

The Role of [^2H]-Labelling in the Determination of the Mechanism of Formation of Benzyne from Benzenediazonium Acetate

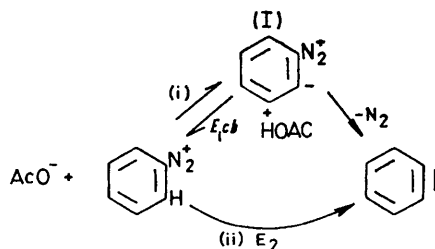
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Summary Contrary to a recent report,¹ we find that [^2H]-[^1H] exchange does not occur during the formation of [$^2\text{H}_2$]- and [^2H]-benzynes from [2,4,6- $^2\text{H}_3$]- and [2- ^2H]-benzenediazonium acetates in the presence of acetic acid.

THAT benzyne is formed by acetate ion-induced elimination from the benzenediazonium ion is now well established.² There remained the question of whether this elimination proceeds stepwise (E_{1cb}) via the betaine (I),^{2,3} by analogy with the corresponding dehydrochlorination of chlorobenzene via the *o*-chlorophenyl anion, or via concerted E_2 elimination without the intermediacy of the betaine (I),⁴ no firm evidence having been provided for either route.

We report the results of experiments using deuteriated benzenediazonium salts which have a bearing on this problem.



In theory, the use of [2,4,6- $^2\text{H}_3$]benzenediazonium acetate in the presence of acetic acid should lead to the loss of one g atom of deuterium only, if E_2 elimination is occurring

[equation (2)], but to more than one g atom of deuterium in the case of the alternative route E_{1cb} , on the assumption that the diazonium cation would undergo D-H rapid exchange with acetic acid via the betaine (I) [equation (1)].

We report that the reaction of [2,4,6- $^2\text{H}_3$]-*N*-nitrosoacetanilide (99% [$^2\text{H}_3$]) in benzene in the presence of tetraphenylcyclopentadienone (1 mol) and acetic acid (2 mol) gave 1,2,3,4-tetraphenylnaphthalene (11%), which had lost only one g atom of deuterium (99% [$^2\text{H}_2$]), and biphenyl (20%) from which no deuterium had been lost (99% [$^2\text{H}_3$]). Comparable results were obtained from reactions of [2,4,6- $^2\text{H}_3$]benzenediazonium fluoroborate in benzene or dichloroethane in the presence of potassium acetate, acetic acid, and tetraphenylcyclopentadienone, or anthracene. Moreover decomposition of [^1H]benzenediazonium fluoroborate in benzene in the presence of potassium acetate, mono-deuterioacetic acid ($\text{CH}_3\text{CO}_2\text{D}$), and tetraphenylcyclopentadienone led to the isolation of 1,2,3,4-tetraphenylnaphthalene containing no deuterium, within experimental error. These results show that only one deuterium atom is being removed in the formation of [$^2\text{H}_2$]-benzyne and that no D-H exchange with acetic acid present in the mixture is taking place. Corresponding reactions with [2- ^2H]benzenediazonium fluoroborate (92% [$^2\text{H}_1$]) in benzene or 1,2-dichloroethane gave biphenyl (92% [^2H]) in the former case, and 1,2,3,4-tetraphenylnaphthalene (55% [^2H]) or triptycene (58% [^2H]).

The simplest interpretation of these results is that reaction proceeds via an E_2 elimination. The alternative E_{1cb} route, via the betaine (I) is only tenable if it is assumed that hydrogen exchange between (I) and acetic acid is very slow compared with its decomposition via nitrogen loss to give benzene.

Publication of our results at this time has been prompted by the very recent report by Buxton and Heaney¹ of an investigation using [2-³H]benzenediazonium chloride (81% [2-³H]), potassium acetate, acetic acid, and anthracene in dichloroethane. These workers reported considerable D-H exchange in the triptycene (18% [³H]) produced in this reaction, which is directly contrary to our observations, and hence concluded that an *E,cb* mechanism *via* the betaine (I) was operative.

After discussion with Dr. Heaney, repetition of this experiment in our laboratory using 2-[³H]benzenediazonium

chloride (94% [³H]) led to triptycene containing 63% [³H], which is at variance with Buxton and Heaney's results but in accord with our earlier experiments. The less than 50% loss of [³H] observed in our case is in accord with the operation of an isotope effect in favour of [¹H].

Dr. Heaney has kindly informed us that a repetition of his experiment in his laboratory has now produced results identical with ours.⁵

(Received, 16th November 1973; Com. 1583.)

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³ J. I. G. Cadogan, *Accounts Chem. Res.*, 1971, 4, 186.

⁴ C. Rüchardt and C. C. Tan, *Angew. Chem. Internat. Edn.*, 1970, 9, 522.

⁵ P. C. Buxton and H. Heaney, Personal communication.