

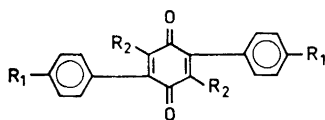
On the Mass Spectral Fragmentation of 2,5-Diphenyl-*p*-benzoquinones

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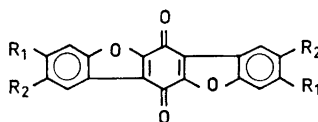
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The mass spectra of 14 2,5-diphenyl-*p*-benzoquinones are measured. The characteristics of the fragmentation patterns are discussed.

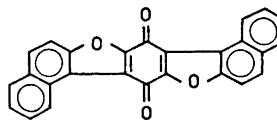
Several studies concerning the mass spectral fragmentation of benzoquinones are available.¹⁻⁹ Most of these, however, concern either relatively simple benzoquinone derivatives, or isoprenoid benzoquinones where the main interest in the fragmentation pattern is due to the side chain. In connection with an investigation of some fungal benzoquinones the mass spectra of several 2,5-diphenyl-*p*-benzoquinones were measured. Because there is, as far as we know, no systematic mass spectral investigation of this type of benzoquinones



- (I) $R_1 = R_2 = H$
- (II) $R_1 = OH; R_2 = H$
- (III) $R_1 = OCH_3; R_2 = H$
- (IV) $R_1 = H; R_2 = OH$
- (V) $R_1 = R_2 = OH$
- (VI) $R_1 = OCH_3; R_2 = OH$
- (VII) $R_1 = OH; R_2 = OCH_3$
- (VIII) $R_1 = R_2 = OCH_3$
- (IX) $R_1 = H; R_2 = Br$



- (X) $R_1 = R_2 = OCOCH_3$
- (XI) $R_1 = R_2 = OCH_3$
- (XII) $R_1 = R_2 = OSi(CH_3)_3$
- (XIII) $R_1 = OCOCH_3; R_2 = H$



(XIV)

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available (however, *cf.* Ref. 10), it seemed to us worthwhile to report the results obtained. In this paper we present the results concerning 2,5-diphenyl-*p*-benzoquinone (I), as well as 13 of its derivatives (II–XIV).

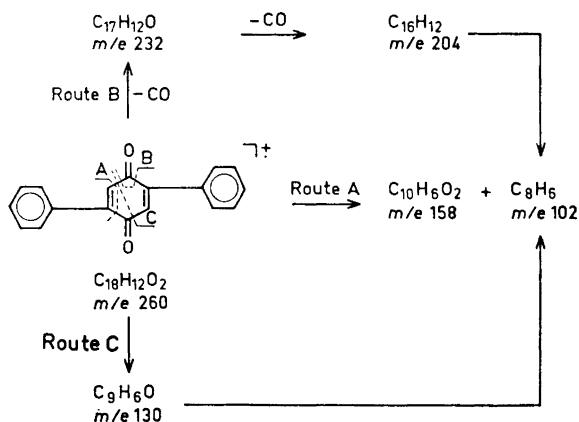
By analogy with the general fragmentation pattern of benzoquinones,¹ three initial fragmentation paths may be suggested.

Route A. Cleavage of the 1–2 and 3–4 bonds.

Route B. Elimination of carbon monoxide (eventually elimination of CHO).

Route C. Fission of the molecule into two halves due to the cleavage of the 1–2 and 4–5 bonds.

These three initial fragmentations, as well as some further cleavages, applied to the case of 2,5-diphenyl-*p*-benzoquinone (I), are presented in Scheme 1.



