Rearrangements of Diphenylamine Derivatives. Part V.[1] Rearrangements of 4-Substituted *N*-Acyldiphenylamines and Related Reactions

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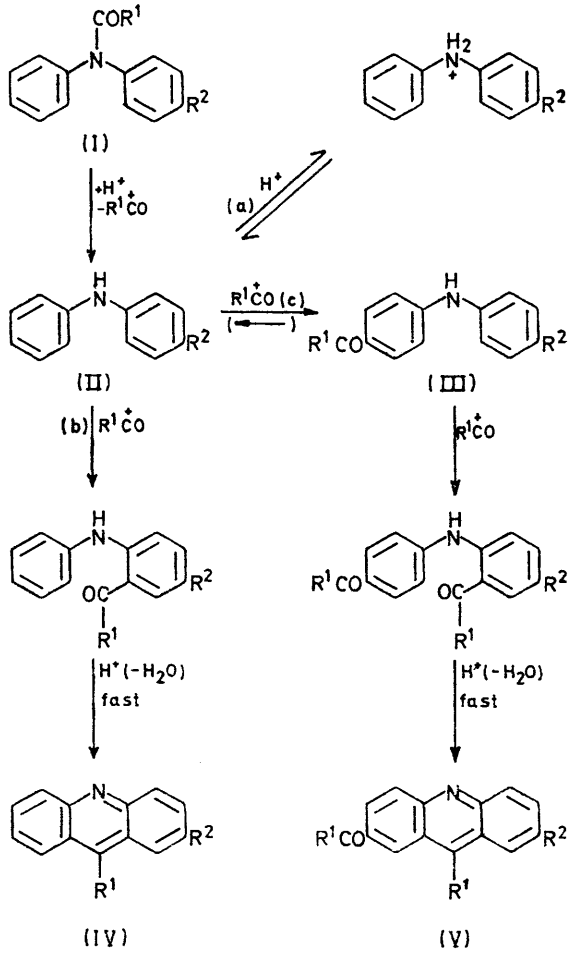
N,4-Dibenzoyldiphenylamine reacts in polyphosphoric acid at 140° to give 4-benzoyldiphenylamine, 4,4'-dibenzoyldiphenylamine, 2-benzoyl-9-phenylacridine, and 2,7-dibenzoyl-9-phenylacridine; the rearrangement of *N*-benzoyl-4-methyldiphenylamine proceeds analogously. *N*-Acetyl-4-benzoyldiphenylamine yields only 4-benzoyldiphenylamine and 4-acetyl-4'-benzoyldiphenylamine, and *N*-butyroyldiphenylamine yields only diphenylamine, 9-propylacridine, and 2-butyroyl-9-propylacridine under similar conditions. *C*-Alkanoylation is facilitated by increased chain-length in the alkanoyl group, but yields of rearrangement products from the *N*-alkanoyl compounds are low. 4-Benzoyldiphenylamine, either alone or in the presence of benzoic acid, is converted into 9-phenylacridine by treatment with zinc chloride at 240°.

FRIES-type rearrangements of *N*-aroyldiphenylamines are now known to be catalysed both by aluminium chloride, to give *C*-aroyldiphenylamines,[1] and by polyphosphoric acid (PPA), which gives both *C*-aroyldiphenylamines and acridine derivatives.[2,3] Both types of rearrangement are believed to be intermolecular, and substituents already present in the diphenylamine rings seem to influence the reaction mainly by their effects on the extent of quaternisation by the catalyst [step (a), Scheme 1, or the analogous reaction with aluminium chloride].[1,2] Thus, *N*,4-dibenzoyldiphenylamine (Ia) undergoes only 52% reaction on treatment with an excess of aluminium chloride at 140° for 1 h, but gives 4,4'-dibenzoyldiphenylamine (IIIa) (77% yield), whereas *N*-benzoyl-4-methyldiphenylamine (Ib) undergoes complete reaction under comparable conditions but yields only 4-methyldiphenylamine (IIb) (60%).[1]

