[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, INSTITUTO VENEZOLANO DE INVESTIGATIONES CIENTÍFICAS]

Competition between Corresponding Derivatives of Aniline and Phenol for Orientational Control[1]

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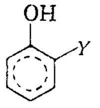
Recent intermolecular competition between aniline and phenol for a triphenylmethyl carbonium ion showed that $NH_2 >$ OH in directive influence in the aromatic ring. These results have been confirmed by further intermolecular competition for the same ion between corresponding derivatives of aniline and phenol. Thus, for the cases of *o*-anisidine and guaiacol, *o*-toluidine and *o*-cresol, and *o*-chloroaniline and *o*-chlorophenol, the competition showed that $NH_2 >$ OH.

The chemical literature contains many contradictory results concerning the relative directing power of the NH_2 and the OH groups. Most of these results have been obtained by intramolecular competition,[3-11] although a few semiquantitative measurements have been published.[12,13]

These conflicting results make it necessary to approach the problem in a different manner. A simpler approach would be that of an intermolecular nonkinetic "competition method"[8] of these two groups with inorganic electrophilic reagents. It is probable that this method has found little application to the problem because of the experimental difficulties involved when the common inorganic reagents are used.

It was recently shown by using this competition method[14] between aniline and phenol with triphenylmethyl carbonium ion that the NH_2 group was stronger than the OH group in orientational control.

To check this result, further intermolecular competitions were examined. In these, the corresponding derivatives of aniline and phenol (0.1 mole of each) competed for the triphenylmethyl carbonium ion (0.01 mole):



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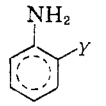

II

Y = corresponding groups: Cl, CH_3, and OCH_3

These compounds were chosen since Y is an activating group and should therefore diminish to a certain almost equivalent degree of the activation of the NH_2 and OH groups in the corresponding compounds. Any coplanarity of the activating groups with the aromatic ring may be reduced by the adjacent substituent, and if this occurs we would expect, as observed in the molecular models, the activation of the NH_2 to be diminished to a greater extent than that of the OH group. Nevertheless, in all cases the results still show that $NH_2 >$ OH.

TABLE I

COMPETITION USING CHLOROTRIPHENYLMETHANE

		Average Yield (%) Position of $(C_6H_5)_3C$			
		Separation *via* KOH-C_2H_5OH[a]		Chromatography	
Compounds	Temp.	4(NH_2 = 1)	4(OH = 1)	4(NH_2 = 1)	4(OH = 1)
o-Anisidine with guaiacol	90–100	69[b]	—	69	—
	135–145	79[b]	—	86	—
o-Toluidine with *o*-cresol	90–100	89	—	76	—
	135–145	82	—	76	—
	Reflux	[c]	—	33[d]	—
o-Chloroaniline with *o*-chlorophenol	90–100	88	—	85	—
	135–145	94	—	91	—
	Reflux	91	—	95	—
Aniline with phenol	90–100	85[e]	—	89	—
	135–145	83[e]	—	79	—
	Reflux	84[e]	5[e]	89	5

[a] Average yield of two runs. Products were identified by mixed melting point. [b] Small yield of $(C_6H_5)_3CH$. [c] Only 56% yield of $(C_6H_5)_3CH$. [d] Also yielded 28% $(C_6H_5)_3CH$. [e] Data taken from G. Chuchani, *J. Chem. Soc.*, 575 (1961).

The conclusions, which are based on the average results of two runs, have only qualitative significance, but they show clearly that the trityl group goes mainly to the *para* position of the various anilines.

The possibility of a solvent effect operating in comparable reactions is a factor that has already

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TABLE II

COMPETITION USING TRIPHENYLMETHYL PERCHLORATE

		Average Yield (%) Position of $(C_6H_5)_3C$			
		Separation *via* $KOH\text{-}C_2H_6OH$[a]		Chromatography	
Compounds	Temp.	$4(NH_2 = 1)$	$4(OH = 1)$	$4(NH_2 = 1)$	$4(OH = 1)$
o-Anisidine with guaiacol	90–100	89	—	78	—
	135–145	70	—	59	—
o-Toluidine with *o*-cresol	90–100	92	—	92	—
	135–145	71	—	79	—
	Reflux	[b]	—	[c]	—
o-Chloroaniline with *o*-chlorophenol	90–100	95	—	91	—
	135–145	90	—	83	—
	Reflux	60	—	57	—
Aniline with phenol	90–100	78[d]	—	88	—
	135–145	—	—	81	—
	Reflux	84[d]	—	83	—

