Rearrangement Reactions of some Simple Ketones and Esters upon Electron Impact

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ATTENTION has recently been drawn[1,2] to the relative rarity of alkyl migrations which have been established to occur in the mass spectrometer. We now report the occurrences, in the spectra of some simple ketones and esters, of fragment ions which necessitate the formation of C–C or C–O bonds upon electron impact.

The compounds in which the examples of C–C and/or C–O bond formation have been established are listed in the Table. In every case the composition of the rearrangement ion has been substantiated by exact mass measurements. Elimination of the ketone carbonyl group in the fragmentation of the β-keto-esters (IV) and (V) is proved by ^{18}O-labelling of the ketone moiety.[3]

The relative abundances quoted in the Table give some indication of the prevalence of the rearrangement ions as they appear in conventionally represented spectra. The importance of the rearrangement processes is indicated in some cases by additional high-resolution measurements. For example, ions at *m/e* 191, 205 (21 and 31% of the base peak) and at *m/e* 165, 178, 179 (11, 13, and 26% of the base peak) in the spectra of (II) and (III) respectively are due to $C_{15}H_{11}^+$, $C_{16}H_{13}^+$ and $C_{13}H_9^+$, $C_{14}H_{10}^+$, $C_{14}H_{11}^+$, all skeletal rearrangement fragments. Further details of these spectra will be reported subsequently.

TABLE

Rearrangement Ions in the Spectra of Some Simple Ketones and Esters

Compound		Rearrangement ion	Migrating group	R.A.*
$MeCO{\cdot}CH_2{\cdot}COMe$ .. (I)		$M^+ - CO$	CH_3	10
$(PhCH{=}CH)_2CO$ .. (II)		$M^+ - CO$	$C_6H_5CH{=}CH$	17
$PhCH{=}CH{\cdot}COPh$ .. (III)		$M^+ - CO$	C_6H_5	10
$MeCO{\cdot}CH_2{\cdot}CO_2Me$ .. (IV)		$M^+ - CO$	CH_3	6
$MeCO{\cdot}CH_2{\cdot}CO_2Et$ .. (V)		$M^+ - CO$	CH_3	4
$MeCO{\cdot}CH_2{\cdot}COPh$ .. (VI)		$C_7H_7^+$	C_6H_5	14
$(Me_2C{=}CH)_2CO$ .. (VII)		$M^+ - C_2H_3O$	—	13
$MeCO_2{\cdot}C{\equiv}C{\cdot}CO_2Me$ .. (VIII)		$M^+ - CO_2$	CH_3	40
$Ph{\cdot}R{\cdot}C(CO_2Et)_2$				
(IX; R=H) ..		$M^+ - CO_2$	C_2H_5	18
(X; R=Et) ..		$M^+ - CO_2$	C_2H_5	7
$PhCH{\cdot}CN{\cdot}CO_2Et$ .. (XI)		$M^+ - CO_2$	C_2H_5	8
$Pr^iCH{\cdot}CN{\cdot}CO_2Et$ .. (XII)		$M^+ - CO_2H$	C_2H_4 or C_2H_5	7

* R.A. = Relative Abundance as % of the base peak.

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