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EXPERIMENTS IN THE FURAN SERIES. XIII.*

INTERACTION OF SUBSTITUENTS ON THE FURAN NUCLEUS CAUSED BY ELECTRON IMPACT

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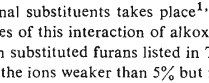
Systematic studies of furan derivatives[1,3] have shown that on fragmentation caused by electron impact mutual interaction of vicinal substituents takes place[1,2] (*ortho*-effect[4]). The aim of this paper is to point to certain features of this interaction of alkoxymethyl and carboxyl groups not yet observed. The spectra of seven substituted furans listed in Table I comprise all ions stronger than 5% of the base peak (100%); the ions weaker than 5% but relevant to the discussion are also given in Table I.



I, $R^1 = CH_3$; $R^2 = CH_3$; $R^3 = H$ *III*, $R^1 = CH_3$; $R^2 = C_2H_5$; $R^3 = CH_3$
II, $R^1 = CH_3$; $R^2 = CH_3$; $R^3 = CH_3$ *IV*, $R^1 = H$; $R^2 = C_2H_5$; $R^3 = CH_3$

* Part XII: This Journal *35*, 3478 (1970).

TABLE I

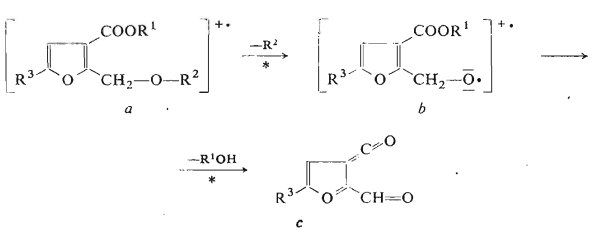
Mass Spectra of Substituted Furans

m/e (Abundance, %)												
					I							
170 (19)	155 (58)	140 (8)	139 (45)	124 (7)	123 (100)	111 (10)	110 (5)	109 (46)	108 (15)	95 (14)	83 (14)	82 (15)
81 (11)	80 (22)	79 (5)	68 (7)	67 (5)	66 (5)	59 (22)	58 (6)	55 (12)	54 (5)	53 (32)	52 (38)	51 (48)
50 (22)	45 (24)	43 (15)	42 (6)	41 (12)	40 (7)	39 (44)	38 (16)	37 (8)	33 (14)	31 (6)	29 (45)	28 (19)
27 (19)	26 (9)											
					II							
184 (30)	170 (5)	169 (62)	154 (11)	153 (84)	141 (8)	138 (8)	137 (81)	125 (8)	123 (19)	122 (8)	109 (8)	95 (8)
94 (13)	81 (5)	79 (5)	65 (5)	59 (11)	53 (11)	52 (8)	51 (13)	50 (8)	45 (16)	43 (100)	41 (5)	39 (11)
29 (13)	28 (11)	27 (5)	15 (32)									
					III							
198 (16)	183 (6)	170 (6)	169 (53)	167 (6)	155 (6)	154 (12)	153 (62)	139 (18)	138 (12)	137 (99)	125 (6)	123 (25)
122 (9)	111 (6)	110 (6)	109 (9)	95 (16)	94 (16)	73 (6)	71 (6)	69 (6)	67 (6)	65 (6)	60 (6)	59 (18)
58 (6)	57 (12)	55 (6)	53 (19)	52 (9)	51 (12)	50 (9)	45 (32)	44 (13)	43 (100)	42 (6)	41 (12)	39 (13)
31 (19)	29 (25)	28 (18)	27 (18)									
					IV							
184 (17)	156 (6)	155 (47)	141 (7)	140 (21)	139 (100)	138 (11)	137 (84)	111 (11)	110 (5)	109 (7)	97 (6)	95 (15)
94 (6)	83 (7)	82 (5)	81 (6)	69 (6)	67 (5)	65 (6)	59 (9)	55 (9)	53 (13)	52 (6)	51 (12)	50 (6)
45 (10)	44 (7)	43 (88)	42 (6)	41 (9)	39 (12)	31 (19)	30 (25)	29 (22)	28 (8)	27 (18)		
					V							
184 (28)	183 (6)	169 (7)	154 (11)	153 (100)	122 (6)	121 (53)	111 (7)	94 (6)	79 (11)	59 (5)	53 (6)	52 (9)
51 (9)	50 (5)	45 (13)	43 (36)	39 (8)	29 (7)	28 (6)	15 (18)					

