

STUDIES IN MASS SPECTROMETRY—XVII¹

REARRANGEMENT PROCESSES IN SOME ESTERS CONTAINING UNSATURATED LINKAGES—THE ELIMINATION OF CO₂ FROM ESTERS

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Abstract. The mass spectra of a variety of propiolate, acetylenedicarboxylate, maleate, fumarate and cyanoacetate esters have been measured. The formation of ions via the elimination of carbon dioxide (with or without the associated loss of other groups) is quite common in these esters. The prevalence of such fragmentation processes, which are of obvious importance with respect to the element-mapping technique, is probably associated with the presence of double or triple bonds (in the vicinity of the ester function) which may be ionized by removal of an electron and thus provide an electron deficient site to which a group (alkyl, alkenyl, etc.) may migrate.

OF OBVIOUS relevance to the technique of element mapping,² is the rigorous evaluation of those processes occurring upon electron impact which involve the migration of atoms other than hydrogen. With reference to this problem, recent publications from our own^{3,4} and other laboratories⁵⁻⁸ have been concerned with (or have noted) the elimination of carbon dioxide from esters upon electron impact. In our own studies^{3,4} only methyl and ethyl esters were examined, but processes involving the elimination of carbon dioxide with consequent skeletal rearrangement seemed particularly prevalent in those esters containing unsaturated linkages (e.g., C≡C³ and C=N^{3,4} bonds) in the vicinity of the ester function. We have now synthesized and examined a variety of propiolates (HC≡CCOOR), acetylenedicarboxylates (ROCC≡CCOOR), maleates and fumarates (ROCCCH:CHCOOR, *cis* or *trans*), cyanoacetates (N≡CCH₂COOR) and isopropylcyanoacetates [(Me)₂CHCH(CN)COOR] in the hope of evaluating the general scope of CO₂ elimination with or without associated loss of other groups in these esters and the influence of the alkyl group (R).

¹ Part XVI, J. H. Bowie, S.-O. Lawesson, J. Ø. Madsen, G. Schroll and D. H. Williams, *Acta Chem. Scand.* in press.

² K. Biemann, *Pure Appl. Chem.* 9, 95 (1964) and K. Biemann, P. Bommer and D. M. Desiderio, *Tetrahedron Letters* 1725 (1964).

³ J. H. Bowie, R. Grigg, D. H. Williams, S.-O. Lawesson and G. Schroll, *Chem. Comm.* 403 (1965).

⁴ J. H. Bowie, R. Grigg, S.-O. Lawesson, P. Madsen, G. Schroll and D. H. Williams, *J. Amer. Chem. Soc.* 88, 1699 (1966).

⁵ M. Fischer and C. Djerassi, *Chem. Ber.* 99, 750 (1966).

⁶ W. H. McFadden, K. L. Stevens, S. Meyerson, A. J. Karabatsos and C. E. Orzech, *J. Phys. Chem.* 69, 1742 (1965).

⁷ P. Natalis and J. L. Franklin, *J. Phys. Chem.* 69, 2935 (1965).

⁸ P. Brown and C. Djerassi, *J. Amer. Chem. Soc.* in press.

Methyl (I), ethyl (II), n-propyl (III), isobutyl (IV), s-butyl (V), allyl (VI) and benzyl (VII) propiolates were synthesized and their mass spectra determined. In each case the compositions of the M-44 and M-45 ions were determined by high resolution measurements. All the esters afforded M-CO₂ and M-HCO₂ ions, whose relative abundances are summarised in Table 1; it is emphasized that none of the hydrocarbon fragments quoted in the Table are present as intact units in the various esters prior to electron impact.

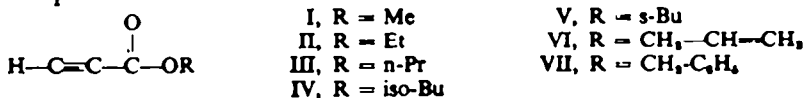


TABLE 1. RELATIVE ABUNDANCES OF M-CO₂ AND M-HCO₂ IONS FROM PROPIOLATE ESTERS (HO=CCOOR)

R	R.A. (%) of M-CO ₂ ion ^a	R.A. (%) of M-HCO ₂ ion ^a
Me	20 (C ₃ H ₄)	15 (C ₃ H ₄)
Et	<1 (C ₄ H ₆) ^b	10 (C ₄ H ₆) ^b
Pr	2 (C ₅ H ₈) ^b	8 (C ₅ H ₈)
iso-Bu	<1 (C ₆ H ₁₀) ^b	3 (C ₆ H ₁₀) ^b
s-Bu	1 (C ₆ H ₁₀) ^b	3 (C ₆ H ₁₀) ^b
CH ₂ -CH=CH ₂	4 (C ₅ H ₆) ^b	8 (C ₅ H ₆)
CH ₂ C ₆ H ₅	34 (C ₇ H ₈)	67 (C ₇ H ₈)

^a R.A. = relative abundance, the base peak arbitrarily being taken as 100: the compositions of the ions are given in parentheses.

^b The peaks in the spectra corresponding to these integral masses were larger because of their doublet nature (as established by high resolution).

