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MODIFIED PHOTOBEHAVIOR OF CARBOXYLIC ACID DERIVATIVES INDUCED BY PROTONATION

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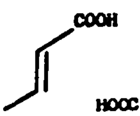
Abstract - A series of carboxylic acid derivatives 1-6 containing a second interacting function have been converted into the corresponding O-protonated species or acylium ions upon treatment with 96% sulfuric acid or oleum, respectively, at room temperature. The resulting stable cations have been spectroscopically characterized and submitted to irradiation. Cis-trans photoisomerization was observed in the ionic species derived from trans-crotonic, fumaric and maleic acids, and maleic anhydride. By contrast protonated crotonolactone $5a^+$ was found to be photostable. Finally, protonated α-bromobutyrolactone $6a^+$ was clean and efficiently dehydrohalogenated to $5a^+$ upon irradiation. Since the normal $n\rightarrow\pi^*$ photoreactions of the uncharged carboxylic acid and their derivatives are inhibited under these conditions, protonation can be envisaged as a chemical selective method for photoprotection of the carboxy group.

INTRODUCTION

Little attention has been paid to photochemically induced transformations of cationic species in strong acid media[1] in spite of the great number of stable cations readily accessible upon direct protonation of uncharged precursors.[2,3]

The photoreactivity of carboxylic acids and derivatives under neutral or basic conditions is also a well documented topic,[4] and has focused the attention of some of us in recent years.[5] Conversely, only a few reports[6] have appeared dealing with the photochemistry of protonated carboxylic acids and derivatives although these cations are stable even in sulfuric acid solution at room temperature.[2,3,7] In order to cover this lack of information we wish to report here our study on the photochemical behavior of a series of simple unsaturated acids (trans-crotonic 1, fumaric 2 and maleic 3) and cyclic acid derivatives (maleic anhydride 4, crotonolactone 5 and α-bromobutyrolactone 6) in strong acid solutions (sulfuric acid and oleum).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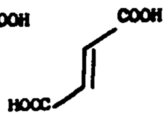
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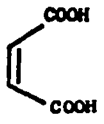
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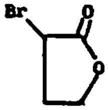
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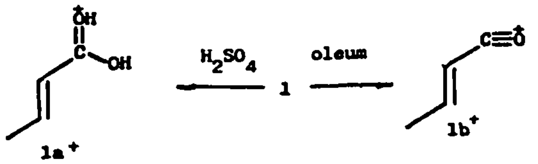
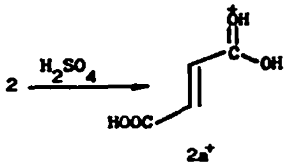
RESULTS AND DISCUSSION

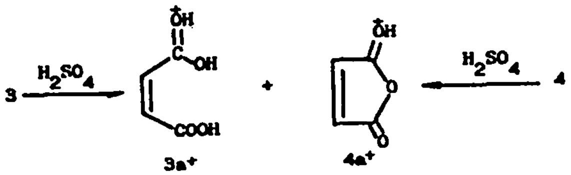
a) Preparation and characterization of cationic species.

O-Protonated trans-crotonic acid 1a$^+$ and the corresponding acylium ion 1b$^+$ were prepared by dissolving the carboxylic acid in concentrated sulfuric acid or oleum, respectively, as described by Deno et al.[8] The treatment of fumaric acid with 96% sulfuric acid afforded a single protonated species 2a$^+$.





By contrast, the protonation of either maleic acid 3 or its anhydride 4 under the same conditions led to a ca. 1:9 equilibrium mixture of the protonated anhydride 4a$^+$ and the protonated acid 3a$^+$. This is in good agreement with data previously obtained based on cryoscopic measurements.[9]



The site of protonation in these compounds, C-versus O-protonation has been subject of controversy in the past.[10] Larsen et al.[11] found indirect evidence for the O-protonation based on the lack of isotopic exchange of the vinylic hydrogen atoms upon protonation with sulfuric acid-d$_2$. We have studied these species by ^{13}C-NMR recording the proton coupled spectra which provide direct and unambigous proof for the O-protonation. The vinyl carbon atoms appear in all instances as double doublets. The carbonyl carbons of 3a$^+$ and 4a$^+$ are a set of five signals which belong to the X part of a high order XAA′ system, while in the case of 2a$^+$ a simple triplet-like absorption pattern is observed (see Table). These data agree well with those reported by Braun[12] for a series of nonprotonated related compounds.

