can be determined. Then, a plot of kt_a *vs.* t_a yields a straight line with a slope equal to k.

DMSO (0.1 *F* TEAP) solutions of *n*-butyl, *sec*-butyl, and *t*-butyl chloride have been prepared with each 0.10 *F* in alkyl halide. A series of reverse chronopotentiograms have been recorded for each solution at 28.0 ± 0.5° for various values of t_a. The current density also has been varied over a minimum range of five for each solution; in the case of *t*-butyl chloride, the range of current density has been ten. In all cases, the ratio of τ_2/t_a is a function only of t_a and is independent of current density. This independence of current density indicates that the reaction is first order in the electroactive species; *i.e.*, superoxide.[13] The pseudo-first-order rate constants, k, for the reaction

$$RCl + O_2^- \longrightarrow RO_2\cdot + Cl^- \qquad (2)$$

are, for *n*-butyl chloride, 3.2×10^{-1} sec^{-1}; *sec*-butyl chloride, 0.6×10^{-1} sec^{-1}; and *t*-butyl chloride, 0.4×10^{-1} sec^{-1}. The rate of the reactions with any of the butyl bromides or butyl iodides is too rapid to measure by this method; *i.e.*, $\tau_2 = 0$.

Attempts have been made to detect hydroperoxide as an eventual product of the reaction to substantiate the belief that the initial product of the reaction is a peroxide radical. The latter would abstract a hydrogen atom from the solvent or the electrolyte to form a hydroperoxide. Large-scale electrolyses have been performed in which solutions of DMSO (0.1 *F* TEAP)–*t*-butyl bromide are kept saturated with oxygen while several hundred coulombs are allowed to pass through the solution. Samples then have been injected into a gas chromatograph and a material exhibiting the same retention time as that of an authentic sample of *t*-butyl hydroperoxide has been detected with two different columns. On this basis, some hydroperoxide is concluded to be formed from the superoxide–alkyl halide reaction. *t*-Butyl hydroperoxide also has been detected by gas chromatography in acetonitrile and acetone in similar experiments.

Summary and Conclusions

The data indicate that tetraethylammonium superoxide reacts with alkyl halide by a nucleophilic displacement of the halide to give peroxide radicals as the initial product. The reaction is first order with respect to superoxide, and occurs with 1:1 stoichiometry. Furthermore, *n*-butyl chloride reacts faster than *sec*-butyl chloride, which is faster than *t*-butyl chloride; alkyl chlorides react slower than bromides and iodides.

The results differ from those reported by Schmidt and Bipp[3] and by Le Berre and Berguer[4] who did not observe reactions for suspensions of potassium and sodium superoxide with alkyl halides. This difference probably is related to the fact that alkali and alkaline earth salts have a large effect on the reactivity of superoxide with water[5] and on its electrochemistry.[6] The greater reactivity of the tetraethylammonium salt implies that it may be of synthetic utility. A preparative procedure for the synthesis of tetramethylammonium superoxide is available.[14]

Registry No.—Superoxide ion, 12185-08-9; *n*-butyl chloride, 109-69-3; *sec*-butyl chloride, 78-86-4; *t*-butyl chloride, 507-20-0.

Acknowledgment.—This work was supported by the National Science Foundation under Grant No. GP-11608.

(14) A. D. McElroy and J. S. Hashman, *Inorg. Chem.*, **3**, 1798 (1964).