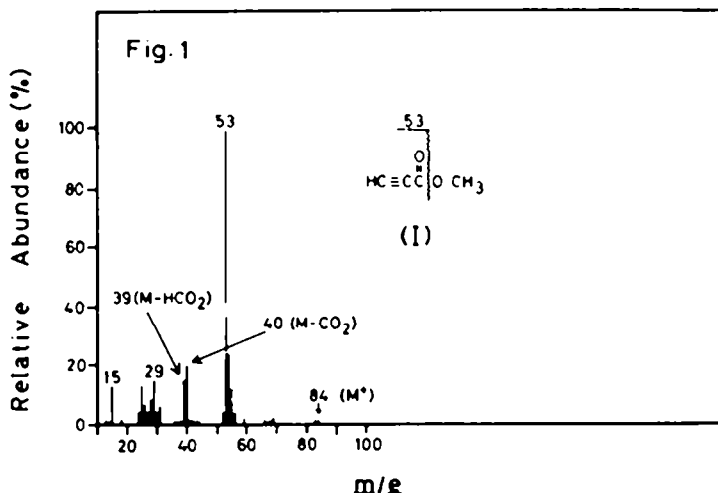
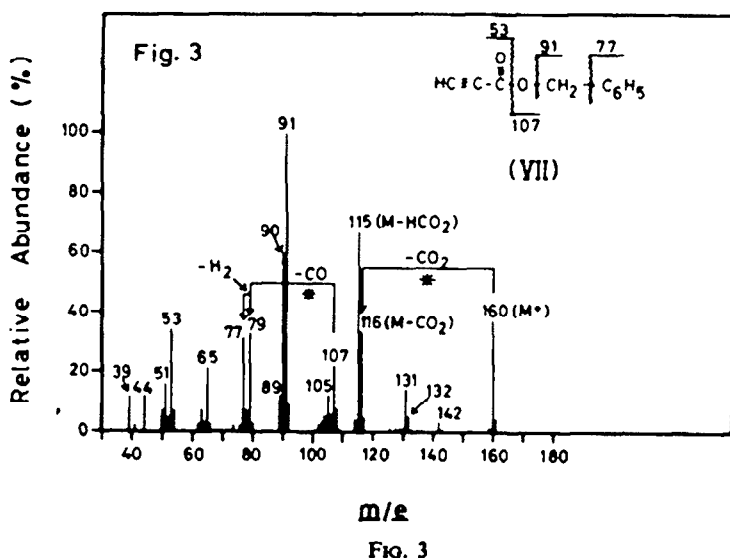
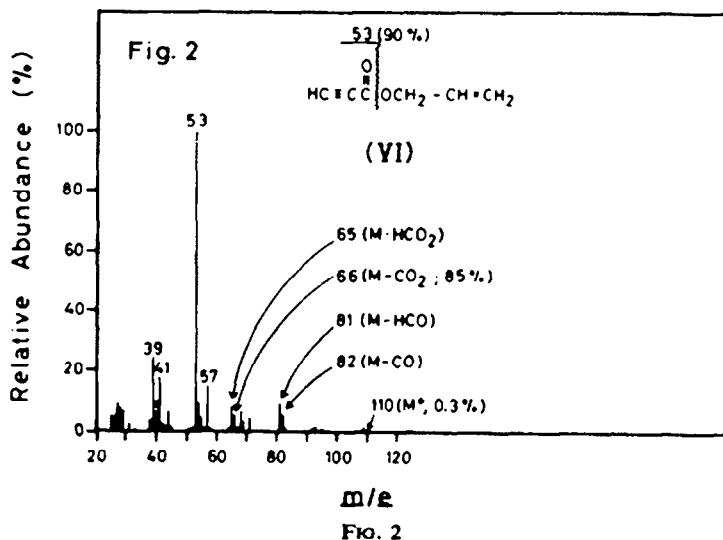


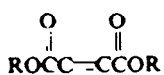
FIG. 1

Representative spectra are reported in detail in Figs. 1-3. The ion which formally corresponds to $\text{H}-\text{C}\equiv\text{C}-\text{C}\equiv\text{O}^+$ (m/e 53) either gives rise to the base peak or is $>90\%$ of the base peak abundance in the spectra of I-VI (see Fig. 1 and Fig. 2). The spectrum (Fig. 2) of allyl propiolate (VI) is also noteworthy for the presence of an



$\text{M}-\text{CO}$ ion [m/e 82, $\text{C}_8\text{H}_6\text{O}^+$, high resolution (H.R.)] which decomposes by loss of a hydrogen radical to m/e 81 ($\text{C}_8\text{H}_5\text{O}^+$, H.R.) as established by an appropriate metastable peak at m/e 80.0. A portion (10%) of the m/e 53 base peak of Fig. 2 is also due to a rearrangement ion (C_4H_5^+); a metastable peak at m/e 34.8 suggests that this ion can arise from the $\text{M}-\text{HCO}$ species (m/e 81) by the elimination of carbon monoxide (calculated value, m/e 34.7). In the spectrum (Fig. 3) of the benzyl ester (VII), a

metastable peak at m/e 114.0 establishes that the $M-HCO_2$ ion (m/e 115) arises, at least in part, from the $M-CO_2$ ion by loss of a hydrogen radical.



VIII, R = Me

IX, R = Et

X, R = n-Pr

XI, R = iso-Pr

XII, R = n-Bu

XIII, R = iso-Bu

XIV, R = s-Bu

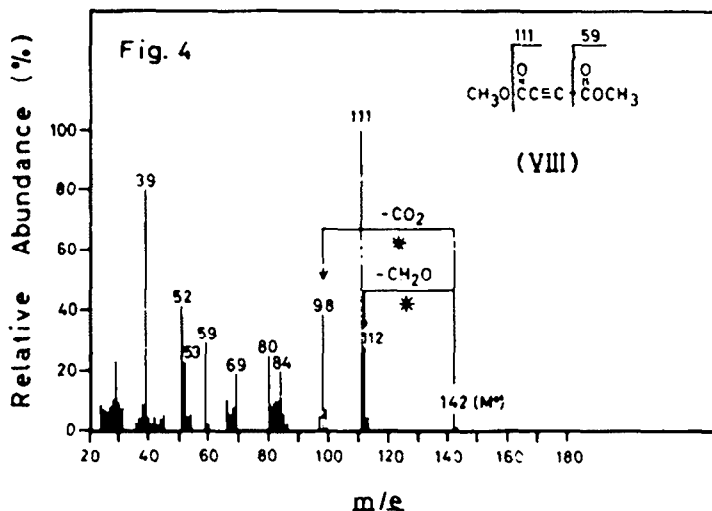
XV, R = $\text{CH}_3-\text{CH}(\text{CH}_3)-$ 