N-Benzoyl Compounds in Polyphosphoric Acid.—We set out to compare the behaviour of the two amides (Ia and b) in the presence of polyphosphoric acid; preliminary investigation by the colour development method[4] indicated that reaction of the *N*,4-dibenzoyl compound (Ia) could best be achieved at 140° during 1 h. Separation of the products from a preparative-scale experiment under these conditions gave 4-benzoyldiphenylamine (IIa) (26%), 4,4'-dibenzoyldiphenylamine (IIIa) (31%), 2-benzoyl-9-phenylacridine (IVa) (9%), and 2,7-dibenzoyl-9-phenylacridine (Va) (17%).

The identities of the benzoyldiphenylamines and of the acridine (Va) were confirmed by comparison with authentic specimens, and the physical properties of the acridine (IVa) were identical with those of the compound previously obtained from the reaction of diphenylamine with benzoic acid in polyphosphoric acid.[2a] The previous identification of this last compound, based on its i.r. and u.v. spectra, was not unambiguous and an attempt to synthesise it during the work described here by a Bernthsen reaction was unsuccessful. Furthermore, it has been shown that although 4-benzoyltriphenylamines are stable in polyphosphoric acid at 120—125°, rearrangement (presumably to the isomeric 2-benzoyl compounds) followed by cyclisation to acridine derivatives can occur at 190—195°.[5] However,



a; R^1 = Ph, R^2 = Bz
b; R^1 = Ph, R^2 = Me
c; R^1 = Me, R^2 = Bz
d; R^1 = $Me[CH_2]_{10}$, R^2 = H
e; R^1 = Pr^n, R^2 = H

SCHEME 1

4-benzoyldiphenylamine (IIa) (92%) is unchanged following treatment with polyphosphoric acid at 140°

[1] Part IV, J. M. Birchall, M. T. Clark, and D. H. Thorpe, *J.C.S. Perkin I*, 1973, 442.
[2] J. M. Birchall and D. H. Thorpe, *J. Chem. Soc.* (*C*), (*a*) 1967, 2071; (*b*) 1968, 2900.
[3] B. Staskun, *J. Org. Chem.*, 1964, **29**, 2856.
[4] F. Uhlig, *Angew. Chem.*, 1954, **66**, 435.
[5] B. Staskun, *J. Org. Chem.*, 1968, **33**, 3031.

for 1 h, and it therefore seems unlikely that migration of the 4-benzoyl group occurs during the reaction of *N*,4-dibenzoyldiphenylamine; consequently, the structure of the 2-benzoyl-9-phenylacridine is not seriously in doubt.

An attempt to achieve an improved synthesis of 2-benzoyl-9-phenylacridine (IVa) by the reaction of 4-benzoyldiphenylamine with benzoic acid (2 mol. equiv.) in polyphosphoric acid at 160° met with only limited success; 4,4′-dibenzoyldiphenylamine (IIIa) (8%), 2,7-dibenzoyl-9-phenylacridine (Va) (51%), and 2-benzoyl-9-phenylacridine (IVa) (18%) were obtained.

Colour development tests with *N*-benzoyl-4-methyldiphenylamine (Ib) showed that, as expected, rearrangement in polyphosphoric acid could probably be achieved at a slightly lower temperature than with the *N*,4-dibenzoyl-compound (Ia), and after 1 h at 130° the 4-methyl compound gave 4-methyldiphenylamine (IIb) (22%), 4-benzoyl-4′-methyldiphenylamine (IIIb) (7%), 2-methyl-9-phenylacridine (IVb) (32%), and 2-benzoyl-7-methyl-9-phenylacridine (Vb) (21%).

