tion was refluxed for 20 hr. A sample of 2-octanol was isolated as described in the 2-octanol isolation procedure (3.70 g, 99% recovery), bp 81–84° at 15 torr. The sample was redistilled to provide 2-octanol, bp 73–74° at 10 torr, $[\alpha]^{19}\text{D}$ + 8.85 ± 0.03°, $n^{23}\text{D}$ 1.4259.

2-Octanol Isolation Procedure.—The hydrolysis mixture or the control (*ca.* 500 ml) was distilled through a 32 × 1.6 cm vacuum-jacketed column packed with single-turn glass helices and fitted with a total reflux, partial take-off head. Ethanol (160 ml) was removed at an 8:1 reflux ratio over a period of 3 hr. The residue was cooled, the column was washed with three 5-ml portions of the distillate, and 20 ml of saturated aqueous sodium hydroxide was added to the combined material. This alkaline mixture was treated with 100 g of anhydrous potassium carbonate, extracted with four 30-ml portions of *n*-pentane, and the combined organic extracts were washed with 30 ml of saturated aqueous sodium chloride and dried with anhydrous potassium carbonate. The *n*-pentane was removed by distillation through a 16 × 2 cm column packed with multiple-turn glass helices; the residue was distilled.

Samples of 2-octanol isolated by this procedure were found to be pure by gas–liquid chromatographic analysis (20% diethylene glycol succinate on Chromosorb-P; 160°, 35 psi of helium).

Studies in Mass Spectroscopy. VI.[1a] Mass Spectra of Substituted Diethyl Malonates

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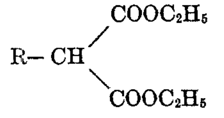
The mass spectra of representative mono- and dialkyl diethyl malonates have been investigated. These molecules break down mainly by loss of an alkyl substituent with hydrogen rearrangement (McLafferty rearrangement). The enolic nature of the resulting fragment is suggested by its subsequent decompositions. Enolic fragments are also apparently formed upon elimination of $COOC_2H_4$ (loss of ester group with hydrogen rearrangement) in the spectra of monoalkyl diethyl malonates.

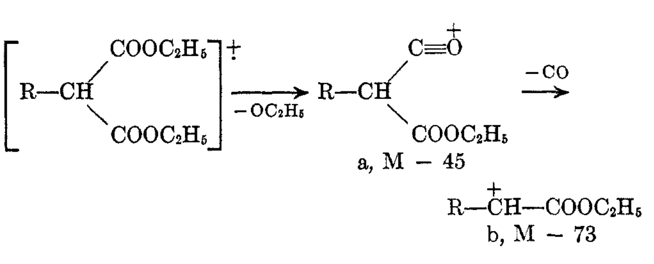
Although the mass spectra of a number of malonic acids have been determined,[2] a detailed study of the synthetically important malonate esters has not been reported. This paper deals with the interpretation of the mass spectra (Table 1 and Figures 1–6) of diethyl malonate and a number of the more important alkyl and aryl derivatives. The most important reactions occurring upon electron impact in many of these compounds appear to lead to enolic fragment ions (as deduced from the further decomposition of these fragment ions). The evidence upon which specific structures for such fragment ions are based comes from allylic cleavage reactions (which occur in a predictable manner); the specific structures aid interpretation of the spectra in a general and self-consistent manner. However, it is emphasized that this is the only evidence available for assigning fragment ion structures, which therefore must be regarded as speculative throughout this paper.

In the spectra of diethyl malonate (I) and the monosubstituted derivatives II–XI, a molecular ion is generally observed only for those cases in which the substituent does not carry a suitable hydrogen atom to participate in the McLafferty rearrangement[3] with a carbonyl group of the ester. Thus, diethyl malonate (I) and the methyl, allyl, phenyl, and benzyl derivatives (II, IV, X, and XI) exhibit molecular ions in their spectra.



I, R = H
II, R = CH_3
III, R = C_2H_5
IV, R = $CH_2CH{=}CH_2$
V, R = n-C_3H_7
VI, R = i-C_3H_7
VII, R = n-C_4H_9
VIII, R = i-C_4H_9
IX, R = t-C_4H_9
X, R = C_6H_5
XI, R = $C_6H_5CH_2$

In general, three important types of fragmentation are evident from the spectra (Table I and Figures 1–4) of these compounds. First, all the spectra contain pronounced (13–100% relative to the base peak) M − C_2H_5O ions (a) which correspond to the base peak when R = H (I) or when R is a small alkyl group [R = CH_3 (II) or C_2H_5 (III)]. Frequently ion a decomposes by elimination of carbon monoxide to an M − $COOC_2H_5$ species, b, as evidenced by appropriate metastable ions in the spectra of III, IV, and VI.