FIG. 4

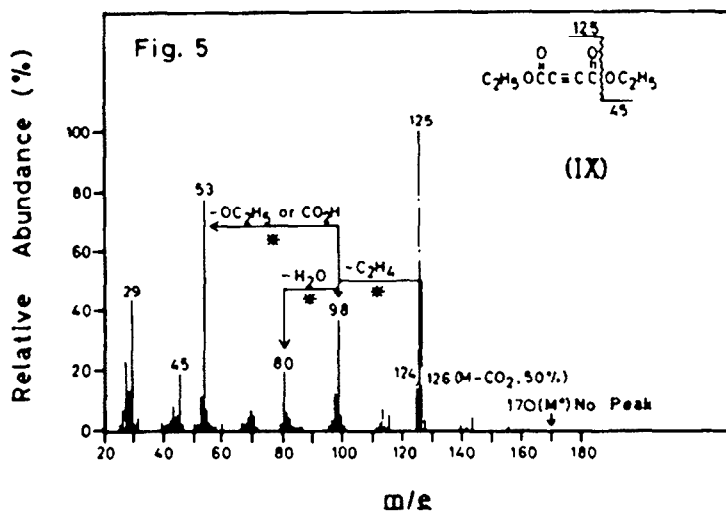


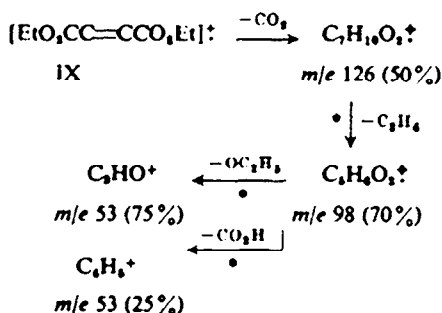
FIG. 5

Since the spectrum (Fig. 4) of dimethyl acetylenedicarboxylate (VIII) contains a $M-CO_2$ species,³ it was of interest to study the prevalence of related ions from ethyl (IX), n-propyl (X), iso-propyl (XI), n-butyl (XII), isobutyl (XIII), s-butyl (XIV) and allyl (XV) esters. In the spectra of the esters (VIII-XIV) containing saturated alkyl groups, significant $M-CO_2$ ions appear only when $R = \text{CH}_3$ (Fig. 4) and $R = \text{C}_2\text{H}_5$ (Fig. 5). Other ions of unusual composition in the spectrum (Fig. 4) of the dimethyl

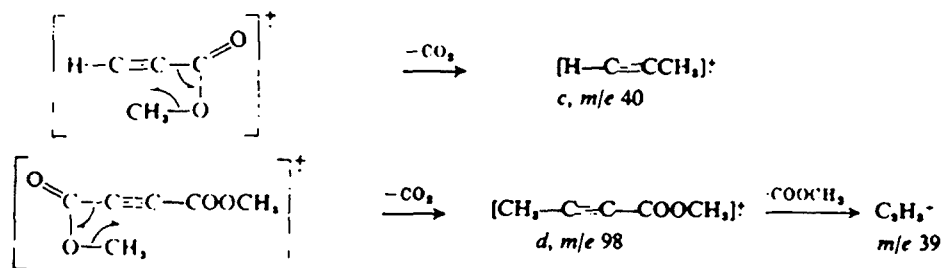
ester (VIII) are m/e 80 ($C_4O_3^+$, formally *a*) and m/e 52 (C_3O^+ , formally *b*). Scheme 1 summarises some of the decomposition modes of diethyl acetylenedicarboxylate (IX) which involve skeletal rearrangement processes and are established by high resolution measurements and appropriate metastable peaks.⁹



Scheme 1



It is appropriate to consider possible mechanisms by which carbon dioxide may be eliminated from propiolates (I–VII) and dimethyl (VIII) and diethyl (IX) acetylenedicarboxylates. In the propiolate esters (I–VII), the alkyl group must migrate to one of the two acetylenic carbon atoms; a four-centre mechanism (e.g., $I \rightarrow c$, m/e 40) appears most plausible and is analogous to the four-centre mechanism proposed by Brown and Djerassi⁶ to account for the loss of carbon dioxide from some organic carbonates. A similar mechanism ($VIII \rightarrow d$, m/e 98) probably operates in the decomposition of dimethyl acetylenedicarboxylate (VIII), since the spectrum (Fig. 4) contains an abundant ion at m/e 39 ($C_3H_3^+$), which may arise by elimination of a carbomethoxyl radical from *d*.



Skeletal rearrangement is very prevalent when diallyl acetylenedicarboxylate (XV) fragments under electron impact (the formation of most of the major ions between m/e 53 and m/e 97 involves the migration of groups other than hydrogen). The compositions of some ion which must arise via skeletal rearrangement in the spectrum (Fig. 6) are listed in Table 2. For purposes of clarity, the formal derivation of each rearrangement ion is indicated in the Table.

⁹ The $C_3H_4O_3^+$ ion may, of course, arise also in part via a pathway which does not involve skeletal rearrangement and hence C_3HO^+ does not necessarily arise via a skeletal reorganisation pathway.

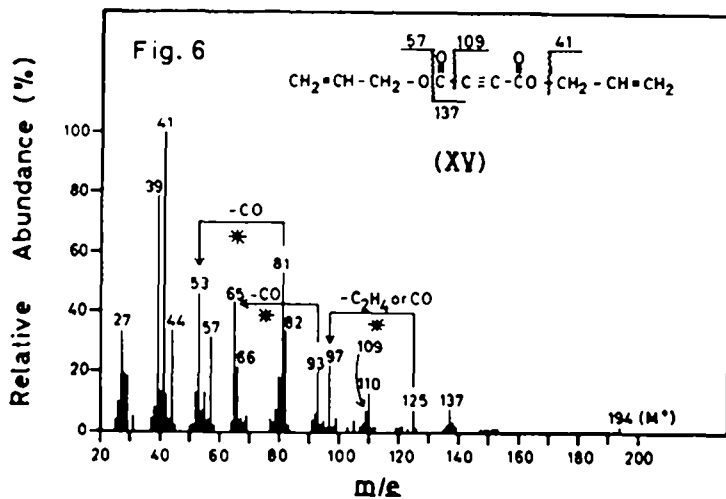


FIG. 6

TABLE 2. SKELETAL REARRANGEMENT IONS FROM DIALLYL ACETYLENE-DICARBOXYLATE (XV)

Ion (m/e)	Composition	Formal derivation
125	$\text{C}_8\text{H}_8\text{O}_2$ (100%)	$\text{M} - \text{CO} - \text{CH}_2 - \text{CH} = \text{CH}_2$
97	$\text{C}_8\text{H}_8\text{O}$ (35%)	$\text{M} - \text{OOCO} = \text{CCO} - \text{H}$
93	$\text{C}_8\text{H}_8\text{O}$ (90%)	$\text{M} - \text{CO}_2 - \text{OCH}_2 - \text{CH} = \text{CH}_2$
82	$\text{C}_8\text{H}_8\text{O}$ (90%)	$\text{M} - \text{CO} - \overset{\text{O}}{\parallel} \text{COCH} - \text{CH} = \text{CH}_2$
81	$\text{C}_8\text{H}_8\text{O}$ (90%)	$\text{M} - \text{CO} - \overset{\text{O}}{\parallel} \text{COCH}_2 - \text{CH} = \text{CH}_2$
66	C_8H_8 (100%)	$\text{M} - \text{CO}_2 - \overset{\text{O}}{\parallel} \text{COCH} - \text{CH} = \text{CH}_2$
65	C_8H_8 (100%)	$\text{M} - \text{CO}_2 - \overset{\text{O}}{\parallel} \text{COCH}_2 - \text{CH} = \text{CH}_2$
53	C_8H_8 (35%)	$\text{C}_8\text{H}_8\text{O} - \text{CO}$