The new 4-benzoyl-4′-methyldiphenylamine and 2-benzoyl-7-methyl-9-phenylacridine were identified initially by spectroscopy, the u.v. spectra again[2] being particularly important in distinguishing the substituted diphenylamine from the acridine system [*K*-bands (log ε): (IIIb) 368 nm (4·44); (Vb) 291 nm (4·60)]. Further evidence for the structures is provided by an unambiguous Goldberg synthesis[6] of the amine (IIIb) from 4′-bromoacetophenone and 4′-methylacetanilide (74% yield after hydrolysis of the intermediate anilide) and its conversion into the acridine (Vb) (70%) by treatment with benzoic acid in polyphosphoric acid. The amine is characterised as its *N*-benzoyl derivative and the acridine as its picrate.

It therefore appears that benzoylation of 4-methyldiphenylamine (IIb) occurs much more readily during the rearrangement of the *N*-benzoyl compound (Ib) in polyphosphoric acid at 130° than in the presence of an excess of aluminium chloride at temperatures up to 180°.[1] Furthermore, comparison of the product distributions from the rearrangements of the amides [(Ia) and (Ib)] in polyphosphoric acid reveals that a much higher proportion of initial benzoylation *ortho* to the nitrogen atom [to give (IV)] occurs during the latter reaction. This is consistent with a preferred initial attack at the 2-position of the ring containing the 4-methyl substituent in (IIb) [step (b), Scheme 1], but at the 4-position of the unsubstituted ring in (IIa) [step (c)].

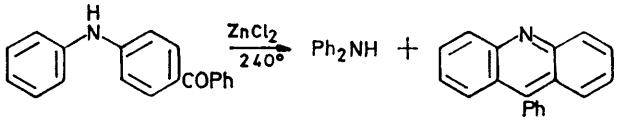
Reactions Involving Alkanoyl Groups.—*C*-Alkanoylation of the diphenylamine system is notoriously difficult,[2a,7-9] and appears to have been achieved only with *N*-benzoyldiphenylamine, acetyl chloride, and aluminium chloride in refluxing carbon disulphide (*ca.* 15% yield of 4-acetyl-*N*-benzoyldiphenylamine)[7] and with diphenylamine and dodecanoic acid in polyphosphoric acid at 140° [25% yield of 2-dodecanoyl-9-undecylacridine (Vd)].[2a] Several unsuccessful attempts to effect a Fries-type rearrangement of *N*-acetyldiphenylamine, in the presence either of aluminium chloride[7,9] or of polyphosphoric acid,[2a] have also been reported. However, rearrangement followed by ring closure occurs in the presence of zinc chloride at 230° to give 9-methylacridine,[10] and photochemical rearrangement of the *N*-acetyl compound has been achieved recently.[11]

The success of the reaction with dodecanoic acid suggested that a contributory factor to the failure of comparable reactions in the acetyl series might be the relative volatility of the acid concerned, but an attempt during the work described here to effect rearrangement of *N*-acetyldiphenylamine in polyphosphoric acid in a sealed tube at 140° gave diphenylamine [52% based on amide consumed (63%)] as the only tractable product. However, *N*-acetyl-4-benzoyldiphenylamine (Ic) reacts with polyphosphoric acid under reflux at 140° to give 4-benzoyldiphenylamine (IIc) (67%) and 4-acetyl-4′-benzoyldiphenylamine (IIIc) (7%), the latter being identified by an unambiguous synthesis from 4′-bromoacetophenone and 4′-benzoylacetanilide (62% yield after hydrolysis of the intermediate anilide). 4-Acetyl-4′-benzoyldiphenylamine (IIIc) (24%) is also obtained from the reaction of 4-benzoyldiphenylamine with a five-fold excess of acetic acid in polyphosphoric acid at 130°. The successful *C*-acetylation in these reactions is attributed to the control exerted by the electron-withdrawing 4-benzoyl group on the extent of protonation at the nitrogen atom [step (a), Scheme 1].

