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STUDIES IN MASS SPECTROMETRY—XX[1]

BOND-FORMING REACTIONS OCCURRING IN THE FRAGMENTATION OF SOME α,β-UNSATURATED ESTERS AND NITRILES UPON ELECTRON IMPACT

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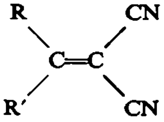
Abstract—Bond-forming reactions which occur in the decomposition of some α,β-unsaturated esters and nitriles upon electron impact are described. The reactions include bond formation between adjacent phenyl and cyanide substituents in structures of type A, and alkoxyl (or hydroxyl) migrations (probably by 1,3-shifts) in systems of type B, to give ions represented by C. A previously described cyclization reaction is shown to facilitate the expulsion of an *ortho*-substituent (at the site of cyclization) in a phenyl ring relative to the corresponding *meta*- and *para*-substituents.

$C_6H_5C(R){=}C(CN)R'$ $\quad$ $R(R')C{=}C(R'')CO_2R'''$ $\quad$ $R(R')\overset{+}{C}{-}OR'''$
A $\quad$ B $\quad$ C

REACTIONS occurring upon electron impact which necessitate bond formation between two atoms X and Y, where neither X nor Y is hydrogen, are of both practical and mechanistic interest. A recent review article[2] has summarized such reactions which have hitherto been reported. The present paper deals with some novel migrations of functional groups which are evident from the mass spectra of a variety of α,β-unsaturated nitriles and esters, represented in general by the structures I–IV.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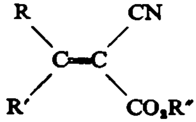
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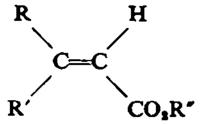
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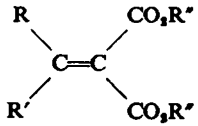
IV

In compounds of the general formula I or II, when R or R′ is phenyl, ions formally corresponding to ionized phenyl cyanide are frequently observed in the spectra. Such ions vary greatly in relative abundance; also aromatic nuclei other than phenyl may participate in the reaction, as may be seen from the data compiled in Table 1. Among the compounds studied, the rearrangement is most prevalent in the spectrum (Fig. 1) of 1,1-dicyano-2-phenylethylene (IX), where the abundance of *m/e* 103 ($C_7H_5N^+$) attains 27% relative to the base peak molecular ion; an appropriate metastable peak establishes that *m/e* 103 is formed in a one-step process from the molecular ion. Although the product ion may conveniently be regarded as ionized phenyl cyanide, there is no evidence to favour C—C bond formation over C—N bond formation in this reaction. These examples appear to be the first reported ones in which an

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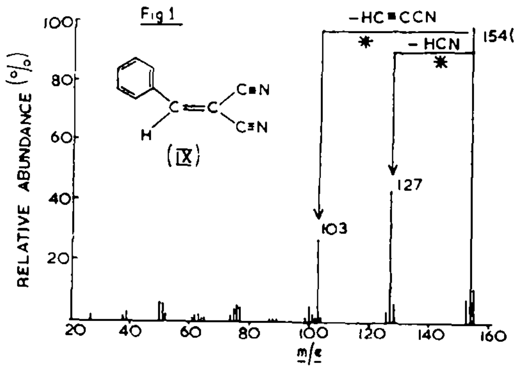
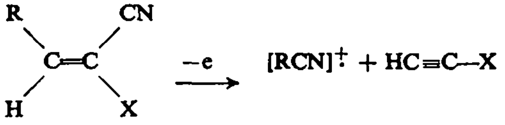
[1] Part XIX, J. Ronayne, D. H. Williams and J. H. Bowie, *J. Am. Chem. Soc.* **88**, 4980 (1966).
[2] P. Brown and C. Djerassi, *Angew. Chem.* in press.