Stable Carbonium Ions. XCIV.[1] Diprotonated Ketocarboxylic Acids and Keto Esters and Their Cleavage to Protonated Ketooxocarbonium Ions in Fluorosulfuric Acid–Antimony Pentafluoride Solution

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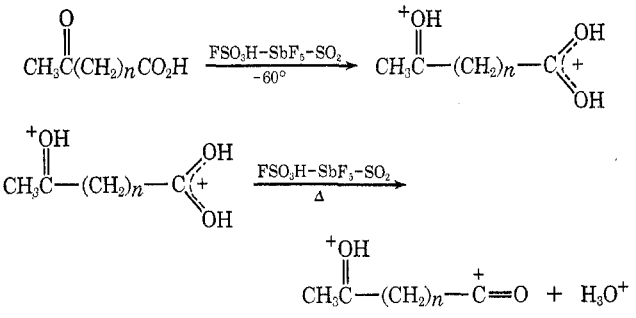
Protonation of a series of keto acids has been studied in FSO_3H–SbF_5–SO_2 solution. O-Diprotonation was observed at low temperature. Two isomeric species were found for protonated acetylvaleric acid and 3- and 4-benzoylbenzoic acids. At higher temperatures acetylbutyric, acetylvaleric, and 2-acetylbenzoic acids underwent dehydration to give the corresponding ketooxocarbonium ions. No cleavage reaction was observed for protonated levulinic acid and 3-acetyl-, 4-acetyl-, 3-benzoyl-, and 4-benzoylbenzoic acids even when solutions were heated up to +50°. Protonated pyruvic acid underwent dehydration and decarbonylation to give the methyloxocarbonium ion. Methyl and ethyl acetoacetates in FSO_3H–SbF_5–SO_2 solution are diprotonated. *t*-Butyl acetoacetate cleaves without observation of the protonated ester to diprotonated acetoacetic acid and the trimethylcarbonium ion.

Our recent investigations of protonated ketones,[3] carboxylic acids,[4] and dicarboxylic acids[5] lead us now to study the protonation of a series of aliphatic and aromatic keto acids in the super acid system, FSO_3H–SbF_5–SO_2. No nuclear magnetic resonance study of protonated keto acids has been reported in the literature, although a number of investigations of protonated carboxylic acids are known.[6–10]

(1) Part XCIII: G. A. Olah and A. T. Ku, *J. Org. Chem.*, **34**, 331 (1969).
(2) (a) National Institutes of Health Predoctoral Research Investigator. (b) NATO Postdoctoral Research Associate, 1967–1968.
(3) G. A. Olah, M. Calin, and D. H. O'Brien, *J. Amer. Chem. Soc.*, **89**, 3586 (1967); G. A. Olah and M. Calin, *ibid.*, **90**, 938 (1968).
(4) G. A. Olah and A. M. White, *ibid.*, **89**, 3591, 7072 (1967).
(5) G. A. Olah and A. M. White, *ibid.*, **89**, 4752 (1967).
(6) T. Birchall and R. J. Gillespie, *Can. J. Chem.*, **43**, 1045 (1965).
(7) H. Hogeveen, A. F. Bickel, C. W. Hilbers, E. L. Mackor, and C. Maclean, *Chem. Commun.*, 898 (1966).
(8) H. Hogeveen, A. F. Bickel, C. W. Hilbers, E. L. Mackor, and C. Maclean, *Rec. Trav. Chim. Pays-Bas*, **86**, 687 (1967).
(9) H. Hogeveen, *ibid.*, **86**, 809 (1967).
(10) M. Brookhart, G. C. Levy, and S. Winstein, *J. Amer. Chem. Soc.*, **89**, 1735 (1967).

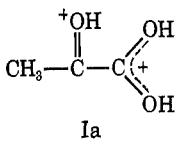
Results and Discussion

In the super acid system, FSO_3H–SbF_5–SO_2 ("magic acid"), all keto acids studied are completely diprotonated at −60°. When raising the temperature, we are able to observe in certain cases cleavage to the protonated ketooxocarbonium ions.

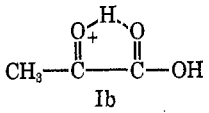


The following keto acids were studied in FSO_3H–SbF_5–SO_2 solution: pyruvic, acetoacetic, levulinic, acetylbutyric, and acetylvaleric acids as well as 2-acetyl-, 3-acetyl-, 4-acetyl-, 2-benzoyl-, 3-benzoyl-, and 4-benzoyl-benzoic acids. The pmr chemical shifts and coupling constants of diprotonated keto acids are summarized in Table I.