The beneficial effect on *C*-alkanoylation of increased chain length in the alkanoyl group is further demonstrated by the reaction of *N*-butyroyldiphenylamine (Ie) with polyphosphoric acid at 140°, which yields diphenylamine (21%), 9-propylacridine (IVe) (14%), and 2-butyroyl-9-propylacridine (Ve) (12%) [the identity of the last compound is established mainly by the close similarity of its u.v. spectrum to that of 2-dodecanoyl-9-undecylacridine (Vd)].[2a] With the exception of the modified Bernthsen synthesis of 9-methylacridine,[10] this is the first successful rearrangement of a simple *N*-alkanoyldiphenylamine to be achieved under thermal conditions, but whether its success depends on improved stability or on improved reactivity of the migrating acylium ion remains in doubt. The fact that the rearrangement of the *N*-butyroyl compound (Ie) yields only acridines whereas the acetylation reactions described above give only diphenylamine derivatives is attributed partly to the presence of the 4-benzoyl group during the acetylations; as in the earlier cases, this should favour step (c) (Scheme 1) rather than step (b).

[6] I. Goldberg, *Ber.*, 1906, **39**, 1691.
[7] S. G. P. Plant and C. R. Worthing, *J. Chem. Soc.*, 1955, 1278.
[8] J. M. Birchall, H. Goldwhite, and E. R. Smith, unpublished observations.
[9] J. F. J. Dippy and J. H. Wood, *J. Chem. Soc.*, 1949, 2719.
[10] F. M. Hamer, *J. Chem. Soc.*, 1930, 995.
[11] H. Shizuka, M. Kato, T. Ochiai, K. Matsui, and T. Morita, *Bull. Chem. Soc. Japan*, 1970, **43**, 67.

Reactions with Zinc Chloride.—Bernthsen's original synthesis of 9-phenylacridine involved the reaction of diphenylamine with benzoic acid in the presence of anhydrous zinc chloride at 260° for 10 h,[12] and the attempted Bernthsen synthesis of 2-benzoyl-9-phenylacridine (IVa) during the work described here involved 4-benzoyldiphenylamine, benzoic acid (2 mol. equiv.), and an excess of zinc chloride at 240° for 24 h. The latter reaction, however, yielded only diphenylamine (14%) and 9-phenylacridine (54%), demonstrating an efficient debenzoylation from the 4-position of the diphenylamine system under these conditions. Confirmation of this result is provided by the formation of the same two compounds during a similar reaction in the absence of benzoic acid (Scheme 2), and the reaction



SCHEME 2

of *N*-benzoyldiphenylamine with zinc chloride at 240° (originally studied by Bernthsen) [12] also gives the same products (23 and 52% yield, respectively).

Acheson has suggested that the formation of acridines under the conditions of the Bernthsen reaction involves a direct Friedel–Crafts acylation at the 2-position of diphenylamine, followed by cyclisation.[13] Albert has criticised this view on the grounds that electrophilic reagents are known to attack diphenylamine mainly at the 4-position,[14] and has supported the suggestion [15] that the reaction proceeds through *N*-acylation followed by a Fries-type rearrangement. Since both 4-benzoylation and *N*-benzoylation have now been shown to be reversible under Bernthsen conditions, while 2-benzoylation is followed by fast irreversible cyclisation,[13] there seems to be little difference between the two approaches to this problem. The ready reversibility of the Friedel–Crafts acylation under Bernthsen conditions also explains why no acylated diphenylamine derivatives have been isolated from Bernthsen reactions.

Consideration of the information now available in this field leads us to the view that 4-acyldiphenylamines are the products of kinetically controlled reactions of diphenylamine with acylium ions, whereas 9-substituted acridines are the thermodynamically preferred products of such reactions. As suggested earlier,[2a] it is possible that *N*-acyl compounds are formed mainly as a result of conventional nucleophilic attack by the nitrogen atom on species containing particularly electron-deficient carbonyl groups [*e.g.* $RCO\cdot\overset{+}{O}H_2$, RCOCl, $R\overset{+}{C}Cl(O\bar{A}lCl_3)$] rather than on free acylium ions.