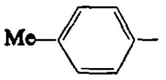
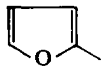
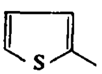
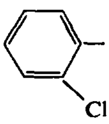


ion is generated with associated bond formation between 1,2-groups attached to a carbon-carbon double bond. The compounds (VI–VIII, X, XI) represented by the general formula II are of unknown stereochemistry, and we are therefore unable to judge whether a *cis*-relationship of the phenyl and cyanide groups is necessary for the rearrangement to occur. However, since *cis-trans* isomerization of double bonds is



V *a*

TABLE 1. RELATIVE ABUNDANCES OF IONS (*a*) IN THE SPECTRA OF COMPOUNDS OF THE GENERAL FORMULA V*

Compound No.	R	X	Composition of "*a*" (*m/e*)	Rel. Ab. (%)
VI	Ph	CO_2Et	C_7H_5N (*m/e* 103)	2
VII	Ph	CO_2H	C_7H_5N (*m/e* 103)	2
VIII		CO_2t-Bu	C_8H_7N (*m/e* 117)	3
IX	Ph	CN	C_7H_5N (*m/e* 103)	27
X		CO_2t-Bu	C_5H_3NO (*m/e* 93)	1
XI		CO_2t-Bu	C_5H_3NS (*m/e* 109)	5
XII		CN	C_7H_4NCl (*m/e* 137/139)	12/4

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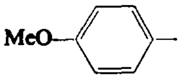
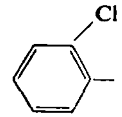
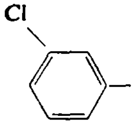
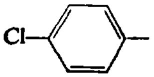
* The compositions of all ions reported in this paper have been established by high resolution measurements. Decomposition processes which are substantiated by appropriate metastable peaks are signified in the figures by an asterisk (*).

known to be a facile process upon electron-impact,[3] a *cis*-relationship would not seem to be a likely prerequisite. The occurrence of this rearrangement process is consistent with the generalization[3] that skeletal rearrangement is frequently facilitated by the proximity of highly unsaturated groups, and with the known propensity[4–6] of nitriles to undergo bond-forming reactions on electron impact.

A second rearrangement process which has been observed involves the migration of an alkoxyl or OH group in the mass spectral fragmentation of compounds represented by the general formulae II–IV. In the general case the reaction is probably best represented as a 1,3-alkoxyl (or OH) shift (XIII → *b*), followed by bond fission as indicated to give *c*.[7]

The compounds which have been found to undergo this fragmentation reaction upon electron impact are listed in Table 2, which also gives the relative abundances

TABLE 2. RELATIVE ABUNDANCES OF IONS (*c*) FORMED BY ALKOXYL OR HYDROXYL MIGRATION IN THE SPECTRA OF SOME α,β-UNSATURATED ESTERS AND ACIDS OF THE GENERAL FORMULA XIII

No.	R	Compound R′	R″	Composition of *c* (*m/e*)	Rel. Ab. (%)
VI	Et	Ph	CN	$C_9H_{11}O$ (*m/e* 135)	5
VII	H	Ph	CN	C_7H_7O (*m/e* 107)	9
XIV	Me	Ph	CN	C_8H_9O (*m/e* 121)	12
XV	H	Ph	H	C_7H_7O (*m/e* 107)	3
XVI	Me	Ph	H	C_8H_9O (*m/e* 121)	2
XVII	Et	Ph	CO_2Et	$C_9H_{11}O$ (*m/e* 135)	28
XVIII	Et		CO_2Et	$C_{10}H_{13}O_2$ (*m/e* 165)	5
XIX	Et		CO_2Et	$C_9H_{10}OCl$ (*m/e* 169/171)	2/0·6
XX	Et		CO_2Et	$C_9H_{10}OCl$ (*m/e* 169/171)	14/5
XXI	Et		CO_2Et	$C_9H_{10}OCl$ (*m/e* 169/171)	14/5
XXII	Et	Me	CN	C_4H_9O (*m/e* 73)	1
XXIII	Et	EtO	CO_2Et	$C_5H_{11}O_2$ (*m/e* 103)	2

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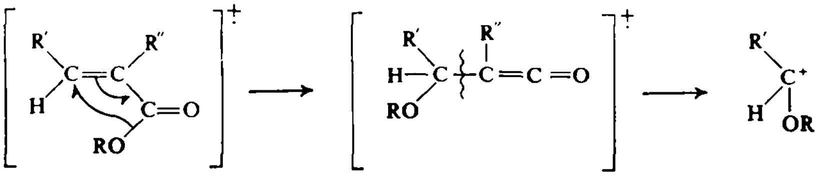
[3] J. H. Bowie, D. H. Williams, P. Madsen, G. Schroll and S.-O. Lawesson, *Tetrahedron* **23**, 305 (1967).