TABLE I
(*Continued*)

m/e (Abundance, %)												
						VI						
184 (20)	155 (10)	140 (26)	139 (100)	123 (10)	121 (26)	95 (10)	79 (16)	55 (5)	53 (5)	52 (6)	51 (8)	45 (6)
43 (36)	41 (5)	39 (7)	31 (7)	29 (12)	28 (5)	27 (9)						
						VII						
198 (24)	169 (8)	167 (20)	155 (8)	154 (28)	153 (100)	139 (10)	137 (8)	123 (16)	122 (12)	121 (60)	109 (8)	
97 (8)	95 (16)	94 (12)	79 (12)	61 (8)	59 (12)	53 (8)	52 (12)	51 (12)	45 (12)	44 (8)	43 (52)	
41 (8)	39 (12)	31 (16)	29 (20)	28 (12)	27 (12)							

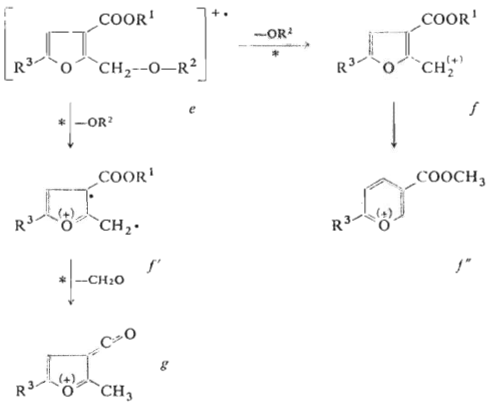
All more abundant fragment ions of compounds *I*—*IV* are formed exclusively by two reaction paths of the decomposition of the molecular ion. In the first one (Scheme 1) the fragmentation is initiated by the splitting off of alkyl R^2 (the discussed[1] splitting off of the alkyl from the ester function contributes very little to this process), and followed by the fragmentation of R^1OH. The resulting ion *c* eliminates then 28 m.u. (most probably CO)[1].



SCHEME 1

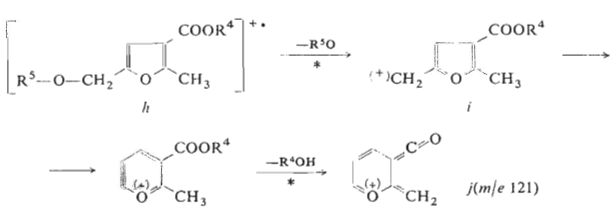
The second fragmentation path (Scheme 2) starts with the expulsion of the OR^2 particle from the molecular ion *e*, and then the formed fragment *f'* eliminates 30 m.u. (CH_2O), and the ion *f''* 28 m.u. (CO). The elimination of the particle CH_2O from the ion $(M - OR^2)^+$ is surprising. Grigg and coworkers[1] observed that ions $(M - COOCH_3)^+$ of methyl 5-methyl-3-methoxycarbonyl-2-furylacetate, for which they proposed structure *f*, eliminated CH_3OH exclusively, but not CH_2O. This may be the result of various structures of the starting compounds, changing

fundamentally the fragmentation paths of the molecular ion. An alternative explanation is based on the differing structures of ions $(M - OR^2)^+$ *f'*, *f''* and ion $(M - COOCH_3)^+$ *f*, which, however, seems rather surprising.



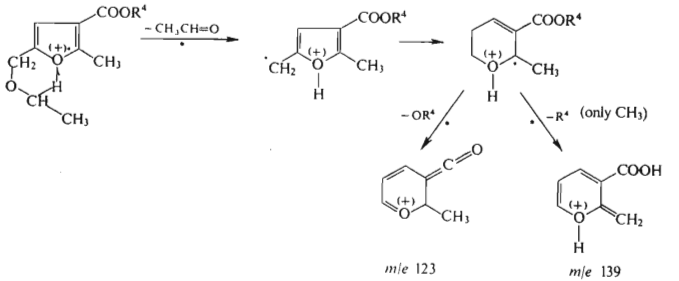
SCHEME 2

The fragmentations of 5-alkoxymethyl derivatives differ appreciably from those of 2-alkoxymethyl derivatives; the most important process of the fragmentation of the molecular ions is the elimination of OR^5 and subsequent elimination of R^4OH (Scheme 3). The loss of R^5 or OR^4 from the molecular ions takes place to a much lesser extent. Further fragmentation of these ions cannot be determined because the corresponding metastable ions are absent. Only in the case of *VI* or *VII* in addition of ions $(M - R^5)^+$ and $(M - OR^4)^+$ the ions $(M - CH_3CH{=}O)^+$ are also formed which are capable of eliminating the particle OR^4 (Scheme 4), and only in the case of *VII* the methyl group, as well.