EXPERIMENTAL

The polyphosphoric acid used was commercial ' tetraphosphoric acid ' [Albright and Wilson (MFG) Ltd.] which contained 80—85% by weight of phosphorus pentoxide. Reactions in polyphosphoric acid were carried out under dry nitrogen. Spence grade H alumina was used for chromatography, and u.v. spectra were measured for solutions in ethanol over the range 210—800 nm. Picrates were obtained by the standard method.[16]

Rearrangements in Polyphosphoric Acid.—(a) N,4-*Dibenzoyldiphenylamine.* The amide (7·54 g, 20 mmol) [1] and polyphosphoric acid (80 g) were stirred under reflux at 140° (bath) for 1 h. A trace of benzoic acid sublimed from the mixture, which rapidly became homogeneous and turned deep orange. The mixture was cooled to 80° and poured into water (400 ml), and the resulting green solid was heated with aqueous 40% sodium hydroxide (200 ml) on a boiling water-bath for 15 min. The precipitated yellow solid (7·40 g) was washed with water, dried in chloroform (Na_2SO_4), and dissolved in boiling ethanol (5 × 100 ml); the yellow solid, which crystallised on cooling, was recrystallised from ethanol (300 ml) (charcoal) to give 4,4'-dibenzoyldiphenylamine (1·68 g), m.p. and mixed m.p. 242—244°,[2a] identified by i.r. spectroscopy. The mother liquors were evaporated to dryness under reduced pressure, and the resulting solid (5·74 g) was dissolved in benzene and chromatographed to give [in order of elution (solvent in parentheses); identifications by i.r. spectroscopy]: 2-benzoyl-9-phenylacridine (0·64 g, 9%) (benzene), m.p. 171—172° (from ethanol) (lit.,[2a] 172°) [*picrate* (Found: N, 9·6. $C_{32}H_{20}N_4O_8$ requires N, 9·5%), m.p. 218—220°]; 4-benzoyldiphenylamine (1·42 g, 26%) (20% chloroform–benzene), m.p. and mixed m.p. 154° (from ethanol); [1] 2,7-dibenzoyl-9-phenylacridine (1·57 g, 17%) (20% chloroform–benzene), m.p. 212—214° (from ethanol) (lit.,[2a] m.p. 213°) [picrate, m.p. 195—196° (lit.,[2a] 195°)]; and 4,4'-dibenzoyldiphenylamine (0·66 g, total yield 31%) (chloroform).

(b) N-*Benzoyl*-4-*methyldiphenylamine.* The amide (8·61 g, 30 mmol) [1] was stirred in polyphosphoric acid (90 g) for 1 h at 130°, and the mixture was then cooled to 80°, poured into water (200 ml), carefully basified with aqueous 40% sodium hydroxide (250 ml), and stirred on a boiling water-bath for 15 min. The orange liquid which separated was extracted with chloroform (3 × 100 ml), and the combined extracts were washed with water (2 × 50 ml), and dried (Na_2SO_4). The chloroform was removed under reduced pressure, and the residual liquid was dissolved in benzene and chromatographed to give: 4-methyldiphenylamine (1·22 g, 22%) (benzene), m.p. and mixed m.p. 89° (from aqueous ethanol) (lit.,[17] 88—89°), identified by i.r. spectroscopy; 2-methyl-9-phenylacridine (2·58 g, 32%) (benzene) (Found: C, 89·0; H, 5·9; N, 5·3. Calc. for $C_{20}H_{15}N$: C, 89·2; H, 5·6; N, 5·2%), m.p. 135—136° (from aqueous

[12] A. Bernthsen, *Annalen*, 1884, **224**, 1.
[13] R. M. Acheson, ' The Chemistry of Heterocyclic Compounds—Acridines,' Interscience, New York, 1956, p. 21.
[14] A. Albert, ' The Acridines,' Arnold, London, 2nd edn., 1966, p. 91.
[15] C. Hollins, ' Synthesis of Nitrogen Ring Compounds,' Benn Bros., London, 1924, p. 67.
[16] F. J. Smith and E. Jones, ' A Scheme for Qualitative Organic Analysis,' Blackie, Glasgow, 1948 p. 91.
[17] A. Takada and H. Nishimura, *Chem. and Pharm. Bull.* (*Japan*), 1962, **10**, 1.

