High Resolution Mass Spectra of Aromatic γ-Dilactones

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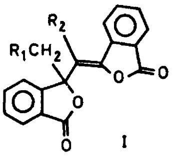
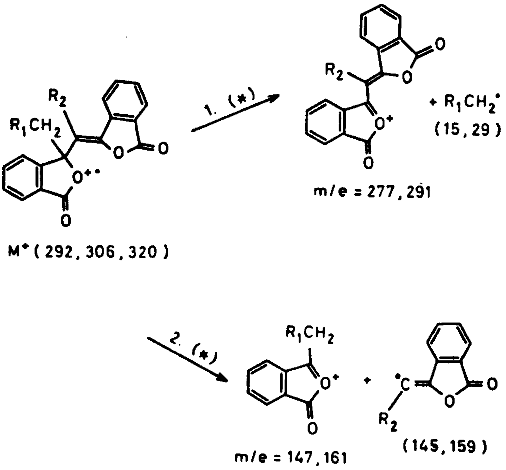
The mass fragmentation of some α,β-unsaturated γ-dilactones formed by condensation of certain γ-keto-acids[1] was recently reported on.[2] When aromatic γ-keto-acids were condensed similar γ-dilactones were formed where the aromatic ring constitutes the α,β-unsaturation (I). The availability of the proper aromatic γ-keto-acids[1] gave in hand γ-dilactones well suited for a study of the effect of other substituents (*i.e.* at the double bond connecting the two lactone rings and at the *sp*³ ring-carbon-atom) on the fragmentation of such systems. The main fragments in the high mass region are given in Table 1.



a : $R_1 = R_2 = H$
b : $R_1 = H;\ R_2 = Me$
c : $R_1 = R_2 = Me$

The molecular ions are involved in two simple bond cleavage processes, both being associated with a change in hybridization at the only *sp*³ ring-carbon atom in the molecules (Scheme 1). The first involves splitting off the R_1CH_2-radical and the other route leads to the carbonium ion believed to be one of the key intermediates in the selfcondensation of the γ-keto-acids.[1]

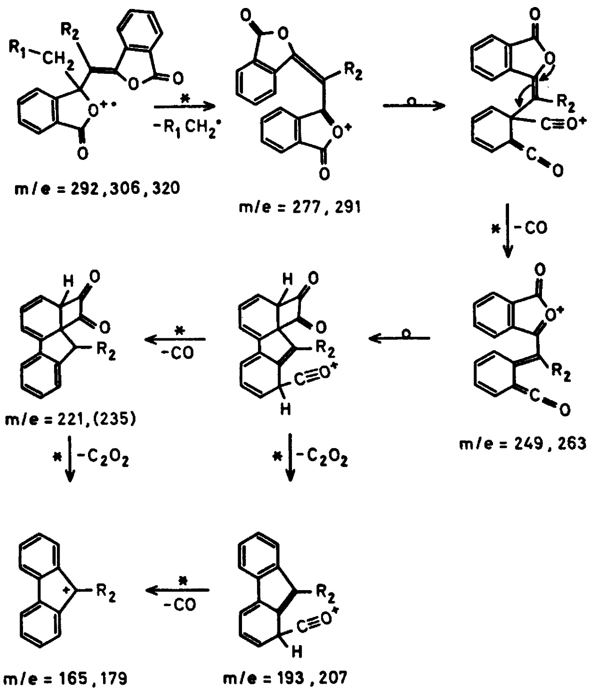
Scheme 1 is interesting in many respects. The structural difference between Ib and Ic lies in the substituent R_1 and therefore the observed variation in fragmentation must be due to the difference in stabilities of the radicals $R_1CH_2^\cdot$ and/or the relative stabilities of the carbonium ions formed by route 2. From measurements of ionization potentials an ethyl group is found to stabilize a carbonium ion better than a methyl group by about 1.9 kcal/mol,[3] and thus the carbonium ion formed by route 2 should be more stable from Ic than from Ib. However, the limit of error of the ionization potential measurements was estimated to 1.2 kcal/mol. On the other hand, most values for stabilities of radicals favor the ethyl radical in comparison to the methyl radical by 3−6 kcal/mol. Thus this greater difference in radical stabilities explains the preference for route 1 for Ic and



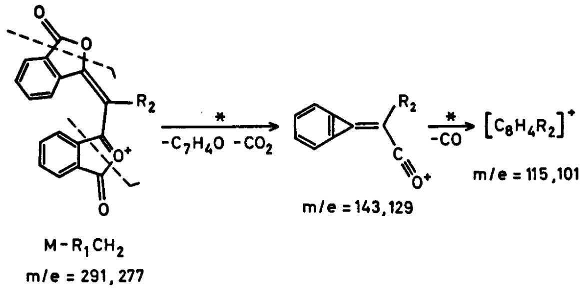
Scheme 1. Consecutive ejection of carbon monoxide (or C_2O_2) leading to fluorenyl cations. Ia. Preferred route: 1. Ib. Preferred route: 2. Ic. Preferred route: 1.

Table 1. Relative intensities of main high masses in the fragmentation of I.