In the mass spectrum of 2,5-diphenyl-*p*-benzoquinone (I) (Fig. 1) Routes B and C are well represented. The absence of the peak corresponding to *m/e* 158 seems to indicate that very little fragmentation occurs according to Route A. However, the spectrum taken at low electron voltage suggests that

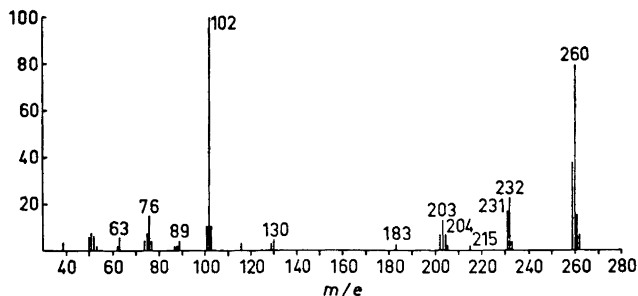


Fig. 1. Mass spectrum (70 eV) of 2,5-diphenyl-*p*-benzoquinone (I).

Table 1. Mass spectra (70 eV) of compounds (II), (III), (IV), (VI), (VIII), (X), (XI), (XII), (XIII) and (XIV). Only the ions of integral mass values having an abundance of 2% of the base peak or greater are recorded. The relative abundance is given in parenthesis.

Compound (II): m/e (%) 39(10), 40(3), 41(4), 42(3), 44(5), 46(2), 50(3), 51(7), 53(6), 55(6), 57(4), 58(12), 62(5), 63(15), 64(6), 65(5), 69(4), 73(3), 74(4), 75(4), 76(4), 77(4), 89(22), 90(5), 91(5), 109(4), 117(7), 118(100), 119(12), 121(6), 132(3), 145(4), 146(5), 147(8), 149(6), 181(3), 189(4), 199(4), 207(3), 219(4), 223(3), 235(6), 236(12), 237(4), 247(9), 248(3), 263(12), 264(13), 265(4), 275(14), 276(4), 291(14), 292(58), 293(14), 294(22), 295(7).

Compound (III): m/e (%) 39(4), 43(5), 45(6), 51(4), 60(5), 62(4), 63(12), 74(2), 75(4), 76(3), 77(2), 88(3), 89(37), 90(3), 94(2), 101(3), 102(5), 103(2), 116(3), 117(27), 118(3), 132(100), 133(9), 135(3), 138(2), 146(3), 160(5), 161(2), 178(3), 188(2), 189(4), 205(2), 206(2), 213(2), 218(3), 221(4), 233(2), 224(2), 249(11), 250(2), 258(2), 261(14), 262(4), 263(2), 264(7), 277(17), 278(4), 289(41), 290(9), 291(9), 292(12), 293(2), 305(8), 320(96), 321(22), 322(16), 323(3).

Compound (IV): m/e (%) 39(5), 51(4), 62(2), 63(6), 64(2), 65(4), 75(2), 76(3), 77(6), 78(2), 89(17), 90(7), 91(6), 102(3), 105(4), 117(2), 118(11), 119(4), 129(10), 130(2), 137(2), 145(2), 146(2), 147(3), 164(2), 173(4), 178(6), 179(3), 189(6), 207(6), 208(2), 218(3), 236(2), 245(2), 246(3), 247(2), 263(2), 264(5), 292(100), 293(19), 294(6).

Compound (VI): m/e (%) 39(10), 41(6), 43(7), 44(10), 50(8), 51(20), 53(6), 55(7), 62(7), 63(10), 65(12), 69(5), 75(5), 76(18), 77(20), 78(12), 79(8), 88(6), 89(13), 90(6), 91(7), 105(17), 108(12), 119(30), 120(18), 121(31), 122(2), 132(6), 133(22), 134(8), 135(11), 139(5), 147(14), 148(33), 149(15), 150(2), 152(6), 153(6), 159(22), 160(6), 162(10), 165(8), 175(6), 176(10), 177(7), 181(5), 188(5), 203(18), 204(2), 237(5), 244(4), 251(4), 253(4), 267(5), 281(4), 309(4), 321(3), 323(3), 324(30), 325(8), 326(3), 337(5), 352(100), 353(24), 354(7).