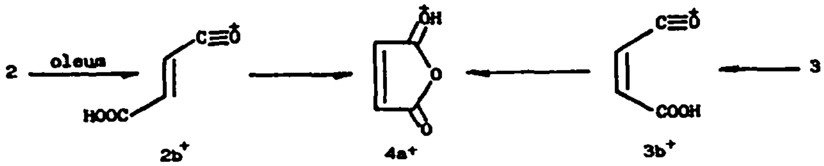
The reaction of acids 2 and 3 with oleum at room temperature resulted in the quantitative formation of O-protonated maleic anhydride 4a$^+$ which should involve the intermediate acylium ions 2b$^+$ and 3b$^+$ respectively. From the results of the protonation of 2 in 96% sulfuric acid can be deduced that simple O-protonation (2a$^+$) cannot account for the double bond isomerization. It is noteworthy the particular ability of 2b$^+$ to undergo a thermal cis-trans isomerization if compared with the thermal stability shown by the trans species 1b$^+$. The double bond cis-trans isomerization must occur through the contribution of a C$_2$-C$_3$ single bonded ketene-like structure I . However, this type of structure should, at first, be more favourable when derived from trans-crotonic acid than in the case of fumaric acid due to the presence in the latter of a α-CO positive charge destabilized owing to the electron withdrawing effect of the carboxy group[13]. Then, the rapid transformation 2b$^+$ → 4a$^+$ must be explained by

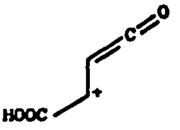
Table.- ^1H and ^{13}C NMR spectral data of the cationic species[a]

Compound	$\delta^b_{^1H}$ for indicated H: 2	3	4	$\delta^b_{^{13}C}$ and (in brackets) J^c_{CH} for indicated C: 1	2	3	4
$1a^+$	6,2	7,9	2,2	180,6 (^2J=6,0)	116,0 (^1J=170,0) (^2J=7,0)	167,3 (^1J=158,0) (^2J=7,0)	20,2 (^1J=130,0) (^2J=3,5) (^3J=2,0)
$1b^+$	6,5	9,0	2,6	151,3[d]	84,7[d]	203,8[d]	22,0[d]
$2a^+$	7,4	7,4	-	173,1 (^2J=5,0)	135,6 (^1J=176,0) (^2J=5,0)	135,6	173,1
$3a^+$	7,1	7,1	-	175,8[d]	137,4 (^1J=177,0) (^2J=1,5)	137,4	175,8
$4a^+$	7,2	7,2	-	168,8[d]	138,5 (^1J=193,0) (^2J=3,5)	138,5	168,8
$5a^+$	6,9	8,7	5,9	187,9	119,3 (^1J=192,0) (^2J=3,0)	168,0 (^1J=184,0) (^2J=3,0)	82,9 (^1J=180,0) (^2J=9,5) (^3J=9,0)
$6a^+$	5,3	2,9	5,4	195,4	38,6 (^1J=168,5)	34,7 (^1J=141,5)	86,4 (^1J=165,5)
$7a^+$	6,1	7,9	2,4	181,6[d]	113,9[d]	170,1[d]	18,2[d]
$7b^+$	6,5	9,0	2,7	157,3[d]	84,4[d]	202,9[d]	26,1[d]

a) For ^1H-NMR literature data see ref. 8 (for $1a^+$and $1b^+$); ref. 11 (for $2a^+$, $3a^+$and $4a^+$). For ^{13}C-NMR see ref. 6a (for $1a^+$)and ref. 2a (for $1b^+$). b) ppm ± 0,1 downfield from TMS. c) Hz ± 0,5. d) J not measured.

