

Rearrangements of Diphenylamine Derivatives. Part IV.¹ Rearrangements of *N*-Aroyldiphenylamines Catalysed by Aluminium Chloride

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N-Benzoyl-, *N*-(*p*-toluoyl)-, and *N*-(*p*-chlorobenzoyl)-diphenylamine react with an excess of aluminium chloride at 140–180° to give the corresponding 4,4'-diaryldiphenylamines and diphenylamine itself. *N*,4-Dibenzoyldiphenylamine gives only 4,4'-dibenzoyldiphenylamine under similar conditions. *N*-benzoyl-4-methyldiphenylamine gives only 4-methyldiphenylamine, and *N*-(*p*-nitrobenzoyl)diphenylamine does not yield tractable products. The reaction of diphenylamine with benzoyl chloride (2 mol. equiv.) and an excess of aluminium chloride at 140° yields *N*-benzoyldiphenylamine and 4,4'-dibenzoyldiphenylamine.

BOTH the Fries-type rearrangement of the corresponding *N*-acyl-compounds and the direct *C*-acylation of aromatic amines have been achieved in recent years under the influence of polyphosphoric acid (PPA) as a solvent-catalyst system.²⁻⁶ However, the cyclisation to acridine derivatives, which accompanies acylation at the 2-position in the diphenylamine^{3a,4a} and triphenylamine³ series, often reduces substantially the yields of free *C*-acyl amines which are obtained. The more conventional catalyst for Fries-type reactions, aluminium chloride, has been used to bring about the Chattaway

rearrangement (usually in poor yield) of *N*-acyl and *NN*-diacyl anilines,⁷⁻⁹ and of *N*-acyl carbazoles,¹⁰ and it has been observed that the presence of a high proportion of aluminium chloride (2.5 mol. equiv.) is necessary for a successful rearrangement of acetanilide.⁸ Even under these conditions, attempted rearrangements of *N*-acyl diphenylamines have failed.^{8,11}

In our work *N*-benzoyldiphenylamine (I) and a six-molar excess of aluminium chloride were kept at 140° for 1 h and gave diphenylamine and 4,4'-dibenzoyldiphenylamine (VII) in 48 and 33% yield, respectively,

¹ Part III, J. M. Birchall, M. T. Clark, H. Goldwhite, and D. H. Thorpe, *J.C.S. Perkin I*, 1972, 2579.

² D. A. Denton and H. Suschitzky, *J. Chem. Soc.*, 1963, 4741.

³ B. Staskun, *J. Org. Chem.*, (a) 1964, **29**, 2856; (b) 1968, **33**, 3031.

⁴ J. M. Birchall and D. H. Thorpe, *J. Chem. Soc. (C)*, (a) 1967, 2071; (b) 1968, 2900.

⁵ H. R. Snyder and C. T. Elston, *J. Amer. Chem. Soc.*, 1955, **77**, 364.

⁶ F. D. Popp, *J. Org. Chem.*, 1962, **27**, 2658.

⁷ D. N. Kursanov, *Zhur. obshchei Khim.*, 1943, **13**, 236; B. I. Ardashev and V. I. Minkin, *ibid.*, 1957, **27**, 1261.

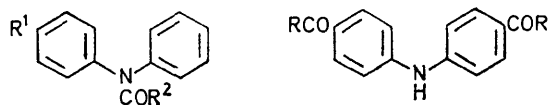
⁸ J. F. J. Dippy and J. H. Wood, *J. Chem. Soc.*, 1949, 2719.

⁹ J. F. J. Dippy and V. Moss, *J. Chem. Soc.*, 1952, 2205.

¹⁰ S. G. P. Plant and S. B. C. Williams, *J. Chem. Soc.*, 1934, 1142.

