HETEROCYCLES, Vol 19, No 9, 1982

CATECHOLIC ION FORMATION FROM 5-SUBSTITUTED 2,2-DIMETHYL-1,3-BENZODIOXOLES MOLECULAR IONS

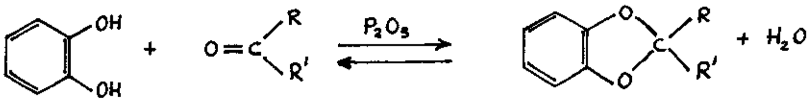
Pietro Traldi* and Umberto Vettori
Centro di Studio per le Sostanze Organiche Naturali del CNR, c/o
Dipartimento di Chimica del Politecnico, 20133 Milano, Italy

Antonio Maccioni and Gianni Podda
Istituto di Chimica Farmaceutica e Tossicologica dell'Università,
Via Ospedale 72, 09100 Cagliari, Italy

Abstract - The presence of catecholic ions in the mass spectra of 5-substituted 2,2-dimethyl-1,3-benzodioxoles is proved to originate from a primary decomposition process analogous to that observed for 2,2-disubstituted 1,3-benzoxathioles.

INTRODUCTION

It is well known that 2,2-disubstituted 1,3-benzodioxoles are easily synthesized by reaction of catechol with ketones[1], as indicated by the following equation.



The chemical cleavage of ethereal bond obtained by the action of Grignard reagents on these compounds, leads to a mixture of catechol, alkanes, alkenes and other minor unidentified products[2].

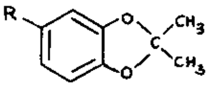
The mass spectrometric behaviour of these compounds has been already studied by Brophy et al.[3] By means of exact mass measurements the composition $C_6H_6O_2$ was found for ions at m/z 110 (the most abundant ions in the mass spectra) and metastable analysis indicated that these are formed, at least in part, from the molecular

---

*Present address: Istituto di Polarografia ed Elettrochimica Preparativa del CNR
Corso Stati Uniti 4, Padova, Italy.

ions of the benzodioxoles under study. A similar process has been observed by us for 2,2-disubstituted benzoxathioles[4]. In that case the presence of 2-hydroxybenzenthiol ions was proved by collisional activation[5] experiments and an analogy with the chemical degradative processes was also underlined.

In the present paper the mass spectrometric behaviour of six 5-substituted 2,2-dimethyl-1,3-*benzodioxoles (**1**-**6**) is described and discussed in detail with the aid* of B/E and B^2/E linked scans[6] and collisional activation experiments for structure investigations.



1 : R=H (M.W.150)

2 : R=Br (M.W.228)

3 : R=NO_2 (M.W.195)

4 : R=CH_3 (M.W.164)

5 : R=NH_2 (M.W.165)

6 : R=$NHCOCH_3$ (M.W.207)

EXPERIMENTAL

Mass spectra were run on a VG Micromass ZAB-2F instrument operating at 70 eV (200 μA). Samples were introduced via all glass heated inlet system at 150°C; the source temperature was 200°C. Metastable ions were detected by B/E and B^2/E linked scan techniques[6]. Collisional activation (CA) spectra were obtained with 7 keV ions colliding with air in the second field free region. Compounds **1** to **6** were analytically pure samples synthesized as described previously in the literature[1].

RESULTS AND DISCUSSION

The 70 eV mass spectra of compounds **1** to **6** are reported in the table.

Table

1 : *m/z* 39(26%), 40(10), 41(24), 43(54), 45(15), 51(14), 52(14), 53(9), 54(9), 55(30), 57(8), 63(15), 64(14), 65(6), 69(8), 76(14), 77(16), 81(6), 82(6), 83(21), 91(9), 92(6), 93(4), 98(9), 103(6), 104(9), 105(13), 107(5), 110(79), 111(5), 122(6), 135(100), 136(9), 150(42), 151(5).

2 : *m/z* 39(26%), 41(35), 43(45), 44(38), 51(29), 62(10), 63(38), 79(9), 81(8), 109(7), 188(78), 190(76), 213(100), 215(98), 228(59), 230(57).

