Tetrahedron Letters No. 45, pp 4329 - 4332, 1971. Pergamon Press. Printed in Great Britain.

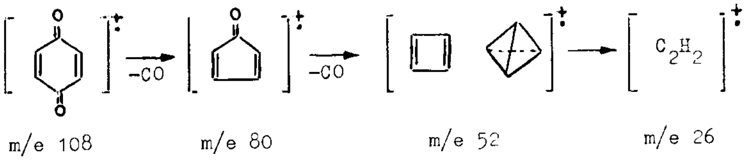
THERMOLYSIS OF QUINONES. THE FLASH-VACUUM THERMOLYSIS OF p-BENZOQUINONE

H.J.HAGEMAN AND U.E.WIERSUM

(AKZO Research Laboratories Arnhem,Corporate Research Department,The Netherlands)

(Received in UK 1 October 1971; accepted for publication 8 October 1971)

Recently we reported[1] the flash-vacuum thermolysis of phenyl-p-benzoquinone. The formation of the major product,naphthalene,was visualised to take place following the loss of two CO molecules from phenyl-p-benzoquinone via intramolecular trapping of either a butadiene diradical,cyclobutadiene,or tetrahedrane by the phenyl group. This process appeared to be reminiscent of the stepwise loss of CO molecules in the mass spectrum of phenyl-p-benzoquinone (parent ion m/e 184),which showed fragment ions m/e 156 (M-CO),and m/e 128 (M-2 CO). This stepwise loss of two CO molecules to C_4H_4 appears to be a general mass fragmentation pathway for p-benzoquinones[2-4]. In the case of p-benzoquinone itself the following scheme has been implied:

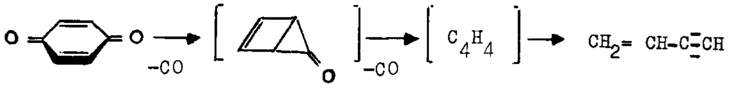


The thermolysis pattern of phenyl-p-benzoquinone to naphthalene (formally a C_4H_3R species) and the electron-impact fragmentation of p-benzoquinone made it of interest to study the flash-vacuum thermolysis of p-benzoquinone itself, in order to trap a possible C_4H_4 species at low temperature. The structure of this species is highly interesting because cyclobutadiene and tetrahedrane are possible candidates,although there is evidence that vinylacetylene is a more stable isomer[5,6].

If the loss of CO molecules takes place in a stepwise manner it must also be considered that cyclopentadienone is a transient intermediate. It has been reported[7] that the flash-vacuum thermolysis of o-benzoquinone at ca.800°C gives a fair yield of 1,8-diketo-4,7-methano-3a,4,7,7a-tetrahydroindene, indicating that in this type of thermolysis the transient cyclopentadienone dimerises rather than loses a further CO molecule.[*]

p-Benzoquinone was flash-thermolysed at 850°C in vacuo.[†] Traces of acetylene were observed. Analysis of the liquid product mixture trapped at low temperature (liq.N_2) showed it to consist of vinylacetylene (70 %),benzene (15.6 %), styrene (8.8 %),phenylacetylene (1.8 %),indene (2.0 %),and a number of other minor products of which toluene and naphthalene were identified. Since no cyclopentadienone dimer was formed in any of our experiments,the conclusion seems inescapable that cyclopentadienone is not intermediary formed in the flash-vacuum thermolysis of p-benzoquinone. This means that the thermolytic degradation of o-,and p-benzoquinone must proceed along fundamentally different pathways.

The question can be raised now whether the vinylacetylene arises from acetylene formed by direct fragmentation of p-benzoquinone. However,since in our hands acetylene formed in other thermolytic processes,e.g. thermolysis (same conditions) of maleic anhydride[9,10] was never accompanied by vinylacetylene,this reaction path can be discounted.[‡] This means that at least one new C-C bond must have been formed before both CO molecules have been expelled, i.e. at some intermediary (cyclic) stage. Excluding then cyclopentadienone we



(I)

feel that a possible cyclic intermediate as bicyclo[2.1.0]pent-4-en-2-one (I) is likely to give a C_4H_4 species (butadiene diradical,cyclobutadiene,or tetrahedrane) ultimately leading to vinylacetylene.

