Reactions between Furfurylidenemalonic Esters and Grignard Reagents. I. Reductions, 1,4-Additions and One Case of 1,8-Addition

GUST.-AD. HOLMBERG, MARIANNE KARLSSON,
OWE ULFSTEDT and MARIANNE OLLI

Institutionen för organisk kemi, Åbo Akademi, SF-20500 Åbo 50, Finland

When methylmagnesium iodide, ethylmagnesium bromide, and isopentylmagnesium bromide react with diethyl furfurylidenemalonate at room temperature, only 1,4-addition products, diethyl 1-(2-furyl)-ethylmalonate, diethyl 1-(2-furyl)propylmalonate, and diethyl 1-(2-furyl)-4-methylpentylmalonate, respectively, are formed. Isopropyl-magnesium bromide and isobutylmagnesium chloride react with the ester to give mainly the 1,4-addition products diethyl 1-(2-furyl)-2-methylpropylmalonate and diethyl 1-(2-furyl)-3-methylbutylmalonate, but also smaller quantities of a reduction product, diethyl furfur-ylmalonate. Benzylmagnesium chloride gives both a 1,4-addition product, diethyl 1-(2-furyl)-2-phenylethylmalonate, and a 1,8-addition product, diethyl 5-benzylfurfurylmalonate. The mass and NMR spectra of the product are discussed.

The reactions between diethyl alkylidenemalonates and Grignard reagents have previously been investigated in this laboratory.[1–4] It has been established that the main reaction is a 1,4-addition of the magnesium compound to the conjugated double bond system $(C=C-C=O)$ of the malonate. Only in the reactions between methylmagnesium iodide and isopropylidenemalonic esters has 1,2-addition been observed. The 1,4-addition is, however, partly or completely suppressed by reduction of the olefinic double bond of the substituted malonate if the alkyl groups of the Grignard reagents and/or the substituents at the olefinic bond are large and branched. The presence of at least one hydrogen atom on the β carbon atom of the Grignard reagent is apparently necessary for the reduction although this fact has not previously been pointed out.

Maxim and Georgescu [5] allowed diethyl furfurylidenemalonate (I) to react with isobutylmagnesium chloride, isopentylmagnesium bromide, and phenyl-magnesium bromide. They reported the isolation of 1,4-addition products, but

$$\text{I} \qquad \text{II} \qquad \text{III}$$

(Structures I, II, III: furfurylidenemalonate and related diethyl ester derivatives)
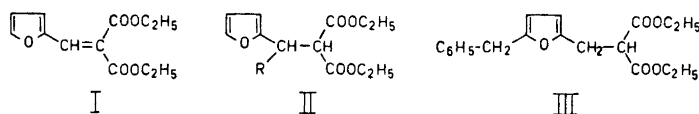
did not mention any reductions which according to the rule quoted above could probably be expected when the first two Grignard reagents react with the malonate.

It therefore seemed justified to investigate the reactions between furfurylidenemalonic ester and different Grignard reagents. Methylmagnesium iodide, ethylmagnesium bromide, isopropylmagnesium bromide, isobutylmagnesium chloride, isopentylmagnesium bromide, and benzylmagnesium chloride were considered to constitute a representative selection of Grignard reagents.

The experiments were first performed on a semimicro scale with a fivefold excess of the Grignard reagent in the way previously described.[2,3] If the products had to be isolated for elemental analyses, recording of NMR spectra, etc., the experiments were repeated on a larger scale.[1] In these experiments, stress was laid more upon pure products than on high yields.

The Grignard reagent with methyl, ethyl, or isopentyl groups gave only 1,4-addition products (II; $R = CH_3$, C_2H_5, and $(CH_3)_2CHCH_2CH_2$, respectively). Isopropylmagnesium bromide gave 94 mol % 1,4-addition product (II; $R = (CH_3)_2CH$) and 6 mol % reduction product (II; $R = H$). With isobutylmagnesium chloride, the mol ratio of 1,4-addition product (II; $R = (CH_3)_2CHCH_2$) and reduction product (II; $R = H$) was 74:26.

