114. *Competition between Aniline and Phenol for a Triphenylmethyl Cation.*

By Gabriel Chuchani.

It has been shown previously that, on tritylation of *o*-aminophenol, the triphenylmethyl group enters the *para*-position with respect to the hydroxyl group. Results now obtained in experiments in which phenol and aniline compete for several trityl reagents reverse the order: *i.e.*, $NH_2 > OH$. The case of *o*-aminophenol is therefore anomalous and may be due to the juxtaposition of the two groups.

Tritylation of *o*-aminophenol [1,2] suggested that the directive power of hydroxyl exceeds that of amino, and similar results have been obtained in the present work by using triphenylmethanol or its perchlorate as tritylating agent. In extension of this work, aniline and phenol (10 mol. of each) were allowed to compete [3] for several trityl reagents (1 mol.) at different temperatures and for a long time. The results given in the Table are of only qualitative significance, but the average yields obtained clearly show that in every case NH_2 predominates over OH in control of orientation in strong acid media. This supports our view [2] that the amino-group is un-ionized at the moment of condensation: if the NH_3^+ group were present we would expect OH to exceed NH_2 in directive power.

Competition between aniline and phenol for triphenylmethyl carbonium ion [a]

Reagent	Temp.	Average yield (%) Posn. of CPh_3	
		4 ($NH_2 = 1$)	4 ($OH = 1$)
Triphenylmethanol [b]	Reflux	82	2
Triphenylmethanol [c]	Reflux	75	0·5
Triphenylmethanol [d]	140—145°	61	12
	Reflux	59	22
Chlorotriphenylmethane	90—100°	85	—
	140—145°	83	—
	Reflux	84	5
Triphenylmethyl perchlorate	100—105°	78	—
	Reflux	84	—

[a] Average isolated yields were taken from three runs; products were identified by mixed m. p. [b] AcOH–HCl. [c] AcOH–H_2SO_4. [d] Without solvent and catalyst.

The anomalous results obtained earlier [1,2] with *o*-aminophenol may be due to the intramolecular changes illustrated in (I)—(IV). If such a chelation occurred intermolecularly in mixtures of aniline and phenol, we should expect to obtain species such as

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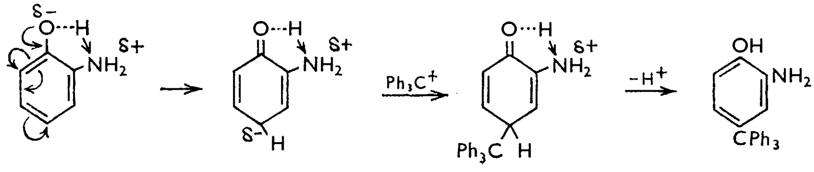
[1] Chuchani, *J.*, 1959, 1753.

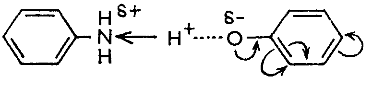
[2] Chuchani, *J.*, 1960, 325.

[3] See (*a*) Ingold and Shaw, *J.*, 1927, 2918; (*b*) Ingold, "Structure and Mechanism in Organic Chemistry," Cornell Univ. Press, 1953, pp. 221—305.

(V). In that case we should have an $:O^-$ group which would be stronger in orientational control than the NH_3^+ group, contrary to the experimental results. The present finding is in agreement with that of inorganic electrophilic substitution in aromatic compounds.



(I) (II) (III) (IV)



(V)

At the same time, our evidence presents further support for the generalization [3b] N > O in orientational control, indicating a decrease in the directing power due to an increase in unshared electrons as the group number increases.[3b,4,5]

EXPERIMENTAL

Triphenylmethyl perchlorate was prepared as described by Gomberg and Cone.[6]

p-Triphenylmethylphenol was prepared from triphenylmethanol and phenol as described by Boyd and Hardy,[7] and also by heating triphenylmethyl perchlorate (0·01 mole) with phenol (0·015 mole) at 80—90° for 5 hr., the solid mass being crystallized from glacial acetic acid; it had m. p. and mixed m. p.[8,9] 284—286° (yield 86%).

p-*Triphenylmethylaniline.*—(*a*) Triphenylmethanol (0·01 mole) and aniline (0·015 mole) were gently refluxed under nitrogen for 17 hr., and the product was crystallized from toluene; it had m. p. 256—258° (yield 60%) alone or mixed with the product from tritylation of aniline.[8,10] (*b*) Triphenylmethyl perchlorate (0·01 mole) was heated with aniline (0·015 mole) at 140—145° for 6 hr., then treated with 20% sodium hydrogen carbonate solution (10 ml.) and dissolved in glacial acetic acid. The mixture was diluted with water (100 ml.), and the solid filtered off and crystallized from toluene; it had m. p. 256—258° (yield 63%) undepressed on admixture with an authentic sample.[8,10]

