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Reaction of Benzyne with *N*-Benzylideneaniline

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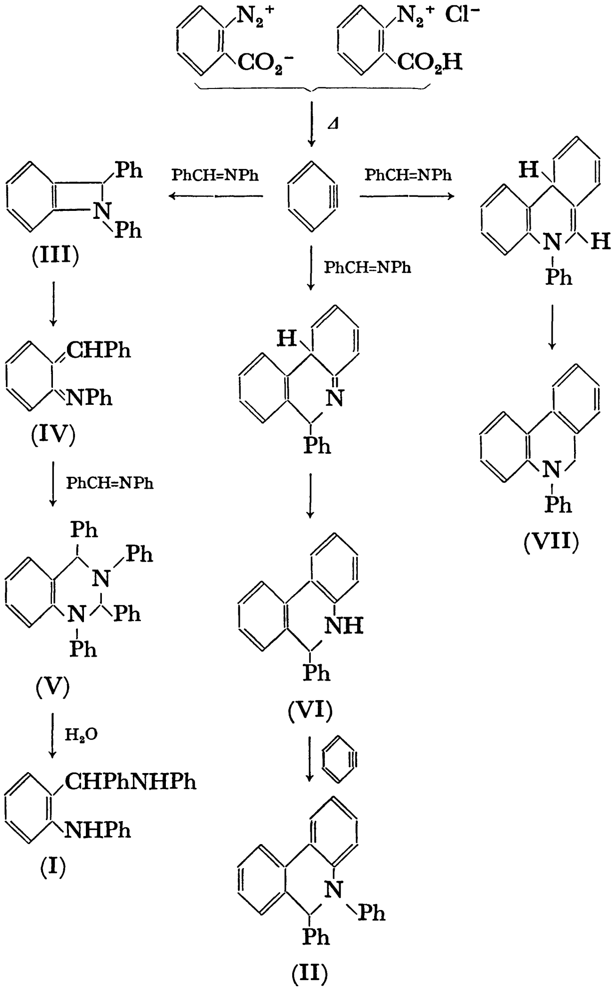
Synopsis. Benzyne, generated from benzenediazonium-2-carboxylate and 2-carboxybenzenediazonium chloride, reacted with *N*-benzylideneaniline to give *N*-(*o*-anilinobenzhydryl)aniline (I) and 5,6-dihydro-5,6-diphenylphenanthridine (II) as final products.

Although benzyne is known to undergo 1,2-cycloadditions with carbon-carbon double bonds,[1] its reactions with carbon-heteroatom double bonds are scarce and only carbonyl groups have been shown to react with benzynes.[2,3] In this paper we wish to report the first example of reaction of benzyne with an azomethine group.

Heating benzenediazonium-2-carboxylate[4] with *N*-benzylideneaniline under reflux in methylene chloride yielded *N*-(*o*-anilinobenzhydryl)aniline[5] (I, 18%[6]) and 5,6-dihydro-5,6-diphenylphenanthridine (II, 8%[6]) together with small amounts of a few unidentified products. Similarly, 2-carboxybenzenediazonium chloride[7] was decomposed with *N*-benzylideneaniline in boiling 1,2-dichloroethane in the presence of propylene oxide to afford the diamine (I, 35%[6]) and the dihydrodiphenylphenanthridine (II, 11%[6]).

In the reaction of benzyne with *N*-benzylideneaniline, the initial formation of a benzazetine (III) by a 1,2-cycloaddition of benzyne to the azomethine group of *N*-benzylideneaniline seems most probable and this benzazetine (III) is converted by ring-opening into a valence tautomer (IV), which undergoes a 1,4-cycloaddition with *N*-benzylideneaniline to yield a tetrahydroquinazoline (V). The formation of the diamine (I) from V during its isolation by chromatography is feasible because of the known susceptibility of 1,2,3,4-tetrahydroquinazolines to acid hydrolysis.[8] Evidence in support of the above reaction courses is found in the reaction of *N*-phenylbenzazetine with *N*-phenylmaleimide.[9] We have also postulated such cycloaddition and ring-opening in the formation of 2,4-diphenyl-1,3-benzodioxin from benzyne and benzaldehyde.[3] The formation of the dihydrodiphenylphenanthridine (II) may be explained in terms of a 1,4-cycloaddition of benzyne with *N*-benzylideneaniline followed by aromatization to 5,6-dihydrophenanthridine (VI) and subsequent *N*-phenylation with benzyne.[10] The last course of the *N*-phenylation was confirmed by a separate synthesis of II by heating benzenediazonium-2-carboxylate with 5,6-dihydro-6-phenylphenanthridine[11] (VI) and thus, the structure of II was confirmed.