Table 1. Mol ratios of 1,4-addition and reduction products formed in the reactions of ethylmagnesium bromide and isopropylmagnesium bromide with different diethyl alkylidenemalonates.[2,3]

Alkalidene group	Ethylmagnesium bromide		Isopropylmagnesium bromide	
	1,4-Addition	Reduction	1,4-Addition	Reduction
Ethylidene	97.7	2.3	82.7	17.3
Propylidene	92.8	7.2	61.3	38.7
Isopropylidene	92.9	7.1	39.4	60.6
Isobutylidene	82.4	17.6	—	100
Neopentylidene	65.4	34.6	—	100

When these results are compared with previous results (*cf.* Table 1), it is observed that diethyl furfurylidenemalonate is less susceptible to reduction than the other examined malonates. This fact is not consistent with the previously quoted rule for the connection between reducibility and the sizes of the substituents of the malonate. Apparently, some other effect operates in the substituent in such a way that diethyl furfurylidenemalonate either is reduced with greater difficulty or is more susceptible to 1,4-addition than the aliphatic alkylidenemalonates. Thus, the mentioned rule seems to be valid only for aliphatic substituents.

The high proportion of reduction product formed in the reaction with isobutylmagnesium chloride is not, however, directly in conflict with the rule about the influence of the size of the alkyl group of the Grignard reagent because a hydrogen atom on a tertiary carbon atom, such as the β carbon of the isobutyl group, is known to react more easily than hydrogen atoms on a primary carbon atom, *i.e.* hydrogen atoms that participated in the reactions in the previously examined cases.

The absence of reduction product among the products of the reaction with isopentylmagnesium bromide exposes another imperfectness of the rule. A large size of the Grignard reagent alkyl group is not alone sufficient to promote reduction.

If these results are noted, the rule as to the alkyl group of the Grignard reagent can be given the following, more exact wording. The 1,4-addition is partly or completely suppressed by reduction of the olefinic double bond of the alkylidenemalonate if the alkyl group of the Grignard reagent is branched at the α or β carbon atom and there is at least one hydrogen atom on the β carbon atom. Some malonates are, however, more easily reduced and in these cases even short and unbranched alkyl groups as in ethylmagnesium bromide can effect reduction of a small portion of the malonate.

The most surprising results are, however, obtained with benzylmagnesium chloride. This Grignard reagent is, of course, not able to reduce the malonate, but instead of giving a single 1,4-addition product, it gives in addition to the 1,4-addition product (II; $R = C_6H_5CH_2$) a 1,8-addition product (III). The mol ratio of the 1,4- and 1,8-addition products is about 65:35.

The formation of the 1,8-addition product apparently involves an extension of the conjugated double bond system to the furan nucleus. Reactions of this type are not usual, although, not unknown. An example is the conjugated addition of Grignard reagents to sterically hindered benzophenones that has been examined especially by Fuson and coworkers.[6] Recently Holm and Crossland [7] investigated the reactions of benzophenone and substituted benzophenones with *t*-butylmagnesium chloride and found that 1,2-, 1,4-, and 1,6-additions occurred concurrently with the formation of benzopinacols. Cases in which the conjugation extends into the furan ring are also known. For example, α-furylethylene reacts with maleic anhydride in a Diels-Alder reaction in which the ethylene double bond and the neighbouring furan double bond form the active diene system.[8] It is easy to understand that such an extention of the double bond system occurs more easily in the furan series than in the benzene series because the furan ring is less aromatic than the benzene ring.

A cyclic mechanism is, of course, excluded, at least for the 1,8-addition.

The fact that the product obtained on hydrolysis of the primary 1,8-addition product with aqueous hydrochloric acid is a furan derivative and not a dihydrofuran derivative as might be expected can easily be explained by the reaction illustrated in Scheme 1. The driving force would be the energy released on restoration of the aromatic furan ring.

As to the question whether the 1,8-addition mechanism is ionic or radical, the present data do not give any definite answer. Holm and Crossland,[7] however, proposed a special kind of radical mechanism when conjugated addition to
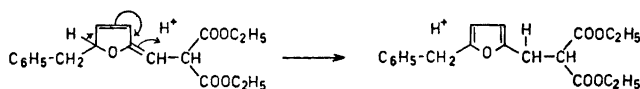
Scheme 1.

aromatic systems occurs. The formation of relatively large quantities of dibenzyl supports such a mechanism in the present reaction.