Protonated pyruvic acid was generated from the sodium salt of pyruvic acid in FSO_3H–SbF_5 solution diluted with SO_2. The pmr spectrum showed the OH protons as a broad resonance at δ 15.0 at −90°. This indicates that the OH protons are exchanging with the solvent acid system, the resonance of which was also broad. The methyl protons which showed no observable coupling appear as a singlet at δ 3.75 which is more deshielded than that of protonated acetone (δ 3.45)[3] and protonated acetic acid (δ 3.18).[4] The highly deshielded singlet methyl absorption at δ 3.75, close to that found for diprotonated 2,4-butanedione (δ 3.90),[11] indicates that pyruvic acid is also diprotonated as shown in Ia. The pmr spectrum of pyruvic acid also displays another small peak at δ 2.90 which is assigned to the methyl protons of the monoprotonated species Ib.

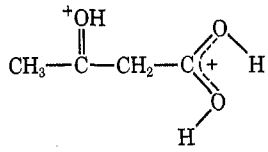


Ia



Ib

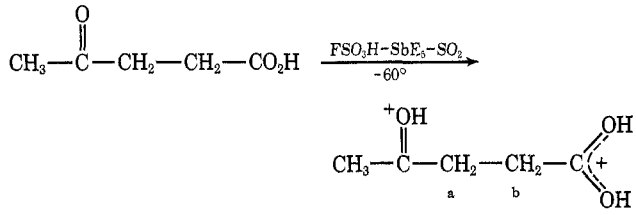
Protonated acetoacetic acid was generated by cleavage of *t*-butyl acetoacetate in 1:1 *M* FSO_3H–SbF_5 solution diluted with SO_2. The pmr spectrum of protonated acetoacetic acid at −80° showed the proton on the keto oxygen, C=OH^+, at δ 16.8 which is at a much lower field than that of protonated aliphatic ketones.[3] This broad resonance could not be resolved even at temperatures as low as −100°. The other two singlet absorptions of equal area at δ 14.10 and 14.27 are assigned to the OH protons of the protonated carboxyl group. As in the case of protonated aliphatic carboxylic acids,[4,5] the hydroxyl protons are in nonequivalent environments. This is interpreted, as in the case of protonated carboxylic acids,[4,5] as a consequence of structure II being the predominant species.



II

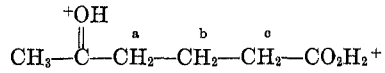
The methyl and methylene protons of protonated acetoacetic acid appeared at δ 3.67 and 5.53, respectively. These absorptions, although somewhat broad, showed no couplings. A small additional peak at δ 9.66 was also observed for protonated acetoacetic acid in FSO_3H–SbF_5–SO_2, even though the precursor, *t*-butyl acetoacetate, had been distilled several times. No assignment of this peak is made at the present time.

Levulinic acid (acetylpropionic acid) is also diprotonated in FSO_3H–SbF_5–SO_2 solution at −60°. It gives a well-resolved pmr spectrum with three singlet



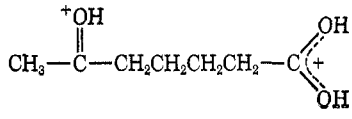
absorptions at δ 15.5, 13.4, and 13.18 for the hydroxyl protons. The lowest field singlet is due to the proton on the keto oxygen, and no coupling with the α protons was observed. The two singlets of equal area at a higher field in the hydroxy region are asigned to the protons on the carboxylic acid oxygens. The reason for the nonequivalence of the two hydroxyl groups is the same as that described for protonated acetoacetic acid. The pmr spectrum of protonated levulinic acid shows the methyl singlet at δ 3.45 and the two methylene triplets a and b at δ 4.25 and 3.85, respectively. Table I summarizes the chemical shifts and coupling constants.

