the ir spectra were recrystallized twice from benzonitrile, washed twice with CCl_4, and pumped dry under vacuum. Nujol mulls were made up by grinding in a drybox.

An additional method of preparation was found to be successful. The methylacetonitrilium ion was obtained by adding an SO_2 solution of CH_3CN to a solution of CH_3Cl in SbF_5–SO_2. The presence of the ion was detected in the nmr spectrum, but no attempt was made to isolate the salt. The spectrum of the ion appears after only a few minutes at temperatures below −10°,

$$CH_3Cl\rightarrow SbF_5 + CH_3CN \xrightarrow{SO_2} CH_3CNCH_3SbF_5Cl$$

while the preparation from CH_3CN-$SbCl_5$ + CH_3Cl required weeks of standing at room temperature.

Ir and Nmr Spectra. A Beckman IR-10 infrared spectrophotometer was used for all ir spectra. Varian Associates Models A-56/60, HA 100, and HA 60 nmr spectrometers were used for the nmr spectra. Nitrogen and carbon decoupling experiments were performed with the aid of a NMR Specialties Model SD-60B heteronuclear spin–spin decoupler. Indor spectra were taken as previously described[23] using a Hewlett-Packard function generator.

Acknowledgment. Support of the work by grants of the National Science Foundation and the National Institutes of Health is gratefully acknowledged. Dr. A. M. White is thanked for the C^{13} measurements and helpful discussions.

(23) G. A. Olah and A. M. White, *J. Amer. Chem. Soc.*, **90**, 1884 (1968).

Stable Carbonium Ions. LXVI.[1] Protonation of Diketones in FSO_3H–SbF_5–SO_2 Solution

George A. Olah and Mihai Calin[2]

Contribution from the Department of Chemistry, Case Western Reserve University, Cleveland, Ohio 44106. *Received February 8, 1968*

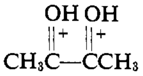
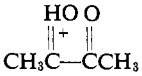
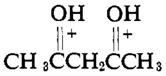
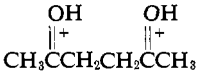
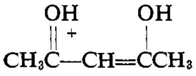
Abstract: 1,2-, 1,3-, and 1,4-diketones were protonated (diprotonated) in FSO_3H-SbF_5-SO_2 solution at −60°. Pmr spectroscopy allowed study of the protonated products.

In continuation of our studies of protonated heteroatom compounds,[3] including protonated ketones,[4] we wish now to report on the investigation of protonated diketones. After our studies were completed, a brief communication by Brouwer[5] appeared, reporting the protonation of acetylacetone, benzoylacetone, and dibenzoylmethane in HF–SbF_5 solution. As our own studies (in FSO_3H-SbF_5 solution) included only one of the diketones investigated by Brouwer (*e.g.*, acetylacetone) and even in this case our observations contain significant new findings, we report them in full.

Results and Discussion

Protonated Aliphatic Open-Chain Diketones. The pmr parameters of protonated diketones have been measured in FSO_3H-SbF_5–SO_2 solution at −60°. It was found that aliphatic diketones like 2,3-butanedione, 2,4-pentanedione, and 2,5-hexanedione are diprotonated in excess 1:1 *M* SbF_5–FSO_3H solution (diluted with sulfur dioxide). At a low concentration of acid (1.5 mol/mol of diketone) there is a tendency toward monoprotonation (as in the case of 2,3-butanedione and 2,3-pentanedione). In all cases there is no indication of resolvable fine structure in the OH resonance (although the peaks are broad), indicating exchange of the proton on oxygen. Table I summarizes the pmr data of protonated aliphatic ketones obtained in FSO_3H–SbF_5–SO_2 solution at −60°.

Table I. Pmr Chemical Shifts of Protonated Aliphatic Diketones[a]

Ion	δ, ppm CH₃	CH₂	$\overset{+}{=OH}$
 $CH_3\overset{OH}{\overset{\|^{+}}{C}}-\overset{OH}{\overset{\|^{+}}{C}}CH_3$ I	−4.0 (−2.3)	...	*b*
 $CH_3\overset{HO}{\overset{\|^{+}}{C}}-\overset{O}{\overset{\|}{C}}CH_3$ II	−3.23 (−2.32)	...	...
 $CH_3\overset{OH}{\overset{\|^{+}}{C}}CH_2\overset{OH}{\overset{\|^{+}}{C}}CH_3$ III	−3.6 (−2.1) (tr, J = 1.0)	−5.70 (−2.3) (q, J = 1.0)	−16.6 (br)
 $CH_3\overset{OH}{\overset{\|^{+}}{C}}CH_2CH_2\overset{OH}{\overset{\|^{+}}{C}}CH_3$ IV	−3.5 (2.2)	−4.3 (−2.7)	−15.5 (br)
 $CH_3\overset{OH}{\overset{\|^{+}}{C}}-CH=\overset{OH}{\overset{\|}{C}}CH_3$ V	−2.52 (br)	−6.13 (br)	...