ethanol) (lit.,[18] 135—136°) [picrate (Found: C, 62·8; H, 3·6; N, 11·0. Calc. for $C_{26}H_{18}N_4O_7$: C, 62·65; H, 3·6; N, 11·2%), m.p. 224—226° (lit.,[19] 226°)]; *2-benzoyl-7-methyl-9-phenylacridine* (2·32 g, 21%) (20% chloroform–benzene) (Found: C, 86·9; H, 5·1; N, 3·7. $C_{27}H_{19}NO$ requires C, 86·8; H, 5·1; N, 3·75%), m.p. 160—161° (yellow plates from ethanol) [*picrate* (Found: C, 65·7; H, 3·8; N, 9·0. $C_{33}H_{22}N_4O_8$ requires C, 65·8; H, 3·7; N, 9·3%), m.p. 232—234°]; and *4-benzoyl-4′-methyldiphenylamine* (0·98 g, 11%) (50% chloroform–benzene) (Found: C, 83·4; H, 5·8; N, 5·0. $C_{20}H_{17}NO$ requires C, 83·6; H, 6·0; N, 4·9%), m.p. 126—127° (yellow plates from ethanol) [*N-benzoyl derivative* (Found: C, 83·1; H, 5·6; N, 3·65. $C_{27}H_{21}NO_2$ requires C, 82·8; H, 5·4; N, 3·6%), m.p. 120—121° (from ethanol)]. The u.v. spectrum of 2-benzoyl-7-methyl-9-phenylacridine shows $\lambda_{max.}$ (log ε) 213 (4·39), 245 (4·64), 257 (4·62), 291 (4·60), 330 (3·67), 348 (3·84), 367 (3·89), and 387 nm (3·65), $\lambda_{infl.}$ 273 (4·56) and 408 nm (3·58); 4-benzoyl-4′-methyldiphenylamine shows $\lambda_{max.}$ 246 (4·19) and 368 nm (4·44), $\lambda_{infl.}$ 267 nm (4·02).

(c) *N-Acetyldiphenylamine*. The amide (4·22 g, 20 mmol) [20] and polyphosphoric acid (50 g) were kept *in vacuo* in a sealed tube for 1 h at 140°. The products were treated as described in (a), and chromatography yielded diphenylamine (1·10 g, 52% based on amide consumed), *N*-acetyldiphenylamine (1·58 g, 37% recovery), and an amorphous brown solid (1·30 g), m.p. >300°, similar to that obtained from the reaction under reflux conditions.[2a]

(d) *N-Acetyl-4-benzoyldiphenylamine*. The amide (3·15 g, 10 mmol) [obtained in 77% yield when 4-benzoyldiphenylamine (20 mmol) [1] was heated under reflux with acetic anhydride (50 mmol) for 5 h] and polyphosphoric acid (40 g) were stirred under reflux at 130° for 1 h. The mixture was treated as described in (a), and the black solid which separated from the alkaline solution was extracted with chloroform (4 × 100 ml) and dried (Na_2SO_4). Evaporation gave a yellow-brown solid (2·26 g), which was recrystallised from benzene (80 ml) and then from ethanol (20 ml) to give yellow plates of *4-acetyl-4′-benzoyldiphenylamine* (0·22 g, 7%) (Found: C, 79·7; H, 5·3; N, 4·3. $C_{21}H_{17}NO_2$ requires C, 80·0; H, 5·4; N, 4·4%), m.p. 221—222° [$\lambda_{max.}$ (log ε) 246 (4·33), 309 (3·94), and 377 nm (4·67)]. The benzene filtrate was chromatographed; elution with 20% chloroform–benzene gave 4-benzoyldiphenylamine (1·82 g, 67%), m.p. and mixed m.p. 154—155°; a black tar (0·19 g) was eluted with benzene.