Finally, it may be mentioned that diethyl 5-benzylfurfurylmalonate has previously been isolated from the reaction products of malonic ester and 5-benzylfurfuryl chloride by Mndzhoyan and Badalyan.[9]

EXPERIMENTAL

Diethyl furfurylidenemalonate, b.p. 183 − 184°/16 mmHg, was prepared from diethyl malonate and furfural with piperidine as catalyst by the method previously used in this laboratory for the preparation of benzylidenemalonic esters.[10,11]

Reactions of methylmagnesium iodide, ethylmagnesium bromide, isopropylmagnesium bromide, isobutylmagnesium chloride, and isopentylmagnesium bromide. The experiments on a semimicro scale were performed exactly according to the previously described method.[2,3] The reaction products were examined on a gas chromatograph connected to a mass spectrometer (LKB 9000). If a substance had to be isolated, the experiment was repeated on the macro scale by the previously described method.[1] The crude products were distilled in a Todd distillation assembly.

Methylmagnesium iodide. The gas chromatogram showed only one peak. The pure product, diethyl 1-(2-furyl)ethylmalonate (II; R = CH₃), was collected at 142°/9 mmHg. (Found: C 61.62; H 7.04. Calc. for $C_{13}H_{18}O_5$: C 61.41; H 7.14.) The NMR and mass spectra, which confirm the structure, are discussed below.

Ethylmagnesium bromide. Only one peak was observed in the gas chromatogram. The pure product, diethyl 1-(2-furyl)propylmalonate, distilled at 143°/8 mmHg. (Found: C 62.95; H 7.55. Calc. for $C_{14}H_{20}O_5$: C 62.67; H 7.51.) The NMR and mass spectra are discussed below.

Isopropylmagnesium bromide. The gas chromatogram showed two peaks. The substance yielding the first peak (peak area 35 mm²) gave in the combined gas chromatograph/mass spectrometer a mass spectrum which was identical with that of diethyl furfurylmalonate (II; R = H). The second peak had an area of 652 mm². When the crude substance was distilled in the Todd assembly, diethyl furfurylmalonate could not be isolated in the pure state, but the main product, diethyl 1-(2-furyl)-2-methylpropylmalonate (II; R = (CH₃)₂CH), was collected at 131°/1 mmHg. (Found: C 63.69; H 7.62. Calc. for $C_{15}H_{22}O_5$: C 63.81; H 7.85.) The mass and NMR spectra are discussed below. The mol ratio of the two reaction products calculated from the peak areas and the compositions of the substances is about 6:94.

Isobutylmagnesium chloride. Two peaks were observed in the gas chromatogram. The compound giving the first peak (area 168 mm²) gave in the combination instrument a mass spectrum identical with that obtained for diethyl furfurylmalonate. The compound giving the second peak (area 641 mm²) gave a mass spectrum that could be expected for diethyl 1-(2-furyl)-3-methylbutylmalonate. Because Maxim and Georgescu[5] have shown that this ester is a product of the reaction of diethyl furfurylidenemalonate and isobutylmagnesium chloride, the experiment was not repeated on the macro scale. The mol ratio of the reaction products calculated from the peak areas and the compositions of substances is about 26:76.

Isopentylmagnesium bromide. The gas chromatogram showed only one peak. The mass spectrum of the substance that gave this peak, however, contained strong peaks at *m/e* 180 and 108 which were not expected. Although Maxim and Georgescu[5] had shown that diethyl 1-(2-furyl)-4-methylpentylmalonate (II; R = (CH₃)₂CHCH₂CH₂) is the main

product, the experiment was repeated on the macro scale. The NMR spectrum of the distilled product, b.p. $158-160°/7$ mmHg, confirmed the structure. The mass and NMR spectra are discussed below.

Reaction between benzylmagnesium chloride and diethyl furfurylidenemalonate. The chromatogram of the products of the semimicro scale experiment showed six peaks. The first peak was due to toluene and the third to bibenzyl. The second and the fourth peaks were small and the substances giving them were not identified. The main products gave rise to the fifth and the sixth peaks and their mass spectra showed that they had been formed by addition of one benzyl group and one hydrogen atom to one molecule of diethyl furfurylidenemalonate. The peak areas of the fifth and sixth peaks were 440 and 232 mm².