Protonated acetylbutyric acid at −60° shows the $HO\overset{+}{=}C<$ proton as a singlet at δ 15.1 and the $CO_2H_2^+$



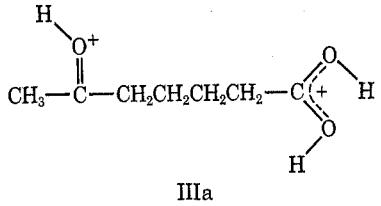
protons as two singlets of equal area at δ 13.1 and 12.9. These two singlets coalesced at −30°. The methyl protons appear as a singlet at δ 3.45. The methylene (a) appears as a triplet at δ 4.1, the methylene (b) as a multiplet centered at δ 2.85, and the methylene (c) as a triplet at δ 3.5. At low temperature, −60°, the C–H protons show broadening and the coupling constants between the methylene protons were evaluated from a spectrum recorded at −30°.

Protonated acetylvaleric acid at −60° shows the $HO\overset{+}{=}C<$ singlet at δ 14.5 and two $CO_2H_2^+$ singlets at

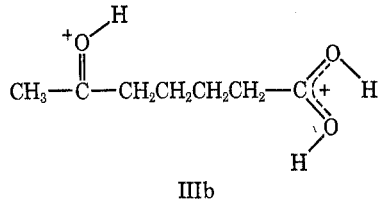


(11) G. A. Olah and M. Calin, *J. Amer. Chem. Soc.*, **90**, 4672 (1968).

δ 12.7 and 12.4 (equal area ratio) indicating that acetylvaleric acid is also diprotonated. No coupling was observed between the $HO{=}C<$ proton and the α-alkyl protons. Hence the structure of the diprotonated species could not be assigned (IIIa or IIIb). The nmr spectrum shows another small peak in the $HO{=}C<$ region (about $^1/_{20}$th the intensity of that at δ 14.5) at δ 14.2 which could possibly be due to another form of the diprotonated acetylvaleric acid (IIIa or IIIb). Since



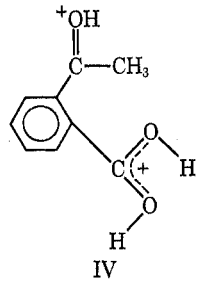
IIIa



IIIb

the intensity of this peak is so low, no further study could be made. The chemical shifts of the alkyl protons are summarized in Table I.

The nmr spectrum of **protonated 2-acetylbenzoic acid** (Table I) in FSO_3H–SbF_5–SO_2 solution[12] at −60° shows two broad low-field absorption peaks at δ 13.53 and 14.73, in the OH region. The higher field OH peak could be resolved into two singlets at δ 13.43 and 13.97 at −90°. This indicates, as in the case of protonted simple carboxylic acids, that the two OH protons of the protonated carboxyl group are nonequivalent, as in structure IV. No coupling of the $HO{=}C<$ proton



IV

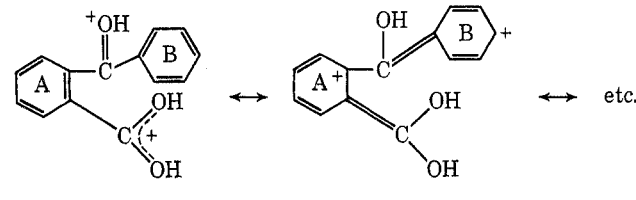
with either methyl or ring protons could be observed. Hence the orientation of the proton on the acetyl oxygen could not be established.

It has been shown that protonated benzoic acid[4,5] gives only a singlet for the OH proton. This is explained to be due to a low barrier of rotation about the C—O bonds. Protonated benzoic acid would be expected to have less double-bond character associated with the C—O bonds than the protonated simple aliphatic carboxylic acids, owing to resonance interaction with the phenyl ring. It is expected that a strong electron-withdrawing group on the ring of protonated benzoic acid would tend to prevent to some extent such resonance interaction. This would make the C—O bond of the carboxyl group more resemble a double bond than in protonated benzoic acid itself. This indeed is in accordance with our observations.

