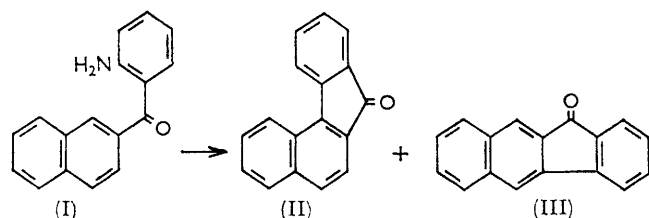


Aromatic Substitution. Part XVII.¹ A New Method of Effecting Pschorr-type Cyclisations

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Pschorr-type cyclisations can be effected by dissolving the appropriate solid diazonium tetrafluoroborate in acetone and heating the solution with one equivalent of pyridine, a procedure known to give rise to aryl radical intermediates. Evidence is presented for the intervention of a homolytic mechanism in the copper-catalysed Pschorr ring-closure.

INTERNUCLEAR cyclisations of the Pschorr type can be effected in a variety of ways^{2,3} and the nature of the reactive intermediate depends upon the method used. Free aryl radicals are undoubtedly involved in the base-catalysed decompositions of the diazonium salt, but there has been much argument concerning the nature of the intermediate in the copper-catalysed decompositions. Huisgen and Zahler⁴ studied the ratio of angular to linear cyclised products in the decomposition of the diazonium tetrafluoroborate of 2-(*o*-aminobenzoyl)-naphthalene (I) and, on the assumption that the ratio (2·4) obtained from the uncatalysed thermal decomposition in aqueous acid reflected attack by the aryl cation

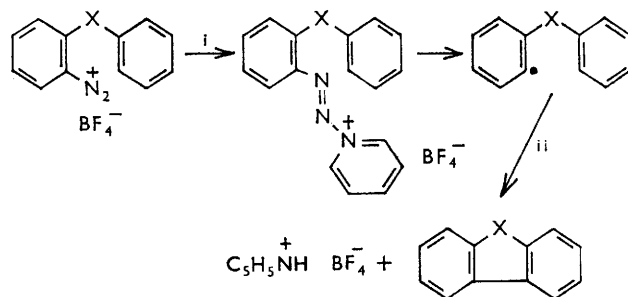


whereas that (9·5) from the acylarylnitrosamine in benzene was characteristic of free-radical attack, they proposed that the copper-catalysed decomposition [(II) : (III) = 4·4] involved a mixture of mechanisms. The aryl radical initially formed could either undergo cyclisation immediately or lose an electron to the copper to give the cation, which would then cyclise with the loss of a proton. The assumption that the decomposition of the acylarylnitrosamine in benzene solution is typical of an unhindered free-radical mode of attack has been questioned.⁵ It was suggested that the high ratio of (II) : (III) obtained when the *N*-nitrosoacylarylamine was decomposed in benzene solution could be due to steric hindrance to the formation of the σ -complex with benzene on the α -side but not on the β -side; this could lead to one conformation cyclising at the α -position of the naphthalene ring while the other could either cyclise at the β -position or react with benzene to give the phenylated product. It was felt⁵ that the fact that the decomposition of the diazonium salt of (I) in alkaline solution also gave an angular to linear ratio of 4·4 indicated that this ratio was characteristic of a free-radical cyclisation. Other evidence for a homolytic process in the copper-catalysed decompositions has been

presented.^{5,6} The radicals formed were not thought to be free, but associated in some way with the surface of the catalyst.³

It was desirable to have a method available for the production of free aryl radicals which would permit a study of Pschorr-type cyclisations involving a homolytic pathway to be carried out in homogeneous solutions, and one which would give yields of cyclised products comparable to those obtained in the copper-catalysed reactions. The nature and effects of the complicating stereochemical factors introduced when the cyclisations are carried out at the surface of a metal are not clear.

The procedure developed for generating free aryl radicals in solution from dry diazonium tetrafluoroborates and one equivalent of pyridine⁷ has now been extended to these cyclisations (see Scheme). The dry diazonium tetrafluoroborate of the appropriate amine was dissolved in dry acetone, one equivalent of pyridine was added, and the solution was heated under reflux until the reaction was complete. No boron trifluoride



Scheme
Reagents: i, C₅H₅N; ii, pyridinium ion-radical.

(indicative of the formation of the aryl cation) was evolved. Instead, addition of dry ether caused precipitation of pyridinium tetrafluoroborate. The yields of cyclised products were comparable to those obtained in the copper-catalysed decompositions. When this procedure was applied to the diazonium salt of (I) the ratio of (II) : (III) was 4·2 to 4·4, confirming that this ratio was indeed characteristic of a homolytic mode of cyclisation in this system, and that no carbonium-ion intermediates were involved in the corresponding copper-catalysed decomposition. It is worth mentioning that, even under the completely anhydrous conditions used

¹ Part XVI, R. A. Abramovitch and G. A. Poulton, *J. Chem. Soc. (B)*, 1967, 267.

² D. F. DeTar, *Org. Reactions*, 1957, **9**, 409.

³ R. A. Abramovitch, in "Advances in Free Radical Chemistry," ed. G. H. Williams, Logos Press, London, vol. 2, in the press.

⁴ R. Huisgen and W. D. Zahler, *Chem. Ber.*, 1963, **96**, 736.

⁵ R. A. Abramovitch and G. Tertzakian, *Canad. J. Chem.*, 1965, **43**, 940.

⁶ A. H. Lewin, A. H. Dinwoodie, and T. Cohen, *Tetrahedron*, 1966, **22**, 1527.