a, M − 45

b, M − 73

Second, loss of one ester group occurs with hydrogen rearrangement to give an M − $COOC_2H_4$ ion (M − 72), whose relative abundance decreases with increasing size of the alkyl substituent as indicated in Table II. The decrease in the relative abundance of the M − 72 fragment is due to the increasing importance of the McLafferty rearrangement as R becomes larger and also the additional tendency for the M − 72 ion to fragment further when R is larger. The further fragmentation of the M − 72 species strongly supports its representation as the enolic form c, perhaps formed *via* a cyclic transition state (see XII → c). Thus, if the alkyl substituent R is large enough to permit loss of an alkyl radical through allylic cleavage in c, then abundant fragment ions corresponding to the formation of d

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[1] (a) Part V: J. H. Bowie, D. W. Cameron, R. G. F. Giles, and D. H. Williams, *J. Chem. Soc.*, in press. (b) To whom inquiries should be addressed.

[2] R. I. Reed and W. K. Reid, *ibid.*, 5933 (1963).

[3] F. W. McLafferty in "Determination of Organic Structure by Physical Methods," Vol. 2, Academic Press, Inc., New York, N. Y., 1962, pp 129–149.

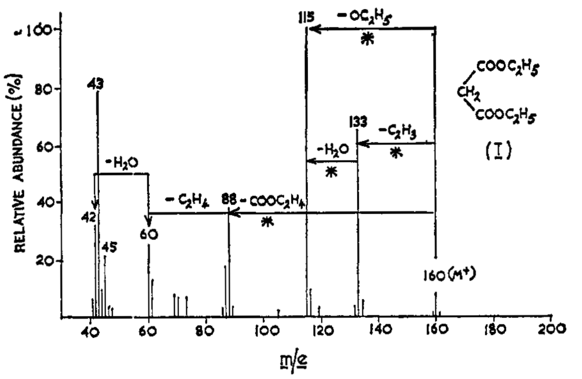


Figure 1.—Mass spectrum of diethyl malonate (I).

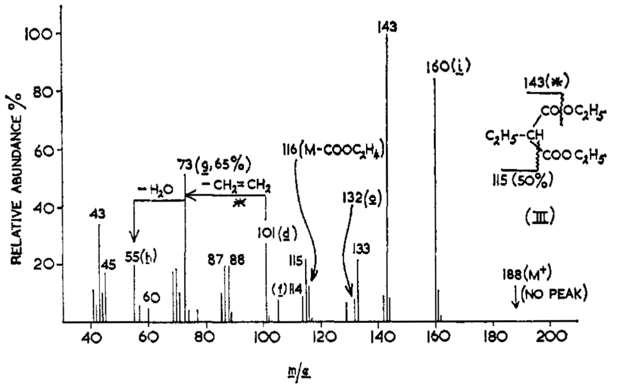


Figure 2.—Mass spectrum of diethyl ethylmalonate (III).

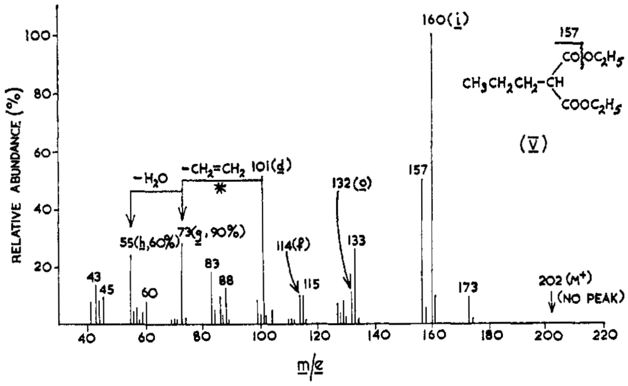


Figure 3.—Mass spectrum of diethyl *n*-propylmalonate (V).