3 : *m/z* 39(40%), 40(8), 41(50), 43(37), 51(17), 53(7), 55(9), 62(11), 63(28), 79(9), 81(10), 91(9), 92(12), 93(8), 109(6), 110(5), 111(12), 124(24) 134(51), 155(19), 179(5), 180(100), 181(10), 195(39), 196(4).

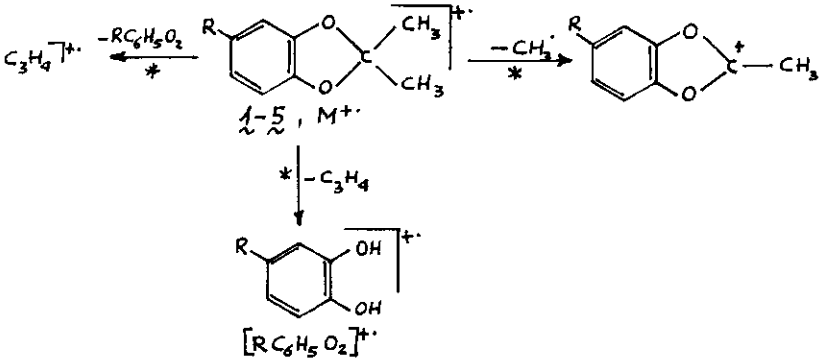
4 : *m/z* 39(30%), 40(15), 41(16), 43(44), 51(31), 52(11), 63(6), 65(6), 66(5), 67

(6), 77(16), 78(40), 79(4), 105(4), 106(20), 107(5), 121(7), 123(18), 124(38), 149(100), 150(10), 164(47), 165(5).

5 : m/z 39(31), 40(33), 41(35), 43(34), 51(16), 52(46), 53(11), 79(67), 96(15), 107(6), 122(12), 124(22), 125(100), 126(7), 150(79), 151(7), 165(84), 166(9).

6 : m/z 50(19%), 51(32), 52(29), 69(15), 77(16), 78(15), 79(43), 91(9), 107(5), 122(16), 124(34), 125(98), 150(100), 151(18), 165(52), 166(7), 192(36), 207(85), 208(9).

As it can be observed, only three intense ions are present, due to $M^{+\cdot}$, $M-CH_3]^+$ and $RC_6H_5O_2]^{+\cdot}$ species. B/E linked scans show the following fragmentation pattern, valid for compounds 1 to 5 only.



Compound 6 shows a primary loss of ketene giving rise to ions at m/z 165 which undergo a similar fragmentation of the molecular ions of 5.

The process due to C_3H_4 loss is very favourable, on the contrary to what observed for 2,2-disubstituted 1,3-benzoxathioles[4], and we have thought interesting to deepen it. First of all it must be underlined that the formation of $RC_6H_6O_2]^{+\cdot}$ ions from benzodioxoles in EI conditions is a primary decomposition process involving the hydrogen atoms of both the 2-methyl groups. This is proved by B^2/E linked scans on these ions (see, for example, figure 1) which indicate the only precursor of these species to be the corresponding molecular ions.

Secondly , the structure of these ions corresponds to that of 4-substituted catechols, as proved by collisional activation experiments (see, for example, fig. 2).

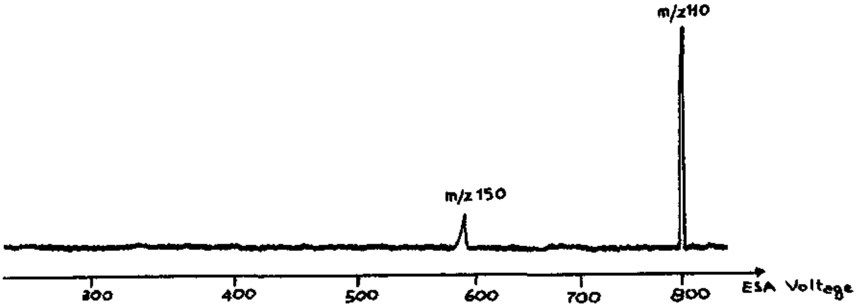


Figure 1. B^2/E linked scan spectrum of m/z 110 ion originating from $M^{+\cdot}$ of compound 1.

