ACTA CHEMICA SCANDINAVICA 25 (1971) 3441–3450

Mass Spectral Studies on Some Naturally Occurring Phloroglucinol Derivatives. Part II.* The Mass Spectra of 6-Methyl-, 6-Ethyl-, 6-Propyl-, and 6-Isopropyl-2,3-dihydropyran-2,4-diones

MAURI LOUNASMAA,[a] ** ARTO KARJALAINEN,[a] CARL-JOHAN WIDÉN[b] and AARRE HUHTIKANGAS[b]

[a] *Department of Chemistry, University of Oulu, Oulu, Finland and* [b] *Department of Pharmacognosy, University of Helsinki, Helsinki, Finland*

The mass spectrometric fragmentation of 6-methyl-, 6-ethyl-, 6-propyl-, and 6-isopropyl-2,3-dihydropyran-2,4-diones (II), (III), (IV), (V), as well as their synthetic 3-acyl intermediates (VI), (VII), (VIII), (IX), were investigated with the aid of high resolution mass spectrometry.

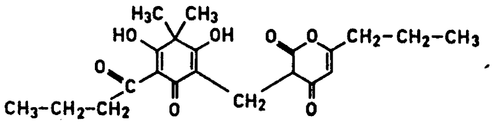
Les fragmentations en spectrométrie de masse de méthyl-6, éthyl-6, propyl-6 et isopropyl-6 dihydro-2,3 pyranediones-2,4 (II), (III), (IV), (V), ainsi que celles de leurs intermédiaires synthétiques acylés en position-3 (VI), (VII), (VIII), (IX), ont été examinées à l'aide de la spectrométrie de masse à haute résolution.

Continuing our studies of the mass spectral behavior of naturally occurring polycyclic phloroglucinol derivatives isolated from rhizomes of different *Dryopteris* species, it was desirable, although there are several publications concerning the mass spectra of pyrones,[1–3] to collect additional information on the fragmentation patterns of simple 2,3-dihydropyran-2,4-diones. This was due to the existence of the 2,3-dihydropyran-2,4-dione ring in some of the above mentioned polycyclic phloroglucinol derivatives, of which perhaps the best known is phloropyron (I).[4–6] In this paper we describe the mass spectral behavior of 6-methyl-, 6-ethyl-, 6-propyl-, and 6-isopropyl-2,3-dihydropyran-2-4-diones (II), (III), (IV), (V), as well as their synthetic 3-acyl intermediates (VI), (VII), (VIII), (IX).

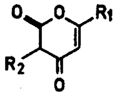
---

* Part I. *Acta Chem. Scand.* **25** (1971) 3428.

** Present address: Institut de Chimie des Substances Naturelles, 91-Gif-sur-Yvette, France.



(I)



(II) $R_1 = CH_3$, $R_2 = H$
(III) $R_1 = CH_3{-}CH_2$, $R_2 = H$
(IV) $R_1 = CH_3{-}CH_2{-}CH_2$, $R_2 = H$
(V) $R_1 = (CH_3)_2CH$, $R_2 = H$
(VI) $R_1 = CH_3$, $R_2 = CH_3CO$
(VII) $R_1 = CH_3{-}CH_2$, $R_2 = CH_3{-}CH_2CO$
(VIII) $R_1 = CH_3{-}CH_2{-}CH_2$, $R_2 = CH_3{-}CH_2{-}CH_2CO$
(IX) $R_1 = (CH_3)_2CH$, $R_2 = (CH_3)_2CHCO$

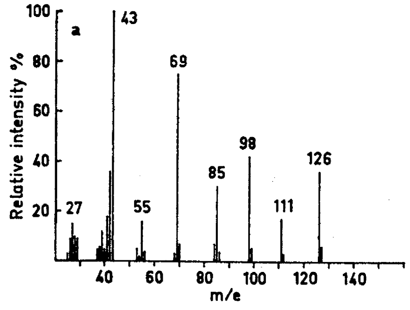


Fig. 1a. Mass spectrum (75 eV) of 6-methyl-2,3-dihydropyran-2,4-dione (II).