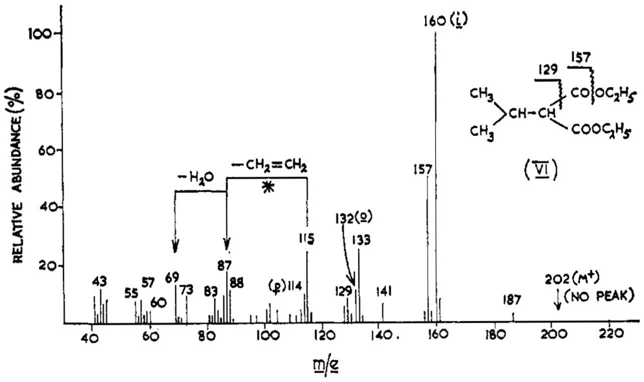
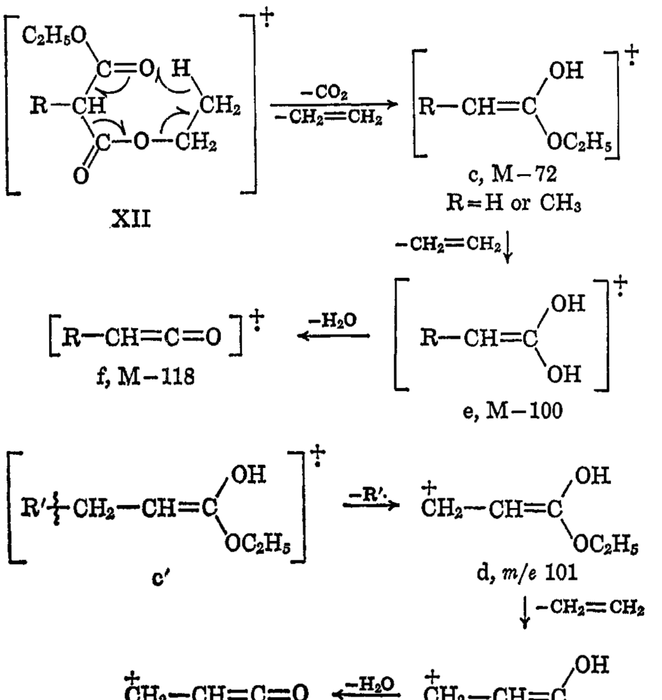
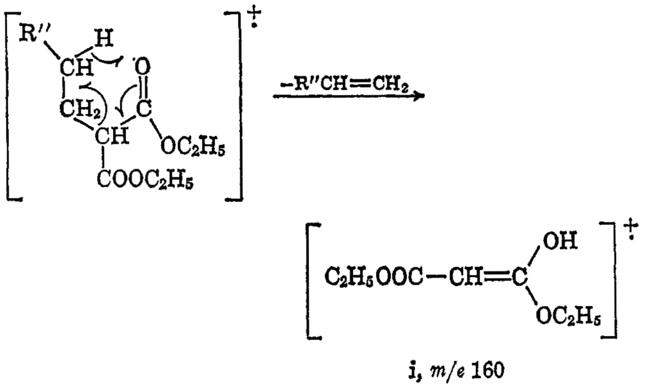


Figure 4.—Mass spectrum of diethyl isopropylmalonate (VI).



from c′ appear in the spectrum. Alternatively, if R is H or CH_3, then c can decompose by successive eliminations of ethylene and water to ions plausibly represented as e and f, respectively; analogous processes may afford g and h from d.

Third, when the McLafferty rearrangement can operate (in III and V–IX), the base peak in the spectrum corresponds to a fragment i (*m/e* 160) in all cases except that of the ethyl derivative III, when the M − OC_2H_5 ion (*m/e* 143, Figure 2) is slightly more abundant.



The evidence which supports the generalizations outlined above may be illustrated by reference to the spectra of diethyl malonate (I) and its ethyl (III), propyl (V), and isopropyl (VI) derivatives (Figures 1, 2, 3, and 4, respectively).[4] The compositions of the ions which give rise to *m/e* 42, 43, 60, 88, and 115 in the spectrum (Figure 1) of I have been established by exact mass measurements. An M − C_2H_3 ion (*m/e* 133 in Figure 1) is also abundant in the spectrum of the methyl derivative II and corresponds to the oxonium ion j.[5] A comparison of Figure 1 with Figures 2–4 clearly indicates that the *m/e* 160 ion in Figures 2–4 has much less tendency to fragment than the diethyl malonate molecular ion. This observation is consistent with its

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(4) Transitions marked by an asterisk, both in these figures and subsequently in the text, indicate a process supported by the presence of an appropriate metastable peak.

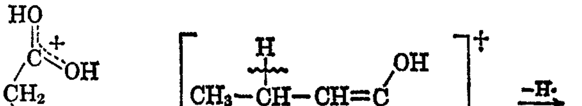
(5) F. W. McLafferty and R. S. Gohlke, *Anal. Chem.*, **31**, 2076 (1959); see also A. G. Harrison and E. G. Jones, *Can. J. Chem.*, **43**, 960 (1965).

TABLE I[a]