It is noteworthy that all the rearrangement ions (with the exception of $\text{C}_8\text{H}_8\text{O}^+$) can formally be generated by a simple cleavage process coupled either with the elimination of CO or CO_2 (necessitating the migration of allyloxy and allyl groups, respectively). The complement to $\text{C}_8\text{H}_8\text{O}^+$ to account for m/e 97 is made up of C_4HO_2^+ (60%) and $\text{C}_5\text{H}_8\text{O}_2^+$ (5%); a strong metastable peak at m/e 75.4 suggests that these ions may arise, at least in part, from m/e 125 (Table 1) by the loss of C_2H_4 or CO, respectively (calculated metastable at m/e 75.3). Some other transitions established by the high resolution measurements and appropriate metastable peaks are summarized in Fig. 6. The most remarkable ions are C_8H_8^+ (m/e 65) and C_8H_8^+ (m/e 66) which formally consist of the carbon atoms of the acetylenic linkage and one allyl group.

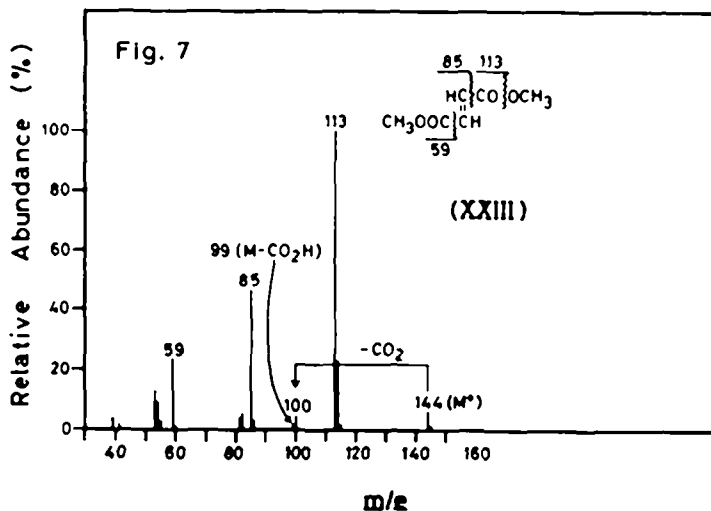
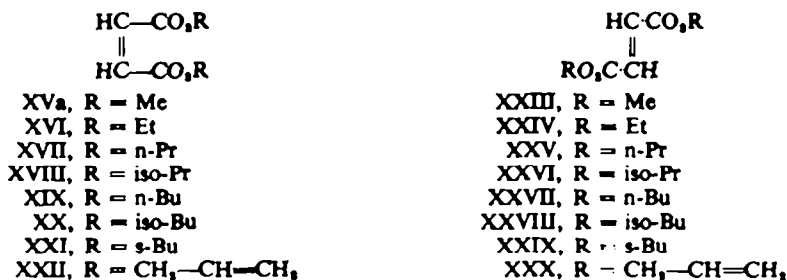
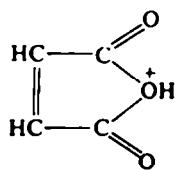
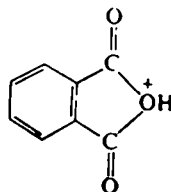


FIG. 7

The maleates and fumarates which have been synthesized and examined are summarized by the formulae XVa-XXX. Of the esters (XVa-XXI and XXIII-XXIX) containing saturated alkyl groups, only the methyl esters (XVa and XXIII) contain M-CO₂ ions (1% and 4% relative abundance, respectively), and M-CO₂H ions (0.3% and 2% relative abundance, respectively—see Fig. 7 for the spectrum of the *trans*-ester XXIII). In the spectrum (Fig. 7) of the *trans*-ester XXIII, *m/e* 99 is a singlet (M-CO₂H), but in the spectrum of the *cis*-isomer XVa is a doublet [M-CO₂H (10%) and C₄H₇O₃ (90%)]. The latter composition corresponds to the ion *e*, the analogue (*f*, *m/e* 149) of which is well authenticated in the spectra of phthalate esters.^{10,11} However, an ion corresponding to *f* is of low abundance (0.5%) in the spectrum of dimethyl phthalate, although it is abundant in the spectra of higher esters.^{10,11} Similarly, although the *m/e* 99 ion (*e*) is of very low relative abundance from dimethyl maleate (XV), it corresponds to the base peak from all the remaining dialkyl maleates [with the exception of the spectrum of di-*iso*-butyl maleate in which *m/e* 57 (C₄H₉⁺) is the base peak and *m/e* 99 the second most abundant ion (65%)]. In addition the *m/e* 99 ion is abundant *but not the base peak* from all the corresponding fumarates (XXIV-XXIX). The relative abundances of *m/e* 99 are summarized for the two series in Table 3.

¹⁰ F. W. McLafferty and R. S. Gohlke, *Analyt. Chem.* **31**, 2076 (1959).

¹¹ C. Djerassi and C. Fenselau, *J. Amer. Chem. Soc.* **87**, 5756 (1965).

*e*, *m/e* 99*f*, *m/e* 149TABLE 3. RELATIVE ABUNDANCES OF *m/e* 99 IONS (*e*) FROM DIALKYL MALEATES AND DIALKYL FUMARATES

Alkyl group	Rel. Ab. <i>m/e</i> 99 (<i>e</i>) (Maleates)	Rel. Ab. <i>m/e</i> 99 (<i>e</i>) (Fumarates)
Me	3	0
Et	100	27
<i>n</i> -Pr	100	36
<i>iso</i> -Pr	100	65
<i>n</i> -Bu	100	43
<i>iso</i> -Bu	65	38
<i>s</i> -Bu	100	62

The situation summarized in Table 3 is *a priori* quite reasonable because the formation of *e* from a fumarate ester could require additional energy to cause isomerisation about the double bond. However, an attempt to illustrate the requirement of extra energy to form *e* from diethyl fumarate (XXIV) did not give an unambiguous result. Utilising the doublet nature of the *m/e* 99 peak [50% of $C_4H_5O_3^+$ (*e*) and 50% of $M-COOC_2H_5$] from diethyl fumarate (XXIV) at 70 eV to monitor the disappearance of *e* on decreasing the energy of the electron beam, it was observed that *m/e* 99 corresponded to *e* (35%) and $M-COOEt$ (65%) at 20 eV, *e* (25%) and $M-COOEt$ (75%) at approximately 15 eV, and solely to $M-COOEt$ in the region of 13 eV. When diethyl maleate (XVI) was then added to the system as the lowest of these electron beam energies, the contribution from *e*, which reappeared on the oscilloscope, was barely significant.

