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(24) Methyl affinities obtained at 85°[20] were combined with isomer distributions from studies at 84–115°[23] to give partial rate factors which were statistically analyzed to give these data: meta only, $\rho = 0.78 \pm 0.37$ (five points, $r = 0.77$, $s_{yx} = 0.16$); meta and para, $\rho = 0.82 \pm 0.37$ (nine points, $r = 0.64$, $s_{yx} = 0.22$).[25] These correlation coefficients are low for ρ values of these sizes,[27] and plots of the data show that the experimental points are widely scattered from the least-squares line.
(25) The ρ values are reported as follows: $\rho = b \pm s_b$ (n points, r, s_{yx}), where b is the slope of the least-squares line, s_b is the standard deviation of the slope, n is the number of points, r is the correlation coefficient, and s_{yx} is the standard deviation from regression.[26a]
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(35) The complete analysis of our methylation data gives, for meta only, $\rho = 0.1 \pm 0.1$ (six points, $r = 0.37$, $s_{yx} = 0.1$); meta and para, $\rho = 0.1 \pm 0.1$ (nine points, $r = 0.44$, $s_{yx} = 0.09$).[25]
(36) Partial rate factors for *p*-nitro and *p*-cyano substituents are not included in these correlations because they lie far off the line determined by the meta substituents alone. The suggestion of van Bekkum and Taft[37,38a] has been followed; meta substituents are used to determine a line and the fit of para substituents to this line is examined. Also see discussion in ref 6.
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Stable Carbocations. CLXXVIII. Carbon-13 Nuclear Magnetic Resonance Spectroscopic Study of Protonated and Diprotonated Acyclic and Cyclic Diketones in FSO_3H–SbF_5–SO_2 Solution[1]

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The carbon-13 NMR chemical shifts for a series of protonated acyclic and cyclic diketones were determined in FSO_3H–SbF_5–SO_2 solution at −60° together with those of their parent diketones. Phenyl-substituted diketones were studied in FSO_3H–SO_2ClF solution at −80° to avoid protonation of the aromatic ring. Protonation of acyclic and cyclic diketones results in deshielding of the carbonyl resonances of the order of 10 ppm and the carbons α to the carbonyl carbons by 5 ppm. The results are discussed in view of other substituent effects and provide an insight into the extent of keto–enol tautomerism operating for the ions and precursors at low temperatures. Diprotonated diketones can also serve as model systems for carbodications.

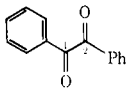
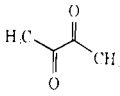
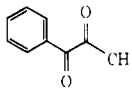
Keto–enol tautomerism is well recognized in 1,2- and 1,3-dicarbonyl compounds.[4] Physical measurements of the extent of keto–enol tautomeric equilibria of acyclic and cyclic diketones is of interest since both tautomers can be observed under suitable conditions. Extensive research efforts have been carried out along these lines utilizing bromine titrations,[5] infrared[6] and ultraviolet spectroscopy,[7] and proton[8] and ^{17}O nuclear magnetic resonance.[9] ^{13}C NMR carbonyl chemical shifts for some acyclic diketones were reported by Stothers and Lauterbur.[10] Proton magnetic resonance studies of protonated 1,3-diketones have been reported by Brouwer.[11]

In our previous investigation of protonated heteroaliphatic compounds, we reported a proton NMR study of protonated diones in FSO_3H–SbF_5–SO_2 solution.[12] We felt it, therefore, of interest to extend this study by undertaking a systematic ^{13}C NMR investigation of protonated 1,2-, 1,3- and 1,4-diketones (as well as their parent compounds) using the Fourier transform method. As protonated ketones can serve as model compounds for carbenium ions, diprotonated diketones are expected to provide similar information about carbodicationic systems. The study of these ions is being reported in detail in a forthcoming paper.

Results and Discussion

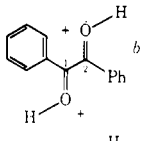
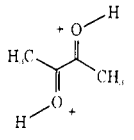
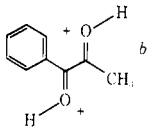
We undertook the ^{13}C NMR study of a series of protonated diketones in the FSO_3H–SbF_5–SO_2 superacid system, and for comparison also studied their neutral parent compounds. FSO_3H–SO_2ClF solution was used for aromatic diketones sensitive to the stronger "Magic Acid" system.

