Tetrahedron Letters No. 8, pp 705 - 706, 1972. Pergamon Press. Printed in Great Britain.

MASS SPECTRA OF KETONES AND DIKETONES CONTAINING PYRIDYL GROUPS

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(Received in UK 5 January 1972; accepted for publication 19 January 1972)

Fragmentation of benzophenone[2] and benzil[3] under electron-impact conditions is essentially simple, the only significant mode of decomposition of the molecular ion in each case being α-cleavage to give the benzoyl cation. Weak peaks are observed, however, corresponding to ions formed by skeletal-rearrangement processes - (M-CO) from benzophenone[2], (M-CHO) and (M-2CHO) from benzil[3].

We now report that monoketones (ArCOAr') and α-diketones (ArCOCOAr') in which at least one of the groups Ar and Ar' is a pyridyl group afford mass spectra which are markedly different from those of benzophenone and benzil respectively in that ions formed by rearrangement processes are often relatively abundant.

More important, however, is the finding that the rearrangements observed for a particular compound are markedly dependent upon the type(s) of pyridyl group(s) initially present in that compound; as such, they are of potential diagnostic use in problems involving structure elucidation. Specifically, with the monoketones, ions due to loss of CO and CHO are particularly noticeable in the spectra of 2-pyridyl derivatives but make little or no contribution to the spectra of 3- or 4-pyridyl derivatives. With the diketones, on the other

Ions observed		Relative abundance (%)					
		Ar = Ph Ar'= Ph	2-Pyr Ph	2-Pyr 2-Pyr	3-Pyr Ph	3-Pyr 3-Pyr	4-Pyr Ph
From ArCOAr'	M	25	36	30	78		60
	M-1	-	30	5	23		3
	M-28	1	51	46	4		-
	M-29	-	18	29	4		-
	[Base peak	$PhCO^+$	Ph^+	Pyr^+	$PhCO^+$		$PhCO^+$]
From ArCOCOAr'	M	5	4	13	4	4	3
	M-28	-	-	3	38	48	18
	M-29	1	4	-	-	2	-
	M-56	-	8	35	-	2	-
	M-57	-	2	10	-	1	-
	[Base peak	$PhCO^+$	Ph^+	Pyr^+	$PhCO^+$	$PyrCO^+$	$PhCO^+$]

hand, ions due to loss of CO and/or CHO are always observed but are particularly important in the case of compounds containing only 3- or 4-pyridyl groups; when 2-pyridyl groups are present, the spectra are characterised by relatively strong peaks due to loss of a second molecule of CO.

Possible structures for the various rearranged ions will be discussed in a full paper to be published elsewhere.

References

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