¹¹ S. G. P. Plant and C. R. Worthing, *J. Chem. Soc.*, 1955, 1278.

based on *N*-benzoyldiphenylamine consumed (71%). A similar reaction in which *N*-(*p*-toluoyl)diphenylamine (II) was treated with aluminium chloride at 140° for 1 h gave a 62% conversion into diphenylamine (50%) and 4,4'-di-(*p*-toluoyl)diphenylamine (VIII) (37%), but *N*-(*p*-chlorobenzoyl)diphenylamine (III) was largely (89%) unchanged after similar treatment. Rearrangement of the chloro-compound (III) at 175° for 1 h gives a 58% conversion into diphenylamine (40%) and 4,4'-di-(*p*-



- (I) R¹ = H, R² = Ph
 (II) R¹ = H, R² = *p*-MeC₆H₄
 (III) R¹ = H, R² = *p*-ClC₆H₄
 (IV) R¹ = H, R² = *p*-NO₂-C₆H₄
 (V) R¹ = Bz, R² = Ph
 (VI) R¹ = Me, R² = Ph
 (VII) R = Ph
 (VIII) R = *p*-MeC₆H₄
 (IX) R = *p*-ClC₆H₄

chlorobenzoyl)diphenylamine (IX) (30%). After an induction period of about 15 min at 140°, *N*-(*p*-nitrobenzoyl)diphenylamine (IV) reacts vigorously with aluminium chloride to give no clear-cut products.

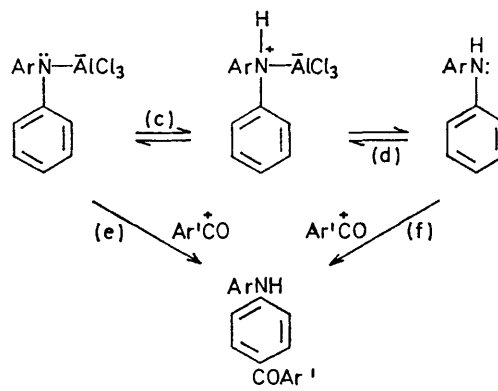
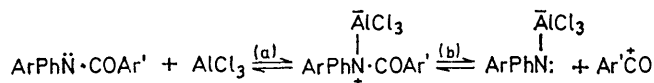
The successful rearrangements just described are consistent with the mechanism shown in the Scheme (the Ar'CO group may also be complexed with aluminium chloride in the early stages of the reaction).¹² The slower reaction given by the *p*-chlorobenzoyl compound (III) is probably the result of the $-I$ effect of the chlorine atom both on the formation of the complex with aluminium chloride [step (a)] and on heterolysis to give the acylium ion [step (b)]. The methyl group in the *p*-toluoyl compound (II) would be expected to have the opposite effect, but apparently this is not sufficiently large to be detected under the conditions of these experiments.

It appears that the use of aluminium chloride for the rearrangement of *N*-aroyldiphenylamines inhibits not only the formation of acridines observed in polyphosphoric acid,^{3a,4} but also the formation of their precursors, the 2-aroyldiphenylamines. This observation is consistent with the suggestion that the high proportion of acylation at the 2-position which occurs in polyphosphoric acid is facilitated by the irreversible rapid cyclisation to acridines which follows.^{4a}

The isolation of diaroyl and not monoaroyl diphenylamines, despite the presence of unsubstituted diphenylamine at the end of each reaction, indicates that the presence of an electron-withdrawing aroyl group in one ring of the diphenylamine molecule facilitates acylation in the other ring [steps (e) and (f)], probably by limiting the extent to which the nitrogen atom will complex with aluminium chloride [step (d)] or with a proton from the hydrogen chloride present as co-catalyst [step (c)].

In accord with this suggestion, *N*,4-dibenzoyldiphenylamine (V) undergoes only 52% conversion during 1 h at 140° in the presence of 6 mol. equiv. of aluminium

chloride to give 4,4'-dibenzoyldiphenylamine (VII) (77% yield). Under identical conditions, *N*-benzoyl-4-methyldiphenylamine (VI) undergoes complete reaction but yields only 4-methyldiphenylamine (60%) and tar; no *C*-benzoylation occurs in this reaction,



SCHEME

and further experiments with the *N*-benzoyl-4-methyl compound (VI) at 90, 120, and 180° also failed to yield 4-benzoyl-4'-methyldiphenylamine. Clearly the presence of the 4-benzoyl-group in (V) retards cleavage of the amide by its effect on step (a), but facilitates *C*-benzoylation by its effect on steps (c) and (d); the 4-methyl group exerts its influence in the opposite direction, and it seems safe to conclude that 4-methyldiphenylamine is completely complexed by aluminium chloride under the conditions of these experiments.