[a] Chemical shifts of parent ketones are in parentheses. *J* values in hertz. Abbreviations used: br, broad; q, quartet; tr, triplet; [b] Not observable even at −100°.

2,3-Butanedione (diacetyl) in excess 1:1 FSO_3H–SbF_5–SO_2 shows a single methyl absorption at −4.0 ppm (Figure 1a). The absorption peak, although somewhat broadened, showed no observable coupling. We interpret the highly deshielded single methyl absorption

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[1] Part LXV: G. A. Olah and T. E. Kiovsky, *J. Amer. Chem. Soc.*, **90**, 4666 (1968).

[2] Postdoctoral Research Investigator, 1966–1967.

[3] For a review see G. A. Olah, *Chem. Eng. News*, **45**, 76 (March 27, 1967).

[4] (a) G. A. Olah, M. Calin, and D. H. O'Brien, *J. Amer. Chem. Soc.*, **89**, 3586 (1967); (b) G. A. Olah and M. Calin, *ibid.*, **90**, 938 (1968).

[5] D. M. Brouwer, *Chem. Commun.*, 515 (1967).

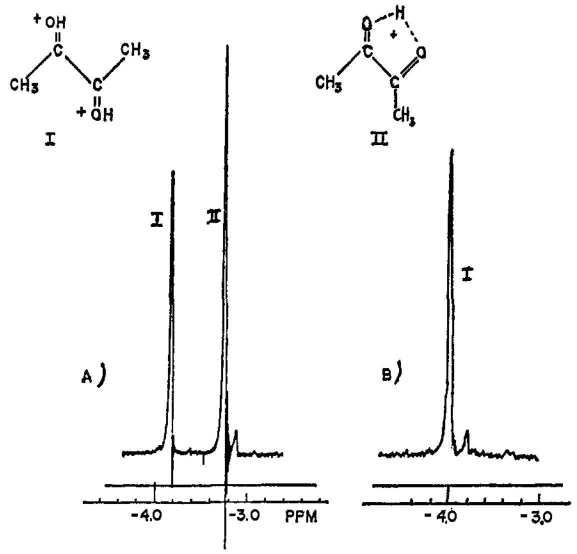
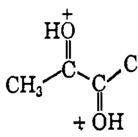


Figure 1. 2,3-Butanedione (diacetyl): (a) in dilute $FSO_3H-SbF_5-SO_2$, and (b) in excess FSO_3H-SbF_5.

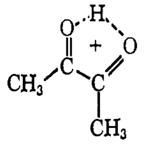
as indicative of the diprotonated ketone I. The methyl absorption is more deshielded, than, for example, in



I

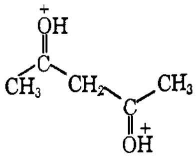
protonated acetone. No $=OH^+$ absorption could be observed, even at −100°, indicating exchange with the solvent.

When the acid concentration in sulfur dioxide solution is decreased, two methyl absorptions (at −3.90 and −3.23 ppm) are observed (Figure 1b), the high-field peak increasing with decreasing acid concentration. Under these conditions monoprotonation of diacetyl (II) is also indicated.

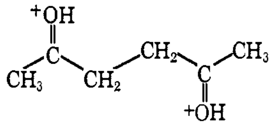


II

2,4-Pentanedione (acetylacetone) (Figure 2) and 2,5-hexanedione (acetonylacetone) (Figure 3) are diprotonated in excess FSO_3H-SbF_5 (1:1).



III



IV

The pmr resonance spectrum of diprotonated 2,4-pentanedione (III) shows the $=OH^+$ absorption as a somewhat broadened single line at −16.6 ppm (indicating the presence of unresolved coupling). The methyl absorption, −3.60 ppm, is a triplet (J = 1.0 Hz) and the methylene absorption (−5.70) a poorly resolved quadruplet, indicating long-range coupling through the sp^2 carbonyl atom (as in protonated methyl ethyl ketone, reported by us previously[4a]).

