Tetrahedron Letters,Vol.27,No.39,pp 4779-4782,1986 0040-4039/86 $3.00 + .00
Printed in Great Britain Pergamon Journals Ltd.

EVIDENCE FOR THE FORMATION OF 1,3- AND 1,4-DEHYDROBENZENES IN THE THERMAL DECOMPOSITION OF DIARYLIODONIUM-CARBOXYLATES

F. Gaviña*, S.V. Luis, V.S. Safont, P. Ferrer and A.M. Costero
Departamento de Química Orgánica, Colegio Universitario de Castellón
Universidad de Valencia, Castellón de la Plana, Spain

Abstract: Generation of m- and p-benzynes in decomposition of diaryliodonium- 3- and 4-carboxylates is demonstrated by three-phase method.

In contrast with the wide number of investigations devoted to the study of the appearance, properties and reactivity of 1,2-dehydrobenzenes (o-arynes) and their polycyclic and heterocyclic analogues[1,2], studies concerning the related 1,3- and 1,4-dehydroarenes have been comparatively limited[2]. For these species, two different structures must be considered, as shown for the parent compounds, 1,3-dehydrobenzene (m-benzyne), I, and 1,4-dehydrobenzene (p-benzyne), II, where besides the respective biradicalic structures (Ia, IIa) the bicyclic (3.1.0) hexatriene (Ib) and butalene (bicyclo(2.2.0)hexatriene, IIb) can be postulated[3]:

Ia **Ib** **IIa** **IIb**

CHART I

Experimental evidence for the generation of a biradicalic 1,4-dehydrobenzene (IIa) in the rearrangement of cis-1,5-hexadiyn-3-ene has been reported by Bergman[4] and the formation of butalene (IIb) from Dewar chlorobenzenes was described by Breslow[5], while a route to bicyclo (3.1.0)hexatriene (Ib) from 4,6-dihalo-2-bicyclo(3.1.0)hexene has been explored by Washburn[6]. However, studies on the formation of such species in 1,3- and 1,4-elimination or fragmentation reactions from benzene derivatives (the most general approach for o-arynes) are limited to the photoinitiated[7] or thermal[8] decomposition of diazonium benzene 3- and 4-carboxylate and some of the results are yet inconclusive.

Connected with our work on o-arynic species[9] and the use of the unambiguous three-phase test for the detection of reactive intermediates[10] we have initiated the study of m- and p-arynes and now we report here the detection of 1,3- and 1,4-dehydrobenzene in the thermal decomposition in solution of diaryliodonium 3- and 4-carboxylates (III and IV, Chart II). These precursors were prepared as

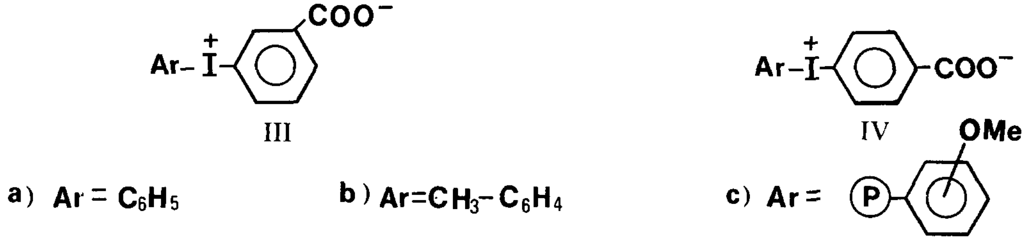
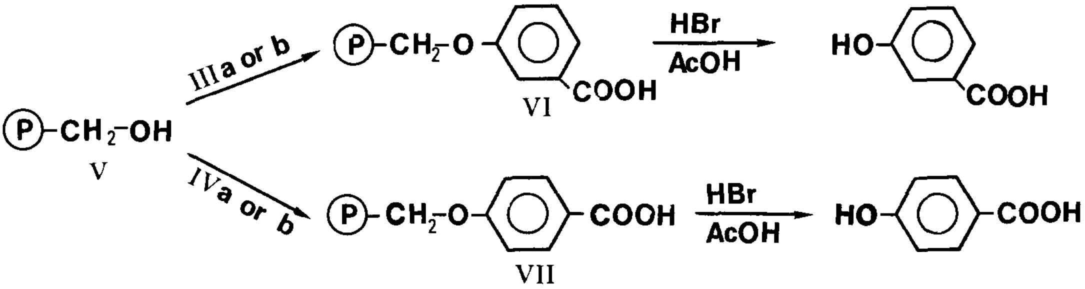


