Preparation of diphenylamines via the Chapman rearrangement

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The optimum conditions have been determined for preparing substituted diphenylamines using the Chapman rearrangement. The rearrangement was best carried out in boiling tetraglyme. Phenyl *N*-phenylcinnamidate rearranged at a lower temperature than the corresponding benzimidate.

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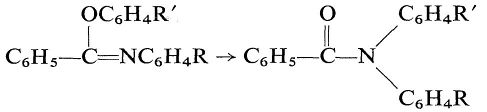
The Chapman rearrangement (1, 2) of phenylbenzimidates (**1**) to benzoyldiphenylamines (**2**) affords a general method (3) for the synthesis of substituted diphenylamines, and is often the only method available (4). The rearrangement is usually carried out by heating the fused imidate to an elevated temperature (280–300°), although this gives a low yield in some cases. Nitrobenzene, diphenyl (5), or diphenyl ether (6) have been used as solvent, but are inconvenient for isolating the product.



$$C_6H_5{-}\overset{OC_6H_4R'}{\overset{|}{C}}{=}NC_6H_4R \rightarrow C_6H_5{-}\overset{O}{\overset{\|}{C}}{-}N(C_6H_4R')(C_6H_4R)$$

1 **2**

It has now been found that the rearrangement can be carried out in nearly quantitative yield by refluxing the benzimidate in tetraethylene glycol dimethyl ether (tetraglyme) (b.p. 276°). The benzoyldiphenylamines were readily isolated by adding water. The reaction could also be carried out in triethylene glycol (b.p. 285°), although with charring and in a lower yield (75–80%). The rearrangement was incomplete in triglyme (b.p. 225°).

The benzimidates (**1**) were prepared by the reaction of a benziminyl chloride with a sodium phenoxide. These chlorides were most conveniently prepared from the benzoylaniline, using a small excess of thionyl chloride (8, 9). The use of phosphorus pentachloride (10, 11) resulted in considerable polymerization on distilling the chloride. The benziminyl chloride in ether was then condensed with the phenol in methanol containing an equivalent of sodium methoxide (1, 4, 12). Dioxane and pyridine have also been used (5, 7) as solvents. It was found that there was no advantage in using sodium methoxide in dimethyl formamide and benzene. Lower yields were obtained with sodium methoxide in tetraglyme, triglyme, or in triethylene glycol. The condensation of the benziminyl chloride in tetraglyme and the rearrangement of the resulting benzimidate without isolation gave only a low yield of product.

A number of substituted benzimidate and benzoyldiphenylamines were prepared (see Table I) in good yield. *N*-Phenylcinnamamide was also prepared by the direct condensation of cinnamic acid and aniline in high yield (91%). The amide was easily converted to the corresponding iminyl chloride by reacting with thionyl chloride. The iminyl chloride reacted smoothly with sodium phenoxide in methanol to give phenyl *N*-phenylcinnamimidate which was rearranged in triglyme in 85% yield, at a lower temperature (225°) than that utilized for the rearrangement of the other compounds studied. Presumably the additional resonance contribution of the cinnamyl group facilitated the rearrangement.

Experimental

Phenylbenziminyl Chloride

Recrystallized benzanilide (19.7 g) was gently heated to reflux with thionyl chloride (15.5 g) for 1 h. The excess thionyl chloride was removed by evacuating at the water pump and the product (28 g, 91%) was distilled, b.p. 115°/6 mm, m.p. 40–41° (lit. (8), m.p. 40°).

Benzo-*p*-toluide (21 g) gave in the same manner *N*-*p*-tolylbenziminyl chloride (32 g, 97%), b.p. 141–144°/10 mm, m.p. 51–52° (lit. (13), b.p. 186°/10 mm).

4-Chlorophenyl-N-phenylbenzimidate
$(1; R = H_1R^1 = pCl)$

p-Chlorophenol (2.32 g) was added to anhydrous methanol (25 ml) containing sodium (0.42 g). Phenylbenziminyl chloride (3.96 g) in ether (15 ml) was added with stirring. The solution was stirred at room temperature overnight, diluted with water, and extracted with ether. The ether solution was washed with 10% sodium hydroxide and water. The product (3.93 g, 80%), m.p. 91–92° (lit. (2), m.p. 92–93°) was recrystallized from methanol.