[4] R. Beugelmans, D. H. Williams, H. Budzikiewicz and C. Djerassi, *J. Am. Chem. Soc.* **86**, 1386 (1964).

[5] J. H. Bowie, R. Grigg, D. H. Williams, S.-O. Lawesson and G. Schroll, *Chem. Comm.* 403 (1965).

[6] J. H. Bowie, R. Grigg, S.-O. Lawesson, P. Madsen, G. Schroll and D. H. Williams, *J. Am. Chem. Soc.* **88**, 1699 (1966).

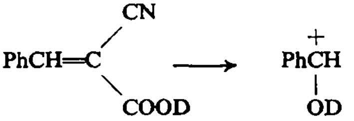
[7] In the representation of concerted processes (e.g., XIII→*b*), the use of a fishhook is not intended to imply any preference for a homolytic process over a heterolytic one.



XIII *b* *c*

and compositions of the product ions. The stereochemistry of compounds VI, VII, XIV and XXII is unknown.

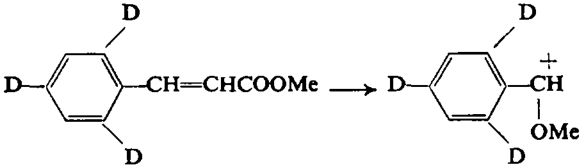
Although high resolution measurements establish all the proposed migrations, additional evidence has been forthcoming from deuterium labelling in a number of cases. Thus the 9% peak at *m/e* 107 in the spectrum of the acid VII is shifted to *m/e* 108 (*d*) in the spectrum of the O-d$_1$-acid VIIa, and the *m/e* 121 rearrangement ion from methyl cinnamate XVI is shifted to *m/e* 124 (*e*) in the spectrum of the d$_3$-derivative XVIa.[8] Similarly, the *m/e* 121 ion in the spectrum (Fig. 2) of methyl α-cyanocinnamate (XIV) is shifted to *m/e* 122 (*f*) in the spectrum of the d$_1$-derivative XIVa, while the *m/e* 135 ion from diethyl benzalmalonate (XVII, see Fig. 3) is quantitatively shifted to *m/e* 138 (*g*) in the spectrum of the d$_3$-derivative XVIIa.



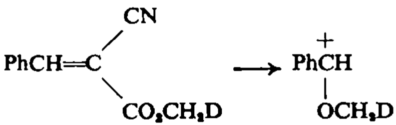
$$PhCH{=}C(CN)COOD \longrightarrow Ph\overset{+}{C}H{-}OD$$