II	m/e	41	43	44	45	55	56	57	73	74	75	87	88	101	102	115	116	128	129	130	147	
	I, %	9	12	10	16	9	30	28	22	76	8	4	10	12	35	10	6	13	100	11	19	
	m/e	174 (M)																				
	I, %	11																				
IV	m/e	41	42	43	44	45	53	54	55	57	60	67	69	70	71	72	81	82	87	88	97	98
	I, %	30	10	30	22	21	20	18	38	20	7	10	14	12	11	6	59	33	10	15	18	88
	m/e	99	100	108	109	110	115	126	127	128	133	153	154	155	160	199	200 (M)					
	I, %	46	11	58	100	8	38	55	93	16	24	16	28	32	9	4	8					
VII	m/e	41	42	43	44	45	55	60	69	70	86	88	91	97	98	99	101	102	104	114	115	116
	I, %	10	5	9	9	9	18	4	20	3	10	14	3	19	4	4	20	3	6	14	18	3
	m/e	132	133	142	143	144	160	161	171	172	173											
	I, %	12	25	5	8	3	100	9	44	6	14											
VIII	m/e	41	43	45	55	56	57	60	69	73	74	86	87	88	97	99	101	104	114	115	127	132
	I, %	11	10	8	18	5	5	4	12	26	3	8	4	10	14	6	24	5	14	13	14	10
	m/e	133	142	143	160	161	171	172	173	201												
	I, %	23	3	5	100	9	23	3	14	3												
IX	m/e	41	43	45	55	57	59	60	69	73	82	83	86	87	88	99	100	101	104	105	114	115
	I, %	10	10	7	10	31	4	5	5	6	5	10	13	14	16	23	6	8	9	5	16	64
	m/e	116	127	132	133	134	155	157	160	161	171	201	216 (M)									
	I, %	3	17	16	35	4	11	10	100	9	15	5	4									
X	m/e	41	43	44	45	46	51	55	57	62	63	64	65	69	73	77	78	79	80	81	83	89
	I, %	5	7	24	17	6	8	7	4	4	11	5	5	5	6	19	6	38	3	3	4	34
	m/e	90	91	92	95	97	105	107	108	117	118	119	120	135	136	137	146	163	164	165	190	191
	I, %	45	86	9	5	5	16	48	5	11	88	29	3	56	76	6	9	100	97	10	27	14
	m/e	192	236 (M)		237																	
	I, %	14	17	57	8																	
XI	m/e	43	44	45	55	65	87	88	89	91	92	102	103	104	105	107	130	131	132	147	148	149
	I, %	4	7	5	5	8	14	10	6	61	8	5	19	18	8	7	8	100	17	16	29	15
	m/e	158	159	160	175	176	177	167	204	205	250 (M)		251									
	I, %	7	55	8	8	93	47	8	6	14	63		11									
XIV	m/e	38	39	41	42	43	44	45	53	55	57	59	69	70	71	73	83	86	87	88	97	98
	I, %	8	11	26	5	24	7	30	5	22	12	8	39	5	10	38	14	8	17	4	19	14
	m/e	99	101	102	113	114	115	116	118	127	129	130	141	142	143	144	145	155	157	160	170	171
	I, %	20	46	3	7	17	54	17	3	10	44	4	15	34	64	24	3	3	8	13	6	48
	m/e	172	173	174	187	188	189															
	I, %	6	33	5	7	100	12															
XVII	m/e	39	41	43	44	45	51	57	73	74	77	78	79	89	91	92	102	103	104	105	107	115
	I, %	4	8	3	7	9	5	8	58	4	12	4	4	3	68	5	3	18	3	15	23	15
	m/e	116	117	118	119	120	131	135	136	145	146	147	149	163	164	174	177	190	191	192	193	218
	I, %	6	48	13	48	6	6	100	17	6	32	11	7	6	7	6	8	7	64	72	9	3
	m/e	219	220	236	264 (M)		265															
	I, %	3	8	3	28		4															

[a] All ions having an abundance greater than 2% of the base peak (arbitrarily taken as 100%) are recorded.

formulation as the enolate i, which can still decompose to a small extent to m/e 133 ($-C_2H_3$), 115 ($-OC_2H_5$), and 88 ($-COOC_2H_4$) as indicated by all the necessary metastable peaks in the spectra of V, VI, VIII, and IX.[6] Most important, whereas the *n*-alkyl derivatives III and V exhibit fairly abundant ions at m/e 101 (d), 73 (g), and 55 (h) (Figures 2 and 3), the corresponding species in the spectrum (Figure 4) of the isopropyl derivative (VI) appear at m/e 115 (k), 87 (l), and 69 (m), the increments of 14 mass units being associated with the α branching of the substituent in VI.[7] As expected m/e 115 is a doublet [$C_5H_7O_3^+$ by loss of C_2H_5O from i (m/e 160) and $C_6H_{11}O_2^+$ (k)] in the spectra of III and VI, since the M − $COOC_2H_4$ ion (n) from III can lose an allylic hydrogen atom to furnish k. However, a $C_6H_{11}O_2^+$ ion cannot arise from the M − $COOC_2H_4$ ion of V by an allylic cleavage, and therefore m/e 115 is a singlet in this spectrum; this observation supports the postulated decomposition mechanism above.



j, m/e 133

n, m/e 116

k, m/e 115 (55% $C_6H_{11}O_2^+$)

l, m/e 87 (55% $C_4H_7O_2^+$)

m, m/e 69 (65% $C_4H_5O^+$)

Extensive exact mass measurements on the spectra of III, V, and VI suggest an additional decomposition mode (Scheme I) of i (m/e 160) and lend further support to the enol formulation.