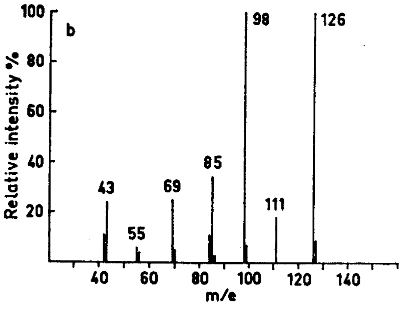


Fig. 1b. Mass spectrum (12 eV) of 6-methyl-2,3-dihydropyran-2,4-dione (II).

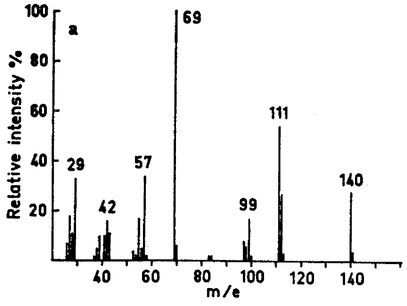


Fig. 2a. Mass spectrum (75 eV) of 6-ethyl-2,3-dihydropyran-2,4-dione (III).

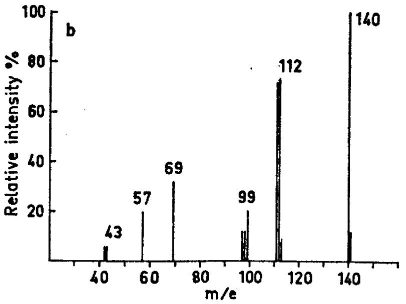


Fig. 2b. Mass spectrum (12 eV) of 6-ethyl-2,3-dihydropyran-2,4-dione (III).

The mass spectra for the compounds (II), (III), (IV) and (V) are presented in Figs. 1 – 4 and the results of accurate mass measurements in Table 1.

Table 1. High resolution measurements.

Ion (*m*/*e*)	Elemental composition	II %	III %	IV %	V %
41	C_2HO	70	70	30	25
	C_3H_5	30	30	70	75
42	C_2H_2O	95	q	80	75
	C_3H_6	5		20	25
43	C_2H_3O	q	85	30	30
	C_3H_7		15	70	70
55	C_3H_3O	q	95	q	90
	C_4H_7		5		10
57	C_3H_5O		q		
69	C_3HO_2	95	q	q	q
	C_4H_5O	5			
70	C_4H_6O			q	
71	C_4H_7O			q	q
84	$C_4H_4O_2$	q		q	q
85	$C_4H_5O_2$	q			
97	$C_5H_5O_2$		q	q	q
98	$C_5H_6O_2$	q	q	q	
99	$C_5H_7O_2$		q		
111	$C_5H_3O_3$	q	q	q	95
	$C_6H_7O_2$				5
112	$C_6H_8O_2$		q	q	q
113	$C_6H_9O_2$			q	q
126	$C_6H_6O_3$			30	
	$C_7H_{10}O_2$			70	q

The relative intensities of the ions presented in the table do not take into account the contribution of isotopic ions. Numerical values are considered accurate to ± 5 % for peaks in excess of 20 % relative abundance. The symbol q refers to a percentage superior to 95 %.

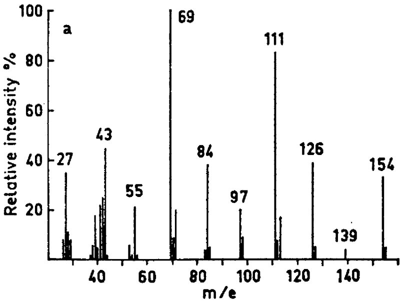


Fig. 3a. Mass spectrum (75 eV) of 6-propyl-2,3-dihydropyran-2,4-dione (IV).

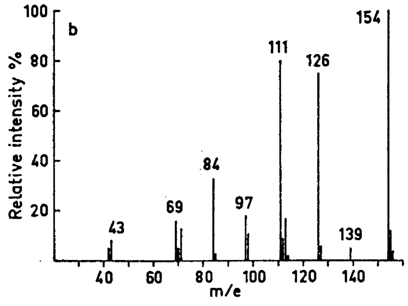


Fig. 3b. Mass spectrum (12 eV) of 6-propyl-2,3-dihydropyran-2,4-dione (IV).