d, m/e 108

VIIa

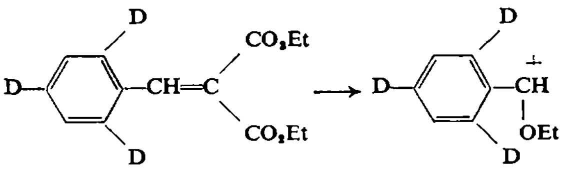


XVIa *e, m/e* 124



$$PhCH{=}C(CN)CO_2CH_2D \longrightarrow Ph\overset{+}{C}H{-}OCH_2D$$

XIVa *f, m/e* 122



XVIIa *g, m/e* 138

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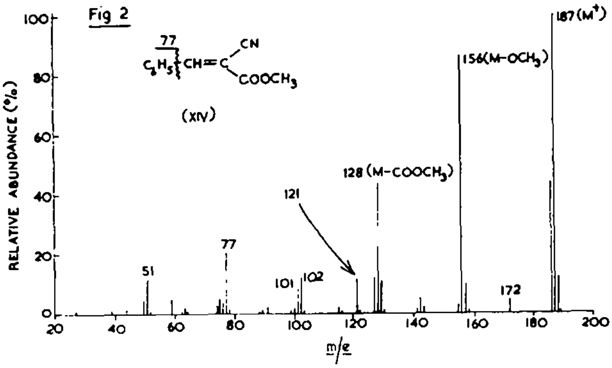
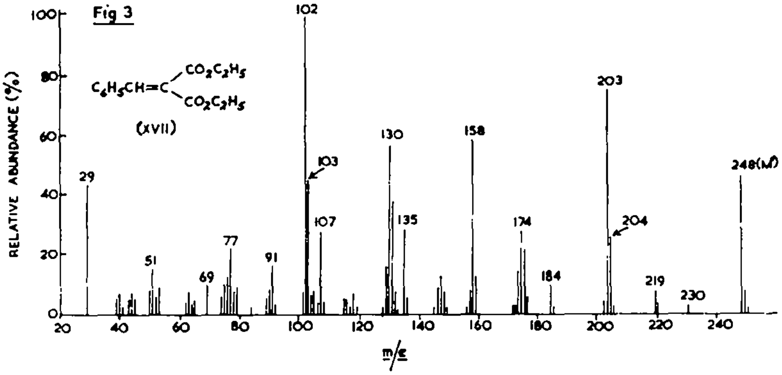
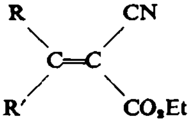
[8] The product ions are represented as benzyl cations merely for convenience, and no preference is implied for these structures over the ring expanded hydroxy- or alkoxy-tropylium ions.[9]

[9] For examples of tropylium ion formation in the mass spectrometer, see H. M. Grubb and S. Meyerson in (F. W. McLafferty ed.) *Mass Spectrometry of Organic Ions* Chap. 10. Academic Press, New York (1963).

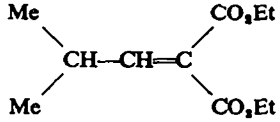
A number of aliphatic α,β-unsaturated ethyl esters which have been examined (XXIV–XXVIII) do not give ions corresponding to ethoxyl migrations, and indeed the data collected in Table 2 suggest that a β-phenyl substituent on the double bond facilitates the production of the rearrangement ions (attention is drawn to the low relative abundance of the rearrangement ions from the aliphatic esters XXII and XXIII). This behaviour may be understood in terms of the favourability of the appropriate bond cleavage in *b* when *R′* is a phenyl substituent, to produce benzyl cations or tropylium ions. However, the possibility of a 1,5-alkoxyl or 1,5-hydroxyl shift (XXIX → *h*), followed by a 1,3-hydrogen shift (*h* → *i*) and subsequent cleavage (*i* → *j*) cannot be excluded when a phenyl substituent is conjugated with the double bond.[10]







Me—CH=CH—CO$_2$Et



XXIV, R = R′ = Me
XXV, R = R′ = Et
XXVI, R = H, R′ = iso-Pr
(or R = iso-Pr, R′ = H)