participation of the neighboring carboxy group that will parallel its π-orbital with that of the C=C double bond (see Figure 1), to allow the formation of C_2-C_3 single bonded ketene-like structures such as II and III, without the formal participation of the destabilized structure I. This effect would be related to the well known enhancement of the S_N2 substitution rate of α-haloesters if compared to that of the simple aliphatic compounds.[14]





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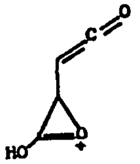

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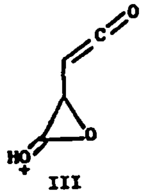

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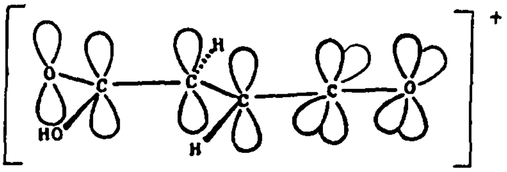
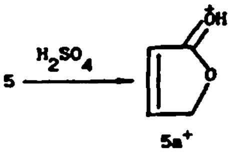
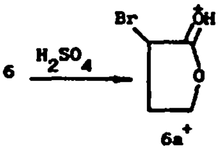


Figure 1

Finally, crotonolactone 5 and α-bromobutyrolactone 6 were dissolved in concentrated sulfuric acid at room temperature leading to the corresponding protonated species 5a$^+$ and 6a$^+$ characterized by their NMR spectra (see Table). The ^{1}H-NMR spectrum of 6a$^+$ in magic acid at low temperature had been reported by Olah and Ku.[13,15] The ^{1}H and ^{13}C NMR spectra of protonated crotonolactone 5a$^+$ correlate well with those of protonated crotonic acid 1a$^+$ allowing to assign the carbonyl oxygen as the protonation site.



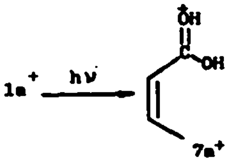
5a$^+$



6a$^+$

b) Photochemistry of cationic species.

The photochemical cis-trans isomerization of protonated trans-crotonic acid 1a$^+$ in fluorosulfuric and magic acid solution at low temperature has been previously reported by Childs et al.[6a,b] We have found similar results upon irradiation of 1a$^+$ in sulfuric acid at room temperature. However, to our knowledgment, none acylium ion has been irradiated so far. So, the irradiation of 1b$^+$ was undertaken also leading to cis-trans isomerization of the double bond. Spectral data of the unknown acylium ion 7b$^+$ are given in the Table. Ion 7b$^+$ is reasonably stable at room temperature and could be stored for several hours without any noticeable degree of thermal isomerization to the more stable trans acylium ion 1b$^+$. So, neither the cis 7b$^+$ or trans 1b$^+$ acylium ions derived from crotonic acid appear to have stable ketene-like structures.

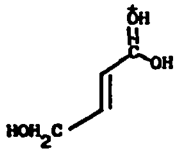


7a$^+$

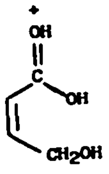
7b$^+$

When fumaric acid 2, maleic acid 3 or maleic anhydride 4 were dissolved in sulfuric acid and the resulting solutions submitted to irradiation, the same mixture of protonated acids 2a$^+$ and 3a$^+$ and the protonated anhydride 4a$^+$ was obtained regardless the nature of the neutral precursor employed. Obviously, the transformation of 4a$^+$ into 2a$^+$ must occur through the intermediacy of 3a$^+$, which was found to be present in the concentrated sulfuric acid solutions of maleic anhydride.

By contrast, we found that protonated crotonolactone 5a$^+$ was reluctant to undergo any light promoted transformation. This behavior is surprising when compared with the manifold photochemical reactivity of 5 and related lactones under neutral conditions.[14] However, this lack of photoreactivity can be correlated with that of protonated cyclohexenone.[1b] The absence of cis-trans isomerization in 5a$^+$ to afford trans 8a$^+$ can be understood since the presence of the cis 8a$^+$ could not be detected in sulfuric acid solutions of the lactone.