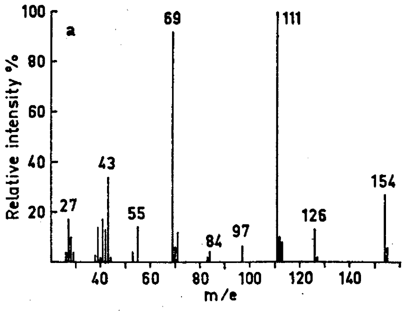


Fig. 4a. Mass spectrum (75 eV) of 6-isopropyl-2,3-dihydropyran-2,4-dione (V).

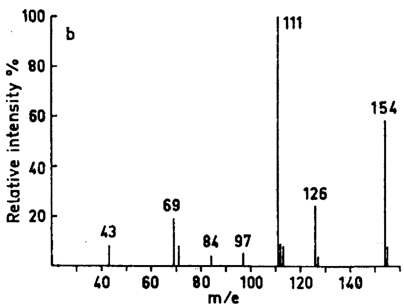
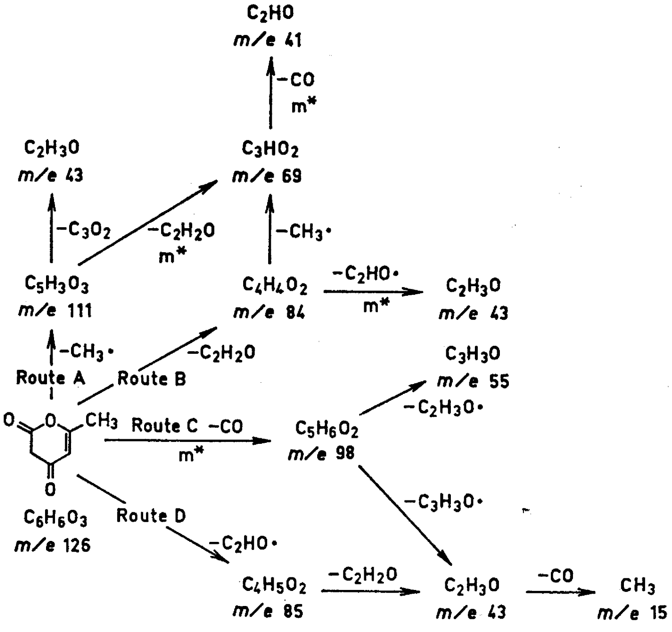


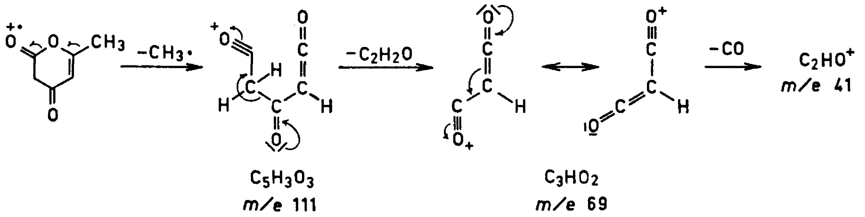
Fig. 4b. Mass spectrum (12 eV) of 6-isopropyl-2,3-dihydropyran-2,4-dione (V).

Scheme 1 shows the fragmentation mode of 6-methyl-2,3-dihydropyran-2,4-dione (II). Transitions supported by metastable peaks in the spectra are marked by m*.

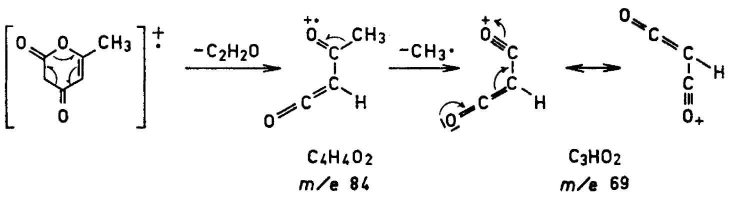


Scheme 1.