Although the spectra of propyl and butyl maleates and fumarates appear to be free of skeletal rearrangement ions, two additional differences between the spectra of these closely related compounds merit comment. First, for any pair of esters (maleate and corresponding fumarate) of the formula $(CHCOOR)_2$, the ratio of the abundances of R^+ to $(R-H)^+$ ions is always greatest for the maleates (see Table 4). The formation of R^+ may be relatively more favourable from the *cis*-esters because of stabilization of the departing radical (formally *g*) as *h*. Second, the relative abundance of RO^+ fragments is always greater when the alkyl group R is α -branched (R = *iso*-propyl or *s*-butyl-- Table 4).

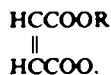
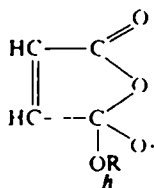
*g**h*

TABLE 4. COMPARISON OF RELATIVE ABUNDANCES OF R^+ , $(R-H)^+$ AND RO^+ IONS FROM PROPYL AND BUTYL MALEATES (*cis*) AND FUMARATES (*trans*)

R	Relative abundances				
	R^+	$(R-H)^+$	$R^+/(R-H)^+$	RO^+	
n-Pr	<i>cis</i>	37	6	6.2	2
	<i>trans</i>	29	15	1.9	3
iso-Pr	<i>cis</i>	46	8	5.7	10
	<i>trans</i>	45	15	3.0	15
n-Bu	<i>cis</i>	60	17	3.5	1
	<i>trans</i>	42	75	0.56	1
iso-Bu	<i>cis</i>	100	24	4.2	1
	<i>trans</i>	55	58	0.95	1
s-Bu	<i>cis</i>	63	18	3.5	6
	<i>trans</i>	20	28	0.71	6

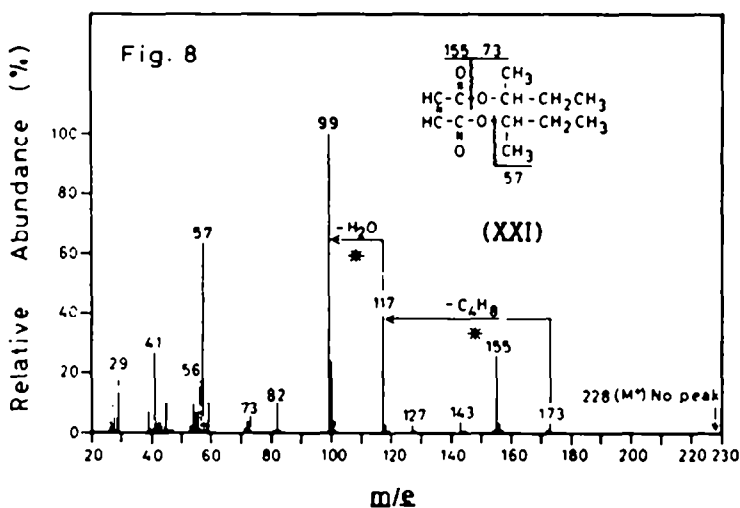


FIG. 8

Some of the general features discussed above may be seen on comparison of the spectra of *s*-butyl maleate (XXI, Fig. 8) and *s*-butyl fumarate (XXIX, Fig. 9), which are reported as representative spectra.

Diallyl maleate does not contain pronounced skeletal rearrangement ions in its spectrum, since the formation of m/e 41 ($\text{CH}_2^+-\text{CH}-\text{CH}_2^+$, base peak) and m/e 99 (e) is so favourable (cf. data accumulated in Tables 3 and 4). However, the spectrum (Fig. 10) of diallyl fumarate is much more interesting and has been extensively investigated by exact mass measurements (Table 5). Once more it is gratifying that all the major skeletal rearrangement fragments are derived by a simple bond cleavage coupled with CO or CO₂ elimination and an associated allyloxy or allyl migration. Where the origin of ions is not immediately obvious (C_6H_6^+ and C_4H_7^+), metastable peaks establish that these fragments arise from C_6H_7^+ and $\text{C}_5\text{H}_7\text{O}^+$ by the elimination of