Bicyclo[2.1.0]pent-4-en-2-one intermediates have been considered before in comparable processes[12-15]. It has also been reported[16,17] that cyclopropenones and cyclopropanones lose CO thermally under mild conditions. The acetylene (traces) observed may arise via decomposition of the C_4H_4-precursor. The formation of benzene, styrene, and the other minor products is interesting but as yet obscure[5,11].

A study of the thermolysis of substituted p-benzoquinones is presently under way in order to obtain a more detailed insight in the reaction mechanism.

---

[*] Very recently Chapman and McIntosh[8] have isolated cyclopentadienone in monomeric form at low temperature from o-benzoquinone.

[†] The thermolysis was carried out in a 12 in. unpacked quartz column, externally heated by a tubular furnace (pressure 0.1 mm). The thermolysate was rapidly quenched on the surface of a trap cooled in liq.N_2, closely coupled to the hot zone. The conversion of the p-benzoquinone at 800°C was negligible, while at 850°C the conversion amounted to ca. 50 %.

[‡] Moreover, thermal oligomerisations have been reported only with energy-rich acetylenes to give mainly cyclic trimers and tetramers besides polymers. Cf.ref.11

REFERENCES

1 H.J.Hageman, and U.E.Wiersum, Chem.Commun., 497 (1971)

2 J.H.Beynon, and A.E.Williams, Appl.Spectroscopy, 14, 156 (1960)

3 J.H.Bowie, D.W.Cameron, R.G.F.Giles, and D.H.Williams, J.Chem.Soc.(B), 335 (1966)

4 T.A.Elwood, and M.M.Bursey, Org.Mass Spectrometry, 1, 537 (1968)

5 E.Hedaya, I.S.Krull, R.D.Miller, M.E.Kent, P.F.D'Angelo, and P.Schissel, J.Amer.Chem.Soc., 91, 6880 (1969)

6 P.B.Shevlin, and A.P.Wolf, J.Amer.Chem.Soc., 92, 406 (1970)

7 D.C.DeJongh,R.Y.VanFossen,and C.F.Bourgeois,Tetrahedron Letters,271,(1967)

D.C.DeJongh,and D.A.Brent, J.Org.Chem.,35,4204 (1970)

8 O.L.Chapman,and C.L.McIntosh, Chem.Commun.,770 (1971)

9 F.O.Rice,and M.T.Murphy, J.Amer.Chem.Soc.,64,896 (1942)

10 A.L.Brown,and P.D.Ritchie, J.Chem.Soc.(C),2007 (1968)

11 R.Fuks,and H.G.Viehe,Ch.8,p.450 in "Chemistry of Acetylenes" (Ed.H.G.Viehe), Marcel Dekker, New York,1969

12 E.Hedaya,M.E.Kent,D.W.McNeil,F.P.Lossing,and T.McAllister, Tetrahedron Letters,3415 (1968)

13 G.Maier,G.Fritschi,and B.Hoppe, Angew.Chem.,82,551 (1970)

14 H.Ona,H.Yamaguchi,and S.Masamune, J.Amer.Chem.Soc.,92,7495 (1970)

15 G.Maier,G.Fritschi,and B.Hoppe, Tetrahedron Letters,1463 (1971)

16 R.Breslow,T.Eicher,A.Krebs,R.A.Peterson,and J.Posner, J.Amer.Chem.Soc.,87,1320 (1965)

R.Breslow,L.J.Altman,A.Krebs,E.Mobacsi,I.Murata,R.A.Peterson,and J.Posner, J.Amer.Chem.Soc.,87,1326 (1965)

R.Breslow,and G.Ryan,J.Amer.Chem.Soc.,89,3073 (1967)

17 N.J.Turro,P.A.Leermakers,H.R.Wilson,D.C.Neckers,G.W.Byers,and G.F.Vesley, J.Amer.Chem.Soc.,87,2613 (1965)