The direct Friedel-Crafts benzoylation of diphenylamine fails when conducted in refluxing carbon disulphide,¹¹ but in the absence of a solvent diphenylamine reacts with benzoyl chloride (2 mol. equiv.) and aluminium chloride (5 mol. equiv.) at 140° during 1 h to give *N*-benzoyldiphenylamine (I) (12%) and 4,4'-dibenzoyldiphenylamine (VII) (60%). This reaction represents the most successful direct *C*-acylation of diphenylamine achieved to date, but comparable results have been reported for the triphenylamine series.^{3b,13,14}

EXPERIMENTAL

Spence Grade H alumina was used for chromatography. Percentage yields are based on starting material consumed in each case.

N-Aroyldiphenylamines were obtained as described earlier from diphenylamine and the appropriate aroyl chloride;^{4b} they gave correct elemental analyses and m.p.s in full agreement with reported data. *N*-Benzoyl-4-methyldiphenylamine (Found: C, 83.7; H, 5.9; N, 5.1. Calc. for C₂₀H₁₇NO: C, 83.6; H, 6.1; N, 4.9%), m.p. 96—

¹³ T. N. Baker, W. P. Doherty, W. S. Kelly, W. Newmeyer, J. E. Rogers, R. E. Spalding, and R. I. Walter, *J. Org. Chem.*, 1965, **30**, 3714.

¹⁴ C. J. Fox and A. L. Johnson, *J. Org. Chem.*, 1964, **29**, 3536.

¹² Cf. H. J. Shine, 'Aromatic Rearrangements,' Elsevier, Amsterdam, 1967, p. 80.

97° (from ethanol), was similarly obtained from 4-methyl-diphenylamine¹⁵ (lit.,¹⁶ m.p. 89–90° for a sample obtained by the Chapman rearrangement of phenyl *N*-*p*-tolylbenzimidate).

N,4-Dibenzoyldiphenylamine.—*p*-Bromobenzophenone (26.2 g, 100 mmol), acetanilide (13.5 g, 100 mmol), anhydrous potassium carbonate (10 g), and copper-bronze (2.0 g) were heated under reflux at 160–180° (bath) for 25 h. The cooled mixture was extracted with ether (3 × 50 ml), and the combined extracts were filtered, washed with water (2 × 25 ml), and dried (Na₂SO₄). Evaporation gave crude *N*-acetyl-4-benzoyldiphenylamine, which was heated under reflux with potassium hydroxide (10.0 g) in ethanol (140 ml) for 5 h; recrystallisation of the resulting solid from ethanol (charcoal) gave 4-benzoyldiphenylamine (21.2 g, 77%) (Found: C, 83.5; H, 5.8; N, 5.2. Calc. for C₁₉H₁₅NO: C, 83.5; H, 5.5; N, 5.1%), m.p. 154–155° (lit.,¹⁷ 155°), the i.r. spectrum of which was consistent with the proposed structure. Treatment with benzoyl chloride in the absence of a catalyst gave a 62% yield of *N*,4-dibenzoyldiphenylamine (Found: C, 82.8; H, 5.1; N, 3.7. Calc. for C₂₈H₁₉NO₂: C, 82.7; H, 5.1; N, 3.7%), m.p. 138° (from ethanol) (lit.,¹⁷ 138° for material prepared by a Chapman rearrangement from *p*-benzoylphenyl *N*-phenylbenzimidate).