Table I
Carbon-13 Chemical Shifts of Acyclic 1,2-Diketones[a]

Precursor	Registry no.	C-1, C-2	Phenyl				CH_3
			Ipso	o-	m-	p-	
	134-81-6	195.4	131.9	130.2	130.7	136.4	
	431-03-8	198.0					22.8
	579-07-7	192.1, 202.5	*b*	130.6	129.3	135.6	25.8

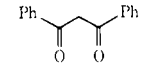
[a] In parts per million from external Me_4Si (capillary). Recorded in SO_2 at −60°. [b] Ipso carbon appears as a small shoulder downfield from ortho carbon.

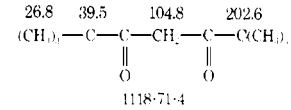
Table II
Carbon-13 Chemical Shifts of Protonated 1,2-Acyclic Diketones[a,c]

Ion	Registry no.	C-1, C-2	Phenyl				CH_3
			Ipso	o-	m-	p-	
	55236-79-8	197.3	128.3	136.2	131.4	145.6	
	55236-80-1	204.0					25.5
	55236-81-2	197.2, 198.3	124.5	139.3	132.0	149.3	29.1

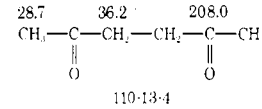
[a] In parts per million from external Me_4Si (capillary). Protonated in FSO_3H-SbF_5-SO_2 at −60°. [b] Protonated in FSO_3H-SO_2ClF. [c] Peaks may be the result of equilibration between several mono- and diprotonated forms. See text.

Table III
Carbon-13 Chemical Shifts of Acyclic 1,3- and 1,4-Diketones[a]

	Registry no.	Carbonyls C-1, C-3	C-2	R'	Phenyl				CH_3
					Ipso	o-	m-	p-	
R = R' = H	600-14-6	189.4	98.9						23.3
R = H; R' = CH_3	815-57-6	198.0, 209.3	60.5, 105.9	12.1					23.0, 28.8
R = R' = CH_3	3142-58-3	211.1	62.3	20.6					25.9
R = H; R' = Ph	5910-25-8	193.7	115.3		136.4	131.5	129.2	127.9	23.6
	120-46-7	185.6	93.4		134.3	127.5	129.2	133.6	



1118-71-4



110-13-4

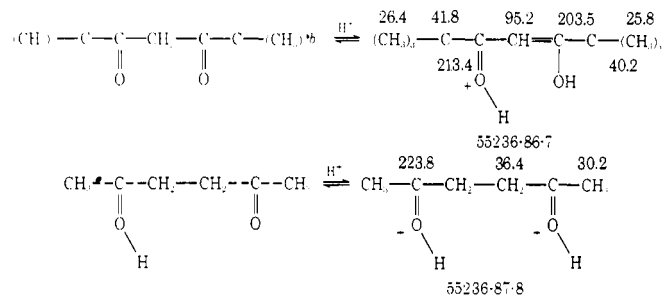
[a] In parts per million from external Me_4Si (capillary). Recorded in SO_2 at −60°. [b] Both diketo and keto-enolic tautomers are present; δ ^{13}C value for enolic tautomers is represented by a shielded carbonyl carbon. See text.

The ^{13}C NMR chemical shift data obtained using the Fourier transform (FT) techniques[13,14] are summarized in Tables I–VI.

The assignment of resonances was made by the now-familiar procedures of Grant and coworkers.[15,16] These include the observation that a polar group exerts a large inductive effect on the shift of a directly attached carbon, and, if symmetry elements are present in a molecule, it is possible to assign signals on the basis of relative intensities. To be assured of the correct assignment, in a number of cases, it was necessary to conduct "off-resonance" proton-decoupling experiments.