2-*Amino*-4-*triphenylmethylphenol.*—(*a*) Triphenylmethanol (0·01 mole) and *o*-aminophenol (0·015 mole) were heated together at 130—135° for 12 hr. The product was heated with glacial acetic acid, diluted with water (200 ml.), and treated with 50% sodium hydroxide solution; the precipitate, crystallized from toluene, had m. p. 287—290° (yield 46%) alone and mixed with a previous specimen.[1,2] (*b*) Triphenylmethyl perchlorate (0·01 mole) was heated with *o*-aminophenol (0·015 mole) at 130—140° for 6 hr. The solid was filtered off and crystallized from toluene; m. p. and mixed m. p.[1,2] 287—289 (yield 51%).

Competition between Aniline and Phenol.—(i) *For triphenylmethanol with hydrochloric acid as catalyst.* A mixture of triphenylmethanol (0·01 mole), aniline (0·1 mole), phenol (0·1 mole), and glacial acetic acid (150 ml.) was heated until homogeneous, then refluxed for 1 week after addition of concentrated hydrochloric acid (4 ml.). After dilution with water (400 ml.), the mixture was treated with 50% sodium hydroxide solution until no more precipitate was formed. The resulting solid was refluxed with ethanolic potassium hydroxide (10 g. in 50 ml.), and the mixture diluted with an equal volume of water and filtered. The solid was crystallized from toluene–ethanol (product A), and the filtrate was acidified with concentrated hydrochloric acid, giving a solid (B). The crystals (A), m. p. 256—258°, were proved (mixed m. p.) to be *p*-triphenylmethylaniline,[8,9] and the solid (B), crystallized from glacial acetic acid, had m. p. alone

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[4] Ingold and Ingold, *J.*, 1926, 1310.

[5] Holmes and Ingold, *J.*, 1926, 1328.

[6] Gomberg and Cone, *Annalen*, 1909, **370**, 193.

[7] Boyd and Hardy, *J.*, 1928, 630.

[8] MacKenzie and Chuchani, *J. Org. Chem.*, 1955, **20**, 338.

[9] Baeyer and Villiger, *Ber.*, 1902, **35**, 1189.

[10] Ullmann and Munzhuber, *Ber.*, 1902, **35**, 2878.

or mixed with *p*-triphenylmethylphenol [8,9] 284—286°. Yields from triplicate runs were: *p*-tritylaniline 78, 93, 75%; *p*-tritylphenol 3, 2, 0·6%, respectively.

(ii) *For triphenylmethanol with sulphuric acid as catalyst.* Conditions were as in (i) except that concentrated sulphuric acid (4 ml.) replaced hydrochloric acid. Yields were: *p*-tritylaniline 81, 66, 78%; *p*-tritylphenol 0·3, 0·3, 0·9%, respectively.

(iii) *For chlorotriphenylmethane.* (*a*) Phenol (0·1 mole) and aniline (0·1 mole) were heated to about 60° until homogeneous, and chlorotriphenylmethane (0·01 mole) was added. The mixture was heated at 90—100° for 24 hr. under nitrogen, then with glacial acetic acid. Working up as in (i) gave: *p*-tritylaniline 78, 93, 84%; and unidentified traces. (*b*) As in (*a*) but with 24 hours' heating at 140—145°. Yields were: *p*-tritylaniline 81, 81, 87%; and unidentified traces. (*c*) As in (*a*) but with 24 hours' heating under reflux. Yields were: *p*-tritylaniline 87, 78, 87%; *p*-tritylphenol 4·5, 5·3, 5·3%, respectively.

(iv) *For triphenylmethanol alone.* (*a*) Phenol (0·1 mole), aniline (0·1 mole), and triphenylmethanol (0·01 mole) were heated at 140—145° for 24 hr. under nitrogen. Working up as in (i) gave: *p*-tritylaniline 60, 57, 66%; *p*-tritylphenol 9, 18, 9%, respectively. (*b*) With 24 hours' refluxing yields were: *p*-tritylaniline 54, 60, 63%; *p*-tritylphenol 30, 18, 18%, respectively.

(v) *For triphenylmethyl perchlorate.* (*a*) Phenol (0·1 mole) and aniline (0·1 mole) were heated at about 60° until homogeneous, and triphenylmethyl perchlorate (0·01 mole) was added. The mixture was heated at 100—105° for 24 hr. Warm glacial acetic acid was added, and the solution diluted with water and treated with 20 ml. of 50% sodium hydroxide solution. The resulting solid was filtered off and separated by the procedure described in (i). The results were: *p*-tritylaniline 76, 81, 77%; and no other product. (*b*) With 24 hours' refluxing yields were: *p*-tritylaniline 82, 88, 82%; and no other product.

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