[a] Average yield of two runs. Products were identified by mixed melting point. [b] Only 57% yield of $(C_6H_5)_3CH$. [c] Yielded only 38% of $(C_6H_5)_3CH$. [d] Data taken from G. Chuchani, *J. Chem. Soc.*, 575 (1961).

caused consideration and discussion.[15–21] Whether it does occur or not is questionable. Several possibilities may be postulated for the ways this effect could take place, although there are objections to every one of them. The first one would involve intermolecular attraction of the anilines and phenols, but has been refuted already.[14] The second case makes reference to similar reaction systems[15–21] where the solvent effect would suggest a nucleophilic substitution with the formation of the tritylphenyl ether or the *N*-tritylaniline followed by the corresponding migration of the trityl group to the *para* position of the aromatic compound. However, Hart and Cassis[22] showed kinetically that interaction of chlorotriphenylmethane with phenol took place by a direct electrophilic attack of the trityl group on the phenol nucleus. Further evidence[23] was presented that the latter mechanism holds for both phenol and aniline.

It should also be added that such effect in the competition reactions may require the participation of the phenolic proton in the dissociation of the trityl reagent followed by electrophilic attack of the carbonium ion generally to the aniline nucleus and rarely to the phenol nucleus. If this were the case, the concentration of phenol would diminish with respect to the concentration of aniline during competition; that is, the proportion would not be equimolecular. On this account, competition reactions of aniline and phenol in different molar ratios[24] for the trityl reagent were carried out and showed no variation in the *p*-tritylated products.

The authors assume that the trityl reagents used in the competition reactions considered may undergo a dissociation favored by the polarity of the aromatic medium. Moreover, there is ample support[22,23] for the above assertion that the probable mechanism is that of direct attack by the two reagents. Thus, the present findings give further support to the generalization[8] that N > O in orientational control.

EXPERIMENTAL[25]

Triphenylmethyl perchlorate was prepared as described by Dauben, Honnen, and Harmon.[26]

I. *Competition between o-anisidine and guaiacol.* (i) *For chlorotriphenylmethane.* (a) *o*-Anisidine (0.1 mole), guaiacol (0.1 mole), and chlorotriphenylmethane (0.01 mole) were heated between 90–100° for 24 hr. under nitrogen. The mixture was dissolved in ethanol and diluted with water; then concentrated hydrochloric acid was added until no more precipitate was formed. The resulting solid was gently refluxed with ethanolic potassium hydroxide (5 g. in 50 ml.), and the mixture diluted with an equal volume of water and filtered. The solid was crystallized from benzene (A), and the filtrate was acidified with concentrated hydrochloric acid.[27] The crystals (A), m.p. 184–185°, proved (mixed melting point) to be *p*-trityl-*o*-anisidine.[10,28] The benzene filtrate was evaporated and the solid mass crystallized from methanol, m.p. 93–94°, unchanged on mixture with an authentic sample of triphenylmethane.[23] Yields from duplicate runs were: *p*-trityl-*o*-anisidine, 74, 64%; triphenylmethane, 6, 17%, respectively. In another experiment chromatographic separation of the initial precipitate was carried out on a column of neutral alumina (75 g. Woelm, grade 1). Elution with benzene gave no triphenylmethane; chloroform removed the colored impurities; finally ethanol eluted *p*-trityl-*o*-anisidine (69%) after crystallization as the only product.

(b) The reaction was carried out as in (a) but with 24 hr. of heating at 135–145°. Yields were: *p*-trityl-*o*-anisidine, 80, 77%; triphenylmethane, 3, 7%, respectively. Chromatographic separation, similar to that described above, gave *p*-trityl-*o*-anisidine (86%) and no other product.

(ii) *For triphenylmethyl perchlorate.* (a) A mixture of triphenylmethyl perchlorate (0.01 mole), *o*-anisidine (0.1

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(21) C. G. Swain and E. E. Pegues, *J. Am. Chem. Soc.*, **80,** 812 (1958).

(22) H. Hart and F. A. Cassis, *J. Am. Chem. Soc.*, **76,** 1634 (1954).