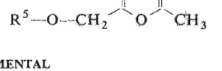
SCHEME 3

In furan derivatives with an alkoxymethyl group adjacent to the carboxyl group the β[3,5](B) and γ(A) cleavage of the substituent at C_2 takes place with equal ease in contrast to analogous substances substituted at C_2 with a $-COCH_2COOR$ ($R = CH_3$, C_2H_5)[1] group, in which the β(B)



SCHEME 4

cleavage largely prevails. Further fragmentation of the product formed on β cleavage (with respect to the position 2 of the furan ring) is also different. In the case of substances *I*—*V* such an ion is further fragmented loosing formaldehyde, while in the case of methyl 5-methyl-3-methoxycarbonyl-2-furylacetate[1] methanol is split off. We consider that this difference is caused by the different distribution of the charge in the molecular ion and probably also by the formation of the ion *f'* from the discussed compounds. During the substitution in the position 5 the γ-cleavage (A) hardly takes place and the β cleavage prevails largely over the other fragmentation paths. The formed ions $(M - OR^5)^+$ probably isomerise (reaction $i \rightarrow i'$) before further fragmentation.



V, $R^4 = CH_3$; $R^5 = CH_3$
VI, $R^4 = H$; $R^5 = C_2H_5$
VII, $R^4 = CH_3$; $R^5 = C_2H_5$

EXPERIMENTAL

Compounds *I*—*VII* were prepared using procedures discussed in detail in paper[6]. Mass spectra were obtained on a single focusing apparatus Gas Chromatograph — Mass Spectrometer LKB 9000 with the magnetic scanning of the mass spectra. The temperature of the ionic source was 290°C, the current of ionising electrons was 50 μA, and their energy 70 eV. Substances *IV* and *VI* were introduced by direct evaporation into the ionic source; the temperature of the direct inlet was 70°C. The remaining compounds *I*, *II*, *III*, *V*, and *VII* were introduced *via* the chromatograph because they were not pure (approx. 10% of impurities). The filling of the chromatography column consisted of 20% Carbowax 20 M on Chromosorb W. The temperature of the column at the moment of the sample injection was set at 100°C and after 3 minutes, the increase was programmed to 250°C. The mass spectrum was registered at the moment when the concentration of the substance in the source of the mass spectrometer was maximum. From the spectrum obtained in this manner the spectrum of the vapour phase of the chromatographic column, measured before or after the elution of the analysed substance, was substracted.

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ORGANIC HERBICIDES. V.*

DERIVATIVES OF 3-MERCAPTO-5-AMINO-1,2,4-THIADIAZOLE

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In this paper we describe the method of preparation and the herbicidal properties of a series of 27 S^3,N^5-disubstituted 3-mercapto-5-amino-1,2,4-thiadiazoles. In this type of compounds we supposed herbicidal effects due to a certain structural similarity with the herbicides of the triazole type. The compounds were prepared by heating S^3-substituted 3-mercapto-5-chloro-1,2,4-thadiazoles (obtained from trichloromethanesulfenyl chloride and corresponding isothiuronium chlorides[1-3]) and amines in alcohol. The yields were above 90%. The prepared compounds are odourless, stable at laboratory conditions, well soluble in common organic solvents, insoluble in water.

For biological testing we made use of Zemánek's method[4] (determination of the inhibition of the growth of wheat and mustard with the tested compounds, untreated plants serving as controls). We found that the majority of compounds displayed the herbicidal effect of the type of growth stimulators (not contact). The measure of these effects is generally lower than necessary for practically utilisable herbicides. The most active of the compounds tested were compounds *IX* and *XV*, *i.e.* those where the substituent R^2 was an isopropylamine group and R^1 and ethylthio- or allylthio group. In contrast to this larger substituents (for example aromatic or heterocyclic) decrease the activity in this type of compounds although these groups by themselves generally do not contribute to increased phytotoxicity. As for the selectivity, the majority of the results indicates a higher effect in mustard, *i.e.* in a representative of large-leaved, dicotyledons.

* Part IV: This Journal *33*, 4416 (1968).