XXVII

XXVIII

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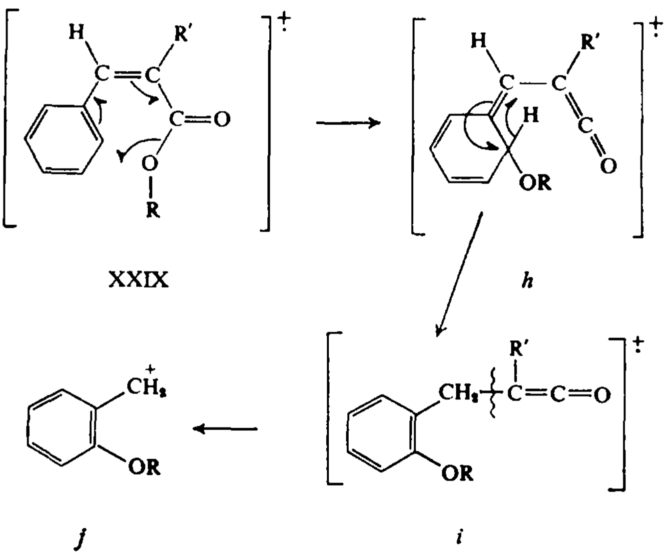
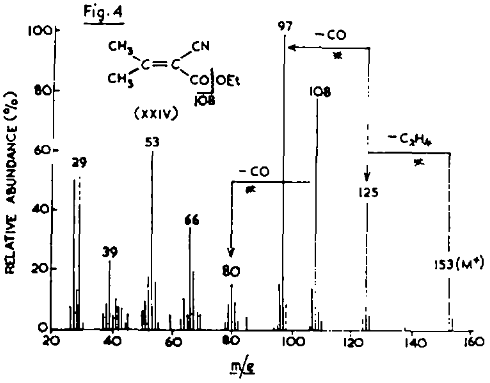
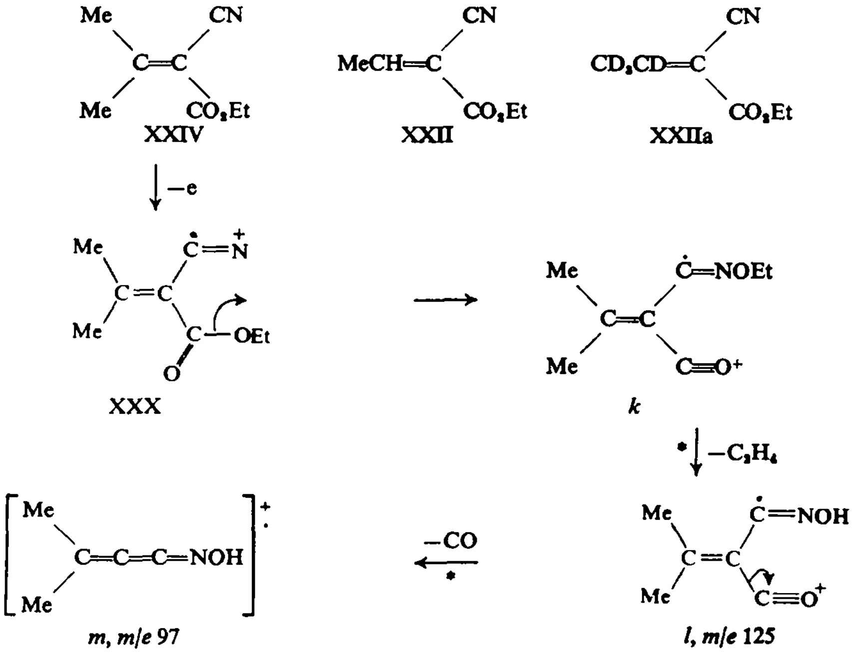
[10] In *trans*-cinnamates, the operation of a 1,5-shift (XXIX → *h*) would of course require isomerization about the double bond prior to rearrangement.



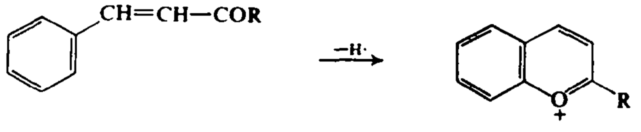
The effect of varying the energy of the electron beam (down to a nominal 11 eV) on both the cyanide (V → *a*) and ethoxyl (XIII → *b* → *c*) migrations has been determined. In the compounds examined at low energies (IX, XXI, XXII), the total ion current carried by the rearrangement fragments was sensibly constant.