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(6) The possibility that a small proportion of the m/e 160 ion in the spectra of diethyl alkylmalonates has the same structure as the diethyl malonate molecular ion cannot be excluded. Moreover, although it is possible that the enolate i is intrinsically less prone to decompose than the diethyl malonate molecular ion, the difference in their behavior could also arise owing to the smaller internal energy of i, which is already the product of an energy-dissipating reaction.

(7) Percentages quoted in the figures indicate the proportion having the required composition, as established by high resolution (hr) measurements.

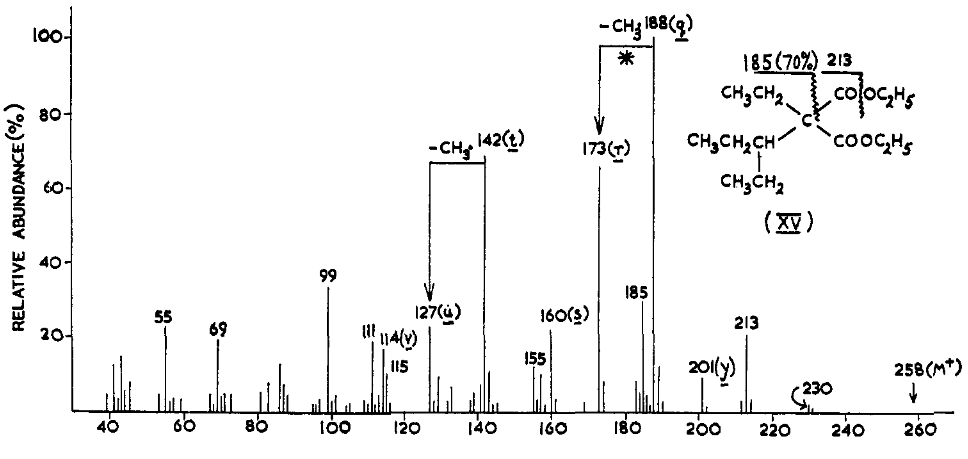


Figure 5.—Mass spectrum of diethyl ethyl(1-ethyl-*n*-propyl)malonate (XV).

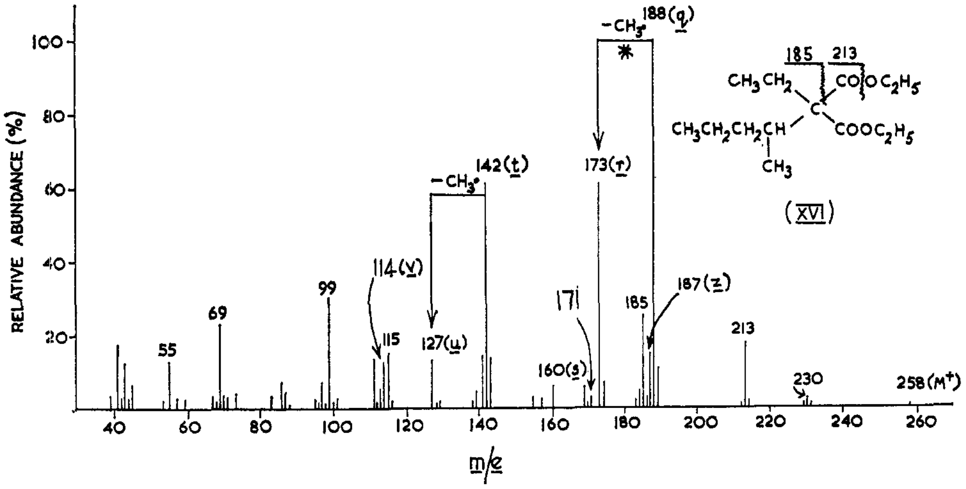


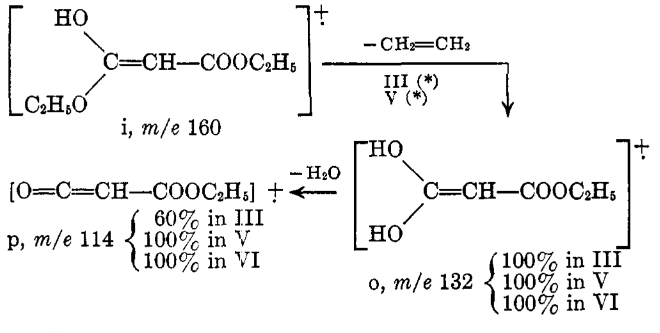
Figure 6.—Mass spectrum of diethyl ethyl(1-methyl-*n*-butyl)malonate (XVI).