When steam was led into the oil that remained after evaporation of the solvent in the macro scale experiment, all compounds except the two main products distilled off. Because the substances could not be separated by chromatography and neither substance crystallized when the mixture was treated with various solvents, a part (5.00 g) was dissolved in ethanol (25 ml) and a solution of potassium hydroxide (5 g) in water (5 ml) and ethanol (25 ml) was added. The mixture was warmed for 2 h in a boiling water bath. The ethanol was distilled off and the residue treated with ether and water. The organic phase was separated and the water solution was acidified. The oil that separated was taken up into ether, the solution dried with sodium sulphate, and the solvent allowed to evaporate slowly at room temperature. The obtained mixture of acids was induced to crystallize by careful addition of ligroin to its chloroform solution. The solid acids were filtered off. The two components of the mixture were then separated by making use of their different rates of solution in chloroform.

From the solution that contained the more rapidly dissolving crystals, an acid that melted at 143° (decomp.) was isolated after repeated crystallization from mixtures of chloroform and ligroin. It was identified as 5-benzylfurfurylmalonic acid by means of its NMR spectrum, which is discussed below. (Found: C 65.57; H 5.06. Calc. for $C_{15}H_{14}O_5$: C 65.69; H 5.15.)

The crystals that dissolved less rapidly in chloroform were purified by fractional crystallization from mixtures of chloroform and ligroin. The pure substance melted at 122° (decomp.) and was identified as 1-(2-furyl)-2-phenylethylmalonic acid by means of its NMR spectrum, which is discussed below. (Found: C 65.50; H 5.16. Calc. for $C_{15}H_{14}O_5$: C 65.69; H 5.15.)
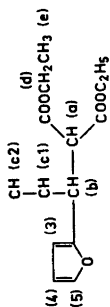
Each acid was reesterified by warming its ethanolic solution containing a small quantity of sulphuric acid for 1 h in a boiling water bath. The reaction mixtures were poured into water and the reaction products extracted with ether. After the ether solutions had been washed with sodium hydrogen carbonate solution and dried with sodium sulphate, they were examined by gas chromatography and mass spectrometry. Because the malonic acids were partly decarboxylated during the esterification, each solution contained one malonic ester and one monocarboxylic ester.

When the mass spectra of these malonic esters were compared with those obtained for the substances of the original reaction mixture giving rise to the peaks 5 and 6, it was observed that the spectra of the substance giving peak 5 and the diethyl ester of 1-(2-furyl)-2-phenylethylmalonic acid, on one hand, and the spectra of the substance giving peak 6 and the diethyl ester of 5-benzylfurfurylmalonic acid, on the other, were identical. The retention times of diethyl 1-(2-furyl)-2-phenylethylmalonate and diethyl 5-benzylfurfurylmalonate corresponded to those of peaks 5 and 6, respectively. The structures of the substances which gave the peaks 5 and 6 had thus been established. The mol ratio of the 1,4- and 1,8-addition products calculated from the peak areas is about 65:35.

The NMR spectra. The most important feature of the NMR spectra of the isolated malonic esters is the AMX line system typical for furans with a single substituent in the α position. The chemical shifts and the coupling constants of this three-proton system are almost identical for all four isolated esters (*cf.* Table 2). These facts show clearly that the furan rings of these esters have not been affected during the reactions. Also the signals due to the protons a, b, c1, and c2 (*cf.* Table 2) confirm the structures. The protons a and b in diethyl 1-(2-furyl)-2-methylpropylmalonate (isopropyl group on C_b) form an AB system, the B lines of which are split into doublets by coupling with the proton c1. The analysis of the spectrum of diethyl 1-(2-furyl)propylmalonate (ethyl group on C_b)

Table 2. Chemical shifts (τ) and coupling constants in the NMR spectra of the isolated malonic esters dissolved in tetrachloromethane.