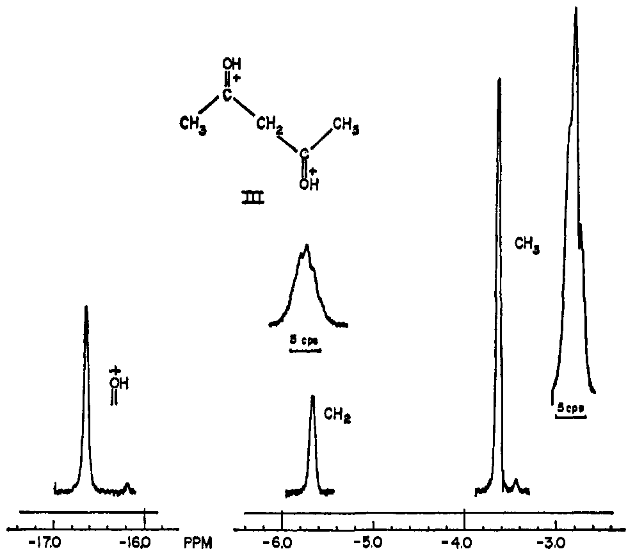


Figure 2. Diprotonated 2,4-pentanedione (acetylacetone).

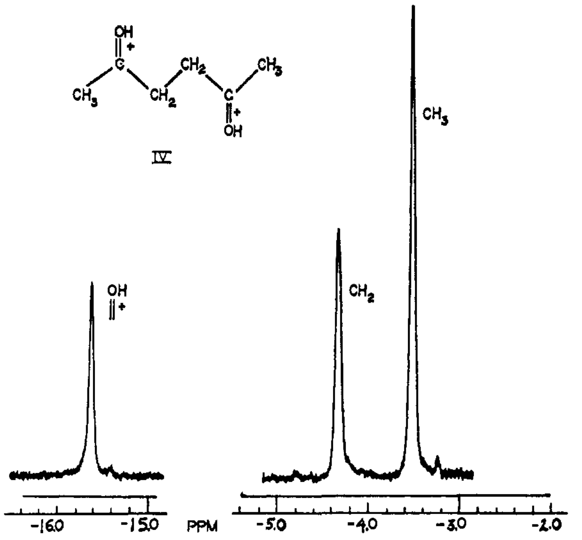
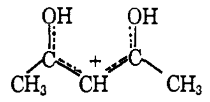


Figure 3. Diprotonated 2,5-hexanedione (acetonylacetone).

In diprotonated acetonylacetone (IV) the $=OH^+$ absorption is at −15.5 ppm (broad), as are the methyl (−3.5 ppm) and the methylene (−4.3 ppm) absorptions, indicating small couplings, not well resolved.

When the acid concentration is decreased only monoprotonation takes place, and the monoprotonated diketones can be observed. In the case of monoprotonated 2,4-pentanedione, the pmr data indicate a dihydroxyallylic structure (V) related to the protonated enolic form of the diketones.



V

Protonated Cyclic Diketones. Protonation of 1,4-diacetylbenzene occurs on both carbonyl oxygen atoms (Figure 4). Coupling of the $=OH^+$ and the methyl

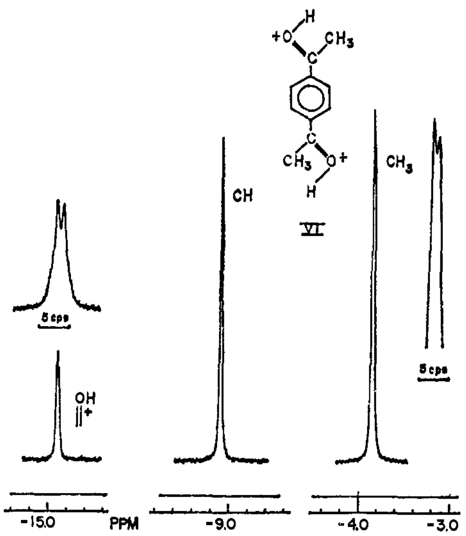


Figure 4. Diprotonated 1,4-diacetylbenzene.