Rearrangements.—(a) *N*-Benzoyldiphenylamine. The *N*-benzoyl-compound (8.21 g, 30 mmol) and anhydrous aluminium chloride (24 g, 180 mmol) were stirred at 140° (bath) for 1 h, then cooled and poured onto crushed ice and 2*M*-hydrochloric acid (50 ml). The precipitated solid was washed with water (2 × 25 ml) and dissolved in chloroform (150 ml); the solution was dried (Na₂SO₄) and evaporated to leave a brown solid (7.86 g), which was crystallised from ethanol (4 × 100 ml) to give 4,4'-dibenzoyldiphenylamine (1.76 g) (Found: C, 82.6; H, 5.2; N, 3.7. Calc. for C₂₈H₁₉NO₂: C, 82.7; H, 5.1; N, 3.7%), m.p. and mixed m.p. 242–244° (lit.,⁵ 243°), identified by i.r. spectroscopy.^{4a} The mother liquor was evaporated to leave a brown solid (5.81 g), which was dissolved in benzene (30 ml) and chromatographed on alumina. The white solid eluted with light petroleum (b.p. 60–80°) was diphenylamine (1.72 g, 48%), m.p. and mixed m.p. 53° (from aqueous ethanol), identified by i.r. spectroscopy, and elution with benzene followed by recrystallisation from aqueous ethanol (charcoal) gave *N*-benzoyldiphenylamine (2.35 g, 29% recovery), m.p. and mixed m.p. 179°. Elution with chloroform and recrystallisation from ethanol then gave 4,4'-dibenzoyldiphenylamine (0.92 g, total yield 2.68 g, 33%), m.p. 242°, and finally a brown intractable tar (0.62 g).

Attempts to improve the conversion into the dibenzoyl compound by increasing the reaction period (5 h) led only to tar formation, and experiments conducted in nitrobenzene or 1,1,2,2-tetrachloroethane as solvents were similarly unsuccessful.

(b) *N*-(*p*-Toluoyle)diphenylamine. A similar procedure with the *N*-(*p*-toluoyle) compound (5.74 g, 20 mmol) and aluminium chloride (16.0 g, 120 mmol) gave, after hydrolysis and drying in chloroform, a brown solid (5.64 g), which crystallised from benzene (40 ml). The resulting solid was recrystallised from ethanol (charcoal) and gave yellow plates of 4,4'-di-(*p*-toluoyle)diphenylamine (1.18 g) (Found: C, 82.7; H, 5.9; N, 3.5. C₂₈H₂₃NO₂ requires C, 82.9; H, 5.7; N, 3.45%), m.p. 205–206°, identified by comparison of its

u.v. spectrum [λ_{max} (EtOH) 256 (log ϵ 4.39) and 385 nm (4.64); λ_{infl} 318 nm (3.89)] with those of the 4,4'-diaryldiphenylamines prepared earlier;^{4b} its i.r. spectrum (mull) shows strong bands at 6.11, 6.25, 6.29, 7.43, 7.63, 7.66, 7.81, 8.55, 8.72, 10.81, 11.88, and 13.25 μm , with a sharp N–H stretching band at 3.01 μm (m). The remaining benzene solution was chromatographed on alumina to give diphenylamine (1.04 g, 50%) [eluted with light petroleum (b.p. 60–80°)], *N*-(*p*-toluoyle)diphenylamine (2.21 g, 38% recovery) (20% chloroform–benzene), and 4,4'-di-(*p*-toluoyle)diphenylamine (0.64 g, total yield 1.82 g, 37%) (chloroform), identified by mixed m.p. determinations and i.r. spectroscopy.

(c) *N*-(*p*-Chlorobenzoyl)diphenylamine. An experiment in which the *N*-(*p*-chlorobenzoyl) compound (6.15 g) and aluminium chloride (16.0 g) were stirred at 140° for 1 h led only to recovery of the starting material (5.50 g, 89%). *N*-(*p*-Chlorobenzoyl)diphenylamine (6.15 g, 20 mmol) and aluminium chloride (16.0 g, 120 mmol) were stirred at 175° (bath) for 1 h, and the products were isolated as described in (b) to give diphenylamine (0.78 g, 40%) [eluted with light petroleum (b.p. 60–80°)], *N*-(*p*-chlorobenzoyl)diphenylamine (2.60 g, 42% recovery) (20% chloroform–benzene), and 4,4'-di-(*p*-chlorobenzoyl)diphenylamine [1.52 g; 1.26 g by crystallisation from benzene and 0.26 g by chromatography (chloroform), 30% total yield] (Found: C, 70.0; H, 4.0; N, 3.4. Calc. for C₂₈H₁₇Cl₂NO₂: C, 70.0; H, 3.8; N, 3.2%), m.p. 225–226° (lit.,^{4b} 223°), identified by mixed m.p. determinations and i.r. spectroscopy.