Table IV
Carbon-13 Chemical Shifts of Protonated 1,3- and 1,4-Acyclic Diketones[a]

	Registry no.	Carbonyls C-1, C-3	C-2	R'	Phenyl Ipso	Phenyl o-	Phenyl m-	Phenyl p-	CH_3
R = R' = H mono-[d]	16962-62-2	198.8	103.1						25.4
R = R' = H di-[d]	55236-82-3	206.2	52.6						33.2
R = H; R' = CH_3	55236-83-4	226.9	57.6	16.3					31.4
R = R' = CH_3	55236-84-5	223.4	62.8	22.9					29.4
R = H; R = Ph[b]	55236-85-6	204.1 193.1	116.6		131.8	130.1	c	c	
b	16292-64-4	188.9 185.3	95.9		128.9	137.6	130.2	138.9	

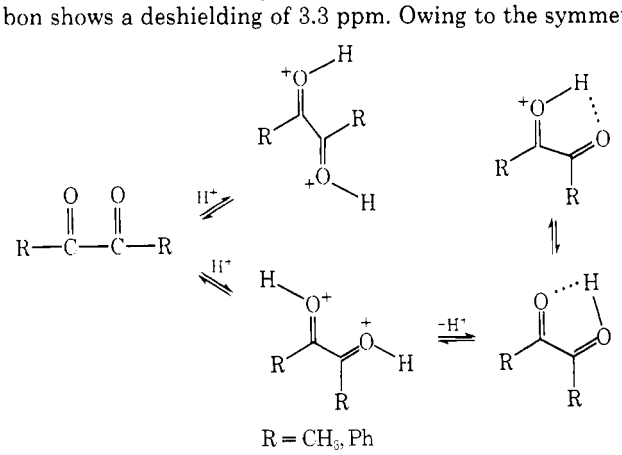


[a] In parts per million from external Me_4Si (capillary). Protonated in FSO_3H-SbF_5-SO_2 at −60°. [b] Protonated in FSO_3H-SO_2ClF at −80°. [c] Protonated 3-phenyl-2,5-pentanedione showed a broad singlet at δ 130.1 making meta and para aromatic carbon shifts. [d] Abbreviations mono- and di- refer to monoprotonation and diprotonation, respectively.

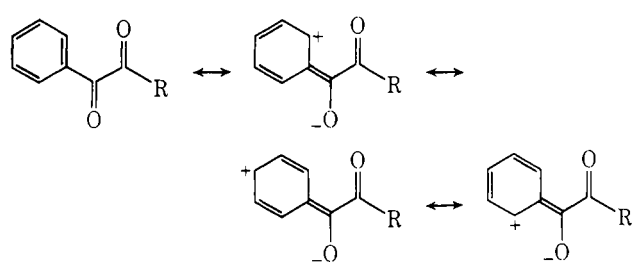
Solvent effects on carbonyl carbon-13 shifts in aprotic solvents have been interpreted in terms of carbonyl π-bond polarity as influenced by polar and van der Waals interactions with the solvent.[17] Our present experimental results may indicate slight solvent–solute interaction between diketone carbonyl groups and sulfur dioxide, but the effect is small and is not a major contribution to the deshieldings that occur for the carbonyl carbon-13 shift upon oxygen protonation.

Carbon-13 chemical shifts of the protonated diketones were measured at −60° in excess of FSO_3H-SbF_5 solution, using SO_2 as diluent. The carbon-13 chemical shifts of protonated aromatic diketones were measured at −80° in SO_2ClF-FSO_3H solution.

1,2-Diketones. Inspection of data in Tables I and II for precursor and protonated aliphatic 1,2-diketones reveals several interesting features. For diacetyl, the adjacent acetyl groups with their significant inductive effect cause shielding of the carbonyl carbons with respect to the carbonyl carbon of acetone. Upon protonation (on oxygen) of diacetyl with FSO_3H-SbF_5-SO_2, a deshielding of 6 ppm is observed for the carbonyl resonance, while the methyl carbon shows a deshielding of 3.3 ppm. Owing to the symmetrical nature of diacetyl, the exact structural geometry of its protonated form is difficult to ascertain. Several protonated forms could be formed which represent mono- and diprotonated cisoid or transoid arrangements of the 1,2-dicarbonyl structure in a rapidly equilibrating system.



