Tetrahedron Vol. 48, No. 39, pp. 8465-8470, 1992
Printed in Great Britain

0040-4020/92 $5.00+.00
Pergamon Press Ltd

DIRECT OBSERVATION AND THERMAL TRANSFORMATIONS OF DICATIONS DERIVED FROM DIBENZOTROPYLIUM IONS

Gregorio Asensio,* Julia Pérez-Prieto, and M. Carmen Rams

Universidad de Valencia, Departamento de Q. Orgánica, Facultad de Farmacia, Avda Blasco Ibañez, 13 E-46010 Valencia Spain

Miguel A. Miranda,* and M. José Sabater

Universidad Politécnica, Departamento de Química, Apdo. 22012 E-46071 Valencia, Spain

(*Received in UK* 24 *June* 1992)

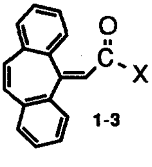
Key Words: Chemical ionization mass spectrometry, dibenzotropylium ions, dications, diprotonation, C- and O-protonation, α,β-unsaturated carboxylic acid derivatives

Abstract: *Carboxylic acid* **1** *and its derivatives* **2**, **3** *treated with triflic acid below* -20°C *afford the dications* $\mathbf{1H_2}^{+2}$-$\mathbf{3H_2}^{+2}$. *Cyclodehydration above* 20°C *(or in the gas-phase, CIMS of* **3**) *leads to the diprotonated ketone* $\mathbf{4H_2}^{+2}$.

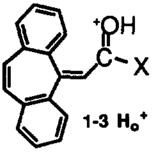
INTRODUCTION

α,β-Unsaturated carboxylic acids undergo O-protonation under strongly acidic conditions at room temperature.[1] The thermochemistry of these species in the temperature range of -60 to 160° in 98% sulfuric acid or triflic acid is characterized by formation of transient C-protonated intermediates from which rearrangement and/or cyclization to O-protonated products occurs.[2] In the search for a substrate suitable to experiment C-protonation at moderate temperature we explored the behavior of dibenzo[a,e]cycloheptatrienylideneacetic acid (**1**) in triflic acid. This led us to observe the unexpected formation of the C,O-diprotonated acid

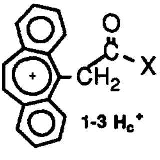
$\underline{1H}_2^{+2}$ which is stable below -20°C but cyclizes to the diprotonated ketone $\underline{4H}_2^{+2}$ at higher temperatures.



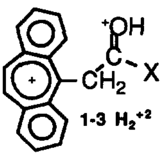
1-3



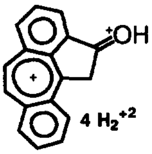
1-3 H_o^+



1-3 H_c^+



1-3 H_2^{+2}



4 H_2^{+2}

1: X=OH 2: X=NHCH₂Ph 3: X=OEt

RESULTS AND DISCUSSION

Compound $\underline{1}$ was prepared according to the method described in the literature.[3] Protonation of $\underline{1}$ was carried out by treatment with triflic acid at -40°C giving a characteristic purple solution which was studied by ^1H and ^{13}C NMR in the temperature range of -40 to +100°C (see Table). The ^{13}C NMR spectrum recorded below -20°C showed a symmetrical pattern with only ten signals corresponding to four quaternary, five tertiary, and one secondary carbon atoms. The high symmetry and the presence of a methylene group evidenced the occurrence of $\underline{C}$-protonation to afford a dibenzotropylium ion, which is in agreement with the deep colour of the solution. The alternative structures $\underline{1H}_c^+$ and $\underline{1H}_2^{+2}$ might be compatible at first with the spectral data. For both ions the down field signals at δ184.6 and 166.3 ppm in the spectrum recorded at -20°C should be assigned to the carbonyl and the C-5 carbon atoms.[4] To allow an unambiguous assignment of these signals the amide $\underline{2}$ was synthesized and protonated under the same conditions for comparison (for spectral parameters see Table). In this case, the corresponding peaks appeared at δ 175.3 and 167.0 ppm, clearly demonstrating that the signals at *ca.* 167 ppm must be assigned to the C-5 carbon in the dibenzotropylium system. This carbon is abnormally shielded if compared to 5-alkyl subtituted model analogues in which the reported values are around 190 ppm,[4] indicative of protonation on the carbonyl oxygen since it is known that the β-carbon in protonated carboxylic acids and derivatives becomes shielded with respect to the neutral precursors.[5] However, the observed deshielding of the carbonyl carbons did not appear by itself large enough to ensure a high degree of protonation unless the positive charge at the β-tropylium moiety could account for the relative small chemical shift increment found.