Compound (VIII): m/e (%) 39(11), 41(11), 43(20), 44(13), 45(4), 50(11), 51(9), 53(6), 56(9), 57(6), 58(7), 62(8), 63(9), 65(19), 74(6), 75(13), 76(40), 77(17), 78(8), 79(8), 87(7), 88(16), 89(11), 90(4), 91(6), 92(5), 104(10), 105(6), 116(8), 117(6), 118(6), 119(100), 120(13), 121(12), 131(6), 132(9), 133(11), 134(5), 135(14), 144(6), 145(7), 146(5), 147(35), 148(8), 149(10), 150(5), 151(4), 152(8), 159(17), 160(5), 161(11), 163(6), 164(7), 165(7), 175(10), 176(13), 189(6), 190(8), 191(5), 195(10), 223(21), 224(6), 235(7), 238(15), 239(4), 250(6), 251(7), 263(2), 266(6), 281(78), 282(17), 283(3), 291(4), 309(40), 310(9), 311(6), 318(5), 319(6), 320(4), 321(4), 332(2), 333(3), 334(4), 335(9), 336(5), 337(28), 338(6), 339(4), 347(11), 348(5), 349(5), 352(21), 353(6), 365(5), 380(100), 381(27), 382(16), 383(4).

Compound (X): m/e (%) 39(7), 40(5), 41(22), 42(57), 43(100), 44(25), 45(5), 58(16), 63(4), 64(22), 65(5), 66(12), 68(9), 69(7), 77(6), 79(5), 91(13), 92(3), 149(7), 172(9), 252(2), 253(6), 254(2), 255(2), 294(4), 295(2), 296(2), 336(7), 337(2), 338(2), 351(12), 352(78), 353(22), 354(11), 355(3), 378(2), 394(17), 395(6), 396(6), 397(2), 436(10), 437(4), 438(6), 439(3), 478(6), 479(3), 480(5), 481(2), 520(4), 521(2), 522(4), 523(2).

Compound (XI): m/e (%) 43(2), 44(3), 47(3), 49(2), 62(2), 69(3), 77(2), 83(17), 85(11), 87(2), 90(2), 133(2), 147(3), 149(3), 152(2), 161(7), 204(9), 205(2), 279(3), 294(2), 307(2), 309(2), 321(2), 322(3), 337(8), 347(3), 348(2), 349(2), 350(2), 365(10), 366(2), 392(2), 393(4), 394(2), 395(2), 408(100), 409(26), 410(7).

Compound (XII): m/e (%) 43(6), 44(8), 45(45), 46(4), 47(3), 57(2), 58(3), 59(5), 66(3), 73(440^a), 74(45), 75(28), 76(3), 91(3), 131(4), 133(3), 147(18), 148(3), 149(6), 229(5), 455(3), 464(7), 465(4), 537(6), 538(3), 539(2), 552(12), 553(6), 554(5), 555(2), 568(9), 569(4), 570(3), 610(2), 611(3), 612(2), 625(17), 626(9), 627(6), 628(3), 640(100), 641(58), 642(35), 643(14), 644(4).

Table 1. Continued.

Compound (XIII): m/e (%) 41(6), 42(24), 43(55), 44(6), 45(15), 50(2), 51(2), 52(2), 53(2), 55(2), 57(2), 58(2), 60(12), 74(2), 75(6), 76(2), 77(3), 79(3), 87(2), 104(3), 131(2), 149(4), 150(4), 151(3), 152(3), 179(3), 207(2), 208(2), 236(3), 263(3), 291(3), 320(100), 321(19), 322(16), 323(4), 334(38), 335(9), 336(6), 348(6), 362(11), 363(3), 364(5), 376(6), 404(4), 406(3).

Compound (XIV): m/e (%) 112(2), 124(3), 125(4), 137(14), 138(23), 166(2), 180(8), 194(10), 274(9), 275(4), 276(9), 277(2), 303(3), 304(2), 332(2), 360(2), 388(100), 389(29), 390(6).