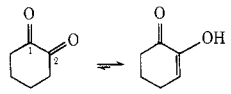
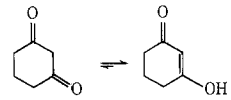
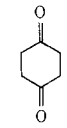
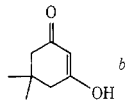
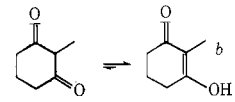
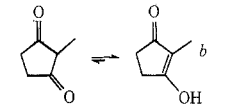
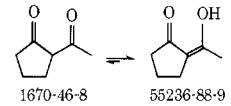
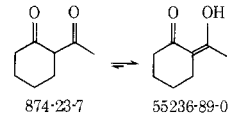
An especially interesting observation is the effect of adjacent dicarbonyl groups on aromatic ring carbons. Maciel reported significant deshielding for carbon-1 of benzophenone presumably as a result of considerable inductive electron withdrawal from the neighboring PhCO substituent.[18] Our results indicate that the para ring carbon is more deshielded than carbon-1 when COCOR (R = CH_3, Ph) is the neighboring substituent. These results are best understood when one considers the following mesomeric structures as contributors to the overall molecular structure. ^{13}C NMR



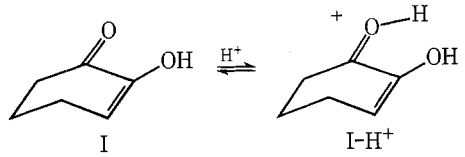
assignments were clarified by off-resonance experiments. [^{13}C-^{1}H coupling observed for the para carbon (doublet), no coupling expected for the ipso carbon (singlet)].

At low temperatures, 1,2-cyclohexanedione shows keto–enol tautomerism. Owing to its position in a closed cyclic system only the cisoid conformation is achieved. The carbonyl resonance is shielded by 11.4 ppm when compared to a monocarbonyl compound, i.e., cyclohexanone. The shielding effect is expected, however, since previous results show a shielding effect of adjacent sp^2 centers.[19] Structure I best represents this tautomer. Unlike its acyclic analog, protonated 1,2-cyclohexanedione can be represented only by I-H^+.

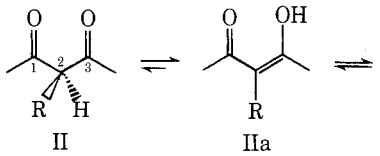
Table V
Carbon-13 Chemical Shifts of Cyclic 1,2-, 1-3-, and 1,4-Diketones[a]

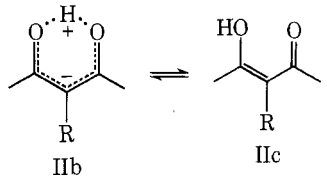
Precursor[b]	C-1	C-2	C-3	C-4	C-5	C-6	$COCH_3$	CH_3
 765-87-7 10316-66-2	197.6	145.3	122.2	22.4	23.2	35.5		
 504-02-9 30182-67-3	209.2	103.7	194.8	31.9	21.9	31.9		
 637-88-7	214.2	34.9						
 3471-13-4	187.5	103.8	187.5	47.4	33.5	47.4		29.4
 1193-55-1 32774-63-3	185.1	110.6		33.4	21.6	33.4		8.1
 765-69-5 5870-63-3	202.5	112.5	142.0	31.1				8.1
 1670-46-8 55236-88-9	216.1 209.6 205.8 174.5	110.8 62.9	36.5	29.8	38.4			25.1 25.0 20.3
 874-23-7 55236-89-0	192.1	108.0	23.8	22.4	24.8	30.5	182.0	21.3

[a] In parts per million from external Me_4Si (capillary). Recorded in SO_2 at −60°. [b] C-1 and C-3 appear as a broad peak in DMSO-d_6 solvent. [b] Registry no. is given below the compound.