CH (c2)
(4) CH (c1) COOCH₂CH₃ (e) (d)
(5) CH—CH (a)
(b) COOC₂H₅

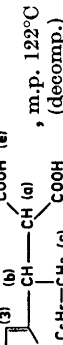| Substituent at C(b)	Chemical shift (τ) of the proton(s) in position									Coupling constants (Hz)						
	5	4	3	a	b	c1	c2	d	e	J_{15}	J_{35}	J_{34}	J_{ab}	J_{bc1}	J_{c1c2}	J_{de}
Methyl	2.75	3.80	4.00	6.43	6.43	8.70	—	5.90 / 6.03	8.80 / 8.90	1.9	0.8	3.0	?	6.7	—	6.9
Ethyl	2.77	3.83	3.98	6.44	6.67	8.34	9.22	5.86 / 6.02	8.77 / 8.94	1.9	0.8	3.0	10.3	6.9	6.9	6.9
Isopropyl	2.77	3.80	3.98	6.23	6.56	8.01	9.14 / 9.18	5.83 / 5.94	8.79 / 8.99	1.9	0.8	3.0	11.0	4.1	4.0	6.9
Isopentyl	2.76	3.83	4.00					5.86 / 6.08	8.76 / 8.92	1.9	0.8	3.0				6.9

Table 3. Chemical shifts (τ) and coupling constants in the NMR spectra of the two malonic acids obtained on hydrolysis of the reaction products of diethyl furfurylidenemalonate and benzyl magnesium chloride.

(3) CH—CH (a) COOH , m.p. 122°C (decomp.)
(4) C₆H₅—CH₂ (c) COOH

(4) CH₂—CH (a) COOH (e) , m.p. 143°C (decomp.)
(5) C₆H₅—CH₂ (b) COOH

Dissolved in deuteriochloroform

Dissolved in a mixture of deuteriochloroform and hexadeuterioacetone

M.p.	Chemical shift (τ) of the proton(s) in position								Coupling constants (Hz)				
	5	4	3	a	b	c	d	e	J_{45}	J_{35}	J_{34}	J_{ab}	J_{bc}
122°	2.66	3.82	4.04	6.25	6.19	6.91	—	1.10	1.7	0.7	3.0	2.6	3.9
143°	—	4.01 / 4.13		6.30	6.48	—	6.11	3.21	—	—	3.1	7.2	—

is almost as simple because the long-range coupling is weak and the B lines are consequently split into triplets. The spectrum of diethyl 1-(2-furyl)ethylmalonate (methyl group on C_b) is more complex due to long-range coupling of the methyl protons with the proton a. When the double resonance technique with irradiation at the methyl frequency 78 Hz was employed, the a and b protons gave only one signal. The chemical shifts of these protons obviously, but surprisingly, lie so close to each other that the AB quartet has collapsed into an A_2 signal. The part of the spectrum of diethyl 1-(2-furyl)-4-methylpentylmalonate (isopentyl group on C_b) due to the methylene and methine protons has not been analysed because the presence of so many protons makes the spectrum extremely complex.

The most important signals in the spectra of the two isolated malonic acids are those from the furan protons (cf. Table 3). The spectrum of the lower-melting acid shows three signals of this type. The chemical shifts and the coupling constants are close in value to those of the furan protons of the above esters. Thus, the furan ring of this substance has not been affected during the formation of its ester. The furan proton signals form in the spectrum of the higher-melting acid an AB quartet, the chemical shifts and coupling constants of which show that the benzyl group has become bounded

Table 4. Series of peaks and major isolated peaks in the mass spectra of furyl substituted diethyl malonates. Relative abundances and masses of the ions giving the peaks are reported.