The close proximity of cyanide and carboethoxy groups, when attached to the same sp^2-hybridized carbon atom (see II), may on occasions lead to abundant M—C_2H_4—CO rearrangement ions. This behaviour is illustrated by reference to the spectrum (Fig. 4) of ethyl isopropylidenecyanoacetate (XXIV), in which appropriate metastable peaks establish the origin of the base peak (*m/e* 97, $C_5H_7NO^+$) from the molecular ion via successive losses of ethylene (to *m/e* 125, $C_6H_7NO_2^+$) and carbon monoxide. Similarly, in the spectrum of the ethylidene derivative XXII, *m/e* 83 ($C_4H_5NO^+$, 16% of the M—OC_2H_5 base peak) arises *via* the successive losses of C_2H_4 and CO from the molecular ion; the spectrum of the d_4-derivative XXIIa establishes that the ethylene is expelled from the ethyl group of the ester. These processes demand the migration of an oxygen atom, presumably as an OEt or OH group. Since a neighbouring cyanide group bound to the sp^2-hybridized carbon atom seems to be necessary for this reaction to occur, one possible representation of the process may be illustrated by the sequence XXX → *k* → *l* → *m* (*m/e* 97). The loss of ethylene from XXIV after ionization to give the acid, followed by a OH migration to the nitrile function might also be entertained since no loss of carbon monoxide is found to precede the expulsion of ethylene.



In some systems represented by the general formula XXXI it has recently been shown[1] that abundant M-1 ions arise via loss of an aromatic hydrogen atom, probably with the production of an aromatic oxonium ion *n*. Waight[11] has demonstrated that such cyclization reactions can lead to the facile loss of an *ortho*-substituent (XXXII → *o*). Since deuterium labelling has established that hydrogen is not lost specifically from the *ortho*-position in the reaction typified by XXXI → *n*,[1] it was of interest to determine whether chlorine was preferentially eliminated from the *ortho*-isomer XIX relative to the *meta*- and *para*-isomers XX and XXI. Whereas the spectra of the *m*- and *p*-isomers are virtually identical (see, for example, Fig. 5), that of the *o*-isomer XIX (Fig. 6) contains no molecular ion, but exhibits a relatively abundant M—Cl ion, the further decomposition of which provides (at least in part) both *m/e* 219 and the base peak (*m/e* 173). These observations strongly indicate a facile chlorine radical elimination via cyclization (XIX → *p*) only in the *o*-isomer.



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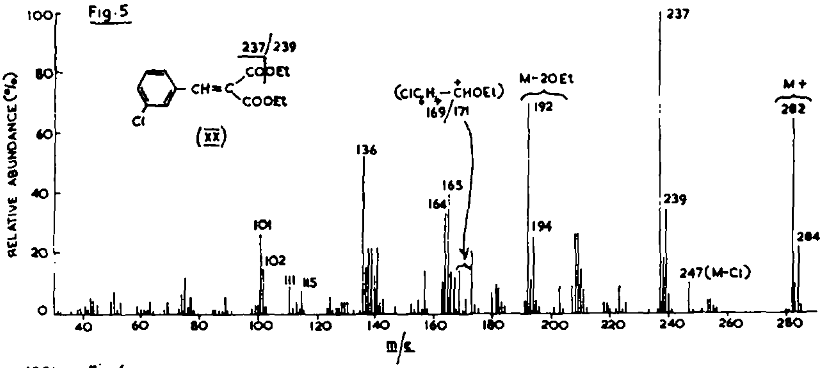
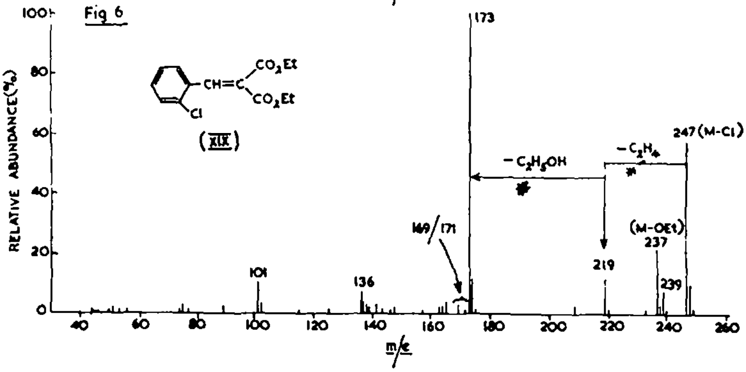
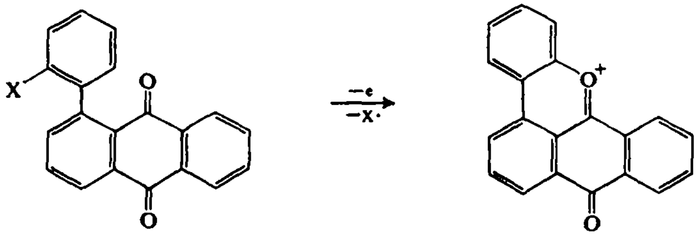
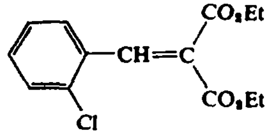
[11] E. S. Waight, Symposium on *Newer Physical Methods in Structural Chemistry*, Oxford (1966).