I I-H^+

1,3-Diketones. Tables III and IV list the carbon-13 chemical shift data for the protonated 1,3-diketones and their precursors. An important feature of these data is the significant deshielding of carbon-2 indicating significant sp^2 character of this carbon. The position of tautomeric


II IIa

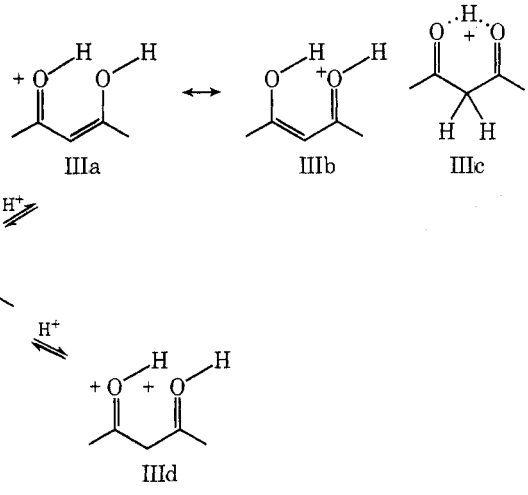

IIb IIc

equilibria is clearly in the direction of the keto–enol form whenever a labile proton is present α to two carbonyl groups in the molecule (as shown by structures IIa–c). However, both tautomers (II and IIa–c) were observed for 3-methyl-2,4-pentanedione, since the carbon α to both carbonyls could be detected as both sp^3 (δ 60.5) and sp^2 (δ 105.9) hybridized forms. Since the carbonyl resonance appears as a singlet absorption for the diketones studied, the precursor can be represented by symmetrical structure IIB indicating significant hydrogen bonding or, equally, by rapid equilibration of IIa with IIc.

By proper variation of molecular structure, the pure diketo tautomer can be observed as in the case of 3,3-dimethyl-2,4-pentanedione. Protonation of the diketo tautomer causes a deshielding of 10 ppm for the carbonyl carbons.

It is significant to note the marked deshielding of aromatic carbon 1 of 3-phenyl-2,4-pentanedione (relative to benzene) at these temperatures due to the enolic contribution of this tautomer which renders the structure to a substituted styrene.

One further interesting aspect of protonation of 1,3-dicarbonyl compounds was the observation of mono- and diprotonated forms. Since the exact nature of the position of

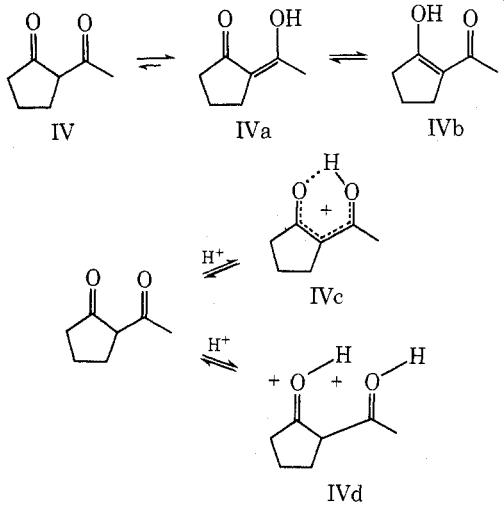


equilibrium was established by measuring the carbon-13 NMR of the precursors (vide supra) the anticipated result was monoprotonation. For example, 2,4-pentanedione shows a deshielding effect of approximately 10 ppm after monoprotonation, and is best represented by resonance structures IIIa,b which account for the observation of one carbonyl resonance. Structure IIIc can be discounted as a monoprotonated contributor III-H^+ since carbon 2 appears as a doublet upon ^1H decoupling.

Using excess superacid, diprotonated structure IIId was obtained which shows a carbonyl singlet 16 ppm deshielded from the neutral parent. Similar results were obtained for 3-methyl-2,4-pentanedione and 3,3-dimethyl-2,4-pentanedione with deshielded absorption for the protonated carbonyls of 23.3 and 12 ppm, respectively.