|	Substituents in the diethyl malonates							
m/e	Furfuryl	1-(2-Furyl)-ethyl	1-(2-Furyl)-propyl	1-(2-Furyl)-2-methylpropyl	1-(2-Furyl)-3-methylbutyl	1-(2-Furyl)-4-methylpentyl	1-(2-Furyl)-2-phenylethyl	5-benzyl-furfuryl
$M^{+\cdot}$	14/240	8/254	11/268	6/282	11/296	9/310	3/330	31/330
$M-45$	6/195	2/209	3/223	2/237	2/251	1/265	—	3/285
$M-46$	—	—	—	—	—	—	2/284	
$M-74$	65/166	38/180	58/194	29/208	27/222	1/236	4/256	40/256
$M-102$	24/138	11/152	9/166	2/180	—	—	—	—
$M-119$	34/121	24/135	38/149	15/163	13/177	7/191	5/211	13/211
$M-146$	27/94	26/108	16/122	2/136	1/150	—	—	(7/184)
$M-159$	100/81	100/95	100/109	70/123	28/137	14/151	34/171	100/171
$M-R$ [a]	—	—	5/239	3/239	1/239	1/239	22/239	1/239
180	—	—	—	—	34/180	100/180	—	—
166	65/166	1/166	9/166	18/166	7/166	3/166	4/166	(2/166)
121	34/121	7/121	34/121	76/121	40/121	19/121	96/121	—
108	—	26/108	16/108	3/108	14/108	21/108	—	—
91	—	—	—	—	—	(3/91)	37/91	39/91
81	100/81	3/81	37/81	37/81	100/81	29/81	2/81	3/81
29	43/29	3/29	5/29	100/29	77/29	15/29	72/29	37/29
27	10/27	15/27	12/27	2/27	27/27	4/27	10/27	13/27
Other abundant ions		16/41	41/158	16/167	18/94		100/170	72/165
		14/39	11/65	16/162	20/65		36/167	20/137
				17/43	27/43		29/139	18/128
				32/122	25/41		18/125	23/105
				20/65	18/39		26/65	
				15/55			12/39	
				43/43				
				22/41				

[a] R = the alkyl group of the Grignard reagent used.

to the furan ring at position 5. Also the signals of the protons a and b in the spectrum of the lower-melting acid (*cf.* the left structure in Table 3) form an AB system in which the signals from proton b are split into triplets due to coupling with the protons c. The signal of these protons is in turn a doublet due to coupling with the proton b. The signal of the methylene protons of the benzyl group in the spectrum of the higher-melting acid is a singlet and the signals of the protons a and b form an ordinary AX_2 system (*cf.* the right structure in Table 3).

The mass spectra were taken on a combined gas chromatograph/mass spectrometer (LKB 9000). Apparent ion series and abundant isolated ions in the spectra are collected in Table 4.

The principal fragmentation seems to be fission of the molecular ion into a malonic ester radical (mass 159) and an ion of mass $M-159$ (IV a and IV b). The relative abundance of this ion decreases with increasing molecular weight in the series of esters with structure II that has an aliphatic side-chain. The decrease begins in the spectrum


$\underline{IV}$a $\underline{IV}$b $\underline{V}$ $\underline{VI}$ $\underline{VII}$
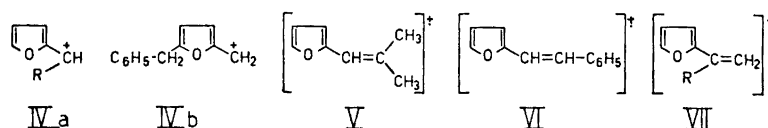
of diethyl 1-(2-furyl)-2-methylpropylmalonate (II; R = $(CH_3)_2CH$), where the abundance of this ion (*m/e* 123) is only 70 %. The situation is, however, not clear. The peak of the ethyl ion (*m/e* 29) is the base peak in this spectrum and is stronger than in the other spectra. This fact might be the principal reason for the lower abundance of the ion $M-159$ in this spectrum. Another reason is the splitting off of a hydrogen atom from the ion $M-159$ with the formation of the ion at *m/e* 122 (V). This secondary fragmentation is still more striking in the spectrum of diethyl 1-(2-furyl)-2-phenylethylmalonate (II; R = $C_6H_5CH_2$), where the peak of the resulting ion (*m/e* 170; VI) is the base peak.
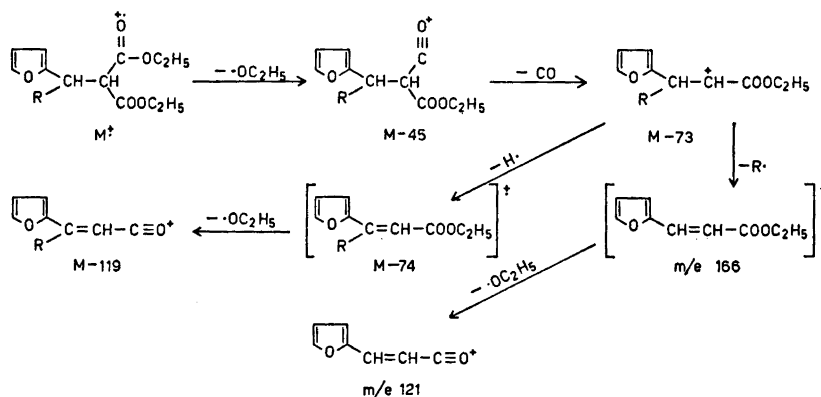
Scheme 2.

