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REARRANGEMENTS IN THE ELECTRON-IMPACT INDUCED FRAGMENTATION OF SOME β-AROYL-α-METHYLPROPIONIC ACIDS

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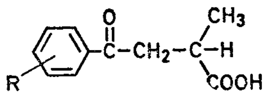
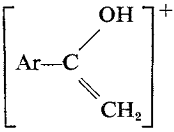
Abstract—A complex rearrangement on electron-impact for β-aroyl-α-methylpropionic acids, involving both hydrogen and hydroxy migration followed by loss of carbon monoxide and allyl radical, is described and discussed. The rearrangement process, resulting in an ion $[ArCOOH_2]^+$, is favoured by electron-withdrawing substituents in the aromatic ring.

Analysis of the mass spectra of β-aroyl-α-methylpropionic acids revealed, in addition to the α-cleavage and the McLafferty rearrangement,[1] a substantial peak at *m/e* [M − 69] for the compounds containing a strongly electron-withdrawing substituent in the aromatic ring (Table 1).

Table 1. Mass spectral data for β-aroyl-α-methylpropionic acids

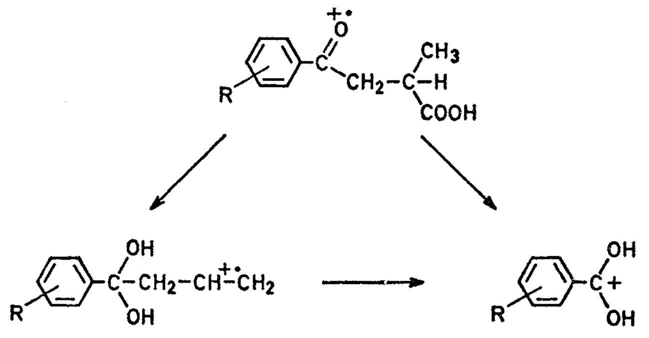


Substituent	*m/e* (relative intensities)			
R	$[M]^{+\cdot}$	$[ArCO]^+$	 $[Ar-C(OH)=CH_2]^{+\cdot}$	$[M-69]^+$
3-NH_2	207(39)	120(100)	135(3)	—
H	192(24)	105(100)	120(10)	123(1)
3-Cl	226(18)	139(100)	154(8)	157(1)
3-CN	217(16)	130(100)	145(16)	148(12)
4-CN	217(9)	130(100)	145(13)	148(9)
3-NO_2	237(5)	150(100)	165(27)	168(14)

The peak at *m/e* [M − 69] was assigned to ion *b* (Scheme 1) on the basis of both accurate mass measurements and determination of the metastable transitions corresponding with the loss of CO_2H_2 in one step from ion *b* (Table 2). Obviously, both hydrogen and hydroxy migration occur in the process leading to ion *b*.

The other metastable transitions listed in Table 2 show that ion *b* is generated both in one and in two steps from the molecular ion. The intensities of the peaks, which prove these transitions, suggest that the latter process is the more important. The intermediate ion *a* in the two-step formation of ion *b* only gives rise to a substantial peak in the spectrum for R = 3-NO_2 (Rel. int. 4%).

At least partly both hydrogen and hydroxy migration take place prior to fragmentation as is shown by the formation of ion *b* from the molecular ion in one step. The rearrangement involves a γ-hydrogen transfer as is demonstrated by (i) the absence of a peak for ion *b* in the spectrum of β-(3-nitrobenzoyl)propionic acid and (ii) the



(*a*) (*b*)

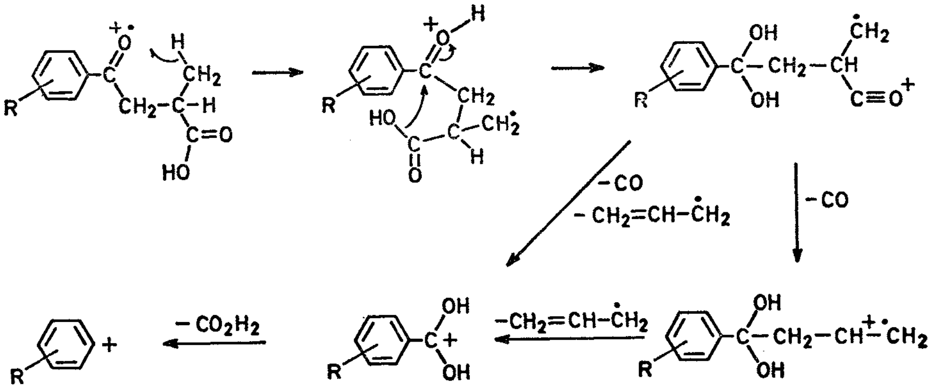
Scheme 1

Table 2. Metastable transitions found by the defocusing technique[2]

Substituent R	Transition $m_1 \rightarrow m_2$	m_1/m_2 Calculated	Found
3-CN	217 → 189	1·148	1·145
	217 → 148	1·466	1·473[a]
	189 → 148	1·277	1·278
	148 → 102	1·451	1·444[a]
3-NO$_2$	237 → 209	1·134	1·130
	237 → 168	1·411	1·420[a]
	209 → 168	1·244	1·241
	168 → 122[b]	1·377	1·388

[a] Peaks were of low intensity.

