61. *Condensation of Chlorotriphenylmethane with* ortho-*Disubstituted Benzenes. Further Evidence on the Systematic Difference of Activation of* ortho- *and* para-*Directing Groups.*

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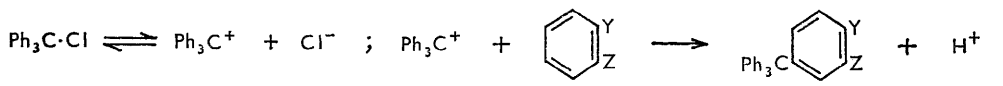
Chlorotriphenylmethane (trityl chloride; triphenylmethyl chloride) is known to condense with aromatic compounds by a plausible direct attack of the triphenylmethyl carbonium ion on the benzene ring without the use of solvents or catalysts. Results now obtained for the difference of directive influence of strong activating substituents in *ortho*-disubstituted benzenes are in agreement with those obtained on tritylation (triphenylmethylation) of the same compounds with triphenylmethanol in acidic media, and thus support the sequence as follows: OH > NH_2 > NHAc > OMe > Me.

Kinetic data [1] and various evidence [2,3] suggest that chlorotriphenylmethane alone condenses with the aromatic ring by direct attack of the triphenylmethyl carbonium ion, and that there was no formation of an ether or *N*-substituted aniline as an intermediate when free OH and NH_2 groups are present as activators. In another view,[4] a pair of activating groups in *ortho*-disubstituted benzenes were suggested to compete for the orientation control:



If Y and Z are different substituents, then in the annexed scheme Y has a more powerful influence on orientation than has Z.

The Table shows that the only compound which was not tritylated was *o*-methylanisole, probably owing to the lack of dissociation of chlorotriphenylmethane. However, it was shown that *o*-methylanisole reacts with triphenylmethanol as recently reported.[4]

Condensation of chlorotriphenylmethane with o-*disubstituted benzenes.*

Compound	Posn. of CPh_3	Diff. in orientation control
o-Cresol	4(OH = 1)	OH > Me
o-Toluidine	4(NH_2 = 1)	NH_2 > Me
o-Acetotoluidide	4(NHAc = 1)	NHAc > Me
o-Methylanisole	N.R.[a]	—
o-Acetanisidide	4(NHAc = 1)	NHAc > OMe
o-Anisidine	4(NH_2 = 1)	NH_2 > OMe
Guaiacol	4(OH = 1)	OH > OMe
o-Aminoacetanilide	4(NH_2 = 1)	NH_2 > NHAc
o-Hydroxyacetanilide [b]	4(OH = 1)	OH > NHAc
o-Aminophenol	4(OH = 1)	OH > NH_2

[a] No reaction below reflux temp. for several days. [b] The NHAc was hydrolysed to NH_2.

Therefore, the general arrangement of the activating groups in order of strength of directive power for tritylation with chlorotriphenylmethane is OH > NH_2 > NHAc > OMe > Me.

This sequence supports the one obtained from tritylation with triphenylmethanol in acidic media [4] and therefore the apparent anomaly reported in the latter work with regard to the absence of free NH_2 groups does not hold, especially since various aniline hydrochlorides have been tritylated in the absence of a catalyst. These facts lead us to consider that OH > NH_2.

Inorganic electrophilic substitution in aromatic compounds has suggested that NH_2

[1] Hart and Cassis, *J. Amer. Chem. Soc.*, 1954, **76**, 1634.
[2] Hickinbottom, *J.*, 1934, 1700.
[3] MacKenzie and Chuchani, *J. Org. Chem.*, 1955, **20**, 338.
[4] Chuchani, *J.*, 1959, 1753.

is the most powerful activating group; nevertheless, there is much evidence [5-7] supporting our view, and Holleman's earlier one,[8] that OH > NH_2. However, these results produced no definite conclusion about control of the orientation of these two groups and more data are required to determine which is the stronger activator.