⁷ R. A. Abramovitch and J. G. Saha, *Tetrahedron*, 1965, **21**, 3297.

here, small amounts of phenols were formed. Phenol formation was also reported⁸ in the copper-catalysed decomposition of the diazonium tetrafluoroborate from *p*-amino-*N*-methyl-*o*'-nitrobenzanilide in acetone solution. Phenol itself was obtained in very low yield, together with some biphenyl, from the pyridine-catalysed decomposition of benzenediazonium tetrafluoroborate in acetone containing benzene. The phenols must arise either by reaction of the radicals with atmospheric oxygen or with the acetone itself.

In the cyclisation of 2-aminobenzophenone, 2,2'-dibenzoylazobenzene (3.7%) was obtained, together with fluorenone (44%), 2-hydroxybenzophenone (10%), and pyridinium tetrafluoroborate (87%). As expected,⁹ cyclisation of 2-aminodiphenyl ether gave a low yield of dibenzofuran (7.5%), together with the deaminated product, diphenyl ether (24%), 2-hydroxydiphenyl ether (9%), pyridinium tetrafluoroborate (94%), and, for the first time, 2,2'-diphenoxyazobenzene (2%), characterised by its analysis. Also as expected, decomposition of the diazonium tetrafluoroborate from 2-amino-*N*-methyl-diphenylamine gave the highest yield (72.5%) of cyclised product (*N*-methylcarbazole) in the series.

EXPERIMENTAL

Reaction of Benzenediazonium Tetrafluoroborate with Benzene in Acetone in the Presence of Pyridine.—The pure dry tetrafluoroborate (0.5 g.) in dry acetone (20 ml.) and dry benzene (5 ml.) was treated with pure dry pyridine (0.22 g.) and the solution was boiled under reflux (CaCl₂ guard tube) for 16 hr. Dry ether was added to the cold solution and the pyridinium tetrafluoroborate (0.325 g.), m. p. 215–218°, which precipitated was filtered off. The filtrate was concentrated, benzene (20 ml.) was added, and the solution was extracted with aqueous sodium hydroxide. The aqueous extract was acidified and extracted with ether to give phenol (0.002 g.) (tribromo-derivative, m. p. 95°). The benzene layer was concentrated and the residue was chromatographed on alumina to give biphenyl (0.042 g.), m. p. 70°, and azobenzene (0.002 g.), m. p. 66°.

Cyclisation of 2-Aminobenzophenone.—The dry diazonium tetrafluoroborate (1.50 g.), m. p. 98–100°, prepared from 2-aminobenzophenone (1.13 g.), was added to degassed dry acetone (20 ml.) and the solution was treated with dry

pyridine (0.424 g.) and boiled under reflux with stirring (CaCl₂ guard tube) for 20 hr. Pyridinium tetrafluoroborate (0.731 g.), m. p. 219–220°, was precipitated by the addition of dry ether. The reaction mixture was then worked up as described above for benzenediazonium tetrafluoroborate, to give 2-hydroxybenzophenone (0.102 g.), m. p. 38° (infrared spectrum identical with that of an authentic sample), fluorenone (0.40 g.), m. p. and mixed m. p. 83–85°, and 2,2'-dibenzoylazobenzene (0.049 g.), m. p. 197–198° (lit.,¹⁰ 201–202°). The infrared spectrum [ν_{\max} (KBr) 1665s, 1590m, 1575w, 1418m, 1150m, 762m, and 698s cm.⁻¹] was also consistent with this structure for the azo-compound.

*Cyclisation of 2-Amino-*N*-methyl-diphenylamine.*—The dry diazonium tetrafluoroborate (1.00 g.) in dry acetone (20 ml.) was treated with pyridine (0.266 g.) and the reaction carried out as described above for the corresponding benzophenone derivative. Pyridinium tetrafluoroborate (0.501 g., 89.1%), 2-hydroxy-*N*-methyl-diphenylamine (1 mg.) (OH band in the i.r. spectrum), *N*-methylcarbazole (0.442 g., 72.5% yield), m. p. 88–89°, and what was probably the orange azo-compound (8 mg.), m. p. 139–143°, were isolated. Insufficient of the orange product was available for further purification and analysis.

Cyclisation of 2-Aminodiphenyl Ether.—From the dry diazonium tetrafluoroborate (4.00 g.) were obtained the following products: pyridinium tetrafluoroborate (2.21 g., 93.9%), 2-hydroxydiphenyl ether (0.231 g., 8.8%) (phenolic OH in the i.r. spectrum), m. p. 103–105° (lit.,¹¹ 106–107°), dibenzofuran (0.178 g., 7.5%), m. p. 85° (lit.,¹¹ 86–87°), 2,2'-diphenoxyazobenzene (0.103 g., 2.0%), m. p. 100–101° [from light petroleum (b. p. 36–56°)] (Found: C, 78.6; H, 5.3; N, 7.6. C₂₄H₁₈N₂O₂ requires C, 78.7; H, 4.9; N, 7.6), and diphenyl ether (0.578 g., 24.1%) (infrared spectrum identical with that of an authentic sample).

*Cyclisation of 2-*o*-Aminobenzoylnaphthalene.*—From the dry diazonium tetrafluoroborate (3.8 g.) and pyridine (0.864 g.), pyridinium tetrafluoroborate (1.69 g., 92.4%), 3,4-benzofluorenone (0.841 g., 33.3%), m. p. 160–161° (lit.,⁴ 160–161°), and 2,3-benzofluorenone (0.201 g., 7.9%), m. p. 152–153° (lit.,⁴ 153–154°), were obtained.

The authors are grateful to the National Research Council for financial assistance.

[6/1463 Received, November 21st, 1966]

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¹⁰ P. Carré, *Bull. Soc. chim. France*, 1909, 5, 283.

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