TABLE II

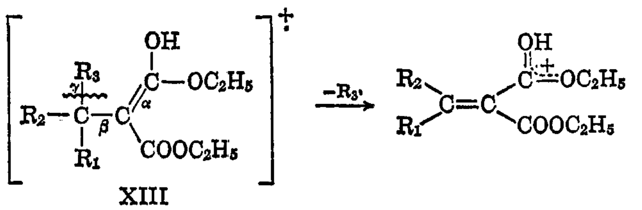
RELATIVE ABUNDANCE OF M − 72 IONS IN THE SPECTRA OF SOME MONOSUBSTITUTED DIETHYL MALONATES

Substituent (R)	H	CH_3	C_2H_5	*n*-C_3H_7	*i*-C_3H_7	*n*-C_4H_9	*i*-C_4H_9	*t*-C_4H_9
Relative abundance of M − 72 ion	38	35	12	2	2	2	1	0

SCHEME I



The spectra of several of the alkyl derivatives establish that a C–C bond of the alkyl group which formally is γ with respect to a carbonyl group (see XIII) is prone to cleavage. The γ bond which is broken is the one which can lead to elision of the largest alkyl radical (Table III). The fragmentation is consistent with the existence of some enol form in the molecular ion of these compounds.



XIII

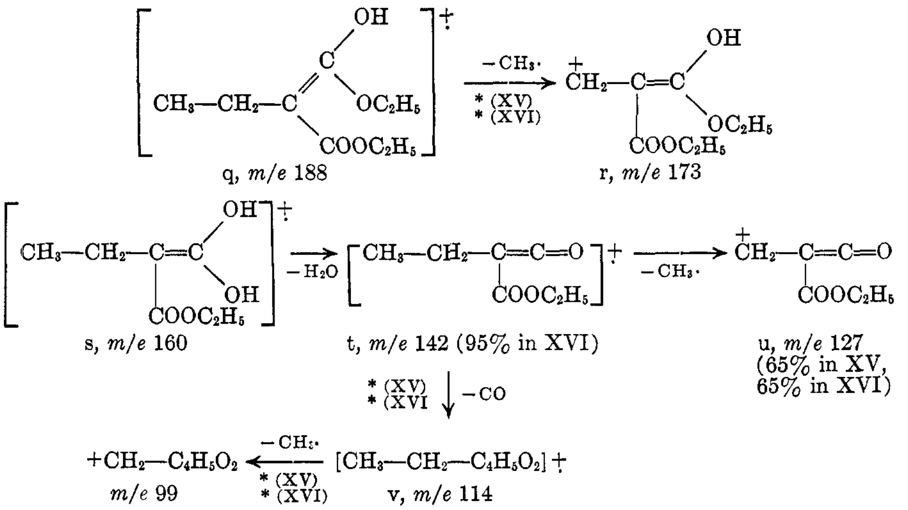
TABLE III

M − R_3 IONS IN THE SPECTRA OF DIETHYL ALKYLMALONATES

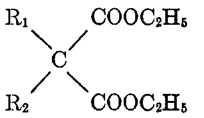
Alkyl substituent	R_3	*m/e* value (rel abundance, %)
n-C_3H_7 (V)	C_2H_5	173 (9)
i-C_3H_7 (VI)	CH_3	187 (3)
n-C_4H_9 (VII)	*n*-C_3H_7	173 (14)
i-C_4H_9 (VIII)	*i*-C_3H_7	173 (14)
t-C_4H_9 (IX)	CH_3	201 (5)

The behavior of the diethyl dialkylmalonates XIV–XVII upon electron impact (the spectra are summarized in Table I) is similar to that of the monosubstituted derivatives and may be illustrated by reference to the spectra (Figures 5 and 6) of the isomeric diethyl ethyl(1-ethyl-*n*-propyl)malonate (XV) and diethyl ethyl(1-methyl-*n*-butyl)malonate (XVI). The two spectra are very similar over-all and in each case the base peak

Scheme II

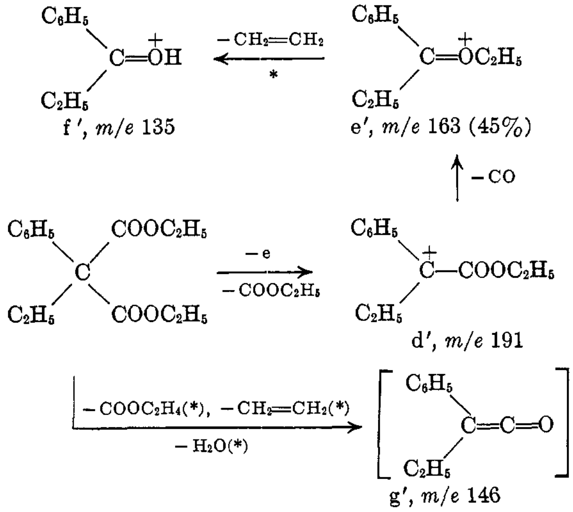


(m/e 188, M − C_5H_{10}) arises from participation of the largest alkyl group in the McLafferty rearrangement. The resulting enolate ion q (m/e 188) decomposes exactly as anticipated, probably to r, s, t, and u and additionally to m/e 114 (v) and 99 (see Figures 5 and 6 and Scheme II above).