[b] The transition 168 → 122 could be explained either by loss of CO$_2$H$_2$ or by loss of NO$_2$ from *b*. High resolution and accurate mass measurement ruled out the latter process.



b *a*

Scheme 2

presence of a substantial peak for ion *b* in the spectrum of β-benzoyl-α,α-dimethylpropionic acid (Rel. int. 14%). Furthermore, in the spectrum of β-(3-nitrobenzoyl)-α-methylpropionic acid -d ion *b* was found to be shifted to *m/e* 149 confirming the hydroxy migration in the rearrangement process.

Conclusively, the observed phenomena may be described by the following fragmentation scheme (Scheme 2).

The first step in the rearrangement of the molecular ion is assumed to be identical with that of the McLafferty rearrangement.[1] In this connection it may be noted, that both the substituents in the aromatic ring and the number of hydrogen atoms in γ-position with respect to the aroyl group affect the two fragmentation processes in an analogous way. The γ-hydrogen transfer and the hydroxy migration are followed by a concerted or stepwise loss of carbon monoxide and an allyl radical to give ion *b*.

The foregoing considerations, if correct, would imply that the McLafferty rearrangement occurs in a stepwise fashion[3] for these compounds. Therefore, further studies on this remarkable rearrangement process are under investigation.

EXPERIMENTAL

The mass spectra were determined on a Varian-MAT SM-1 mass spectrometer operating at 70 eV, by using a direct insertion probe. Accurate masses were determined at high resolution ($m/\Delta m \geqslant 10^4$).

The elemental analyses were performed by Mr M. van Leeuwen. β-(3-nitrobenzoyl)propionic acid[4], β-benzoyl-α-methylpropionic acid (I)[5] and β-benzoyl-α,α-dimethylpropionic acid[6] were prepared according to the literature.

β-(3-nitrobenzoyl)-α-methylpropionic acid (II). A cold mixture of 15 ml of nitric acid (1·52) and of 28 ml of sulphuric acid (1·84) was added during 30 mins to a stirred suspension of 25 g (0·13 mole) of I in 40 ml of sulphuric acid (1·84) at 0°. The mixture was then poured into water and the resulting solid crystallized from ethanol/water to yield 18 g (58%) of II, m.p. 177 to 178°. (Found: C, 55·5; H, 4·7; N, 5·9. $C_{11}H_{11}NO_5$ requires C, 55·69; H, 4·67; N, 5·91%).

β-(3-aminobenzoyl)-α-methylpropionic acid (III), m.p. 152 to 153° (water), was obtained in 95% yield by hydrogenation of II in ethanol at room temperature and atmospheric pressure in the presence of 10% palladium on carbon. (Found: C, 63·8; H, 6·4; N, 6·8. $C_{11}H_{13}NO_3$ requires C, 63·75; H, 6·32; N, 6·76%).

β-(3-chlorobenzoyl)-α-methylpropionic acid (IV). Diazotation of 5·0 g (0·024 mole) of III, followed by the Sandmeyer reaction with cuprous chloride yielded 3·6 g (66%) of IV, m.p. 103·5 to 104·5° (ethyl acetate/petroleum ether). (Found: C, 58·3; H, 5·0. $C_{11}H_{11}ClO_3$ requires C, 58·29; H, 4·89%).

β-(3-cyanobenzoyl)-α-methylpropionic acid (V). Diazotation of 2·5 g (0·012 mole) of III, followed by the Sandmeyer reaction with cuprous cyanide yielded 3·7 g of a high melting solid. Extraction of this solid with 50 ml of hot ethyl acetate and evaporation of the solvent gave 1·3 g (50%) of V, m.p. 168 to 169° (ethyl acetate/petroleum ether). (Found: C, 65·9; H, 5·1; N, 6·3. $C_{12}H_{11}NO_3$ requires C, 66·35; H, 5·10; N, 6·45%).

β-(4-cyanobenzoyl)-α-methylpropionic acid (VI). 24·0 g (0·178 mole) of acetanilide and 20·0 g (0·174 mole) of methylsuccinic anhydride were added to 92 g (0·69 mole) of aluminium chloride in 100 ml of carbon disulphide at 0° and the mixture was stirred for 2 hrs. After standing for 2 days the reaction mixture was worked up in the usual way to yield 13·0 g (30%) of *β-(4-acetamidobenzoyl)-α-methylpropionic acid*, m.p. 200 to 201°. The product was heated under reflux with 46 ml of hydrochloric acid (1:1) for 2 hrs. Diazotation of the resulting mixture, followed by the Sandmeyer reaction with cuprous cyanide yielded 22 g of a high melting solid. Working-up as described for V gave 5·0 g (44%) of VI, m.p. 135 to 136° (ethyl acetate/petroleum ether). (Found: C, 66·0; H, 5·2; N, 6·3. $C_{12}H_{11}NO_3$ requires C, 66·35; H, 5·10; N, 6·45%).

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