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^{13}C Magnetic Resonance of Benzylmalonic Acid and of Some Malonato Complexes of Aluminium(III)

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There has been recent interest in the acidity of the α-protons in the malonate group, both in the esters [1] and in malonate coordinated to cobalt [2].

We report in this paper preliminary results of the ^{1}H and ^{13}C n.m.r. studies of benzylmalonic acid and the aluminium(III) complexes of malonic, ethyl- and benzylmalonic acids. The results show that benzylmalonic acid undergoes exchange with deuterium from solvent D_2O in acid and in basic solution. In neutral solution, no exchange takes place in $CDCl_3$, but slow exchange occurs in D_2O. The similar observations for malonic and ethylmalonic acids will be reported later [3].

In D_2O solution, the complexes $[Al(mal)_3]^{3-}$, $[Al(etmal)_3]^{3-}$ and $[Al(bzylmal)_3]^{3-}$ are stable to hydrolysis, and do not exchange protons with the solvent.

Experimental

The aluminium malonato complexes were prepared by a modification of the method of Bailar and Jones [4] for the tris(oxalato) complex. Thus, potassium tris(malonato)aluminate(III) hexahydrate, potassium tris(ethylmalonato)aluminate(III) trihydrate and potassium tris(benzylmalonato)aluminate(III) trihydrate were prepared by the addition of the appropriate potassium hydrogen malonate to the required amount of freshly prepared aluminium hydroxide. The filtered mixtures were concentrated on a rotary evaporator, and set aside to crystallise. Analyses were satisfactory. The measurement of n.m.r. spectra will be described elsewhere [3].

TABLE I. ^{1}H N.m.r. Signals of Benzylmalonic Acid in $CDCl_3$ (δ in ppm *vs.* TMS).

CH_2	doublet	3.25	(J = 7.63 Hz)
CH	triplet	3.75	
C_6H_5	singlet	7.25	
CO_2H	broad	9.36	

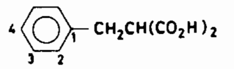
Results and Discussion

The ^{1}H n.m.r. spectral data of benzylmalonic acid in $CDCl_3$ are reported in Table I. In this solvent there is no change in the spectrum for 24 hours. In D_2O solution the spectrum is more complicated as a consequence of the slow exchange reaction:

$$C_6H_5CH_2CH(CO_2H)_2 \rightleftharpoons C_6H_5CH_2CD(CO_2D)_2$$

After 30 minutes, the singlet of the high field (CH_2) pattern has increased at the expense of the low field (CH) triplet. After 24 hours the low field triplet has disappeared and the high field pattern has become a singlet, showing the presence of $C_6H_5CH_2$·$CD(CO_2D)_2$.

TABLE II. ^{13}C N.m.r. Signals of Benzylmalonic Acid and Derivatives (δ in ppm *vs.* TMS).

				$Al(bzylmal)_3^{3-}$
	D_2O soln.	D_2O/NaOD	Na_2CO_3/D_2O[b]	
CO_2H	173.21	179.86	180.00	177.38
C_1	138.63	141.66	141.72	140.50
C_2, C_3	129.53	129.38	129.46	129.62, 129.38
C_4	127.71	126.95	127.04	127.25
CH	54.42[c]	61.7[a]	61.21	55.41
CH_2	35.17	37.11	37.24	36.19

[a] Split signal showing presence of CH and CD. [b] Acid neutralised with Na_2CO_3, salt dried and dissolved in D_2O. [c] Singlet of fresh solution rapidly collapses to split signal of CH and CD.

TABLE III. ^{13}C N.m.r. Signals of Ethylmalonic Acid and Derivatives (δ in ppm *vs.* TMS).

	D_2O soln.[a]	$D_2O/NaOD$[a]	Na_2CO_3/D_2O[a,b]	$Al(etmal)_3^{3-}$
CO_2H	174.28	180.88	180.86	178.50
CH	54.05	–	61.64	54.85
CH_2	22.80	22.40	22.38	24.54
CH_3	11.73	13.00	13.04	12.48

[a]From ref. 3. [b]As Table II.

TABLE IV. ^{13}C N.m.r. Signals of Malonic Acid and Derivatives (δ in ppm *vs*, TMS).

	D_2O[a]	$D_2O/NaOD$[a]	Na_2CO_3/D_2O[a,b]	$Al(mal)_3^{3-}$
CO_2H	171.57	178.49	178.37	175.49
CH_2	42.33	49.44	48.90	42.40
	41.43	48.73		
	40.64	47.92		

[a]From ref. 3. [b]As Table II.

The ^{13}C n.m.r. spectral data of benzylmalonic, ethylmalonic and malonic acids are shown in Tables II–IV.

The addition of a proton to the anion of benzylmalonic acid produces an upfield shift in the carboxyl and α-carbon resonances both of 6.79 ppm. The CH_2 and C_1 resonances are slightly more shielded, with upfield shifts of 2.07 and 3.09 ppm respectively. The C_2, C_3 and C_4 resonances show deshielding with small downfield shifts. When the anion is complexed with Al^{3+}, the increased shieldings of the carboxyl and the α-carbons are smaller (2.62 and 5.8 ppm, respectively), and the increased shielding of the CH_2 carbon is smaller (1.05 ppm). The C_2 and C_3 resonances are resolved in the complex.

A similar trend is observed for ethylmalonate. On acidification, the carboxyl and α-carbons show large increases in shielding of 6.58 and 7.35 ppm, respectively. The ethyl group shows a smaller upfield shift. On coordination to Al^{3+}, there are smaller upfield shifts for the carboxyl and α-carbons (2.36 and 6.79 ppm), whereas the methylene carbon of the ethyl group is now deshielded (2.16 ppm). However, the methyl group carbon is shielded by 0.56 ppm.

In general the resonances for the Al^{3+} complexes fall between those found for the free acids and those for their sodium salts, with the exception of the CH_2 resonance in the ethyl group of $[Al(etmal)_3]^{3-}$. Thus coordination of the anion by Al^{3+} in general produces shielding.

There exists the possibility of geometrical isomers in the tris complexes of C-substituted malonate. This point, and the reactions of such complexes are under investigation.

References

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