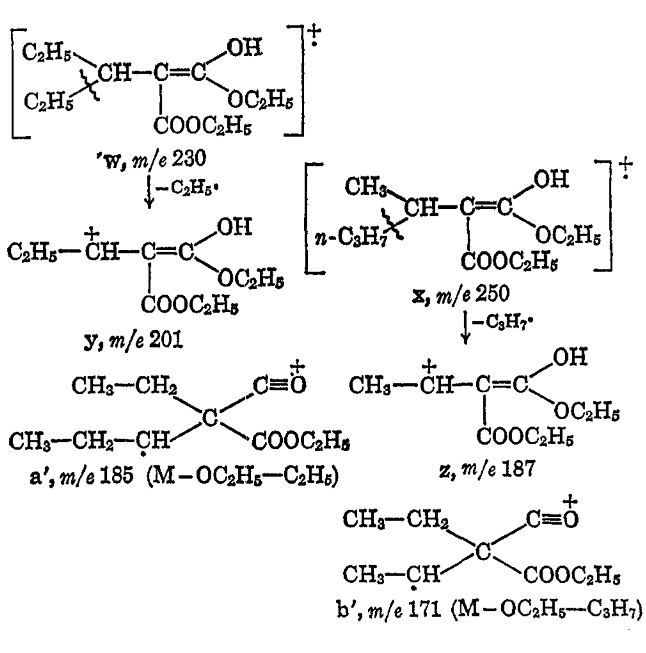
XIV, $R_1 = R_2 = C_2H_5$
XV, $R_1 = C_2H_5$; $R_2 = CH(C_2H_5)_2$
XVI, $R_1 = C_2H_5$; $R_2 = CH(CH_3)$-n-C_3H_7
XVII, $R_1 = C_2H_5$; $R_2 = C_6H_5$

Scheme III[a]



[a] The compositions of all fragments represented in this scheme have been established by exact mass measurements.

Alternatively, the McLafferty rearrangement may involve the ethyl substituent in both XV and XVI, but as expected this process occurs to a much smaller extent, to give m/e 230 ions which are structurally different from XV and XVI (w and x, respectively). The enolic ions w and x should decompose by elimination of an ethyl radical and a propyl radical, respectively, to afford m/e 201 (y) and 187 (z). In fact the presence of m/e 201 and the virtual absence of m/e 187 in Figure 5, and *vice versa* in Figure 6, constitutes the main difference between the two spectra, as predicted.



An additional difference between the behavior of XV and XVI, which is uncovered by high-resolution measurements, is that m/e 185 is a doublet [$C_{10}H_{17}O_3^+$ (30%) and $C_{11}H_{21}O_2^+$ (70%)] in the spectrum of XV, but a singlet ($C_{11}H_{21}O_2^+$) in the spectrum of XVI. The $C_{10}H_{17}O_3^+$ species from XV corresponds to a′ and consequently an m/e 171 ion (b′) is the corresponding fragment from XVI; a small m/e 171 ion is in fact present in Figure 6 and absent in Figure 5.

If one of the substituents which replaces the active methylene hydrogens is a phenyl group, as in diethyl phenylethylmalonate (XVII), then the fragmentation pattern follows a somewhat different course. The McLafferty rearrangement in the spectrum of XVII is not an important process, but instead a large proportion of the decomposition takes place by complete loss of an ester group, perhaps because the resulting carbonium ion d′ (m/e 191, see Scheme III) is relatively favorable. Appropriate metastable peaks and exact mass measurements indicate that *m/e* 191 decomposes further by successive losses of carbon monoxide and ethylene to *m/e* 163 (45% of $C_{11}H_{15}O^+$) and 135 (100% of $C_9H_{11}O^+$ and the base peak of the spectrum). Both of these ions must be skeletal rearrangement fragments,[8] most plausibly arising as indicated in Scheme III, although either ethyl group could in principle be eliminated in passing from e′ to f′. The usual sequence of loss of an ester group (with hydrogen rearrangement), ethylene, and then water is operative and terminates in the formation of a $C_{10}H_{10}O^+$ fragment (*m/e* 146, represented as g′).