(e) *N-Butyroyldiphenylamine*. The amide (4·78 g, 20 mmol) [21] and polyphosphoric acid (50 g) were stirred at 140° for 1 h, and the products were treated with water and aqueous 40% sodium hydroxide and dried (Na_2SO_4) in chloroform. The resulting viscous liquid (4·38 g) was dissolved in benzene (30 ml) and chromatographed to give diphenylamine (0·81 g, 21%) [light petroleum (b.p. 60—80°)], 9-propylacridine (0·62 g, 14%) (benzene) (Found: C, 86·6; H, 6·9; N, 6·2. Calc. for $C_{16}H_{15}N$: C, 86·8; H, 6·8; N, 6·3%), m.p. 72—73° (from ethanol) (lit.,[22] m.p.) 72—75°), identified by i.r. and u.v. spectroscopy, *2-butyroyl-9-propylacridine* (0·70 g, 12%) (20% chloroform–benzene) (Found: C, 81·8; H, 7·3; N, 4·8. $C_{20}H_{21}NO$ requires C, 82·4; H, 7·3; N, 4·8%), m.p. 119—120° (from ethanol) [$\lambda_{max.}$ (log ε) 212 (4·12), 252 (4·58), 276 (4·80), 348 (3·78), and 367 nm (3·87), $\lambda_{infl.}$ 244 (4·48), 333 (3·53), 382 (3·65), and 400 nm (3·54)], and a black tar (2·17 g) (chloroform).

Acylation of 4-Benzoyldiphenylamine.—(a) *With benzoic acid*. The amine (5·40 g, 20 mmol), benzoic acid (7·32 g, 30 mmol), and polyphosphoric acid (140 g) were stirred at 160° for 1 h. The mixture was cooled to 80° and poured into water (400 ml), and the resulting green solid was heated with aqueous 40% sodium hydroxide (100 ml) on a boiling water-bath for 15 min, then washed with water, and dried (Na_2SO_4) in chloroform. Evaporation of the chloroform left a brown solid (6·38 g), which was chromatographed to give 2-benzoyl-9-phenylacridine (1·29 g, 18%), 2,7-dibenzoyl-9-phenylacridine (4·72 g, 51%), and 4,4′-dibenzoyldiphenylamine (0·60 g, 8%), identified by mixed m.p. determinations and i.r. spectroscopy.

(b) *With acetic acid*. 4-Benzoyldiphenylamine (2·73 g, 10 mmol), acetic acid (3·00 g, 50 mmol), and polyphosphoric acid (60 g) were stirred at 130° for 1 h. The products were separated as described for the rearrangement of *N*-acetyl-4-benzoyldiphenylamine, to give 4-acetyl-4′-benzoyldiphenylamine (0·29 g, 24% based on amine consumed) and 4-benzoyldiphenylamine (1·69 g, 62% recovery), identified by mixed m.p. determinations and i.r. spectroscopy, and a black tar (3.12 g).

4-Benzoyl-4′-methyldiphenylamine.— 4′-Bromobenzophenone (26·2 g, 100 mmol), 4′-methylacetanilide (14·9 g, 100 mmol), anhydrous potassium carbonate (10·0 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), dried (Na_2SO_4), and evaporated. The resulting *N*-acetyl compound was heated under reflux with potassium hydroxide (10·0 g) in ethanol (140 ml) for 5 h and the brown solid which separated on cooling was recrystallised from ethanol (charcoal) to give 4-benzoyl-4′-methyldiphenylamine (21·2 g, 74%), m.p. and mixed m.p. 126—127°, spectroscopically identical with the sample obtained by rearrangement of *N*-benzoyl-4-methyldiphenylamine.

2-Benzoyl-7-methyl-9-phenylacridine.— 4-Benzoyl-4′-methyldiphenylamine (2·87 g, 10 mmol) and benzoic acid (3·66 g, 30 mmol) were stirred under reflux in polyphosphoric acid (70 g) at 130° for 1 h. The mixture was cooled to 80°, poured into water (400 ml), warmed with aqueous 40% sodium hydroxide (100 ml), and extracted with chloroform (3 × 50 ml). The combined extracts were dried (Na_2SO_4) and evaporated, and the resulting solid was recrystallised from ethanol to give 2-benzoyl-7-methyl-9-phenylacridine (2·56 g, 70%), m.p. and mixed m.p. 160—161°, spectroscopically identical with the sample obtained from the rearrangement of *N*-benzoyl-4-methyldiphenylamine.