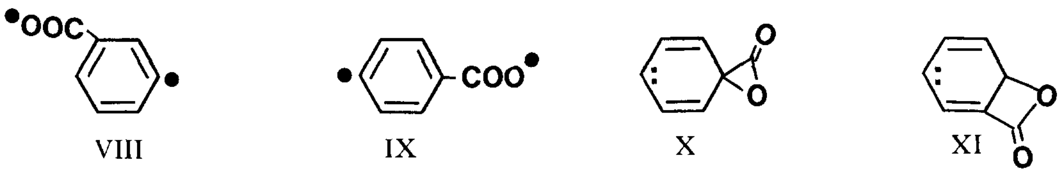
CHART II

described for the related o-compounds[9,11]. For polymers IIIc and IVc, the starting material was a Merrifield's resin (2.3 mmol Cl/g) and both of them were obtained with a functionalization degree of about 1.2-1.3 mequiv/g. A hydroxybenzylic polymer (V) prepared from the same chloromethylated polymer (2.4 mequiv/g) was chosen as a adequate trapping agent. When either IIIa, IIIb, IVa or IVb were heated in diglyme (150-160ºC) in the presence of V[12], the respective m- or p-hydroxybenzoic acid was isolated after hydrolysis of the resulting polymers (VI and VII, Scheme I). Phenol which should be the expected product from the trapping of I or II was not detected in any case. Direct nucleophilic attack by the polymer on the diaryliodonium salt could explain this result[13],



SCHEME I

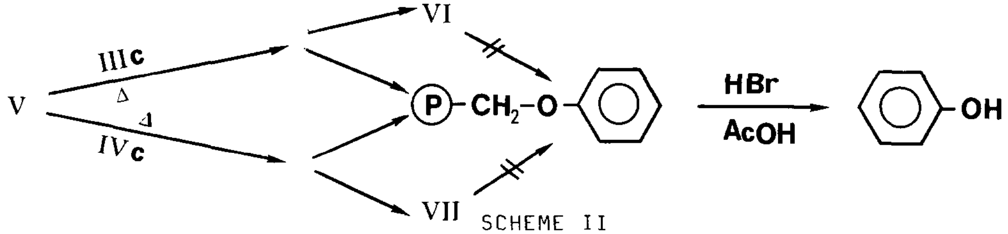
but the absence of substitution on the other arylic moiety as shown by the non appearance of phenol (from IIIa and IVa) or p-cresol (from IIIb and IVb) after hydrolysis, seems to exclude this possibility. So, the general mechanism for this kind of reactions[13b,c] via radical intermediates must be considered. The biradical intermediates VIII and IX (Chart III) can explain the obtention of hydroxybenzoic acids and also the formation of a complex mixture of polymeric esters as the main product in the thermal decomposition of diaryliodonium compounds III and IV. Another possibility is that the intermediates are carbenes like X or XI, which undergo slow decarboxylation[7].



VIII IX X XI

CHART III

Resins IIIc and IVc were used as precursors in three phase experiments where intermediates are liberated from polymer-bound precursors and pass through the solvent to a second polymer in which they are trapped. Direct reaction between the trapping resin and precursor is excluded. In our case, the hydrolysis of the trapping polymer (V) yielded a mixture of hydroxyacid (3- or 4-) and phenol (Scheme II), where the first one was always in excess over phenol (about 5:1).