Table. ^{13}CNMR Spectral Data for the Observed Ionic Species and their Precursors

Precursors[a] and Ions[b]	Temp. (°C)	δ_C (ppm) for indicated C				
		$\underline{C}O$	$\underline{C}H_2CO$	$\underline{C}$-5	$CO O\underline{C}H_2$ or $CONH\underline{C}H_2$	Others
1	20	167.2		154.1		139.9, 136.5, 133.8, 133.6, 132.0 131.0, 129.8, 129.2, 129.0, 128.9 128.8, 128.6, 127.3, 124.4
$1H_2^{+2}$	-40	186.9	41.9	164.9		145.6, 145.3, 139.8, 137.9, 135.4 133.8, 130.9
	-20	184.6	42.2	166.3		145.4, 144.8, 139.6, 137.8, 135.1 133.5, 130.8
2	20	166.6		148.8	43.4	139.6, 137.5, 135.3, 133.6, 133.4 131.3, 130.6, 129.1, 128.8, 128.5 128.4, 128.1, 127.8, 127.6, 127.3 126.8
$2H_2^{+2}$	-20	175.3	44.5	167.0	49.6	147.8, 142.4, 140.4, 137.7, 136.4 132.3, 132.1, 131.6, 130.2, 129.5
3	20	166.8		157.0	61.1	140.7, 136.8, 134.5, 134.2, 132.4 131.4, 129.8, 129.6, 129.3, 129.0 127.6, 123.4, 15.0
$3H_2^{+2}$	-20	187.2	45.1	167.4	78.9	147.9, 147.5, 142.2, 140.2, 137.7 136.2, 132.8, 12.9
	20	182.7	45.6	170.4	74.1	147.5, 146.6, 141.8, 140.1, 137.1 135.6, 132.9, 13.8
$4H_2^{+2}$	-20	216.0	47.1	172.9		150.6, 149.4, 149.2, 146.0, 145.5 145.2, 145.0, 141.9, 140.0, 139.6 138.0, 137.4, 137.1, 136.3
	20	211.7	47.1	175.1		149.3, 148.7, 146.4, 145.2, 145.0 144.9, 144.8, 141.9, 139.1, 139.0 137.1, 136.8, 136.7, 136.1
	55	210.8	47.0	175.1		149.1, 148.7, 146.1, 145.1, 144.9 144.9, 144.7, 141.9, 139.1, 139.0 137.1, 136.7, 136.5, 135.8
	70	209.6	47.1	175.6		148.8, 148.6, 145.4, 144.8, 144.7 144.6, 144.5, 141.9, 139.4, 138.9 136.9, 136.6, 135.7, 135.7
	80	208.9	47.0	175.9		148.6, 148.5, 145.0, 144.8, 144.6 144.6, 144.4, 141.9, 139.6, 138.8 136.8, 136.5, 135.7, 135.3
	100	207.6	47.3	176.5		148.5, 148.4, 144.9, 144.7, 144.5 144.4, 144.3, 142.0, 140.0, 138.8 136.7, 136.5, 135.7, 134.7

