a solution of 1:1 *M* HF-SbF_5 (6 mmol) in SO_2 (2 ml) at −78°. The reaction was carried out in a sealed reaction tube fitted with a pressure screw cap. After 5 hr at room temperature, the sealed tube was cooled and opened and the solvent removed under vacuum.

Acknowledgment. Support of our work by the National Institutes of Health is gratefully acknowledged.

References and Notes

(1) (a) Part CLXXXI: G. A. Olah and G. Liang, *J. Org. Chem.*, **40**, 2108 (1975); (b) postdoctoral research associates.
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Stable Carbocations. CLXXXIII.[1a] Haloacetylium Ions

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Abstract: Haloacetylium ions were prepared using methods previously developed for obtaining acylium fluoroantimonate salts. The monochloro-, monobromo-, and monoiodoacetylium ions were obtained as stable species and studied by NMR spectroscopy in SO_2, while the monofluoroacetylium ion was found to be in equilibrium with its oxygen and fluorine coordinated donor-acceptor complexes. Dichloro- and difluoroacetylium and, in contrast to previous reports, also the trifluoroacetylium ion could not be obtained as stable species due to their rapid decarbonylation. The ^1H, ^{19}F, and ^{13}C NMR spectra of prepared haloacetylium ions are discussed in relation to structural aspects and the stability of the halogen substituted acetylium ions.

Acylium ions constitute by now a well-characterized class of stable carbocations.[2] However, no study of halogenated aliphatic acylium ions, except the work of Lindner and Kranz concerning the trifluoroacetylium ion,[3] has previously been reported. These ions are of interest as intermediates in haloacylation reactions and also of theoretical interest concerning the effect of introduction of halogen atoms on the stability of acylium ions and the possibility of halogen participation.

In carbenium ions, halogen substitution of the carbenium center affects stabilization by electronic "back-donation",[4] i.e., by conjugation of the nonbonded halogen electron pairs into the vacant p orbital. Halogen substitution at adjacent or further removed carbons on the other hand causes destabilization due to the inductive electronic effect of the electronegative halogen atoms. This is clearly the case for fluorine but, with chlorine, bromine, and iodine, halogen participation involving halonium ion type mesomeric forms can also be expected.[5a,b]

In the case of acylium ions, three mesomeric forms (**1, 2,** and **3**) are involved in providing stabilization of the ions. All

$$\underset{\mathbf{1}}{R{-}C{\equiv}O^{+}} \longleftrightarrow \underset{\mathbf{2}}{R{-}\overset{+}{C}{=}O} \longleftrightarrow \underset{\mathbf{3}}{\overset{+}{R}{=}C{=}O}$$

these mesomeric forms will be destabilized by the inductive effect of halogen substitution. While possible chlorine, bromine, or iodine neighboring group participation could lead to the stabilizing halonium ion form **4**, such an effect is un-