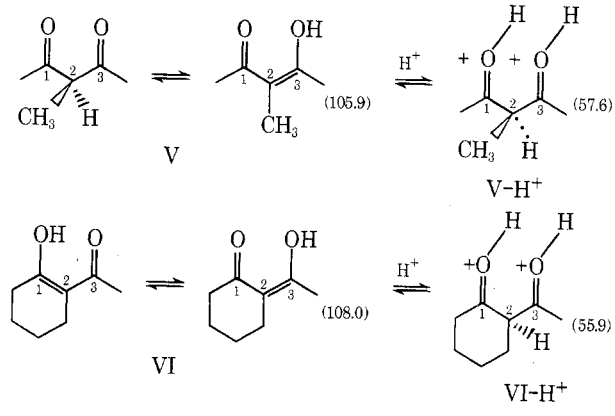
Cyclic 1,3-dicarbonyl compounds demonstrate similar trends both in degree of enolic contribution and in deshielding of charge upon protonation, as can be seen in Tables V and VI. Incorporation of more than one carbonyl in a ring system showed varied results (see also cycloalkanones studied by Roberts).[20,21] One example in this series of cyclic 1,3-dicarbonyl compounds, 5,5-dimethyl-1,3-cyclohexanedione, shows this preference for the keto–enolic tautomeric form, as indicated by the olefinic type absorption of the α carbon relative to both carbonyls (δ ^{13}C 103.8).

Examples of 1,3-dicarbonyl compounds representing α-acetylated cycloalkanones were also studied. ^{13}C NMR parameters for 2-acetylcyclopentanone and 2-acetylcyclohexanone can be seen in Table V. For 2-acetylcyclopentanone, an equilibrating tautomeric system can be best represented by structures IVa and IVb, since four different keto–enolic carbons were observed in the carbon-13 spectrum.



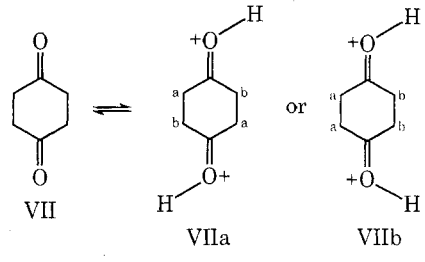
^{13}C NMR parameters for monoprotonated 2-acetylcyclopentanone (IVc) and diprotonated 2-acetylcyclopentanone (IVd) are also shown in Table VI.

^{13}C NMR data indicate the preference of keto–enolic tautomeric forms for 2-acetylcyclohexanone (VI) at the temperatures employed. As previously mentioned, both tautomers were observed for 3-methyl-2,4-pentanedione (V), the acyclic analog of VI. Numerical values in parentheses indicate ^{13}C NMR chemical shifts for carbon 2 of precursors and ions; values for precursors show typical olefinic carbon shieldings. Although monoprotonation of VI was



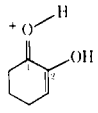
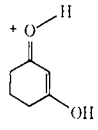
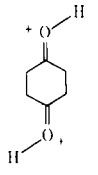
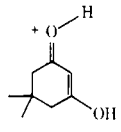
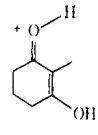
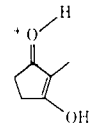
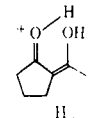
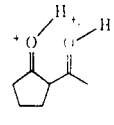
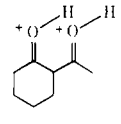
anticipated, the ^{13}C NMR chemical shift data for V-H^+ reveal carbon 2 as δ ^{13}C 57.6 and carbon 2 for VI-H^+ δ ^{13}C 59.9, results which best describe diprotonated ions. Diprotonated structures would thus explain the highly deshielded carbonyl resonances of the order of 35.1 ppm for the ring carbonyl and 43.8 ppm for the acetyl carbonyl carbon for VI-H^+. The larger deshielded value for the acetyl carbonyl carbon could then be explained by the additional deshielding effect of a directly attached methyl group. Diprotonated species V-H^+ shows a deshielding of 23.3 ppm from the precursor (an average value is reported since two carbonyl absorptions are observed when both tautomers are present).