^a m/e 640 used as base peak.

the peak at m/e 102, which in the normal spectrum represents the base peak, arises partly from the molecular ion. This indicates that the cleavage of the 1–2 and 3–4 bonds (Route A) takes place, but in this case the charge remains mainly in the acetylenic moiety. This phenomenon is a general feature in the mass spectral fragmentation of 2,5-diphenyl-*p*-benzoquinones and is especially pronounced in the cases where positions 3 and 6 are unsubstituted [compounds (I), (II) and (III)].

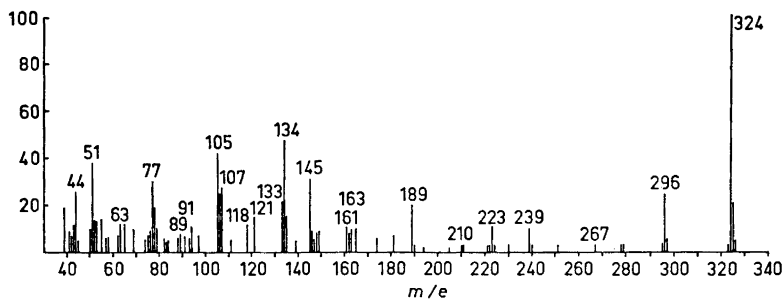


Fig. 2. Mass spectrum (70 eV) of 2,5-bis-(*p*-hydroxyphenyl)-3,6-dihydroxy-*p*-benzoquinone (V).

The mass spectra of the hydroxy-*p*-benzoquinone derivatives investigated (IV), (V), and (VI) (Fig. 2 and Table 1) show a fragmentation pattern basically analogous to that of 2,5-diphenyl-*p*-benzoquinone (I) (Fig. 1). The base peak in these spectra corresponds to the molecular ion. This is in agreement with earlier observations of Williams *et al.*,¹ concerning the mass spectral behaviour of hydroxybenzoquinones.

According to Williams *et al.*¹ the cleavage of the 1–2 and 4–5 bonds (Route C) of hydroxybenzoquinones occurs mainly with hydrogen rearrangement from the hydroxyl group. This process is also seen from the mass spectra of compounds (IV), (V), and (VI) (Fig. 2 and Table 1), by the presence of peaks at m/e 147 ($C_9H_7O_2^+$), m/e 163 ($C_9H_7O_3^+$), and m/e 177 ($C_{10}H_9O_3^+$), respectively. These hydroxybenzoquinone compounds also show peaks at m/e 173 ($C_{10}H_5O_3^+$), m/e 189 ($C_{10}H_5O_4^+$), and m/e 203 ($C_{11}H_7O_4^+$). A plausible

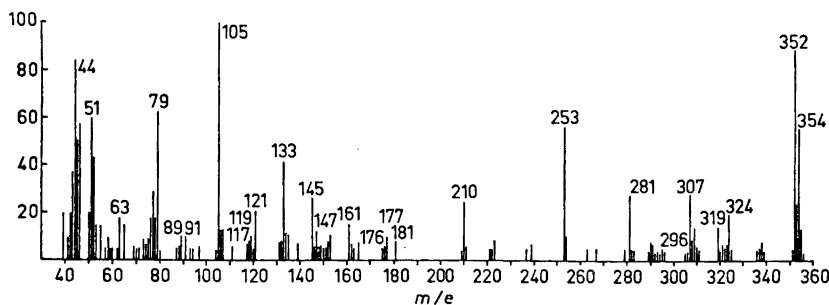


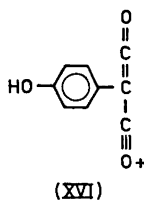
Fig. 3. Mass spectrum (70 eV) of 2,5-bis-(*p*-hydroxyphenyl)-3,6-dimethoxy-*p*-benzoquinone (VII).

explanation for these peaks is the cleavage of the 1–2 and 3–4 bonds (Route A) with hydrogen rearrangement.

The mass spectra of the methoxy-*p*-benzoquinone derivatives investigated (VII) and (VIII) (Fig. 3 and Table 1) show fragmentation patterns, where Routes A, B and C are involved. However, because the positions 3 and 6 of the quinone ring are substituted, the cleavage of the 1–2 and 3–4 bonds (Route A) (combined with the remaining of the charge in the acetylenic moiety), is much less pronounced than in the above mentioned case of 2,5-diphenyl-*p*-benzoquinone (I).