Another important fragmentation, which seems to occur in all cases, is illustrated in Scheme 2. The absence of the ion $M-45$ and the presence of the ion $M-46$ in the spectrum of diethyl 1-(2-furyl)-2-phenylethylmalonate (II; R = $C_6H_5CH_2$), however, call for caution. The low relative abundance of the ion $M-74$ in the spectrum of diethyl 1-(2-furyl)-4-methylpentylmalonate (II; R = $(CH_3)_2CHCH_2CH_2$) might be explained by the McLafferty rearrangement illustrated in Scheme 3. It is quite clear that diethyl
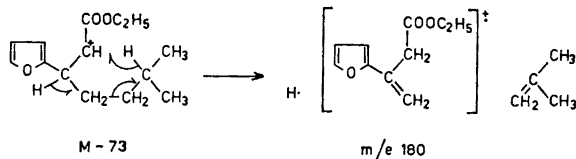
Scheme 3.

5-benzylfurfurylmalonate (III) does not give the ions of masses 121 and 166 in Scheme 2. The ion with the latter mass in the spectrum of this ester must be a result of a rearrangement and the fragment ion does not necessarily have the structure given in Scheme 2.

The ions of the series $M-146$ seem to be of the type illustrated by structure VII, although a simple mechanism for their formation cannot be proposed. Their origins seem to be the ions $M-74$. This hypothesis is supported by the presence of the ion $M-146$ in all spectra where the ion $M-74$ is abundant and by the absence of the $M-146$ ion from the spectrum of diethyl 1-(2-furyl)-4-methylpentylmalonate (II; $R=(CH_3)_2CH$ CH_2CH_2), where the abundance of the ion $M-74$ is low. The ion $M-146$ is apparently replaced by the ion at m/e 108 in the last-mentioned spectrum, which ion is related to the ion at m/e 180 in the same way as the ions $M-146$ are to the ions $M-74$.

No explanation has been found for the presence of the ions of the series $M-102$.

The ions at m/e 91 (benzyl ∼ cycloheptatrienyl cation), 81 (furfuryl ∼ pyranyl cation), 29 (ethyl), and 27 (ethenyl) are self-explanatory.

The elemental analyses were performed by Janssen Pharmaceutica, Analytical Department, Beerse, Belgium. *Statens naturvetenskapliga kommission* (Finland) has supported the work.

REFERENCES

1. Holmberg, G. A. *Acta Chem. Scand.* 12 (1958) 229.
2. Holmberg, G. A. and Lundell, R. *Acta Acad. Aboensis, Ser. B* 26 (1967) No. 12.
3. Holmberg, G. A., Virtanen, E. and Bäckström, T. *Acta Chem. Scand.* 23 (1969) 1304.
4. Holmberg, G. A. and Sjöholm, R. *Acta Chem. Scand.* 24 (1970) 2490.
5. Maxim, N. and Georgescu, E. *Bull. Soc. Chim. France* [5] 3 (1936) 1114.
6. Fuson, R. C. In Stone, F. G. A. and West, R. *Advan. Organometal. Chem.* 1 (1964) 221.
7. Holm, T. and Crossland, I. *Acta Chem. Scand.* 25 (1971) 59.
8. Herz, W. *J. Am. Chem. Soc.* 68 (1946) 2732.
9. Mndzhoyan, A. L. and Badalyan, V. E. *Arm. Khim. Zh.* 22 (1969) 671, as abstracted in *Chem. Abstr.* 72 (1970) 21590.
10. Holmberg, G. A. *Acta Acad. Aboensis, Math. Phys.* 16 (1949) No. 6.
11. Holmberg, G. A. *Acta Chem. Scand.* 13 (1959) 859.