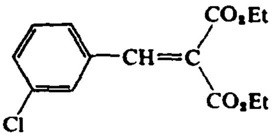




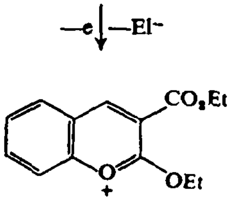
XXXII *o*



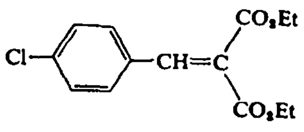
XIX



XX



p



XXI

While the elimination upon electron impact of stable neutral species (e.g., CO) from organic molecules with bond-formation between the terminal portions can no longer be regarded as very unusual,[2] the possible migration of groups in concerted electrocyclic reactions (e.g., XIII → *b* or XXIX → *h*) appears to be a rarer phenomenon, examples of which are of great mechanistic interest. However, it is emphasized that if the ionization process is regarded as occurring by removal of a π-electron from the olefinic double bond of XIII, then the alkoxyl (or hydroxyl) migration may be visualized to occur to a benzylic carbonium ion centre, in analogy to other cases.[11a]

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EXPERIMENTAL

All mass spectra were determined using an AEI MS 9 mass spectrometer operating at 70 eV and a source pressure of approximately 1×10^{-7} mm Hg. Samples were introduced through a heated inlet system (at approximately 150°) or by the direct insertion technique.

Compound XV was obtained commercially. We have previously[12] reported the preparation of VIII, X and XI.

Diethyl *m*-chlorobenzalmalonate (XX) was prepared by condensation of *m*-chlorobenzaldehyde with diethylmalonate, yield 28%, b.p. 135°/0·5 mm, n_D^{25} 1·5380. (Found: C, 59·33; H, 5·38; Cl, 12·50. Calc. for $C_{14}H_{15}O_4Cl$: C, 59·49; H, 5·36; Cl, 12·71%.)

The following Knoevenagel products were prepared by reported methods (compound and Ref. given), VI,[13] VII,[14] IX,[15] XII,[15] XIV,[16] XVI,[17] XVII,[18] XVIII,[19] XIX,[20] XXI,[21] XXII,[22] XXIII,[23] XXIV,[24] XXV,[25] XXVI,[26] XXVII,[27] XXVIII.[28]

The isotopically labelled ester XIVa was prepared by condensation of benzaldehyde with monodeuterated methyl cyanoacetate, which was obtained from the acid by esterification with diazomethane in a dioxane-deuterium oxide mixture.[29] Yield 89%, m.p. 87–88°.

Ethyl d_4-ethylidenecyanoacetate (XXIIa) was prepared by condensation of d_4-acetaldehyde with ethyl cyanoacetate, yield 69%, b.p. 99°/11 mm., n_D^{25} 1·4456.

The spectrum of the deuterated acid VIIa was obtained by introducing the acid VII into the spectrometer in the presence of D_2O.[30]

Methyl 2,4,6-d_3-cinnamate (XVIa) was prepared by a previously described[1] procedure. Diethyl 2,4,6-d_3-benzalmalonate (XVIIa) was available from the condensation of 2,4,6-d_3-benzaldehyde[1] with diethyl malonate.

[11a] R. G. Cooks and D. H. Williams, *Chem. Comm.* 51 (1967).

[12] S.-O. Lawesson, E. H. Larsen and H. J. Jacobsen, *Arkiv. Kemi* 23, 453 (1965).

[13] W. Baker and A. Lapworth, *J. Chem. Soc.* 127, 563 (1925).

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