5,6-Dihydro-5-phenylphenanthridine (VII), which might be formed by an alternative way of a 1,4-cycloaddition of benzyne with *N*-benzylidneaniline, was not observed in the reaction products. Since steric hindrance exerted in the transition states producing VI and VII seems to be the same, the selective formation of VI may suggest that the concerted formation of two carbon-carbon bonds in the 1,4-addition is preferable to that of carbon-carbon and carbon-nitrogen bonds.



All other attempts to isolate similar products in the reaction of benzyne with substituted *N*-benzylideneaniline such as *N*-(4′-methylbenzylidene)-4-toluidine, *N*-(4′-methoxybenzylidene)-4-anisidine, and *N*-(4′-chlorobenzylidene)-4-chloroaniline have failed.

Experimental

Reaction of N-*Benzylideneaniline with Benzyne Generated from Benzenediazonium-2-carboxylate.* A suspension of benzenediazonium-2-carboxylate, prepared from 20 mmol of anthranilic acid according to the procedure described in the literature,[12] in methylene chloride (120 ml) was dried over Molecular Sieves (10 g) at 0 °C with stirring for 5 hr. To the suspension *N*-benzylideneaniline (12 mmol) was added and the mixture was heated under reflux for 1.5 hr. The dark brown reaction mixture was filtered and the filtrate, upon evaporation of the solvent, gave a brown oily residue, which was chromatographed on silica gel (120 g). Elution with cyclohexane gave a pale yellow oil (0.48 g), which, after rechromatography, afforded 0.27 g (8%) of 5,6-dihydro-5,6-diphenylphenanthridine (II) as colorless needles and small amounts of two unidentified products (mp 146—152 °C and 128—130 °C). Elution with cyclohexane–benzene (9: 1) afforded a small amount of crystallines (mp 117—138 °C), while elution with cyclohexane–benzene (5: 1) afforded 0.38 g (18%) of *N*-(*o*-anilinobenzhydryl)aniline (I), mp 134—135 °C (lit,[5] 134—135 °C). Further elution with cyclohexane–benzene (1: 1) gave aniline and benzaldehyde.

5,6-Dihydro-5,6-diphenylphenanthridine (II) (Found: C, 90.02; H, 6.03; N, 4.30%. Calcd for $C_{25}H_{19}N$: C, 90.05; H, 5.74: H, 4.20%), mp 138—140 °C, ν_{max} (Nujol) 3070, 3040, 1592, 1496, 1438, and 1260 cm^{-1}, *m/e* 333 (M^+), δ ($CDCl_3$) 5.93 (1H, s), 6.84—7.50 (16H, m), and 7.68—7.90 (2H, m).

Chromatography of the brown oily residue over basic alumina or florisil gave similarly compounds I and II, but no tetrahydroquinazoline (V) was isolated in any experiments. The reaction carried out in the absence of Molecular Sieves yielded I and II in somewhat decreased yield along with a small amount of triphenylamine, the reaction product of benzyne with aniline, which may be formed by hydrolysis of *N*-benzylideneaniline. When the reaction was carried out in methylene chloride not strictly dried, only diphenyl- and triphenylamines were obtained, and neither I nor II was isolated.

Reaction of N-*Benzylidneaniline with Benzyne from 2-Carboxybenzenediazonium Chloride.* 2-Carboxybenzenediazonium chloride[7] (10 mmol) was heated under reflux for 1 hr with *N*-benzylideneaniline (7 mmol) in the presence of propylene oxide (1.7 ml) in 1,2-dichloroethane (100 ml). The red reaction mixture was concentrated under reduced pressure and the residue was chromatographed on silica gel. Compounds I (35%) and II (11%) were isolated in a similar way described before.

5,6-*Dihydro*-5,6-*diphenylphenanthridine (II).* Benzenediazonium-2-carboxylate, prepared from 5 mmol of anthranilic acid, was heated with 5,6-dihydro-6-phenylphenanthridine[11] (VI, 3 mmol) in methylene chloride (50 ml) under reflux for 1 hr. The brown reaction mixture was concentrated and the residue was submitted to purification by chromatography on silica gel to give 5,6-dihydro-5,6-diphenylphenanthridine (II, 35%), mp 138—140 °C, which was identical (mixed melting point) with the product obtained from benzyne and *N*-benzylideneaniline.

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6) Yield of I was based on *N*-benzylideneaniline used and that of II based on anthranilic acid or 2-carboxybenzenediazonium chloride.

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