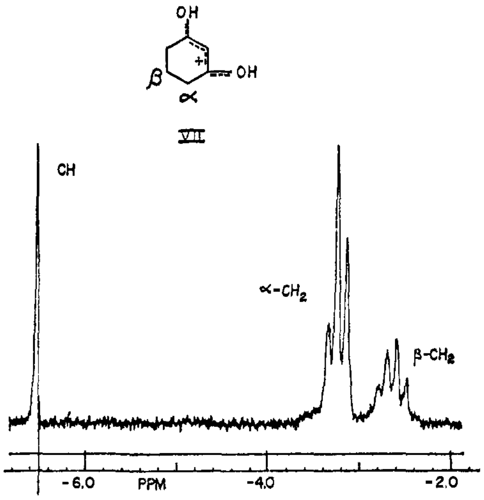
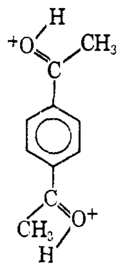


Figure 5. Protonated 1,3-cyclohexanedione.

resonances of the diprotonated species VI is observed. As would be expected, the proton on oxygen is *cis* to the methyl group, and the coupling observed corresponds to the allylic-type coupling observed for protonated methyl ketones.



VI

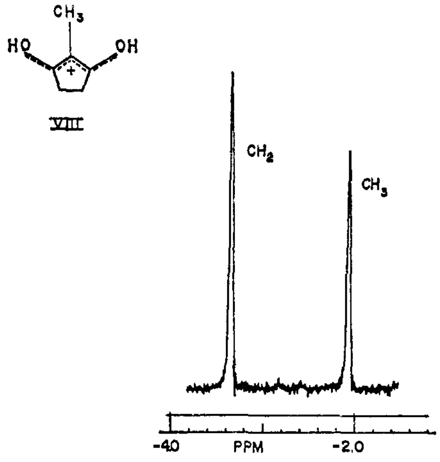


Figure 6. Protonated 2-methyl-1,3-cyclopentanedione.

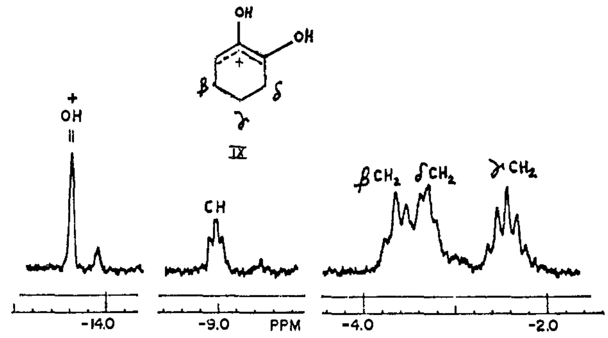
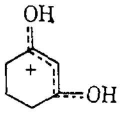
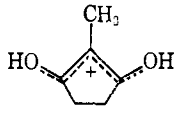


Figure 7. Protonated 1,2-cyclohexanedione.

Protonation of some alicyclic diketones was also studied under the same conditions. They were found to be monoprotonated or diprotonated depending on the type of ketone and the strength and concentration of acid used. 1,3-Cyclohexanedione (VII) (Figure 5) and 2-methyl-1,3-cyclopentanedione (VIII) (Figure 6) are only monoprotonated in the strong acid system FSO_3H–SbF_5–SO_2, probably because in this case the enol form is more stable than that of the aliphatic ketones. Our previous observation of the protonation of 2-cyclohexen-1-one[4b] is in accord with present results.

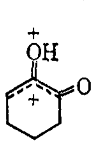


VII

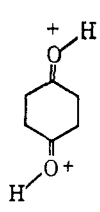


VIII

1,2-Cyclohexanedione seems also to be monoprotonated (IX) (Figure 7), but the OH resonance is observable, whereas it is not observable in the case of monoprotonated 2,3-butanedione. Protonation of 1,4-cyclohexanedione (X) (Figure 8) shows a simple pattern



IX



X

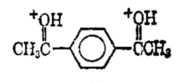
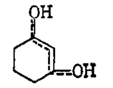
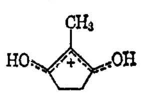
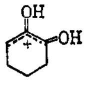
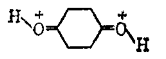
of a diprotonated species. Pmr data of the protonated cyclic ketones investigated are summarized in Table II.

Experimental Section

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

Spectra. Varian Associates Models A56-60A and HA-60-IL nmr spectrometers with variable-temperature probes were used for all spectra. Coupling constants are believed accurate to 0.1 Hz.