SCHEME II

These results confirm the intermediacy of species as the indicated in Chart III, while the formation of the benzyl phenyl ether functionality on the trapping resin requires the occurrence of the species I and II as free intermediates in solution[14]. Both, 1,3- and 1,4-dehydrobenzene intermediates are most likely generated in this process through decarboxylation of species VIII-XI. Concerted fragmentation from betaines III or IV to give I or II seems to be excluded as a main pathway by the absence of any detectable amounts of I or II in the two-phase experiments. These results also suggest that the generation of dehydrobenzenes from VIII - XI is a relatively slow process compared to the trapping of these species by the hydroxybenzylic polymer V. So, only in three phase experiments, with higher dilution conditions which will favour unimolecular decomposition of VIII - XI over intermolecular processes and were the reaction of the intermediate with the trapping resin is delayed, at least some tenths of a second[10c], the species I and II are formed and reach the reactive sites of the second resin in an amount enough to be detected.

Thus, according to previous experimental work on these intermediates, our own data seems likely to agree better with a biradicalic structure for I and II. More detailed studies on this subject and on the complete mechanisms of this processes are in progress.

ACKNOWLEDGEMENT

Finantial support for this work was provided by the Comisión Asesora de Investigación Científica y Técnica. Project No 1470/82

REFERENCES AND NOTES

1. a) Hoffmann, R.W.; "Dehydrobenzene and Cycloalkynes", Academic Press, New York 1967; b) Reinecke, M.G.; Tetrahedron, 38, 427 (1982)
2. Levin, R.H. "Reactive Intermediates", Jones, M.; Moss, R.A. Eds J. Wiley, New York, vol I, pp 1-26 (1978); II, pp 1-14 (1981); III, pp 1-18 (1985)
3. a) Noell, J.O.; Newton, M.D.; J. Am. Chem. Soc., 101, 51 (1979); b) Malar, E.J.P.; Jug, K.; Tetrahedron, 42, 417 (1986)
4. a) Lockhart, T.P.; Comita, P.B.; Bergman, R.G., J. Am. Chem. Soc., 103, 4082 (1981); b) Lockhart,T.P., Bergman, R.G.; J. Am. Chem. Soc., 103,4091 (1981)
5. Breslow, R.; Napierski, J.; Clarke, T.C.; J. Am. Chem. Soc., 97, 6275 (1975)
6. Wshburn, W.N.; Zahler, R.; Chen, I.; J. Am. Chem. Soc., 100, 5863 (1978)
7. Berry, R.S.; Clardy, J.; Schafer, M.E., Tetrahedron Lett., 1003, 1011 (1965)
8. Hoyos de Rossi, R.; Bertorello, H.E.; Rossi, R.A.; J. Org. Chem., 35, 3328, (1970); ibid, 36, 2905 (1971)
9. Gaviña, F.; Luis, S.V.; Costero, A.M.; Gil, P.; Tetrahedron, 42, 155 (1986)
10. Rebek, J.Jr; Gaviña, F.; J. Am. Chem. Soc., 97, 3453 (1975)
11. Beringer, F.M.; Lillien, I.; J. Am. Chem. Soc., 82, 725 (1960)
12. In our experiments a 2-3 times excess of the precursor III or IV was always used.
13. a) Beringer, F.M.; Brierley, A.; Drexler, M.; Grindler, E.M., Lumpkin, C.C.; J. Am. Chem. Soc., 75, 2708 (1953); b) Beringer, F.M.; Falk, R.A.; J. Chem. Soc., 4442 (1964); c) Gronowitz, S., Holm, B.; Tetrahedron, 33, 557 (1977)
14. Decarboxylation of polymeric benzylcarboxyphenyl ether to give polymeric benzylphenyl ether has to be excluded. Heating in the same conditions of the former resin, even for longer periods of time did not produce any decarboxylation product. In the same way, the conversion of hydroxybenzoic acids to phenol did not occur in the hydrolysis process, even in more drastic conditions

(Received in UK 8 July 1986)