Finally, it should be noted that both XVII and diethyl phenylmalonate (X) lose carbon dioxide (hr) from their molecular ions to form *m/e* 220 and 192 (8 and 17% or the base peaks, respectively), thus necessitating ethyl migrations in both cases.[8]

Experimental Section

This investigation was carried out using an A.E.I. MS9 double-focussing mass spectrometer. Spectra were obtained with an ionizing energy of 70 ev at a source pressure between 0.1 × 10^{-6} and 1.0 × 10^{-6} mm. Samples were introduced into the ionization chamber *via* a heated inlet system operating at a temperature of approximately 150°.

[8] For numerous examples of skeletal rearrangement processes occurring in ketones and esters upon electron impact, see J. H. Bowie, R. Grigg, D. H. Williams, S.-O. Lawesson and G. Schroll, *Chem. Commun.*, (London), 403 (1965); W. H. McFadden, K. L. Stevens, S. Meyerson, G. J. Karabatsos, and C. E. Orzech, *J. Phys. Chem.*, **69**, 1742 (1965); P. Natalis and J. L. Franklin, *ibid.*, **69**, 2943 (1965).

Structure of Two Solanone Precursors from Tobacco[1]

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Received December 7, 1965

Two acyclic diterpenoid precursors of solanone have been isolated from tobacco and identified as diastereoisomers of 6,8-dihydroxy-11-isopropyl-4,8-dimethyl-14-oxo-4,9-pentadecadienoic acid.

The genesis of the tobacco terpenoid solanone[2] (III) is of interest because of the apparent violation of the isoprene rule. Almost all of the available III in tobacco is presumed to be in the form of thermally unstable precursors, and the isolation of a carboxylic acid precursor preparation from Burley tobacco has been described.[3] In this report, we wish to describe the isolation and identification of two diastereoisomeric solanone precursors, Ia and b, from tobacco.

A mixture containing Ia and b (Scheme I), which occur in the acid form in tobacco, was obtained by a modification of the published solvent-extraction procedure.[3] The mixed acids were not readily separated by adsorption chromatography, but their methyl esters (IIa and b) were easily separated from one another by thin layer chromatography (tlc) on silica gel G using diethyl ether as the developing solvent. Both Ia and b, obtained by saponification of IIa and b, thermally decompose in the injector block of a gas chromatograph at 250° to yield III in 15.9 and 13.5 wt %, respectively. It is assumed that the thermal decomposition is almost instantaneous since there is no broadening of the gas–liquid partition chromatography (glpc) peak of III. Mass spectral examination of IIa and b showed that both gave cracking patterns characteristic of III, and the III molecular ion was one of the most intense mass fragments in both spectra. The yields of Ia and b from Burley tobacco amounted to 0.04 and 0.03%, respectively, on a dry tobacco weight basis.

The acidic precursors and their methyl esters were slightly unstable in storage even at 0° and slowly decomposed in acidic media. The methyl esters, which were the more stable form, were used in the identification studies, and spectral data were obtained on samples immediately after isolation. Both IIa and b were indicated to be pure by tlc on four different adsorbants.

Infrared spectra of both IIa and b show strong hydroxyl bands at 3410 cm^{-1}, two carbonyl functions at 1740 and 1720 cm^{-1}, and a *trans* double bond band at 970 cm^{-1}. The only differences in these spectra occur in the 1100–1000- and 930-cm^{-1} regions. Both compounds gave mass spectra with small parent peaks at *m/e* 368 and intense peaks at 350 and 332 which correspond, respectively, to the loss of one and two molecules of water from the parent ion.

Nuclear magnetic resonance (nmr) data and assignments obtained on deuteriochloroform solutions of IIa and b are presented in Table I. In each case, the resonances were consistent with the presence of five oxygen atoms: two in hydroxyl functions, one in a methyl ketone carbonyl, and two in the carboxylate group. Thus, the mass spectral parent peaks of 368 for IIa and b must correspond to the empirical formula $C_{21}H_{36}O_5$. The three olefinic protons apparent in the nmr spectra must be due to the *trans* double bond indicated by infrared evidence and a trisubstituted double bond. These double bonds are not conjugated since IIa and b do not absorb above 220 mμ in the ultraviolet spectrum. Lack of reaction of IIa and b with sodium metaperiodate indicates that the hydroxyl groups in each compound are not vicinal.

Nmr data obtained on IIa and b in dry pyridine provided further structural information. In this solvent, the δ 1.40 methyl resonance and the δ 4.77 multiplet of IIa are shifted about 0.30 ppm to lower field which confirms their assignments, respectively, to that of a methyl group and a single proton attached to hydroxyl-bearing

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[1] Presented at the Nineteenth Tobacco Chemists' Research Conference, Lexington, Ky., Oct 26–28, 1965.

[2] R. R. Johnson and J. A. Nicholson, *J. Org. Chem.*, **30**, 2918 (1965).

[3] R. B. Griffith, R. R. Johnson, and A. D. Quinn, U. S. Patent 3,174,485 (1965).