4-Acetyl-4′-benzoyldiphenylamine.— 4′-Bromoacetophenone (9·95 g, 50 mmol), 4′-benzoylacetanilide (11·95 g, 50 mmol),[23] anhydrous potassium carbonate (5·0 g), and copper-bronze (1·0 g) were kept under reflux at 160—180° (bath) for 25 h. The cooled mixture was extracted with chloroform (3 × 50 ml), and the combined extracts were washed with water (2 × 25 ml), dried (Na_2SO_4), and evaporated. The resulting *N*-acetyl compound was hydrolysed with potassium hydroxide (5·0 g) in refluxing ethanol

[18] A. Bonna, *Annalen*, 1887, **239**, 55.
[19] H. Jensen and F. Rethwisch, *J. Amer. Chem. Soc.*, 1928, **50**, 1146.
[20] A. A. Berlin, *J. Gen. Chem.* (*U.S.S.R.*), 1944, **14**, 430.
[21] E. V. Meyer and A. Nicolaus, *J. prakt. Chem.*, 1910, **82**, 530.
[22] A. Volpi, *Gazzetta*, 1891, **212**, 228.
[23] A. Döbner, *Annalen*, 1881, **210**, 246.

(70 ml), and the free amine was recrystallised from ethanol (charcoal) to give 4-acetyl-4′-benzoyldiphenylamine (9·77 g, 62%), m.p. and mixed m.p. 221—222°, spectroscopically identical with the sample obtained from the rearrangement of *N*-acetyl-4-benzoyldiphenylamine.

Reactions Under Bernthsen Conditions.—(a) *4-Benzoyldiphenylamine and benzoic acid.* The amide (2·73 g, 10 mmol), benzoic acid (2·56 g, 21 mmol), and anhydrous zinc chloride (4·20 g, 30 mmol) were heated under reflux at 240° (bath) for 24 h. The mixture was dissolved in hot ethanol (100 ml), and the solution was poured into aqueous ammonia (s.g. 0·880; 50 ml) and kept for 24 h. Water (700 ml) was added, and the precipitated solid was washed with water, dried at 60° for 4 h, and digested with benzene (4 × 50 ml) until only white zinc oxide remained. The solution was concentrated (to 10 ml) and chromatographed, to give diphenylamine (0·24 g, 14%) [light petroleum (b.p. 60—80°)] and 9-phenylacridine (1·38 g, 54%) (20% chloroform–benzene) (Found: C, 89·7; H, 5·2; N, 5·8. Calc. for $C_{19}H_{13}N$: C, 89·4; H, 5·1; N, 5·5%), m.p. 184° (from ethanol) (lit.,[12] 184°) [picrate, m.p. 227° (lit.,[24] 227·7°)], identified by i.r. spectroscopy; a black tar (0·94 g) was eluted with chloroform.

(b) *Rearrangement of 4-benzoyldiphenylamine.* The amine (2·73 g, 10 mmol) and anhydrous zinc chloride (4·20 g, 30 mmol) were heated under reflux at 240° (bath) for 24 h. Treatment of the products as in (a) gave diphenylamine (0·19 g, 11%), 9-phenylacridine (1·22 g, 48%), and tar (1·18 g).

(c) *Rearrangement of* N-*benzoyldiphenylamine.* The amide (2·73 g, 10 mmol) and anhydrous zinc chloride (4·20 g, 30 mmol) were kept at 240° for 24 h and then treated as described above to give diphenylamine (0·38 g, 23%), 9-phenylacridine (1·32 g, 52%), and tar (0·91 g).

One of the authors (M. T. C.) thanks the S.R.C. for a Research Studentship.

[2/2877 *Received*, 22*nd December*, 1972]

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