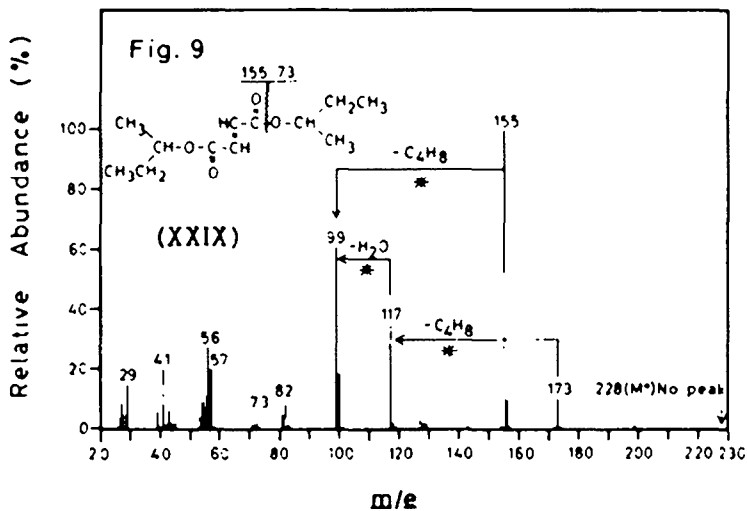


FIG. 9

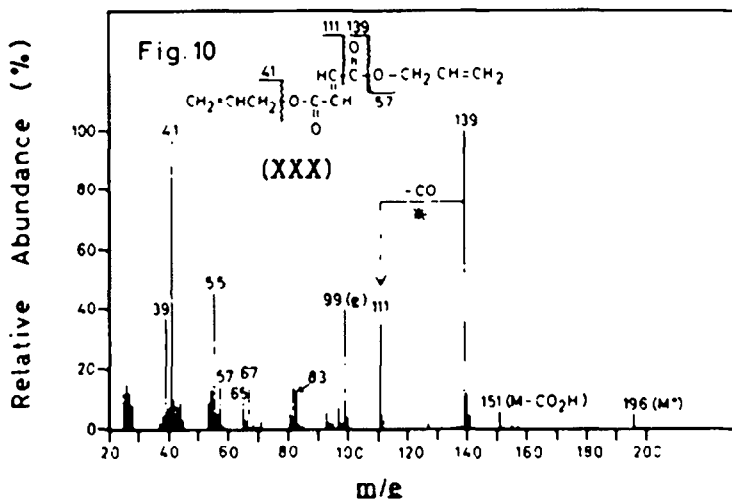
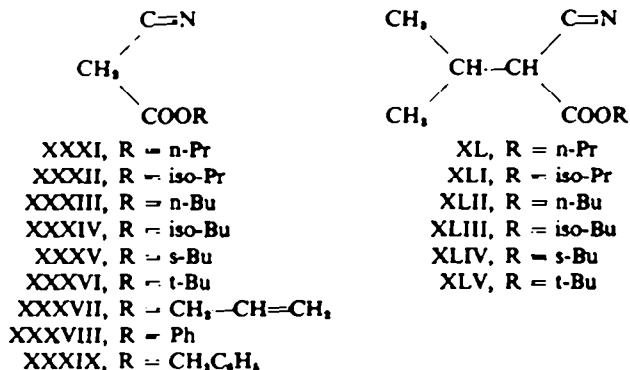


FIG. 10

TABLE 5. SKELETAL REARRANGEMENT IONS FROM DIALLYL FUMARATE (XXX)

Ion (m/e)	Composition	Formal derivation
151	C ₉ H ₁₁ O ₂ (100%)	M - CO ₂ H
83	C ₈ H ₇ O (90%)	M - CO - $\begin{array}{c} \text{O} \\ \parallel \\ \text{COCH}_2\text{CH}=\text{CH}_2 \end{array}$
67	C ₈ H ₇ (100%)	M - CO ₂ - $\begin{array}{c} \text{O} \\ \parallel \\ \text{COCH}_2\text{CH}=\text{CH}_2 \end{array}$
65	C ₈ H ₆ (100%)	C ₈ H ₇ - H ₂
55	C ₈ H ₇ O (25%)	C ₈ H ₇ O - CO



H₂ and CO respectively. The driving force for the former reaction is perhaps the formation of a resonance stabilised cyclopentadienyl cation (C₅H₅⁺).

A series of alkyl cyanoacetates (XXXI–XXXIX) and of alkyl isopropylcyanoacetates (XL–XLV) have been synthesized because methyl and ethyl cyanoacetates were previously observed to give M–CO₂H ions, while ethyl isopropylcyanoacetate eliminates CO₂ with associated expulsion of a hydrogen atom or of a methyl group of the isopropyl substituent.⁴ High resolution measurements on the spectra of the simple cyanoacetates (N≡CCH₂COOR, XXXI–XXXIX) establish that analogous processes occur in the higher esters with the exception of t-butyl cyanoacetate (XXXVI) and phenyl cyanoacetate (XXXVIII); the tendency is particularly pronounced in the spectra of the allyl and benzyl esters (Table 6 and also Fig. 11). The spectrum of the benzyl ester in which the active methylene hydrogens have been replaced by deuterium establishes that the hydrogen expelled with CO₂ is derived almost exclusively from the benzyl group.

In the series of isopropylcyanoacetates [(Me)₂CHCH(CN)COOR, XL–XLV], the relative abundance of M–CO₂–CH₃ ions decreases with increasing size and increasing branching of R as summarised in Table 7. It is quite feasible that the tendency of

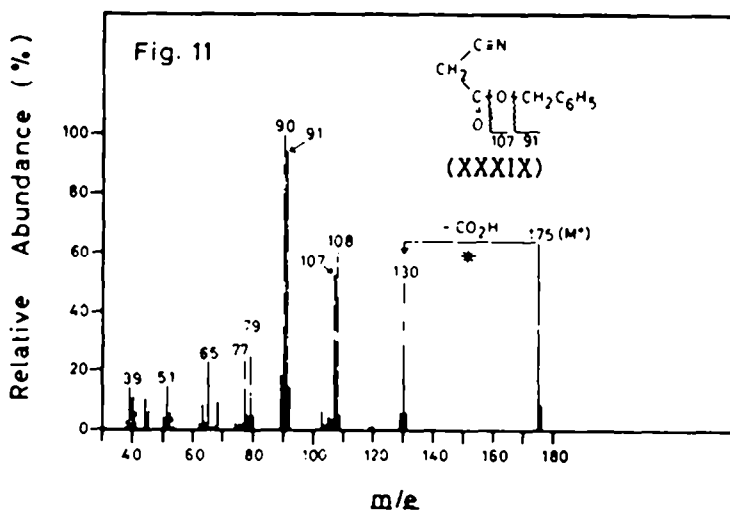


FIG. 11

TABLE 6. SOME SKELETAL REARRANGEMENT IONS FROM SIMPLE CYANO-ACETATES ($\text{N}\equiv\text{C}-\text{CH}_2\text{COOR}$)

R	M-CO ₂ H (Rel. Ab. %)	Other (Rel. Ab. %)
Me ^a	10	M-CO ₂ (14)
Et ^a	10	..
n-Pr	3	M-CO ₂ -CH ₃ (5) M-CO ₂ (3)
iso-Pr	7	..
n-Bu	1	M-CO ₂ -CH ₃ (5)
iso-Bu	1	M-CO ₂ -CH ₃ (5) M-CO ₂ CH ₃ (10)
s-Bu	1	..
t-Bu
CH ₂ =CH-CH ₃	16	..
Ph
CH ₂ C ₆ H ₅	50	..

TABLE 7. RELATIVE ABUNDANCE OF M-CO₂-Me IONS FROM ALKYL ISOPROPYLCYANOACETATES [(Me)₂CHCH(CN)COOR]

R	Et ^a	n-Pr	iso-Pr	n-Bu
Rel. Ab. %	27	5	2	1
R	iso-Bu	s-Bu	t-Bu	
Rel. Ab. %	2	1	0	

these M-CO₂-Me ions to decompose further may increase with increasing size and branching of R and hence their relative abundance is not a reliable measure of the preponderance of the rearrangement process. Unfortunately, the decomposition products of M-CO₂-Me species can have compositions which may also arise via simple cleavage pathways and hence it is not possible to evaluate this effect in these cases. However, the absence of appropriate metastable peaks which might establish any such decompositions of M-CO₂-Me ions, coupled with the drastic reductions in intensity of the M-CO₂-Me peaks, make it seem probable that the extent of the rearrangement does decrease with increasing size and branching of R.