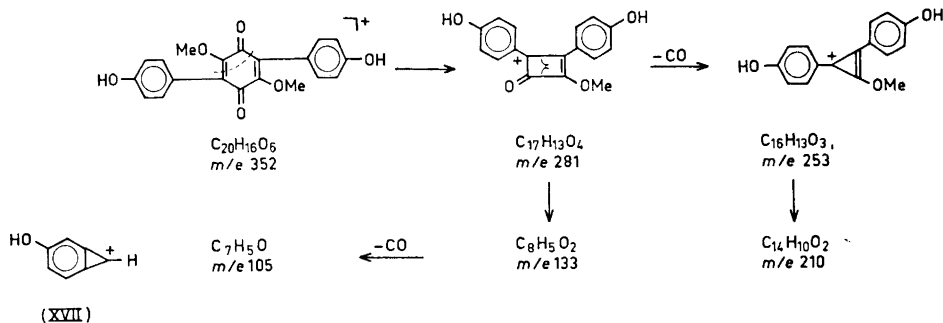
In the case of 2,5-bis-(*p*-hydroxyphenyl)-3,6-dimethoxy-*p*-benzoquinone (VII) the peaks at m/e 324 and 296 (weak) are obviously due to successive losses of carbon monoxide from the molecular ion (Route B). The initial fragmentation according to Route C is responsible for the formation of the ion $C_{10}H_8O_3^+$ (m/e 176).

Williams *et al.*¹ have pointed out that the most general feature of the spectra of methoxybenzoquinones is associated with the appearance of an ion, which, in the case of 2,5-bis-(*p*-hydroxyphenyl)-3,6-dimethoxy-*p*-benzoquinone (VII) would be (XVI) ($C_9H_5O_3^+$; m/e 161).



Williams *et al.*¹ have also found that another common process leads to pronounced $M-71$ peaks. This process arises from the formal loss of two molecules of carbon monoxide and a methyl group from the molecular ion. This process and some further fragmentations applied to the case of 2,5-bis-(*p*-hydroxyphenyl)-3,6-dimethoxy-*p*-benzoquinone (VII) are shown in Scheme 2.

A plausible representation for the ion of $C_7H_5O^+$ corresponding to the base peak at m/e 105 is the cation (XVII). As indicated by the spectra (Fig. 3 and Table 1) both these processes take place in the fragmentation of compounds (VII) and (VIII).



Scheme 2.

The mass spectrum of 2,5-diphenyl-3,6-dibromo-*p*-benzoquinone (IX) (Fig. 4) shows three molecular peaks at m/e 420, 418, and 416, the intensities of which correspond to the relative abundance of the bromine isotopes. The fragmentation of this compound is very much dominated by the presence of the two bromine atoms. The cleavage of the first bromine atom leads to the ions of m/e 339 and 337, which can then lose the second one giving rise to the ion of m/e 258. A bromine atom may also be eliminated under form of hydrogen bromide (peaks at m/e 338 and 336). The formal loss of two molecules of hydrogen bromide and two molecules of carbon monoxide from the molecular ions leads to the ion of m/e 200.

Due to the low volatility, the fungal 2,5-diphenyl-*p*-benzoquinone derivative (XVIII), known as thelephoric acid, does not give a readable mass spectrum. However, the conversion of the compound into more volatile derivatives permits its mass spectral investigation. Thus the corresponding tetra-acetate