(d) *N*,4-Dibenzoyldiphenylamine. The *N*,4-dibenzoyl compound (3.77 g, 10 mmol) and aluminium chloride (8.00 g, 60 mmol) were stirred at 140° for 1 h. The mixture was hydrolysed, dried in chloroform, and then dissolved in hot benzene (30 ml); 4,4'-dibenzoyldiphenylamine (1.21 g), m.p. 242–244° [from ethanol (charcoal)] crystallised on cooling. The mother liquor was chromatographed on alumina to give *N*,4-dibenzoyldiphenylamine (1.81 g, 48% recovery) (eluted with benzene) and 4,4'-dibenzoyldiphenylamine (0.31 g, total yield 1.52 g, 77%) (chloroform), identified by mixed m.p. determinations and i.r. spectroscopy, and a tar (0.3 g).

(e) *N*-Benzoyl-4-methyldiphenylamine. This compound (5.74 g, 20 mmol) and aluminium chloride (16.0 g, 120 mmol) were stirred at 140° for 1 h, and the resulting mixture was hydrolysed with 2*M*-hydrochloric acid and dried in chloroform. The resulting brown solid (5.58 g) was dissolved in benzene (30 ml) and chromatographed to give 4-methyldiphenylamine (2.20 g, 60%), m.p. and mixed m.p. 89° [from ethanol (charcoal)] (lit.,¹⁵ 88–89°), eluted with benzene and identified by i.r. spectroscopy; the only other product detected was a black tar (2.56 g), eluted with chloroform. A similar reaction on the same scale at 90° for 1 h gave *N*-benzoyl-4-methyldiphenylamine (5.11 g, 90% recovery) and tar (0.30 g); a reaction at 120° for 1 h gave *N*-benzoyl-4-methyldiphenylamine (2.79 g, 49%), 4-methyldiphenylamine (1.36 g 73%), and tar (1.21 g); and a reaction at 180° for 1 h gave 4-methyldiphenylamine (1.09 g, 30%) and tar (4.10 g).

Friedel-Crafts Benzoylation of Diphenylamine.—Diphenylamine (4.25 g, 25 mmol) was added slowly to benzoyl chloride (7.02 g, 50 mmol) and anhydrous aluminium chloride (16.75 g, 125 mmol), and the mixture was stirred

¹⁵ A. Takada and H. Nishimura, *Chem. and Pharm. Bull. (Japan)*, 1962, **10**, 1.

¹⁶ O. H. Wheeler, F. Roman, M. V. Santiago, and F. Quiles, *Canad. J. Chem.*, 1969, **47**, 503.

¹⁷ M. P. Lippner and M. Tomlinson, *J. Chem. Soc.*, 1956, 4667.

at 140° (bath) for 1 h. The cooled products were poured onto crushed ice and 2M-hydrochloric acid (50 ml), and the resulting brown solid was washed with water, dried in chloroform, and dissolved in hot benzene (40 ml). 4,4'-Dibenzoyldiphenylamine (3.42 g), m.p. and mixed m.p. 242—244° (from ethanol), crystallised out when the solution cooled, and the mother liquor was chromatographed on alumina to give diphenylamine (0.82 g, 19% recovery),

N-benzoyldiphenylamine (0.72 g, 12%), m.p. and mixed m.p. 179° (from ethanol), and 4,4'-dibenzoyldiphenylamine (1.36 g, total yield 4.78 g, 60%).

We thank The Rubber Regenerating Co. Ltd. for a grant and the S.R.C. for a research studentship (to M. T. C.).

[2/1638 Received, 11th July, 1972]