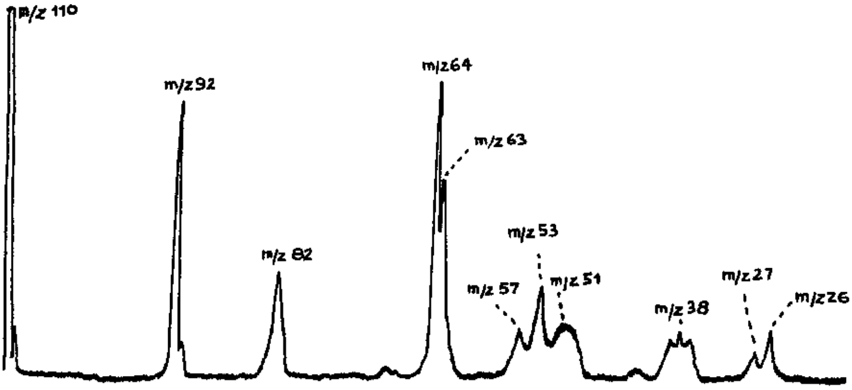
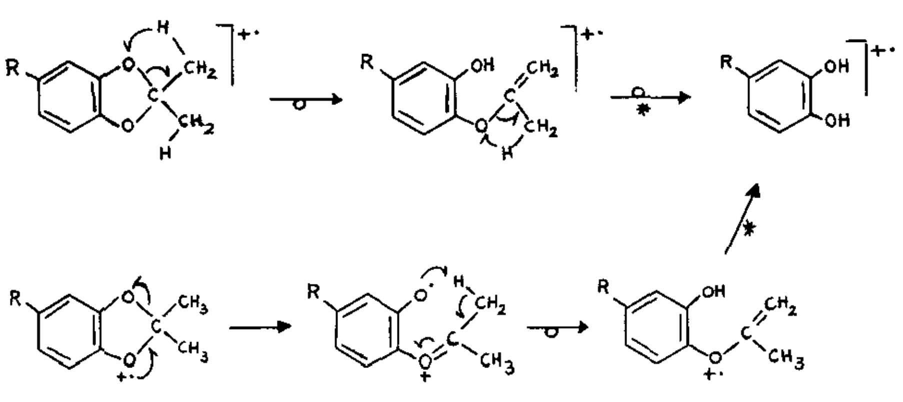


Figure 2. Collisional activation spectrum of m/z 110 ion originating from $M^{+\cdot}$ of compound 1, identical to that of $M^{+\cdot}$ of catechol.

Then we suggest for the formation of these ions the following mechanisms:



Analogously to the 1,3-benzoxathioles, the four center mechanism is suggested by the presence of a wide metastable peak corresponding to this transition in the

MIKE spectra of these compounds.

Finally, the primary $CH_3^{\cdot}$ loss leads to a very stable cation. It is to underline how this cation is stable in solution chemistry also, as reported in literature[7], giving a good correspondence between the data obtainable by mass spectrometry and those of solution chemistry.

REFERENCES

1. G.Sloof, Rec.Trav.Chim., 1935, **54**, 995.
2. S.Cabiddu, A.Maccioni and M.Secci, Ann.Chim.(Rome), 1971, **61**, 432.
3. J.J.Brophy, G.Crank, H.Minh and D.Nelson, Org.Mass Spectrom., 1980, **15**, 435.
4. P.Traldi, U.Vettori, A.Maccioni and G.Podda, Org.Mass Spectrom., in press.
5. K.Levsen and H.Schwartz, Angew.Chem.Internat.Edn., 1976, **15**, 509.
6. A.P.Bruins, K.R.Jennings and S.Evans, Int.J.Mass Spectrom.Ion Phys., 1978,**26**,395.
7. K.Dimroth, P.Heinrich and K.Schromm, Angew.Chem., 1965, **77**, 873;
   D.A.Tomalia, Brev.U.S., 1968, 68-17;
   H.Volz and G.Zimmermann, Tetrahedron Letters, 1970, 3597.

Received, 20th February, 1982