

# Acid-catalysed decomposition of diazofluorene<sup>†</sup>

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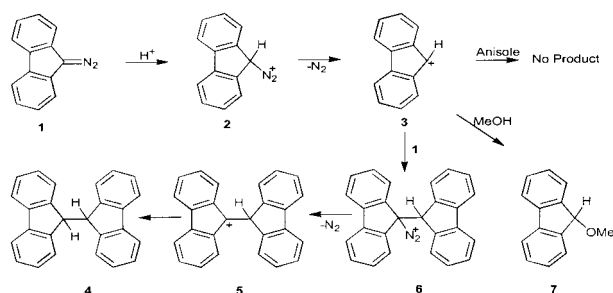
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Upon irradiation, diazofluorene undergoes reductive dimerisation to give 9,9'-bifluorene through the intermediacy of a carbene intermediate and treatment of diazofluorene with Lewis or Brønsted acids also yields the same product, but through the intermediacy of a cation intermediate.

Aryldiazoalkanes produce triplet carbenes in solution.<sup>1-6</sup> Triplet aryl carbenes abstract hydrogen from solvents with the formation of radicals and products of radical recombination.<sup>7</sup> The photolysis of diazofluorene in cyclohexane solution, for example, afforded 9-cyclohexylfluorene and 9,9'-bifluorene.<sup>8</sup> However, such dimerisation in the presence of acid catalysts has not been reported earlier.

In this article, we report a comparative study of reductive dimerisation of diazofluorene under photochemical conditions and in the presence of acid catalysts. Irradiation of diazofluorene in hexane or a mixture of hexane and methanol gave 9,9'-bifluorene (**4**) through the intermediacy of the 9-fluorenyl radical. We have now observed that the treatment of a hexane solution of diazofluorene with either toluene-*p*-sulfonic acid or anhydrous AlCl<sub>3</sub> also gives **4** as the only product. When the reaction was repeated in the presence of methanol (one equivalent) and toluene-*p*-sulfonic acid, 9-methoxyfluorene (**7**) and 9,9'-bifluorene (**4**) were obtained in a 57:43 ratio. Attempted reactions in methanol or a mixture of methanol and hexane, but in the absence of acid catalyst, did not yield any new product. Diazofluorene was isolated in near-quantitative amounts even after prolonged stirring. These observations indicate the probable involvement of the fluorenyl cation intermediate **3** in the reductive dimerisation of diazofluorene. It is interesting to note that cation **5** is not trapped either by methanol or diazofluorene under the conditions selected by us. We attribute the reluctance of **5** to undergo further reactions, including E1 elimination to yield 9,9'-bifluorenyl, to steric reasons. Based on our results, it is not possible to establish the exact nature of the hydride transfer to **5**. Our attempts to gain further evidence for the involvement of fluorenyl cation **3**, and thereby to develop an attractive route to commercially-important triaryl-methane derivatives, by trapping experiments with a reactive aromatic compound such as anisole, were not successful.

A possible mechanism for the formation of various products under acid-catalysed conditions is presented in Scheme 1.



Scheme 1

## Experimental

**Irradiation of diazofluorene:** Diazofluorene (0.96 g, 5 mmol) in hexane (25 ml) was irradiated for 24 h using a high-pressure mercury lamp (250 W). The solvent was removed under reduced pressure and the residue was chromatographed over silica gel. Elution with hexane gave 9,9'-bifluorene (**4**) (0.58 g, 70%). m.p.: 246 °C<sup>8</sup>; <sup>1</sup>H NMR (90 MHz, CDCl<sub>3</sub>): δ = 5.85 (s, 2H) and 7.1–7.9 (m, 16H); <sup>13</sup>C NMR (22.5 MHz, CDCl<sub>3</sub>): δ = 81, 121, 125, 128, 129, 141, 144.

**Reaction of diazofluorene with toluene-*p*-sulfonic acid:** Diazofluorene (0.96 g, 5 mmol) in hexane (25 ml) was stirred with toluene-*p*-sulfonic acid (0.86 g, 5 mmol) in hexane (25 ml) for 12 h. The product formed was separated by column chromatography. Elution with hexane gave 9,9'-bifluorene (**4**) (0.50 g, 58%). Similar results were obtained when a hexane solution of diazofluorene was treated with one equivalent of anhydrous aluminium chloride.

**Reaction of diazofluorene with toluene-*p*-sulfonic acid in presence of methanol:** Diazofluorene (0.96 g, 5 mmol) and methanol (0.16 g, 5 mmol) in hexane (25 ml) was stirred with toluene-*p*-sulfonic acid (0.86 g, 5 mmol) in hexane (25 ml) for 12 h. The products formed were separated by column chromatography. Elution with hexane gave 9-methoxyfluorene (**6**) (0.34 g, 36%). Further elution gave 9,9'-bifluorene (**4**) (0.22g, 27%).

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