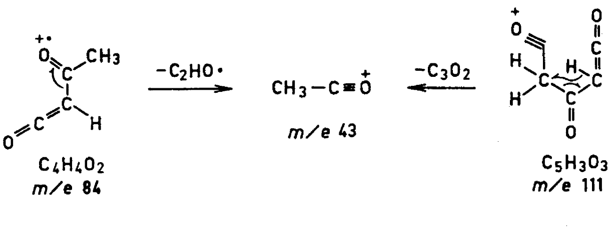
An important peak in the mass spectrum of this compound is that due to $C_3HO_2^+$ at m/e 69. A metastable peak shows that it is derived partly from the ion of m/e 111 ($C_5H_3O_3^+$), which itself is formed from the molecular ion by ejection of $CH_3\cdot$. Loss of carbon monoxide from the ion of m/e 69 leads to the C_2HO^+ ion of m/e 41.



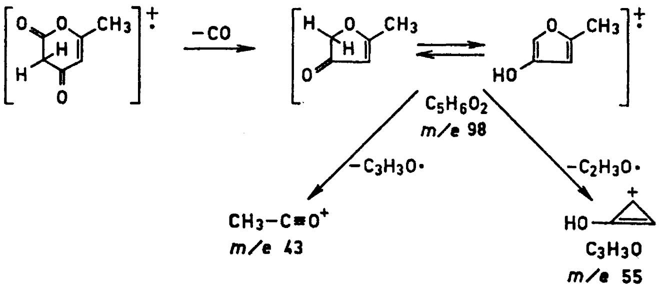
According to the general fragmentation mode of 4-pyrones proposed by several authors,[1] the formation of the resonance stabilized ion of *m*/*e* 69 may also be formulated as a retro-Diels-Alder cleavage leading to the $C_4H_4O_2^{\cdot+}$ ion (*m*/*e* 84), followed by the cleavage of CH_3. (route B). The charge remains partly on the other component, giving the $C_2H_2O^+$ ion (*m*/*e* 42). There is, however, no metastable peak present to support this fragmentation path.



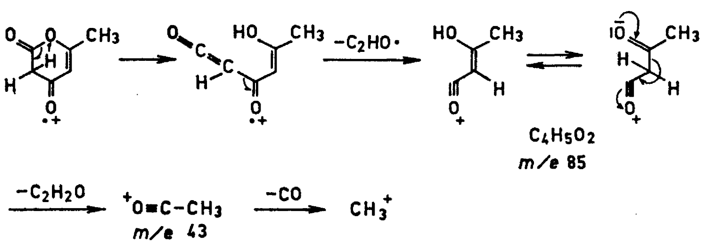
The base peak in the spectrum is that due to $C_2H_3O^+$ at *m*/*e* 43. A metastable peak suggests that this ion is derived partly from the ion of *m*/*e* 84 by loss of a C_2HO unit. The $C_2H_3O^+$ ion may also be formed by ejection of carbon suboxide from the ion of *m*/*e* 111 (route A), as well as from the ions of *m*/*e* 98 and *m*/*e* 85, as depicted in routes C and D.



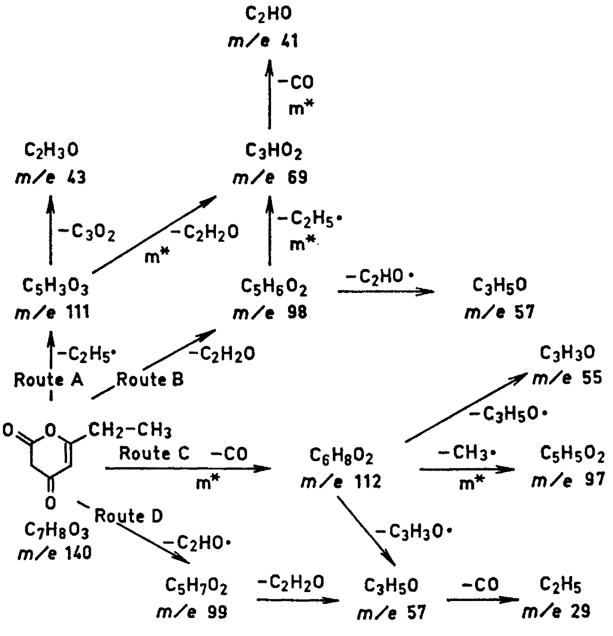
The elimination of carbon monoxide from the molecular ion (route C), leading to the $C_5H_6O_2^{\cdot+}$ ion of *m*/*e* 98 (strong metastable peak) is a process of general importance in the fragmentation of 2-pyrones.[1] In deciding the initial site of cleavage of carbon monoxide, the choice between the two carbonyl groups was made by analogy with the known fact[1] that a 2-pyrone releases carbon monoxide much more readily than a 4-pyrone.



