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THE MASS-SPECTRA OF DIMEDONE DERIVATIVES OF ALDEHYDES

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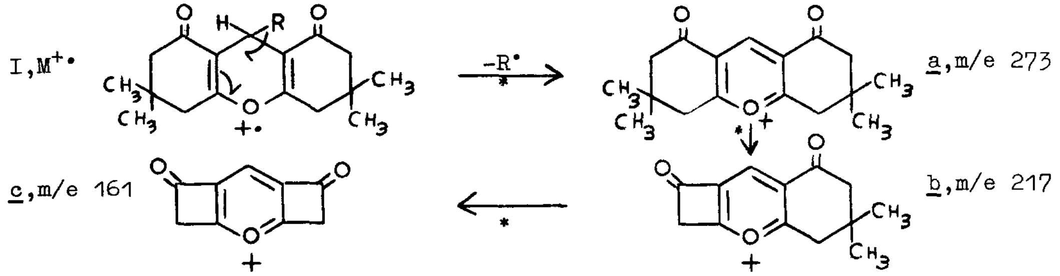
Although the mass-spectra of common derivatives of aldehydes such as oximes (1), semicarbazones (2), and 2,4-dinitrophenylhydrazones (3,4,5) have been analysed and rationalized in terms of intact molecule structures, no such analysis has been reported for the mass-spectra of dimedone (5,5-dimethyl-1,3-cyclohexanedione) derivatives of aldehydes. We find that the anhydro-dimedone-derivatives (I) of aldehydes R-CHO give simple mass-spectra with only three significant fragment ions being formed. Since methods are known for small-scale preparation of these compounds, they are very suitable for mass-spectral analysis of trace amounts or mixtures of aldehydes.

The base peak of all the spectra examined is the ion a, $C_{17}H_{21}O_3$, formed directly from the parent ion by loss of R•, and it is suggested that it owes its stability to its aromatic pyrilium ion structure. The fragment ions at m/e 217 (b) and 161 (c) are formed by successive losses of C_4H_8 in retro-Diels-Alder processes (6):



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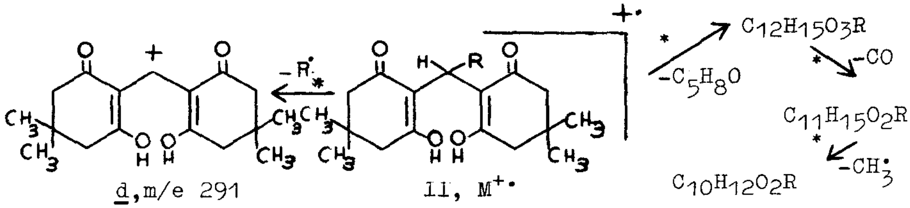
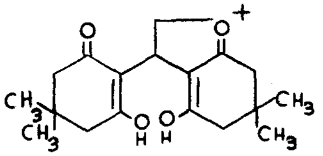
* Indicates that a metastable ion was observed for the transition concerned.

The mass-spectra of the non-cyclized dimedone derivatives (II) are much more complex and their nature depends considerably upon the structure of the original aldehyde. In all the cases examined the molecular ion is intense and the following sequences of decomposition are evident, although the relative intensities of the fragment ions are very variable.



d, m/e 291 II, $M^{+\cdot}$

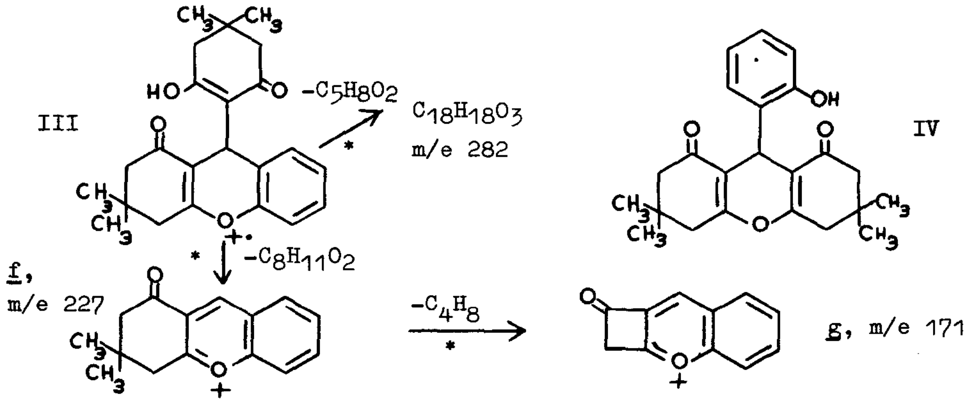
A feature noted when R is an alkyl group ($\geqslant C_2H_5$) is fission to give a homologue of d. This ion is presumably stabilized as e by cyclization. A similar cleavage has been observed with some 2-alkyldimedones (8).



e, m/e 305

Mass-spectra of deuterium-labelled compounds permitting a complete rationalization of the decompositions observed will be reported in the full paper. All derivatives of type II have a prominent peak corresponding to the ion $(CH_3)_2C{=}CH{-}C{\equiv}O^+$ (m/e 83) which has been observed as the base peak of the mass spectra of dimedone and various 3-substituted and 3,3-disubstituted dimedones (7,8,9). It is interesting to note that little or no dehydration (thermal or impact-induced) is observed in the spectra of any of the non-cyclized derivatives.