The other benzimidates (see Table I) were prepared in the same manner.

TABLE I

Physical constants of compounds

	Benzimidates (**1**)				Benzoyldiphenylamines (**2**)			
Substituents	Yield (%)	Melting point (°C)	Lit. melting point (°C)	Reference	Yield (%)	Melting point (°C)	Lit. melting point (°C)	Reference
$R = R^1 = H$	81	104–105	105	6	96	180–181	180	1
$R = Me, R^1 = H$	82	116–118	117–119	14	96	89–90*	—	—
$R = H, R^1 = p$Br	75	89–90	83–84	6	80	178–180†	—	—
$R = Me, R^1 = p$Br	65	136–138‡	—	—	85	117–180§	—	—
$R = H, R^1 = m$Br	80	84–85‖	—	—	75	132–134¶	—	—
$R = H, R^1 = m$MeO	83	77–78	79–80	2	86	123	121	2
$R = H, R^1 = p$Cl	80	91–92	92–93	2	87	110	110	2
$R = H, R^1 = o$Cl	77	89–90	88	1	91	95	95–96	1

*Anal. Calcd. for $C_{20}H_{17}NO$: C, 83.59; H, 5.92. Found: C, 84.16; H, 5.74.
†Anal. Calcd. for $C_{19}H_{14}BrNO$: C, 64.79; H, 4.00. Found: C, 64.65; H, 4.13.
‡Anal. Calcd. for $C_{20}H_{16}BrNO$: C, 65.58; H, 3.85. Found: C, 65.87; H, 4.03.
§Found: C, 65.5; H, 3.92.
‖Anal. Calcd. for $C_{19}H_{14}BrNO$: C, 64.79; H, 4.00. Found: C, 64.45; H, 3.84.
¶Found: C, 64.52; H, 4.21.

N-Benzoyl-4-chlorodiphenylamine (2; $R = H_1R^1 = p$Cl)

4-Chlorophenyl-*N*-phenylbenzimidate (1.5 g) in tetraglyme (15 ml) was heated under reflux for 4 h. The cooled solution was then poured into water, and the solid recrystallized from ethanol (1.3 g, 87%), m.p. 110° (lit. (2), m.p. 110°).

The other diphenylamines (see Table I) were prepared similarly.

N-Phenyl-N-phenylcinnamimidate

A mixture of cinnamic acid (15 g) and aniline (12 g) was heated under reflux at 180° for 2 h. The excess aniline was distilled off *in vacuo*, and the residue of *N*-phenylcinnamamide (22.1 g, 91%) was washed with water and dried, m.p. 149–150° (lit. (14), m.p. 151–152°).

A mixture of *N*-phenylcinnamamide (22 g) and thionyl chloride (12 g) was submitted to the same procedure as before. Distillation of the product gave a light-brown liquid, b.p. 170–175°, 5 mm. On cooling a solid was obtained (25 g, 80%), m.p. 60–61°.

N-Phenylcinnaminyl chloride (2.8 g) was reacted with phenol (1.1 g) in the presence of sodium methoxide (0.6 g) as before to give an oily product. This was chromatographed on alumina and the product eluted with hexane and benzene giving crystals (1.7 g, 48%), m.p. 65–66°, from benzene–hexane. Infrared: 1600 cm^{-1} (CON), 1480 cm^{-1} (C═N), and 1250 cm^{-1} (C—O—Ar).

Anal. Calcd. for $C_{21}H_{17}NO$: C, 84.25; H, 5.72; N, 4.69. Found: C, 84.36; H, 5.66; N, 4.75.

N-Cinnamoyldiphenylamine

Phenyl-*N*-phenylcinnamimidate (1.2 g) was heated under reflux in triglyme (15 ml) for 3 h. The product (1.0 g, 84%) was recrystallized from ethanol, m.p. 153–155° (lit. (13), m.p. 154–156°).

Acknowledgments

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