The $C_4H_5O_2^+$ ion of *m/e* 85 is regarded as being derived from the molecular ion by loss of a $C_2HO\cdot$ radical (route D). The spectrum taken at low electron voltage (Fig. 1b) supports this view. Further loss of ketene leads to the above mentioned $C_2H_3O^+$ ion of *m/e* 43, which may eject a neutral carbon monoxide molecule.

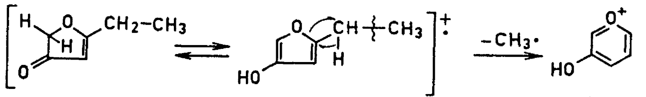


The fragmentation of 6-ethyl-2,3-dihydropyran-2,4-dione (III) differs from that of the 6-methyl compound mainly in route C (Scheme 2).



Scheme 2.

The presence of a peak at *m/e* 97 may be explained by assuming β-cleavage of the $C_6H_8O_2^{\cdot+}$ ion (*m/e* 112). This leads to a resonance stabilized ion or by ring expansion to a fully aromatic pyrylium ion.[7] In the case of the 6-methyl compound the same process would require the cleavage of a hydrogen radical, which is energetically less favored and does not take place to a detectable extent.



$C_6H_8O_2$ *m/e* 112

$C_5H_5O_2$ *m/e* 97

The base peak of the spectrum occurs at *m/e* 69 and is due to the resonance stabilized $C_3HO_2^+$ ion. The much lower intensity of the peak due to $C_2H_3O^+$ at *m/e* 43 (85 % of the total intensity of the peak at *m/e* 43) compared with the intensity in the case of the 6-methyl compound is due to the fact that in this case the ion can be formed only by the loss of carbon suboxide from the ion of *m/e* 111 (route A). The other processes mentioned above in connection with the 6-methyl compound lead to the $C_3H_5O^+$ ion of *m/e* 57, as depicted in Scheme 2.

The fragmentation of 6-propyl-2,3-dihydropyran-2,4-dione (V) is largely similar to that of the 6-ethyl compound, except, of course, for fragmentations due to McLafferty rearrangement of the side chain. The loss of carbon suboxide from the $C_5H_3O_3^+$ ion (*m/e* 111), to give the $C_2H_3O^+$ ion, is supported by a metastable peak at *m/e* 16.7. The base peak is again at *m/e* 69 and is due to the resonance stabilized $C_3HO_2^+$ ion. The peak at *m/e* 126, which according to accurate mass measurements, is a doublet, is due to $C_7H_{10}O_2^{\cdot+}$ (70 %) and $C_6H_6O_3^{\cdot+}$ (30 %). The peak at *m/e* 97, which is due to the $C_5H_5O_2^+$ ion derived from the $C_7H_{10}O_2^{\cdot+}$ ion by β-cleavage, is of higher relative intensity than that in the spectrum of the 6-ethyl compound. This is due to the more favorable cleavage of an ethyl radical than of a methyl radical. The $C_6H_6O_3^{\cdot+}$ ion is formed from the molecular ion by loss of a neutral ethylene molecule (McLafferty). Further stepwise losses of ketene lead to the $C_4H_4O_2^{\cdot+}$ ion (*m/e* 84) and the $C_2H_2O^{\cdot+}$ ion (*m/e* 42).

The loss of carbon monoxide from the $C_6H_6O_3^{\cdot+}$ ion (*m/e* 126), supported by the presence of a metastable peak, leads to the $C_5H_6O_2^{\cdot+}$ ion (*m/e* 98). Further cleavage of this ion may be depicted analogously as in the case of 6-methyl-2,3-dihydropyran-2,4-dione (II) (route C).