Ambiguities in the structures of certain aldehyde dimedone derivatives. have been removed by a consideration of their mass-spectra. Structures III and IV have been considered for the anhydro-compound from salicylaldehyde (10,11,12,13), but mass-spectrometry clearly shows III to be correct. As expected for this structure a major process is the loss of $C_8H_{11}O_2$ from the molecular ion to give the chromenyl cation f, rather than loss of C_6H_5O leading to a as expected for IV. The ion f undergoes the expected retro-Diels-Alder reaction to g. As with compounds of type II, loss of C_5H_8O from the molecular ion is also a prominent process with III, and leads to the base peak of the spectrum at m/e 282.

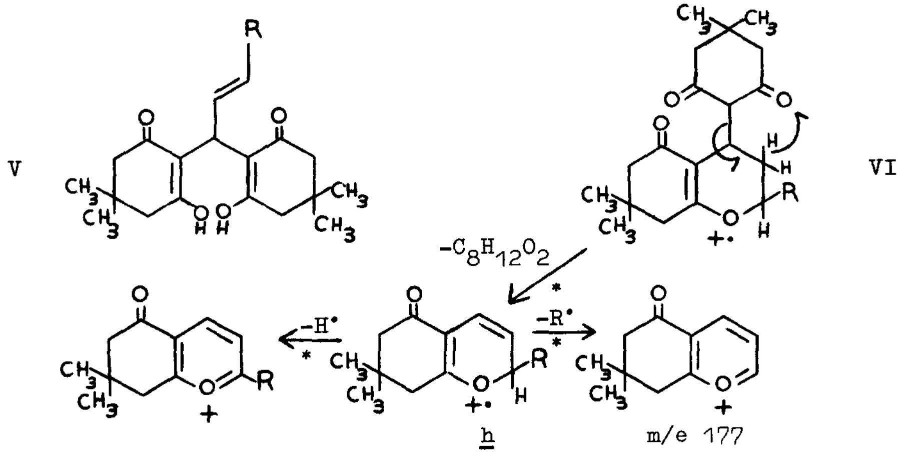

III

IV

f, m/e 227

g, m/e 171

The initial condensation products of α,β-unsaturated aldehydes and dimedone also present structural ambiguities (11,12,14). Thus the product from crotonaldehyde may be formulated as the "normal" adduct V ($R=CH_3$) or as its cyclic ether isomer VI ($R=CH_3$). The mass-spectrum points to VI as the correct structure, since the parent ion eliminates dimedone to produce an ion whose mode of formation and subsequent decomposition suggest formulation h ($R=CH_3$):


V

VI

h

m/e 177

A similar sequence of decompositions is observed with the cinnamaldehyde derivative, supporting its formulation as the cyclic ether VI (R=Ph). The n.m.r. spectra of these derivatives also support this formulation. Neither shows any olefinic proton absorption. With the cinnamaldehyde compound a one-proton double doublet centred at τ 5.1 (J = 2.7 and 13.5 c/s) can be correlated with the single benzylic proton coupled to the magnetically non-equivalent protons of the adjacent methylene group.

Mass-spectra were determined using an AEI MS9 instrument, and exact masses were measured with heptacosafluorotributylamine as a standard.

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TABLE I. Partial Mass Spectra

Compound	R	Spectrum											
I	CH_3	m/e	288	273	217	161	133	83					
		I(%)	4	100	13	8	4	4					
	C_2H_5	m/e	302	273	217	161	133	83					
		I(%)	0.3	100	13	10	8	9					
	Ph	m/e	350	349	273	217	161	133	83				
		I(%)	70	6	100	15	14	8	10				
II	H	m/e	292	291	208	180	165	83					
		I(%)	100	0.5	15	23	100	95					
	CH_3	m/e	306	305	291	222	194	179	83				
		I(%)	100	0.9	12.5	11	41	83	91				
	C_2H_5	m/e	320	305	291	236	235	208	207	193	83		
		I(%)	53	20	16	2	3.3	8.4	6.5	42	100		
	n-C_6H_{13}	m/e	376	305	292	291	264	263	249	83			
		I(%)	61	71	15	76	2.2	5.2	12	100			
	†C_9H_{17}	m/e	416	332	314	305	299	292	291	287	273	83	
		I(%)	4.4	9.2	12	10	6.6	13	4	6.7	10	100	
	Ph	m/e	368	291	284	283	256	241	83				
		I(%)	100	1	5.5	8	33	78	100				
III	--	m/e	366	282	227	171	115	83					
		I(%)	43	100	98	72	68	34					
VI	CH_3	m/e	332	314	299	192	191	179	177	83			
		I(%)	28	54	28	33	13	64	72	100			
	Ph	m/e	394	376	254	253	241	229	228	227	198	177	83
		I(%)	19	16	66	14	38	17	8.5	13	14	13	100

†R-CHO is citronellal