4-Acetylbenzoic acid in FSO_3H–SbF_5–SO_2 is also diprotonated. The pmr spectrum shows two OH singlets with an area ratio of 1:2 at δ 14.8 and 13.1. The higher field OH resonance is due to the OH of the protonated carboxyl group and the lower field OH is due to the proton on acetyl oxygen. The OH resonance of the carboxyl group could not be resolved even at a temperature as low as −100°. This is due to the fact that the inductive effect of the $HO{=}C<$ group is decreased as the separation of the two functional groups is increased. The aromatic protons gave an AB quartet centered at δ 8.86. The chemical shifts are summarized in Table I.

Protonated 3-acetylbenzoic acid shows two singlet resonance at δ 14.3 and 12.7 with a relative area ratio of 1:2. Again, the lower field OH resonance is assigned to the proton on the acetyl oxygen; the higher field OH resonance is due to the proton on the carboxyl group oxygen. These resonances are less deshielded than that of diprotonated 2- and 4-acetylbenzoic acid since the $HO{=}C<$ and $-CO_2H_2$ groups of protonated 3-acetylbenzoic acid are not directly conjugated. The resonance of the OH protons of the carboxyl group is a singlet even at a temperature as low as −100°. Table I summarizes the chemical shifts.

2-Benzoylbenzoic acid is diprotonated in FSO_3H–SbF_5 diluted with SO_2. The pmr spectrum shows two low-field singlets in the OH region at δ 13.3 and 12.9 for the proton on benzoyl oxygen and the carboxyl group, respectively. The chemical shift of the proton on benzoyl oxygen appears at a higher field than that of protonated 2-acetylbenzoic acid (δ 14.7). The resonance at δ 13.3 is a singlet even at a temperature as low as −100°. This is believed to be due to a low barrier to rotation about the C—OH bonds of the protonated carboxyl group. It is evident that the resonance interaction of the A ring and the protonated carboxyl group is still substantial. The positive charge of $HO{=}C<$ is substantially deceased by the resonance interaction with ring B, as shown above. The electron-withdrawing ability of the protonated benzoyl group $C_6H_5C(=OH)-$ is not strong enough to prevent the resonance interaction of ring A and the carboxyl group.

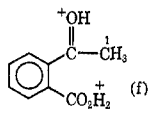
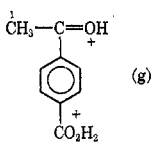
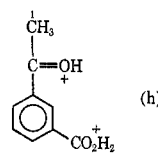
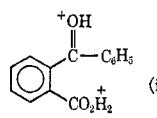
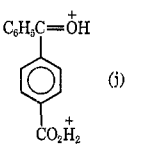
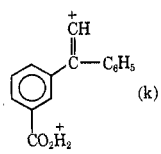


The pmr spectrum of **protonated 4-benzoylbenzoic acid** shows two absorption peaks for the proton on the benzoyl oxygen in a relative ratio of 60:40 indicating, as in the case of protonated ketones,[3] that two isomeric

(12) A 4:1 *M* FSO_3H–SbF_5 solution was used for all benzoic acid derivatives. This solution was used in preference to the 1:1 *M* acid since, in the latter solution, spectra were less well resolved particularly at higher temperature. The spectra obtained in both acids were in other respects identical.

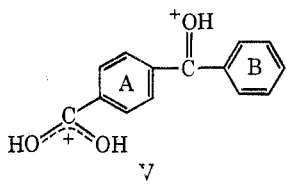
TABLE I

NMR CHEMICAL SHIFTS (IN PARTS PER MILLION)[a] AND COUPLING CONSTANTS (IN HERTZ) OF PROTONATED KETO ACIDS IN FSO_3H–SbF_5 SOLUTION