The fragmentation of 6-isopropyl-2,3-dihydropyran-2,4-dione (V) resembles largely the fragmentation of the other 6-alkyl compounds. The base peak of the spectrum occurs at *m/e* 111, and accurate mass measurements show that it is a doublet due to $C_5H_3O_3^+$ (95 %) and $C_6H_7O_2^+$ (5 %). The $C_5H_3O_3^+$ ion is derived from the molecular ion by ejection of $C_3H_7\cdot$, and the $C_6H_7O_2^+$ ion by β-cleavage of the $C_7H_{10}O_2^{\cdot+}$ ion (*m/e* 126) (route C).

The presence of minor quantities of 6-propyl-2,3-dihydropyran-2,4-dione (IV), as an impurity, might explain the small peak due to $C_5H_5O_2^+$ at *m/e* 97, and that due to $C_4H_4O_2^{\cdot+}$ at *m/e* 84. The peak at *m/e* 97 may partly result from rearrangement of the isopropyl side chain and subsequent β-cleavage of an ethyl radical, which is energetically more favored than the β-cleavage of a methyl radical.

An important peak at *m/e* 69, due to the resonance stabilized $C_3HO_2^+$ ion, is also present in the mass spectrum of 6-isopropyl-2,3-dihydropyran-2,4-dione (V).

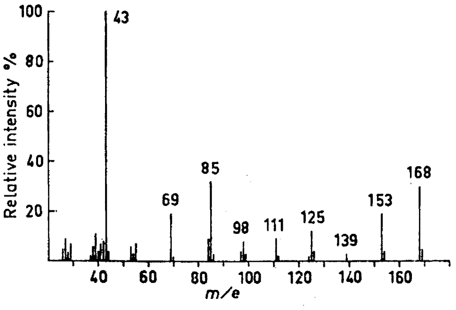


Fig. 5. Mass spectrum (75 eV) of 3-acetyl-6-methyl-2,3-dihydropyran-2,4-dione (VI).

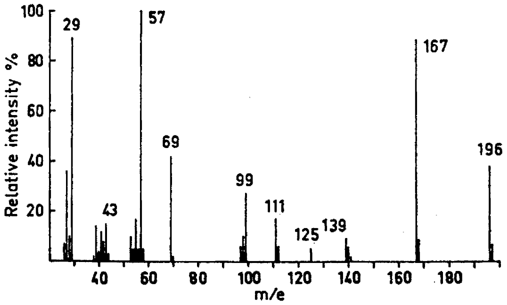


Fig. 6. Mass spectrum (75 eV) of 3-propionyl-6-ethyl-2,3-dihydropyran-2,4-dione (VII).

The fragmentations of all the 3-acyl derivatives of the 6-alkyl-2,3-dihydropyran-2,4-diones (VI), (VII), (VIII), (IX) (Figs. 5–8) are very

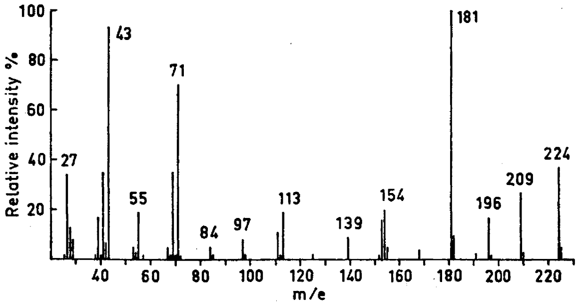


Fig. 7. Mass spectrum (75 eV) of 3-butyryl-6-propyl-2,3-dihydropyran-2,4-dione (VIII).