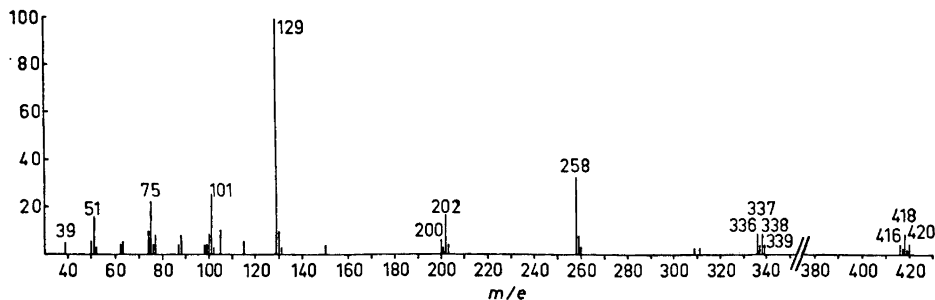
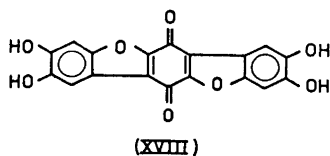


Fig. 4. Mass spectrum (70 eV) of 2,5-diphenyl-3,6-dibromo-*p*-benzoquinone (IX).

shows the molecular peak at m/e 520 (Table 1) in accordance with the proposed structure (X). The fragmentation is very much dominated by successive losses of acetoxy groups in the form of ketene, as indicated by appreciable peaks at m/e 478, 436, 394, and 352. The existence of these peaks may be used for quantitative determination of hydroxyl groups in telephoric acid (XVIII). In the mass spectrum of the corresponding tetramethyl ether (XI) (Table 1) the base peak at m/e 408 corresponds to the molecular ion. Fragmentation is very poor except for the cleavage of the $\text{CH}_3\cdot$ radical from one of the methoxyl groups followed by losses of two CO units. There is also some fission of the molecule into two halves according to Route C.



The tetra-trimethylsilyl ether derivative of telephoric acid (XII) shows a strong molecular peak at m/e 640 (Table 1). The mass spectrum exhibits only a few other peaks in the higher mass region except for the peaks at m/e 625 ($\text{M}^+ - \text{CH}_3\cdot$) and 568 ($\text{M}^+ - \text{C}_3\text{H}_9\text{Si}$). The peaks at m/e 75 and 73 (base peak), which are always observed in the mass spectra of trimethylsilyl ethers,¹¹ are caused by $(\text{CH}_3)_2\text{Si}=\overset{+}{\text{O}}\text{H}$ and $(\text{CH}_3)_3\text{Si}^+$, respectively. The peaks at m/e 147 and 59 are artifacts. The first one is due to an ion formed by expulsion of a methyl group from hexamethyldisiloxane and the second one to a small amount of acetamide present, which is formed during the preparation of trimethylsilyl ether derivative (XII) using trimethylsilylacetamide.¹²

The compound (XIII) (Table 1) shows a fragmentation pattern analogous to that of compound (X), as may be expected. Thus the main fragmentation, as indicated by the peaks at m/e 362 and 320 (base peak), consists of losses of the acetoxy group in the form of ketene from the molecular ion ($\text{C}_{22}\text{H}_{12}\text{O}_8^+$; m/e 404).

In the mass spectrum of compound (XIV) (Table 1) the base peak at m/e 388 corresponds to the molecular ion. Although the fragmentation is very poor Routes B and C can be recognized in the spectrum.

Several mass spectra examined exhibit peaks at $\text{M}+2$ due to the corresponding hydroquinones formed by dismutation reactions in the ionization chamber.^{5,9,13,14,15}

Moreover, in several cases doubly charged molecular and other ions are formed, as indicated by the presence of small peaks, due to doubly charged ^{13}C isotopic ions (not presented in the figures or in Table 1), at 1/2 mass unit higher than the corresponding fragment.¹⁶ This means that, *e.g.*, the peaks assigned above to the fission of the molecules into two halves (*cf.* Route C) are partly due to doubly charged molecular ions.

Mass spectra were recorded on a Hitachi Perkin-Elmer RMU-6E double-focusing mass spectrometer using direct sample insertion into the ion source which was at a tem-

perature between 120° and 150°. In several cases relatively high probe temperatures (about 300°) were necessary for sufficient vaporization of samples.

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