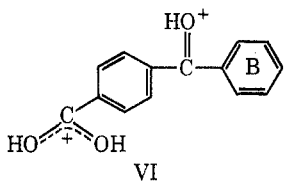
Keto acids	Temp, °C	^{+}OH ‖ –C–	$CO_2H_2^+$	H_1	H_2	H_3	H_4	H_5	Aromatic H
$CH_3\overset{+OH}{\overset{\|}{C}}-CO_2H_2^+$ (a)	−90	15.0	15.0	3.75 2.90					
$CH_3\overset{+OH}{\overset{\|}{C}}CH_2CO_2H_2^+$ (b)	−80	16.8	14.1 14.3	3.67	5.53				
$CH_3-\overset{+OH}{\overset{\|}{C}}CH_2CH_2CO_2H_2^+$ (c)	−60	15.5	13.4 13.2	3.45	4.25 (t, 6.0)[b]	3.85 (t, 6.0)			
$CH_3-\overset{+OH}{\overset{\|}{C}}CH_2CH_2CH_2CO_2H_2^+$ (d)	−60	15.1	13.1 12.9	3.45	4.1 (t, 7.0)	3.5 (t, 7.0)	2.85 (m)		
$CH_3-\overset{+OH}{\overset{\|}{C}}-CH_2CH_2CH_2CH_2CO_2H_2^+$ (e)	−60	14.5 14.20	12.5 12.6	3.25	3.70 (m)	3.30 (m)	2.10 (m)	2.10	
 (f)	−90	14.9	13.4 13.9	3.75					8.26–9.20
 (g)	−60	14.8	13.1	3.75					8.86
 (h)	−60	14.3	12.7	3.63					8.13–9.46
 (i)	−60	13.3	12.9						7.83–9.13
 (j)	−60	13.4 13.1	12.95						7.90–9.00
 (k)	−60	13.2 13.0	12.7						7.90–9.30

[a] Referred to external TMS. [b] Multiplicity: t = triplet; q, quartet; m = multiplet.

species (V and VI) are present. The assignment of the two isomers could not be made, because no coupling



V



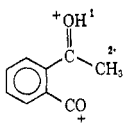
VI

was observed between this OH proton and ring protons. Only a singlet is observed for the OH protons of the protonated carboxyl group. As in the case of protonated 2-benzoylbenzoic acid, the resonance interaction of ring A with the protonated carboxyl group is still great.

3-Benzoylbenzoic acid in FSO_3H–SbF_5–SO_2 solution is also diprotonated. The pmr spectrum of protonated 3-benzoylbenzoic acid shows two singlets with relative

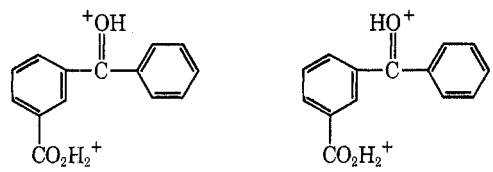
TABLE II

NMR CHEMICAL SHIFTS (IN PARTS PER MILLION)[a] AND COUPLING CONSTANTS (IN HERTZ) OF KETOOXOCARBONIUM IONS

Ketooxocarbonium ions	Temp, °C	H_1	H_2	H_3	H_4	H_5	H_6	Ar H
$CH_3-\overset{+}{C}(OH)-CH_2CH_2CH_2CO^+$ (a)	−40	15.5	3.55	4.20 (m)	4.70 (t, 8)[b]	3.10 (m)		
$CH_3-\overset{+}{C}(OH_3)-CH_2CH_2CH_2CH_2CO^+$ (b)	−20	14.80	3.30	3.90 (m)	4.50 (t, 7.0)	2.50 (m)	2.20 (m)	
 (c)	−60		3.85					8.73–9.30

[a] Referred to external TMS. [b] Multiplicity: t = triplet; m = multiplet.