1,4-Diketones. 1,4-Cyclic and acyclic diketones were also studied by ^{13}C NMR spectroscopy. The ^{13}C NMR chemical shift data for the studied compounds can be found in Tables III and IV. According to ^{13}C NMR assignments, it was determined that neither cyclic nor acyclic 1,4-diketones exist in the enolic form when compared to 1,2- and 1,3-dicarbonyl compounds, where the preference for the keto–enol tautomeric forms predominates at these temperatures. α methylene carbons appear at the expected resonance positions as well as the carbonyl carbons. Diprotonation of the carbonyl carbons occurs for both cyclic and acyclic 1,4-diketones studied. A deshielding of 15 ppm was observed for 2,5-hexanedione and 30 ppm for 1,4-cyclohexanedione. If one considers diprotonation of 1,4-cyclohexanedione, two structures (VIIa and VIIb) can be formed



where a and b designate the equivalent carbons. An exact differentiation between structures VIIa and VIIb cannot be made, since both structures would exhibit two methylene signals in the ^{13}C NMR spectrum.

Table VI
Carbon-13 Chemical Shifts of Protonated 1,2-, 1,3-, and 1,4-Cyclic Diketones[a]

Ion	Registry no.	C-1	C-2	C-3	C-4	C-5	C-6	$COCH_3$	CH_3
	55236-90-3	215.9		106.4	66.0	45.8	66.0		
	55236-91-4	206.8	106.0		32.0	21.7	32.0		
	55236-92-5	245.5	35.4	34.6					
	55236-93-6	203.2	103.1	203.2	43.2	34.7	43.2		26.6
	55336-94-7	200.7	113.3	200.7	31.1	19.7	31.1		6.0
	55236-95-8	203.8	115.5	203.8	30.0	30.0			4.4
	55236-96-9	200.2	110.3	26.0	22.0	36.7		188.2	18.4
	55236-97-0	248.1	62.3	29.0	31.6	43.9		237.9	21.3
	55236-98-1	227.7	59.9	32.3	30.8	36.4	42.3	225.8	27.0

[a] In parts per million from external Me_4Si (capillary). Protonated in FSO_3H-SbF_5-SO_2 at −60°. [b] Abbreviations mono- and di- refer to monoprotonation and diprotonation, respectively.

Conclusions

Keto–enol equilibrating tautomers were generally observed at low temperatures for 1,2- and 1,3-acyclic and cyclic diketones. Only 1,4-diketones and suitably substituted 1,3-diketones (e.g., 3,3-dimethyl-2,4-pentanedione) could be observed in pure diketo tautomeric forms. Monoprotonation of these keto–enol tautomers (on oxygen) results in only relatively significant deshielding for the carbonyl carbon, while more significantly deshielded resonances are observed for the diprotonated species in excess of "Magic Acid" solutions.

Experimental Section

Materials. All diketones were commercially available materials and were purified prior to use.

Preparation of Protonated Diketones. Protonated diketones were prepared by adding the diketone (0.5 ml) to a stirred solution of 1:1 FSO_3H–SbF_5 (1.5 ml) in an equal volume of SO_2 at −76°. Samples prepared in this manner gave spectra which showed no appreciable chemical shift differences with temperature or small concentration variations. The acid was always in excess as indicated by an acid peak at about δ 10.9 ppm in the ^1H NMR spectrum. The ^{13}C NMR spectra of protonated diketones were recorded only if the ^1H NMR data matched the reported values in the literature.[22] For diketones not yet reported, the structure of the protonated forms could be established from the ^1H NMR spectral data (chemical shifts, multiplicity patterns, and peak area integration). After the ^{13}C NMR spectrum of a protonated diketone was obtained, the sample was again checked by ^1H NMR spectroscopy to determine if any decomposition had occurred. Samples of protonated aromatic diketones were prepared by dissolving the diketone (0.5 ml) in SO_2ClF (0.5 ml). This solution was added dropwise to a rapidly stirred solution of FSO_3H (2 ml)–SO_2ClF (1 ml) at −76°. The acid was always in excess as indicated by an acid peak at about δ 10.4 ppm in the ^1H NMR spectrum. The ^{13}C NMR spectra of protonated aromatic diketones were recorded at −80°.

NMR Spectroscopy. ^1H NMR spectra were obtained on a Varian Associates Model A56/60-A spectrometer equipped with a variable temperature probe.