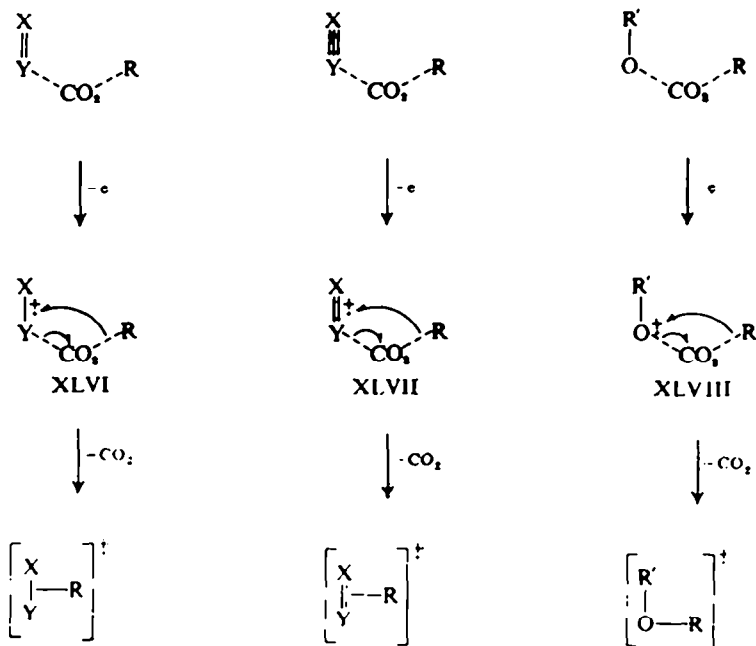
With all the information which has been gathered in the course of this study, some useful generalizations can probably now be made as to the tendency of esters to eliminate CO₂ or CO in ABC⁺ → AC⁺ reactions upon electron impact. First, there do not appear to be any reported examples of *completely saturated* esters (RCOOR')¹² affording M-CO, M-CO₂ or M-CO₂H ions, although butyl propionate¹¹ and neo-pentyl esters¹³ expel formaldehyde. However, all those esters which have been reported to undergo alkyl/aryl migrations with elimination of CO₂ (see Refs. 3-8 and the results reported in this paper) either contain double or triple bonds,

¹² For details of the mass spectra of such esters see R. Ryhage and E. Stenhagen (Edited by F. W. McLafferty) Chap. 3. "Mass Spectrometry of Organic Ions" Academic Press, New York (1963); R. Ryhage and E. Stenhagen, *Arkiv Kemi* 13, 523 (1959); A. G. Sharkey, J. L. Shultz and R. A. Friedel, *Analyt. Chem.* 31, 87 (1959); J. H. Beynon, R. A. Saunders and A. E. Williams, *Ibid.* 33, 221, (1961) and F. M. Trent, F. D. Miller and G. H. Brown, *Appl. Spectroscopy* 15, 64 (1961). The elimination of CO from formates [D. Van Raalte and A. G. Harrison, *Canada J. Chem.* 41, 2054 (1963)] only of course requires hydrogen migration.

¹³ D. R. Black, W. H. McFadden and J. W. Corse, *J. Phys. Chem.* 68, 1237 (1964).

or lone pair electrons (in addition to those associated with the —COO-portion of the ester). It is therefore proposed that CO₂ elimination with associated group migration (other than hydrogen) is in general facilitated by removal of a π -electron (from a double or triple bond—see XLVI and XLVII, respectively, which Y---C represents 1 or 2 σ -bonds) or of a lone pair electron to afford an electron deficient site to which the group can migrate. Particularly pertinent to this concept are the alkyl migrations recently found to occur in *saturated* dialkyl carbonates by Brown and Djerassi;⁸ the electron deficient site to which the R group can migrate is then located on oxygen⁸ (see XLVIII). Depending on the nature of the groups R and R' and the nature of groups attached to the atoms X and Y, additional atoms may of course be expelled in association with the CO₂ elimination.

The concept is also useful in understanding the loss of formaldehyde from some saturated esters,^{11,13} because in these cases the electron deficient site may be provided by ionisation within the carbonyl group. In addition, other esters which have been reported to lose CO₂ (neo-pentyl benzoate,⁶ phenyl pivalate⁵ and t-butyl benzoate⁵)



contain unsaturation in aromatic rings. It is emphasised that generation of an electron deficient site by removal of lone-pair or π -electrons is not visualized as a prerequisite for skeletal rearrangement, since even saturated hydrocarbons may reorganise to some extent in this fashion upon electron impact,¹⁴ but rather as a factor which will promote facile CO₂ elimination.

Although the unsaturated esters which we have investigated vary widely in structure, some useful general trends are indicated. In many cases (but not all), the tendency is for the methyl and ethyl esters to undergo CO₂ eliminations to a greater extent than propyl and butyl esters, probably because more alternative

¹⁴ P. N. Rylander and S. Meyerson, *J. Amer. Chem. Soc.*, **78**, 5799 (1956).

reactions are open to the latter groups. Also it is obvious that allyl and benzyl esters studied are particularly prone to undergo $ABC^+ \rightarrow AC^+$ reactions, which is understandable in terms of units of unsaturation present in both "acid" and "alcohol" portions of the ester.^{14a} Finally, although the composition of some ions initially suggest that their origins must be complex, simple cleavages with associated CO or CO₂ elimination from the ester group will usually account for their formation. Obviously, the possibility of analogous processes occurring must be borne in mind when natural products are examined by mass spectrometry.

EXPERIMENTAL

Mass spectra: an A.E.I. MS 9 mass spectrometer with the heated inlet system, and source, at a temp of 150–180°. High resolution measurements were performed at a resolution of 15,000 (10% valley definition).

All compounds were freshly distilled and their purities routinely checked by NMR and mass spectrometry. If any doubt remained as to the purity of a compound, this was additionally checked by VPC.