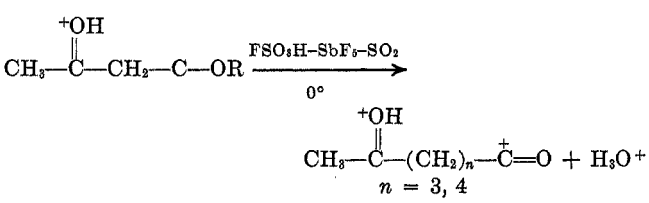
ratio of 40:60 for the proton on the benzoyl oxygen, indicating that two isomeric species (VII and VIII) are



VII VIII

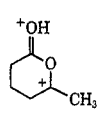
present. Assignment of the two isomers could not be made based on the present data. As in the case of protonated 2- and 4-benzoylbenzoic acid, the protons of the protonated carboxyl group appear only as a singlet at δ 12.7 which could not be resolved even at −100°. Table I summarizes the chemical shifts.

Cleavage of Diprotonated Keto Acids to Protonated Ketooxocarbonium Ions.—The mode of cleavage of diprotonated aliphatic keto acids is dependent on the distance between the keto and carboxyl groups. **Acetylbutyric and acetylvaleric acids** undergo complete dehydration at 0° to give the corresponding protonated ketooxocarbonium ions and an equimolar amount of H_3O^+.



An increase of deshielding is observed for all the protons of protonated ketooxocarbonium ions. The largest deshielding is observed in the methylene protons next to the carbonium carbon.[13] The chemical shifts and coupling constants of the protonated oxocarbonium ions are summarized in Table II.

(13) The possibility that the ions formed might be protonated cyclic ions, such as

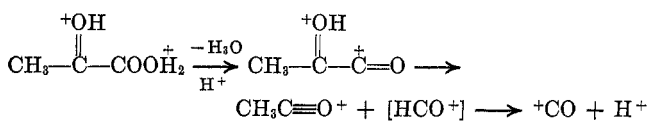


is ruled out based on this observation. In the cyclic ion one would expect that the methylene and the methyl protons originally next to the protonated keto group would be deshielded substantially.

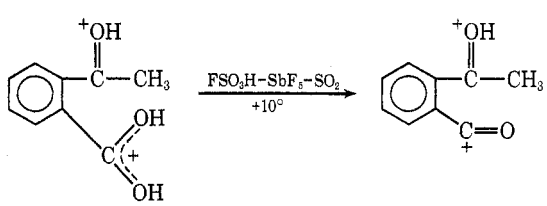
Diprotonated **levulinic acid** is very stable. No cleavage was observed even when the solution was heated to a temperature as high as +60°.

The cleavage reaction of diprotonated **acetoacetic acid** takes place slowly at 0° and gives a complex and yet unidentified mixture of products.

Protonated **pyruvic acid** undergoes cleavage at −20° to give the methyloxocarbonium ion (singlet at δ 4.05). The cleavage reaction can be rationalized in the following way.



Protonated **2-acetylbenzoic acid** undergoes dehydration at +10° to give 2-acetylphenyloxocarbonium ion. The proton on the acetyl oxygen is not observed, probably exchanging with the acid solvent system. The formation of the oxocarbonium ion is evident from the increase of the H_3O^+ peak which appears at δ 10.25 and the increased deshielding of the phenyl ring protons of the oxocarbonium ion. The chemical shifts are summarized in Table II.



Protonated **2-benzoylbenzoic acid** undergoes dehydration and acylation at room temperature to give diprotonated anthraquinone which gave an nmr spectrum identical with that obtained from the authentic material.

Protonated **3-** and **4-acetylbenzoic acid** and **3-** and **4-benzoylbenzyic acid** are very stable. No indication for the formation of the ketooxocarbonium ion was observed even when the solution was heated to +60°.