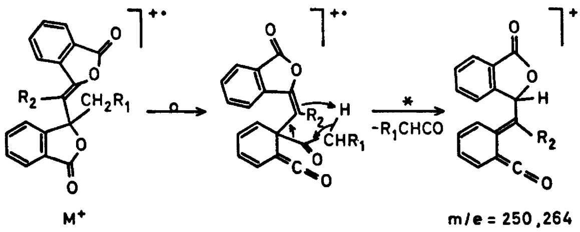
Ia		Ib		Ic		Fragment
Rel. int.	*m/e*	Rel. int.	*m/e*	Rel. int.	*m/e*	
8	292	6	306	3	320	M^+
100	277	20	291	100	291	$M-R_1CH_2$
22	250	3	264	1	264	$M-R_1\ CH=C=O$
26	249	4	263	3	263	$M-R_1CH_2CO$ (or $M-R_1CH_2,-CO$)
3	221	0	235	0	235	$M-R_1CH_2,-2CO$
15	193	5	207	5	207	$M-R_1CH_2,-3CO$
16	165	1	179	0.4	179	$M-R_1CH_2,-4CO$
19	147	100	147	8	161	$M-R_2C_9H_4O_2$
29	129	22	143	54	143	$M-R_1CH_2,-C_7H_4O,-CO_2$
9	101	10	115	20	115	$M-R_1CH_2,-C_7H_4O,-CO_2,-CO$



Scheme 2. Fragmentation of $\text{M-R}_1^{\cdot}\text{CH}_2$.



Scheme 3. Competitive fragmentation of molecular ion.



Scheme 4. Ketene ejection from molecular ion.

route 2 for Ib. The different fragmentation preference for Ia and Ib must lie in the relative stabilities of the entities carrying the substituent R_2. Again the radical stabilities seems to be more important, *i.e.* a methyl group (compared to a hydrogen atom at a double bond) must be more effective in stabilizing radicals than carbonium ions.

Similar to the aliphatic analogues, fragmentations involving consecutive losses of carbon monoxide are observed. The metastable defocusing technique once again revealed that two molecules of carbon monoxide (or C_2O_2) are ejected simultaneously. These fragmentations leading to fluorenyl cations are dealt with in Scheme 2. The rearrangement of $[M-R_1CH_2]^+$ and the intermediate formation of α-diketones before ejection of C_2O_2 are processes discussed earlier.[2]

As seen from Table 1 the path through $m/e = 221$ (Ia) or $m/e = 193$ (Ia) and 207 (Ib and Ic) is preferred only to some extent. In fact, the fragmentation route in Scheme 1 is very prominent only for Ia. When $R_2 = Me$ (Ib and Ic) another route seems to be of more importance. Here fragmentation of $M-R_1CH_2$ directly to $m/e = 143$ is preferred, demonstrated by the observation of the proper metastable peak (Scheme 3).

As for the aliphatic analogues,[2] metastable peaks indicating the elimination of ketenes from I are observed. In these aromatic dilactones such processes must involve rearrangements destroying the aromatic structure in one of the aromatic rings.

However, compared with other processes, only for Ia this represents a major fragmentation path.

Experimental. Mass spectra (70 eV, ion source temperature 230 °C) were obtained on an AEI MS 902 mass spectrometer connected to an AEI DS 30/64/H data system. Peak compositions were within 4 ppm of calculated values. Metastable peaks were observed in the spectra and confirmed by the metastable defocusing technique.

1. Kolsaker, P. and Berner, E. *Tetrahedron 29* (1973) 1095.
2. Kolsaker, P. *Org. Mass Spectrom. 7* (1973) 535.
3. Lossing, F. P. *Mass Spectrometry*, McGraw, New York 1963, p. 442.

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The Dimerization of Coniferyl Alcohol in Aqueous Sodium Hydroxide*

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p-Hydroxyarylglycerol *β*-aryl ether structures (*1*), present originally as such or formed during degradation, have been shown to be the major site of lignin fragmentation in kraft pulping.[1] Structures of type *1* fragment to give predominantly *trans*-coniferyl alcohol (*2*).[2] This undergoes further transformation, in part via its extended quinone methide *3*. By this process the side chains of units derived from *2* and *3* condense to the final product, kraft lignin. The present paper is concerned with the elucidation of some of the reactions by which *2* reacts with the kraft lignin being formed.

Heating of *2* in dilute aqueous sodium hydroxide for 2 h at 170 °C gives a polymer.[2a,3] Little monomeric or dimeric material remains. The most characteristic feature of this polymer (in a strict sense it should be termed a telomer) is the absence of the *γ*-hydroxymethyl group present in its precursor *2*. This was demonstrated by recording the NMR-spectrum of the acetylated polymer. A similar polymer can be made by alkaline treatment of *γ*-coniferyl benzoate, which is believed to give primarily the quinone methide *3*.[4]

Suitable choice of the conditions of heating coniferyl alcohol in dilute sodium hydroxide (120 °C 1 h) afforded considerable amounts of dimeric material. Gas chromatography of the trimethylsilylated reaction mixture [bis(trimethylsilyl)trifluoracetamide in pyridine] showed that the dimer fraction has two major components (*A* and *B*). Small amounts of these were collected and analyzed by high resolution mass spectroscopy. The fragmentation pattern and determinations of exact masses of the molecular ion (*B*) and of a prominent fragment (*A*) suggested structures *4* and *5* for *A* and B, respectively. Compound *4* is the 1,8-addition product of the carbanion of *2* to the quinone methide *3*. Proton abstraction from solvent by the anion of *4* gives a quinone methide (*6*) which undergoes cyclization with preferential reaction by the less hindered primary hydroxyl group, yielding *5*.

p-Coumaryl alcohol reacted in the same way as *2*, giving major amounts of the non-meth-

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* Part IV of the series "Degradation of Lignin by Kraft Cooking", Part III, Ref. 2a.