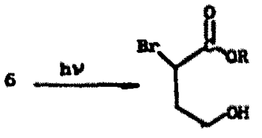
trans **8a$^+$**



cis **8a$^+$**

It is agreed that electronic excitation of α-haloesters results in an efficient homolytic cleavage of the carbon-halogen bond, the products mostly being derived from subsequent radical reactions.[4a] We have also studied the photochemistry of the protonated α-bromobutyrolactone $6a^+$ as a thirth type of functionalized carboxylic acid derivative in order to determine how protonation modifies the photobehavior. Ion $6a^+$ upon irradiation was clean and efficiently dehydrohalogenated to yield protonated crotonolactone $5a^+$. This compound could arise at least via two different reaction paths: a) heterolytic cleavage of the carbon-bromine bond (or homolytic cleavage followed by electron transfer) to give the corresponding carbenium ion and subsequent deprotonation, or b) less probably, nucleophilic substitution of bromide by the water contained in the 96% sulfuric acid used as solvent, followed by acid promoted dehydration. This prompted us to carry out the irradiation of bromolactone **6** in neutral protic solvents for comparison. The irradiation in methanol led to the bromohydroxyester **9** by solvolytic cleavage of the lactone ring remaining the carbon-bromine bond unaffected. Likewise, the irradiation in water was attempted, but DMSO had to be added as cosolvent for solubility reasons. Under these conditions hydrolysis of the lactone to afford the bromohydroxyacid **10** was the only observable photoreaction. These facts allow to rule out the nucleophilic substitution reaction path.

$$6a^+ \xrightarrow[(-HBr)]{h\nu} 5a^+$$



9: R = OCH_3
10: R = H

The unexpected dehydrohalogenation observed in the photolysis of protonated α-bromobutyrolactone $6a^+$ is relevant to the understanding of the photochemical behavior of α-halocarboxylic acid derivatives in the photo-Friedel-Crafts reaction. For instance, ethyl chloroacetate reacts with benzene in the dark under Friedel-Crafts conditions (aluminum chloride catalysis) to give mono-, di- and triethylbenzene, showing that the reactivity of the C-Hal bond is inhibited by the presence of the α-carboxy group. Conversely,[16,17] under irradiation only ethyl phenylacetate is obtained although aluminum chloride coordinate with both halogen and carbonyl oxygen in the ground state. To explain these facts inhibition of carbonyl coordination with the Lewis acid has been argued based on reverse π-electron polarization in the excited state. However, both the dehydrohalogenation of $6a^+$ now reported and the aluminum chloride catalyzed photo-Friedel-Crafts reaction, accomodate well with the photoreactivity of simple alkyl bromides which exhibit almost exclusive ionic photobehavior in viscous solvents[17,18] were the radical pairs formed by homolysis of the carbon-halogen bond remain in the solvent cage a time long enough to allow electron transfer to compete effectively with diffusion of the radicals. Then, it could be concluded that the photobehavior of carboxylic acid derivatives containing a second interacting function[15,19] is, under acid catalysis (protic or Lewis acid), that own of the isolated second function being suppressed all the normal $n \rightarrow \pi^*$ photoreactions characteristic of the non protonated carboxy group. Thus, protonation can be envisaged as a chemical selective method for photoprotection of the carboxy group, based on disturbing the absorption properties in difunctional substrates. Work is in progress to determine the scope and limitations of this methodology.

EXPERIMENTAL

General. Proton spectra were obtained at 60-MHz using a Hitachi Perkin-Elmer Model R-24 B NMR spectrometer. ^{13}C-spectra were recorded with a Bruker WP 80 SY NMR spectrometer using dioxane as external standard (capilar). All chemical shifts (δ) (^{1}H and ^{13}C) are reported in ppm relative to TMS.

Preparation of the ions.
Neutral substrates used were commercial material, except α-bromobutyrolactone and crotonolactone that were synthesized following known procedures.[20] Ions were prepared by slow addition, with efficient stirring, of either concentrated sulfuric acid (96%) or oleum (63% SO_3) to a substrate cooled in an ice-water bath, to get a ca. $7x10^{-3}$ M solutions.

Irradiations.
Ions solutions were placed into quartz tubes surrounding a centrally positioned quartz . cooling jacket (external diameter 55 mm) containing a 125 W medium-pressure mercury lamp. The temperature was keeped below 30° by means of a water bath.

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