Protonated alkyl acetoacetates.—Methyl, ethyl, and *t*-butyl acetoacetates) were examined in FSO_3H–SbF_5–SO_2 solution. At −80° two low-field peaks in the hydroxyl region were observed for both protonated

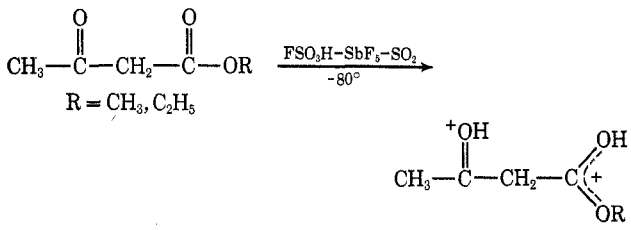
TABLE III

NMR CHEMICAL SHIFTS (IN PARTS PER MILLION),[a] AND COUPLING CONSTANTS (IN HERTZ) OF PROTONATED KETO ESTERS OF CARBOXYLIC ACIDS IN FSO_3H–SbF_5–SO_2 SOLUTION AT −60°

Acetoacetates	H_1	H_2	H_3	H_4	H_5	H_6	H_7
$CH_3\overset{3}{C}(^+OH)\overset{2}{=}CH_2\overset{4}{C}(^+OH)\overset{1}{=}OCH_3$ (a)	16.7[b]	14.2	3.66	5.43	5.05		
$CH_3\overset{3}{C}(^+OH)\overset{2}{=}CH_2\overset{4}{C}(^+OH)\overset{1}{=}O\overset{5}{C}H_2\overset{6}{C}H_3$ (b)	16.3[b]	13.7	3.63	5.35	5.50 (q, 7.0)[c]	1.93 (t, 7.0)	

[a] Referred to external TMS. [b] Observed below −80°. [c] Multiplicity: q, = quartet; t, = triplet.

methyl and ethyl acetoacetates, indicating that the acetoacetates studied were diprotonated on the two carbonyl oxygens. At temperatures higher than −80°, the proton on acetyl oxygen could not be observed, and



the peak for the acid system is also broad, indicating an occurrence of proton exchange. No coupling was observed between the hydroxyl protons with either the acetyl or methylene protons; hence the orientation of the OH protons could not be established. Chemical shifts and coupling constants of the protonated acetoacetates are given in Table III.

Protonated *t*-butyl acetoacetate could not be observed even when solutions of *t*-butyl acetoacetate in FSO_3H–SbF_5–SO_2 were prepared and examined at −80°. The pmr spectra obtained corresponded only to protonated acetoacetic acid (see previous discussion) and *t*-butyl cation (singlet at δ 4.2).

Experimental Section

Materials.—With the exception of acetylvaleric acid and 4-acetylbenzoic, 3-acetylbenzoic, and 3-benzoylbenzoic acids, all the keto acids were commercially available materials and used without further purification.

Acetylvaleric acid was prepared by the oxidation of 2-methylcyclohexanone with chromic trioxide in dilute sulfuric acid solution.[14]

m- and *p*-acetylbenzoic acid were prepared by the hydrolysis of the corresponding cyanoacetophenone,[15] which in turn was prepared by means of the Sandmeyer reaction[16,17] from the corresponding aminoacetophenone. *m*-Benzoylbenzoic acid was prepared by the reaction of benzoic anhydride and benzoyl chloride in the presence of zinc chloride at high temperature.[18]

Spectra.—A Varian Associates Model A-56/60A nmr spectrometer with variable-temperature probe was used for all spectra.

Preparation of Protonated Keto Acids.—Samples of protonated keto acids were prepared by dissolving approximately 1.5 ml of FSO_3H–SbF_5 (1:1 *M* solution) in an equal volume of sulfur dioxide and cooling to −78°. The keto acids (approximately 0.2 ml) were dissolved in 1 ml of sulfur dioxide, cooled to −78°, and with vigorous agitation slowly added to the FSO_3H–SbF_5 acid solution. The acid solution was always in large excess as indicated by the large acid peak at about δ 10.9 to 12.0.

Registry No.—Table I—a, 24621-23-6; b, 24621-24-7; c, 24621-25-8; d, 24621-26-9; e, 24621-27-0; f, 24621-28-1; g, 24621-29-2; h, 24621-30-5; i, 24621-31-6; j, 24621-32-7; k, 24621-33-8; Table II—a, 24621-34-9; b, 24621-35-0; c, 24605-68-3; Table III—a, 24621-36-1; b, 19220-71-4.

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