^{13}C NMR spectra were obtained in part on a modified Varian Associates Model HA-100 spectrometer equipped with a FT-100 Fourier transform accessory (V-4357 pulsing and control unit); a broad-band proton decoupler of 25.14 MHz was derived from a gated power amplifier capable of putting out approximately 80 W into the transmitter coils. The pulse width used was 35 μsec, and

the pulse interval 1.5 sec. The available computer memory (4000 input channels) and the need to provide multichannel excitation over the region of interest (seeep width 6800 Hz) limited the data acquisition time to 0.2 sec.

The free induction signal derived after each pulse was signitized and accumulated in a Varian 620/i computer (8K). Approximately 5000–7000 accumulations were made to obtain each spectrum. Field frequency regulation was maintained by a homonuclear internal lock system. The lock used was the proton-decoupled carbon-13 resonance of a 60% carbon-13 labeled methyl iodide sample contained in a precision coaxially spaced capillary (o.d. ca. 0.2 and 0.4 mm) inserted in the sample NMR tube (5 mm o.d.).

Fourier transformation of the accumulated free induction signal gave the frequency spectrum,[23,24] from which was measured the chemical shift of each signal, relative to the reference methyl iodide signal. All the chemical shifts reported here have been corrected to a Me_4Si reference by the relationship

$$\text{ppm } (Me_4Si) = \frac{H_2(\text{obsd}) - 977 - T\,(°C) \times 0.70}{25.2}$$

The ^{13}C NMR spectra for the remaining protonated diketones and precursors were obtained on a Varian Associates Model XL-100 spectrometer equipped with a broad decoupler and variable temperature probe. The instrument operates at 25.2 MHz for ^{13}C, and is interfaced with a Varian 620L computer. The combined system was operated in the pulse Fourier transform mode, employing a Varian Fourier transform accessory. Typically 3000–5000 pulses, each of width 20–30 μsec, needed to be accumulated in order to give a satisfactory signal to noise ratio for all signals of interest. Field frequency stabilization was maintained by locking on the ^{19}F external sample of fluorobenzene. Chemical shifts were measured from the ^{13}C signal of 5% ^{13}C enriched tetramethylsilane in a 1.75-mm capillary held concentrically inside the standard 12-mm sample tube.

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

Registry No.—FSO_3H–SbF_5, 33843-68-4; SO_2ClF, 13632-84-8; SO_2, 7446-09-5.

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Stable Carbocations. CLXXXI.[1] Dihydrodibenzotropylium and Dibenzotropylium Ions. Neighboring Methyl, Cyclopropyl, and Phenyl Substituent Effects in Geometrically Constrained Systems

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A series of dihydrodibenzotropylium and dibenzotropylium ions have been prepared under stable ion conditions and characterized by NMR spectroscopy. Neighboring methyl, cyclopropyl, and phenyl substituent effects are discussed in terms of ^{13}C NMR shift changes. The relative ability of neighboring methyl, cyclopropyl, and phenyl substituents in stabilizing carbenium ions via either inductive or conjugative charge-delocalizing effects is further discussed.

Methyl, cyclopropyl, and phenyl groups stabilize carbenium ions by inductive and/or resonance (conjugative) effects.[2–5] The degree of conjugation between π or σ bonds in phenyl or cyclopropyl rings with a neighboring empty p orbital on a carbenium center is significant in the degree of delocalization it can exercise and depends upon the orientation of these substituents. Since a phenyl group is larger than a cyclopropyl group, in a given sterically crowded system the former might be affected more in its ability for conjugative stabilization (i.e., effective overlap between p and π orbitals) than the latter. Therefore, if steric inhibition of conjugation becomes significant or overwhelming, phenyl-substituted carbenium ions might become less stable than either the parent (unsubstituted) or alkyl-substituted analogs. A typical example is seen in the case of dibenzotropylium ions.[6] The parent (unsubstituted) ion ($pK_{R^+} = -3.7$) is found to be considerably more stable than the phenyl-substituted ion ($pK_{R^+} = -5.7$) based on comparison of the corresponding pK_{R^+} values.[6a] The decrease in stability of the lattter ion is explained by the fact