Experimental

General Procedure.—Chlorotriphenylmethane and the *o*-disubstituted benzene were mixed in an approximately 1 : 1 molar ratio with the latter in very slight excess, without solvent or catalyst, in a two-necked flask, fitted with a thermometer, air condenser, and drying tube.

4-*Trityl*-o-*cresol.* This was prepared as described by van Alphen.[9]

4-*Trityl*-o-*toluidine.* Chlorotriphenylmethane (0·01 mole) and *o*-toluidine (0·01 mole) were heated at 115—120° for 3 hr. The solid mass was treated with 10 ml. of 20% sodium hydroxide solution and crystallised from ethanol; it had m. p. 215—216° (74%), undepressed on admixture with a previous specimen [4] (Found: C, 89·0; H, 6·5; N, 4·1. Calc. for $C_{26}H_{23}N$: C, 89·4; H, 6·6; N, 4·0%).

4-*Trityl*-o-*acetotoluidide.* Chlorotriphenylmethane (0·01 mole) and *o*-acetotoluidide (0·01 mole) were heated at 135—145° for 4 hr. The solid, crystallised from xylene, had m. p. 261—262° (69%) alone or mixed with 4-trityl-*o*-acetotoluidide [4] (Found: C, 86·1; H, 6·3; N, 3·4. Calc. for $C_{28}H_{25}ON$: C, 85·9; H, 6·4; N, 3·6%).

4-*Trityl*-o-*acetanisidide and* 5-*trityl*-o-*aminoacetanilide.* These were prepared as before.[4]

4-*Trityl*-o-*anisidine.* Chlorotriphenylmethane (0·01 mole) was heated with *o*-anisidine (0·01 mole) at 135—140° for 18 hr. The solid was treated with 10 ml. of 20% sodium hydroxide solution and crystallised from benzene; it had m. p. 184—185° (44%) alone or mixed with the product from tritylation of *o*-anisidine with triphenylmethanol in acid [4] (Found: C, 85·3; H, 6·2; N, 3·9. Calc. for $C_{26}H_{23}ON$: C, 85·5; H, 6·3; N, 3·8%).

4-*Tritylguaiacol.* Chlorotriphenylmethane (0·01 mole) and guaiacol (0·01 mole) were heated at 120—125° for 30 hr. The product, crystallised from small amounts of glacial acetic acid, had m. p. and mixed [4] m. p. 188—189° (56%) (Found: C, 85·0; H, 6·0. Calc. for $C_{26}H_{22}O_2$: C, 85·2; H, 6·1%).

2-*Amino*-4-*tritylphenol.* (a) Chlorotriphenylmethane (0·01 mole) was heated with *o*-hydroxyacetanilide at 120—125° for 20 hr. The solid, treated with 10 ml. of 20% sodium hydrogen carbonate solution and crystallised from boiling toluene, had m. p. 286—288° (83%) alone or mixed with the product of tritylation of *o*-aminophenol; [4] therefore the acetyl group was cleaved (Found: C, 84·8; H, 6·6; N, 3·9. Calc. for $C_{25}H_{21}ON$: C, 85·5; H, 6·0; N, 4·0%). (b) Chlorotriphenylmethane (0·01 mole) and *o*-aminophenol (0·01 mole) were heated at 135—140° for 18 hr. The product, treated with 10 ml. of 20% sodium hydrogen carbonate solution and crystallised from boiling toluene, had m. p. and mixed [4] m. p. 286—288° (79%) (Found: C, 84·0; H, 6·4; N, 4·0%).

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[5] Kohn and Fink, *Monatsh.*, 1930, **56**, 137.
[6] Ferguson, *Chem. Rev.*, 1952, **50**, 60.
[7] Francis, Hill, and Johnston, *J. Amer. Chem. Soc.*, 1925, **47**, 2211.
[8] Holleman, *Chem. Rev.*, 1925, **1**, 200.
[9] van Alphen, *Rec. Trav. chim.*, 1927, **46**, 287.