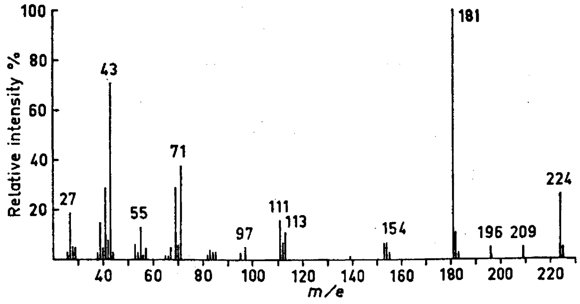
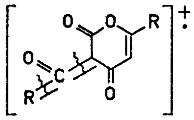
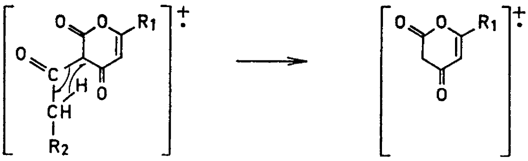


Fig. 8. Mass spectrum (75 eV) of 3-isobutyryl-6-isopropyl-2,3-dihydropyran-2,4-dione (IX).

much dominated by the 3-acyl group. The main fragmentation pattern may be explained by assuming fission of the bonds adjacent to the acyl carbonyl group (α-cleavage) and retention of the charge by either part.



The spectra show also elements of fragmentation patterns of the corresponding 6-alkyl-2,3-dihydropyran-2,4-diones due to the following rearrangement.



EXPERIMENTAL

Mass spectra were recorded on a Hitachi Perkin-Elmer RMU – 6E double-focusing mass spectrometer. The compounds (II) – (VII) were introduced *via* a direct insertion system, the compounds (VIII) and (IX) *via* an all-glass heated inlet system, with an ion chamber temperature between 100° and 130°. Low voltage studies were carried out at 12 eV nominal energy, accuracy ± 1 eV. Exact mass measurements were performed with a resolution of 10 000 (40 % valley definition).

The compounds (II) – (IX) were synthetized by the procedure of Kögl and Salemink.[8] They had the following physical properties: (II) m.p. 188 – 189° (lit.[9] m.p. 188 – 189°; lit.[10] 186 – 186.5°), (III) m.p. 99 – 102° (lit.[8] m.p. 103.5°), (IV) m.p. 94 – 95° (lit.[8] m.p. 94 – 95°), (V) m.p. 91 – 92° (lit.[8] m.p. 86°), (VI) m.p. 110° (lit.[11] m.p. 108°), (VII),m.p 70°, b.p. 106°/0.3 mm (lit.[12] m.p. 72°), (VIII) b.p. 140 – 142°/0.15 mm (lit.[8] b.p. 112 – 115°/ 0.08 mm), (IX) b.p. 128 – 130°/0.25 mm (lit.[8] b.p. 97 – 101°/0.07 mm).

One of the authors (M. L.) wishes to thank Dr. B. C. Das, at the Institut de Chimie des Substances Naturelles, Gif-sur-Yvette, France, for a fruitful discussion during a visit to Gif-sur-Yvette in autumn 1970.

REFERENCES

1. Budzikiewicz, H., Djerassi, C. and Williams, D. H. *Mass Spectrometry of Organic Compounds*, Holden-Day, San Francisco 1967, pp. 208 – 210, and references therein.
2. Brown, P. and Green, M. M. *J. Org. Chem.* **32** (1967) 1681.
3. Reed, R. I. and Takhistov, V. V. *Some Newer Phys. Methods Struct. Chem. Proc. Symp.* **1966** 39; *Chem. Abstr.* **70** (1969) 36951.
4. Penttilä, A. and Sundman, J. *Acta Chem. Scand.* **15** (1961) 893.
5. Penttilä, A. and Sundman, J. *Acta Chem. Scand.* **17** (1963) 1886.
6. Penttilä, A. and Sundman, J. *J. Pharm. Pharmacol.* **22** (1970) 393.
7. Budzikiewicz, H., Djerassi, C. and Williams, D. H. *Mass Spectrometry of Organic Compounds*, Holden-Day, San Francisco 1967, p. 617.

8. Kögl, F. and Salemink, C. A. *Rec. Trav. Chim. Pays-Bas* **71** (1952) 779.
9. Collie, J. N. *J. Chem. Soc.* **59** (1891) 607.
10. Berson, J. A. *J. Am. Chem. Soc.* **74** (1952) 5172.
11. Horning, E. C., Ed., *Org. Syn. Coll. Vol.* **3** (1955) 231.
12. v. Pechmann, H. and Neger, F. *Ann* **273** (1893) 186.

Received February 4, 1971.