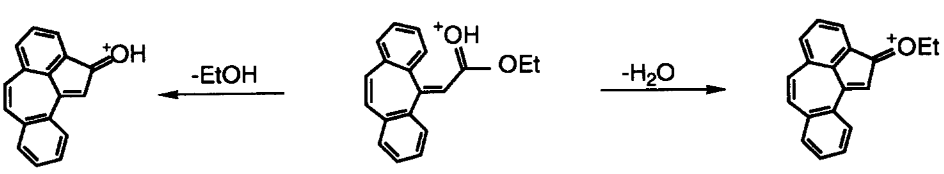
---

[a] In $CDCl_3$, [b] in CF_3SO_3H

A fact usually associated to protonation on the carbonyl oxygen in carboxylic esters is the deshielding of the carbon bound to the ether oxygen due to the contribution of oxonium ion structures.[5] For this reason, in order to ascertain the dicationic character of the species formed upon protonation of compound 1 in triflic acid, we synthesized and submitted to protonation under the same conditions the ethyl ester 3.[3] In this case ion $3H_2^{+2}$ was obtained as evidenced by the 17 ppm deshielding of the methylene carbon of the ethyl group (see Table).

It is evident from the temperature dependent ^{13}C NMR spectra that i) a reversible protonation of $1H_c^+$ between -40 and -20°C and ii) an irreversible cyclization of $1H_o^+$ above 20°C takes place in the temperature range studied. Thus, a 2.3 ppm deshielding of the carbonyl carbon is observed at the lower temperature indicating a small increment in the degree of O-protonation. This effect should be expected according to the exothermic nature of the protonation which is consistent with the displacement of the equilibrium to the right. The parallel 1.4 ppm shielding of C-5 in the tropylium ring can be attributed to the β-effect (see above) due to the higher degree of protonation at the carbonyl site. The same trend was observed in the temperature dependent spectra of all the ions studied (see Table). On the other hand, compound 1 dissolved in triflic acid cyclized above 20°C to the diprotonated ketone $4H_2^{+2}$. The same transformation took place in compound 3 although at slower rate which allowed to record the spectrum of $3H_2^{+2}$ at this temperature. The most striking spectral feature associated to this intramolecular acylation was the increase in the number of peaks due to the unsymmetrical nature of the new ion (see Table).

For comparison of these results in solution with the gas-phase behavior of protonated species we recorded the CIMS spectrum[6] of the ester 3 with methane as reactant gas. The base peak was that corresponding to the [MH^+] ion from which water or ethanol were lost, to give the ions with *m/z* 259 (14%) and 231 (53%) respectively.



m/z 231 (53%)

$3H_o^+$

m/z 259 (14%)

In summary, treatment of the carboxylic acid 1 or its derivatives 2 and 3 with triflic acid at low temperature affords the corresponding O,C-diprotonated species $1H_2^{+2}$-$3H_2^{+2}$. At higher temperatures cyclization to the diprotonated ketone $4H_2^{+2}$ is observed. The gas-phase ion chemistry (CIMS of 3) can be correlated with this latter behavior observed in solution.

Acknowledgements-We thank the Comision Interministerial de Ciencia y Tecnología proyect PB87-0989 and proyect PB90-0412. M.J. Vicente Arana is gratefully acknowledged by the high-resolution MS at Sercicio Interdepartamental de Investigación de la Universidad Autónoma de Madrid.

EXPERIMENTAL

^1H and ^{13}C NMR spectra were recorded with a Varian Gemini 200 NMR spectrometer. Dioxane or acetone (used for spectra recorded at low temperatures) served as the external standard (capillary tube). Chemical shifts (δ) are reported in ppm relative to TMS. CIMS spectra were recorded with a Hewlett Packard 5988A spectrometer, using methane as reagent gas. Electron impact mass spectra were recorded, at a 70 eV by magnet scan, on a magnetic sector VG-Autospec.

Ions were prepared by slowly adding, with efficient stirring, the cooled compound to a quantity of neat trifluoromethanesulfonic acid sufficient to give a ca. 1M solution.