Alkyl propiolates. The following compounds were prepared by literature methods: I,¹⁵ II,¹⁶ IV¹⁵ and VI.¹⁷

Compounds III, V and VII were synthesized by mixing propiolic acid with the corresponding alcohol (using conc H₂SO₄ as catalyst) and allowing the mixture to stand at room temp. for 1 week.

Compound	B.p.	Yield	Analysis (%)		
			C	H	
III	65°/50 mm	23%	Calc.	64.27	7.19
			Found	63.70	6.92
V	80°/66 mm	24%	Calc.	66.64	7.99
			Found	66.78	8.63
VII	122°/18 mm	25%	Calc.	74.99	5.03
			Found	74.54	5.51

Dialkyl acetylenedicarboxylates. The following compounds were prepared by literature methods: VIII,¹⁸ IX,¹⁹ X,¹⁹ XI,¹⁹ XII,¹⁹ XIII²⁰ and XV.¹⁷ Di-*s*-butyl acetylenedicarboxylate (XIV) was synthesized by heating acetylenedicarboxylic acid and *s*-butyl alcohol in benzene (with conc H₂SO₄ as a catalyst) under reflux for 2 hr (using a water separator); b.p. 88°/0.1 mm, yield 46%. (Found: C, 63.85; H, 8.04. Calc. C, 63.70; H, 8.02%.)

Dialkyl maleates. Diallyl maleate (XXII) was a purified commercial sample. The following compounds were prepared by literature methods: XV,¹⁸ XVI,²¹ XVII,²² XIX²³ and XX.²⁴ Compounds

Compound	B.p.	Yield	Analysis (%)		
			C	H	
XVIII	104°/9 mm	85%	Calc.	59.98	8.05
			Found	59.98	8.09
XXI	130°/10 mm	79%	Calc.	63.13	8.83
			Found	62.93	8.61

^{14a} In this respect, it is somewhat surprising that phenyl cyanoacetate (XXXVIII) does not furnish a skeletal rearrangement ion in its spectrum.

¹⁵ I. F. Grove, *Ann. appl. Biol.* **35**, 38 (1948).

¹⁶ K. V. Auwers, *Chem. Ber.* **65**, 146 (1932).

¹⁷ C. D. Heaton and C. R. Noller, *J. Amer. Chem. Soc.* **71**, 2948 (1949).

¹⁸ E. H. Huntress, T. E. Lesslie and J. Bornstein, *Org. Synth.* **32**, 55 (1952).

¹⁹ G. H. Jeffrey and A. I. Vogel, *J. Chem. Soc.* 674 (1948).

²⁰ F. Adickes, *J. Prakt. Chem.* [2] **6**, 275 (1943).

²¹ V. M. Mitchovitch, *Bull. Soc. Chim. Fr.* [5] **4**, 1667 (1937).

²² G. H. Jeffrey and A. I. Vogel, *J. Chem. Soc.* 658 (1948).

XVIII and XXI were synthesized by heating maleic acid and the appropriate alcohol (with conc H_2SO_4 as catalyst) under reflux in benzene for 2 hr using a separator to remove the water formed during the reaction.

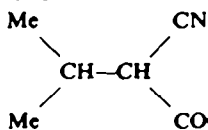
Dialkyl fumarates. The following compounds were synthesized by literature methods: XXIII,²⁰ XXIV,²¹ XXV,²² XXVII,²³ XXVIII²⁴ and XXX.²⁴

Compounds XXVI and XXIX were prepared in the same manner as that outlined above for the maleates.

Compound	B.p.	Yield	Analysis (%)		
				C	H
XXVI	102°/9 mm	71%	Calc.	59.58	8.05
			Found	59.96	8.03
XXIX	127°/9 mm	67%	Calc.	63.13	8.83
			Found	63.51	8.83

Compound	B.p.	Yield	Analysis (%)			
			C	H	N	
XXXV	100°/10 mm	58%	Calc.	59.55	7.85	9.92
			Found	59.45	7.67	10.05
XXXVII	101°/10 mm	60%	Calc.	57.59	5.64	11.20
			Found	57.40	5.80	11.38
XXXVIII	m.p. 41°	12%	Calc.	67.07	4.38	8.69
			Found	66.78	4.29	8.84
XXXIX	115°/0.05 mm	63%	Calc.	68.56	5.18	8.00
			Found	68.65	5.12	8.21

Compound	B.p.	Yield	Analysis (%)		
			C	H	
XL	103°/10 mm	63%	Calc.	63.88	8.94
			Found	63.41	8.88
XLI	93°/10 mm	63%	Calc.	63.88	8.94
			Found	63.53	8.82
XLII	115°/8 mm	58%	Calc.	65.54	9.35
			Found	65.66	9.32
XLIII	109°/10 mm	58%	Calc.	65.54	9.35
			Found	65.40	9.41
XLIV	104°/9 mm	68%	Calc.	65.54	9.35
			Found	65.55	9.41
XLV	96°/10 mm	60%	Calc.	65.54	9.35
			Found	65.42	9.18



²⁰ R. Anschütz, *Chem. Ber.* 12, 2279 (1879).

²⁴ V. P. Golendefew, *J. Gen. Chem., U.S.S.R.* 10, 1539 (1940).

Alkyl and aryl cyanoacetates. The following compounds were prepared by literature methods: XXXI,²⁵ XXXII,²⁶ XXXIII,²⁶ XXXIV²⁵ and XXXVI.²⁷ Compounds XXXV, XXXVII and XXXIX were synthesized by heating cyanoacetic acid and the appropriate alcohol (in benzene, using conc. H₂SO₄ as catalyst) under reflux for 2 hr (using a water separator). Compound XXXVIII was prepared by the general method outlined in Ref. 27.

Alkyl isopropylcyanoacetates. Compounds XL, XLI, XLII, XLIII and XLIV were prepared by alkylation of the Na salt of the cyanoacetate ester with isopropyl iodide in the alcohol corresponding to the ester. Compound XLV was available by alkylation of the Na salt of t-butyl cyanoacetate (prepared using NaH) with isopropyl iodide in dioxan.

Acknowledgement—The authors from Aarhus University wish to thank the Statens Almindelige Videnskabsfond for a grant.

²⁵ J. Guinchant, *Ann. Chim. Fr.* [9], 9, 30 (1918).

²⁶ A. Karvonen, *Ann. acad. sci. Fennicae* 20, 18 (1924).

²⁷ R. E. Ireland and M. Chaykovsky, *Org. Synth.* 41, 5 (1961).