Table II. Pmr Data of Protonated Cyclic Diketones[a]

Ion	δ, ppm CH$_3$	CH$_2$	CH	$=\overset{+}{O}H$
 VI	−3.8 (−2.6) (d) J = 1.2	...	−9.1	−14.9 (qu) J=1.2
 VII		α −3.22 (tr) J = 5.9 β −2.64 (qu) J = 5.9	−6.52 (s)	b
 VIII	−2.08	−3.34		b
 IX		β −3.65 (m) δ −3.26 (m) γ −2.92 (p) J = 6.0	−9.02 (tr) J = 6.0	−14.0 (br)
 X	...	−4.0 (−2.7)	...	−15.7

[a] J values in hertz. Abbreviations used are: s, singlet; d, doublet; tr, triplet; qu, quadruplet; p, pentuplet; m, multiplet. [b] Not observable even at −100°.

Preparation of Protonated Diketones. Samples of protonated diketones were prepared by dissolving approximately 1.5 ml of FSO$_3$H–SbF$_5$ (1:1 *M* solution) in an equal volume of sulfur dioxide and cooling to −76°. The diketone (approximately 0.2 ml) was dissolved in 1 ml of sulfur dioxide, cooled to −76°, and with vigorous agitation slowly added to the acid solution. Samples prepared in this manner gave nmr spectra (generally taken at −60°) which showed no appreciable chemical shift differences with temperature or small concentration variations. The acid was always in excess of the aldehyde as indicated by the large acid peak at about −10.9 ppm.

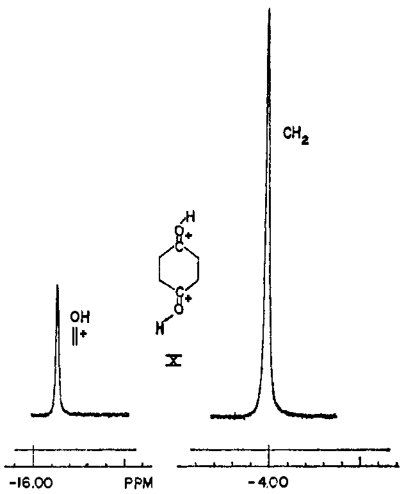


Figure 8. Diprotonated 1,4-cyclohexanedione.

Acknowledgment. Support of this research by grants of the National Institutes of Health and the National Science Foundation is gratefully acknowledged.

Halonium Ion Formation *via* 1,4-Halogen Participation. Five-Membered-Ring Tetramethylenehalonium, 2-Methyltetramethylenehalonium, and 2,5-Dimethyltetramethylenehalonium Ions[1]

George A. Olah and Paul E. Peterson

Contribution from the Department of Chemistry, Case Western Reserve University, Cleveland, Ohio 44106, and the Department of Chemistry, St. Louis University, St. Louis, Missouri 63156.

Received February 8, 1968

Abstract: Tetramethylene- and 2-methyltetramethylenechloronium, -bromonium, and -iodonium ions were formed by ionization of 1,4-dihalobutanes and 1,4-dihalopentanes, respectively, in antimony pentafluoride–sulfur dioxide solution at −60°. 2,5-Dimethyltetramethylenehalonium ions were formed by protonation of 5-halo-1-hexenes in fluorosulfonic acid–antimony pentafluoride–sulfur dioxide. Selected five-membered-ring halonium ions were shown by nmr observation to be stable for brief periods of time even at temperatures in the range −30–0°, depending on the structure.

Three-membered-ring ethyleniodonium, -bromonium, and -chloronium ions, long postulated as intermediates in reactions involving 1,2-halogen participation or in additions of halogen to alkenes, have recently been observed by nmr spectroscopy in antimony pentafluoride–sulfur dioxide solutions.[2] We now report the observation of the analogous five-membered-ring ions which are formed by 1,4-halogen participation from 1,4-dihalobutanes in SbF$_5$–SO$_2$ solution.

1,4-Halogen participation was postulated to occur in 4-iodo- and 4-bromo-1-butyl tosylate acetolysis,[3] but the indications for participation, enhanced reaction rates and special salt effects, were not very pronounced. As outlined below, examples of 1,4-halogen partic-

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[1] Stable Carbonium Ions. LXVII. Part LXVI: G. A. Olah and M. Calin, *J. Amer. Chem. Soc.*, **90**, 4672 (1968).

[2] G. A. Olah and J. M. Bollinger, *ibid.*, **89**, 4744 (1967); **90**, 947, 2587 (1968).

[3] R. E. Glick, Ph.D. Thesis, University of California at Los Angeles, Los Angeles, Calif., 1954.