Ethyl dibenzo[a,e]cycloheptatrienylideneacetate 3 *($C_{19}H_{16}O_2$):* This compound was prepared according to the literature method,[3] by reaction of dibenzo[a,e]cycloheptatrienone with triethyl phosphonoacetate, in the presence of sodium hydride, using DMSO as solvent. IR and UV spectral data were in agreement with the literature values. The compound was obtained as a solid and was recrystallized from hexane, (m.p. 68 °C) (lit.:[3] viscous oil). The ^1H NMR spectral data (not previously reported) were as follows: $\delta_H(CDCl_3)$ 7.5-7.3(m, 8H), 7.0(d, 1H), 6.9(d, 1H), 5.9(s,1H), 4.0(q, 2H), 1.1(t, 3H) ppm.

Dibenzo[a,e]cycloheptatrienylideneacetic acid 1 *($C_{17}H_{12}O_2$):* This compound was prepared by hydrolysis of the ethyl ester following a literature method.[3] Physical, IR and UV-spectral data were in agreement with the literature values.[3] The ^1H NMR spectral data (not previously reported) were as follows: δ_H(DMSO-d_6) 7.5-7.3(m, 8H), 7.05(d, 1H) 6.95(d, 1H), 5.9(s, 1H) ppm.

N-Phenylmethyldibenzo[a,e]cycloheptatrienylideneacetamide **2** *($C_{24}H_{19}NO$):* Ammonium chloride (50 mg) was added to a stirred mixture of ethyl dibenzo[a,e]cycloheptatrienylideneacetate (2.66 g, 0.01 mol) and phenylmethylamine (4.94 g, 0.05 mol). The reaction mixture was refluxed for seven hours. Then, the mixture was treated with water, extracted with ether and the organic layer dried with anhydrous sodium sulfate. Solvent was removed under reduced pressure to give a white solid (1.56 g, 99%) which was recrystallized from hexane, (m.p. 149°C). High-resolution MS calcd for $C_{24}H_{19}NO$ (M^+) 337.1467, found 337.1448.
ν_{max}(KBr) 3440, 3060, 3020, 1660, 1510 cm^{-1}; δ_H($CDCl_3$) 7.5-7.2(m, 13H), 6.9(s, 2H), 6.05(s, 1H), 5.3(s, 1H), 4.35(dd, 1H), 4.25(dd, 1H) ppm.

REFERENCES

1. a) Olah, G.A.; White, A.M.; O'Brien, D.H.; *Chem. Rev.* **1970**, *70*, 561-591; b) Childs, R.F.; Lund, E.F.; Marshall, A.G.; Morrisey, W.J.; Rogerson, C.V.; *J. Am. Chem. Soc.* **1976**, *98*, 5924-5931; c) Amat, A.M.; Asensio, G.A.; Castello, M.J.; Miranda, M.A.; Simón-Fuentes, A.; *Tetrahedron*, **1987**, *43*, 905-910.
2. a) Amat, A.M.; Asensio, G.A.; Castelló, M.J.; Miranda, M.A.; Simón-Fuentes, A.; *J.Org. Chem.* **1987**, *52*, 4790-4792; b) Amat, A.M.; Asensio, G.A.; Miranda, M.A.; Sabater, M.J.; Simón-Fuentes, A.; *J. Org. Chem.* **1988**, *53*, 5480-5484; c) Asensio, G.A.; Miranda, M.A.; Pérez-Prieto, J.; Sabater, M.J.; Simón-Fuentes, A.; *Angew. Chem. Int. Ed. Engl.* **1990**, *29*, 1146-1147.
3. Bergmann, E.D.; Solomonovici, A.; *Synthesis* **1970**, *2*, 183-189.
4. Olah, G.A.; Liang, G.; *J. Org. Chem.* **1975**, *40*, 2108-2116.
5. Olah, G.A.; Westerman, Ph.W.; *J. Org. Chem.* **1973**, *38*, 1986-1992.
6. Harrison, A.G. *Chemical Ionization Mass Spectrometry*; CRC Press: Boca Raton, FL, 1983.