(23) C. A. MacKenzie and G. Chuchani, *J. Org. Chem.*, **20,** 336 (1955).

(24) In one set of reactions 0.1 mole of phenol and 0.01 mole of the trityl reagent were refluxed with amounts of aniline up to 0.2 mole; in another, 0.1 mole of aniline and 0.01 mole of the trityl reagent were refluxed with the phenol proportion varied up to 0.2 mole.

(25) Melting points were taken on a Fisher-Johns block and are uncorrected.

(26) H. J. Dauben, L. R. Honnen, and K. M. Harmon, *J. Org. Chem.*, **25,** 1442 (1960).

(27) This step was done to precipitate any final phenolic product present, although in no case was such a compound obtained.

(28) R. A. Benkeser and R. B. Gosnell, *J. Org. Chem.*, **22,** 327 (1957).

mole), and guaiacol (0.1 mole) was heated at 90–100° in darkness for 24 hr. and under nitrogen. Working up as in (i) (a) gave only *p*-trityl-*o*-anisidine, 90, 88%. Separation by chromatography as above gave *p*-trityl-*o*-anisidine (78%).

(b) With 24 hr. of heating at 135–145° yields were: 84, 55% (determined by the ethanolic potassium hydroxide separation) and 50% (chromatographic method) of *p*-trityl-*o*-anisidine.

II. *Competition between o-toluidine and o-cresol.* (i) *For chlorotriphenylmethane.* (a) *o*-Toluidine (0.1 mole), *o*-cresol (0.1 mole), and chlorotriphenylmethane (0.01 mole) were heated at 90–100° for 24 hr. under nitrogen. The reaction mixture was dissolved in ethanol, and the ethanolic potassium hydroxide method (I, i, a) described above was followed. The product on crystallization with ethanol, gave *p*-trityl-*o*-toluidine, which had m.p. 215–216° alone or mixed with an authentic specimen.[10,29] Yields were 87, 91%, and no other product. Chromatographic separation as above (I, i, a) of the initial reaction product dissolved in a small amount of benzene, gave on elution with chloroform and ethanol a 76% yield of *p*-trityl-*o*-toluidine as the only product.

(b) The reaction was carried out as in (a) but 24 hr. of heating at 135–145°. Yields were *p*-trityl-*o*-toluidine, 85, 79%, by the ethanolic potassium hydroxide separation, and 76%, by chromatography. No other product was obtained.

(c) The work-up was as in (a) but with 24 hr. of heating under gentle reflux. Yields of triphenylmethane were 49, 63%; and by chromatography, 33, 28%, plus an unidentified oil.

(ii) *For triphenylmethylperchlorate.* (a) *o*-Toluidine (0.1 mole), *o*-cresol (0.1 mole), and triphenylmethylperchlorate (0.01 mole) were heated at 90–100° for 24 hr. in darkness and under nitrogen. The mixture was dissolved in ethanol, and separation was carried out by the ethanolic potassium hydroxide procedure (I, i, a). Yields were *p*-trityl-*o*-toluidine, 88, 96%, and no other product. Chromatographic separation (II, i, a) gave 92% of *p*-trityl-*o*-toluidine as the only product.

(b) The reaction was carried out as in (a) but with 24 hr. of heating at 135–145°. Yields were *p*-trityl-*o*-toluidine, 78, 63%; chromatography gave 79% of *p*-trityl-*o*-toluidine, and no other product was isolated.

(c) With 24 hr. of refluxing, yields were triphenylmethane, 63, 52%; and by chromatography, 33, 43%.

III. *Competition between o-chloroaniline and o-chlorophenol.* (i) *For chlorotriphenylmethane.* (a) *o*-Chloroaniline (0.1 mole), *o*-chlorophenol (0.1 mole), and chlorotriphenylmethane (0.01 mole) were heated at 90–100° for 24 hr. under nitrogen. Working up by the ethanolic potassium hydroxide procedure (I, i, a) gave, on crystallization with acetone-water, only *p*-trityl-*o*-chloroaniline, m.p. 188–189° alone or mixed with a previous specimen.[30] Yields from duplicate run were *p*-trityl-*o*-chloroaniline, 84, 92%, and no other product. In another run the reaction product, in the minimum quantity of benzene, was chromatograph as in (I, i, a); elution with benzene and chloroform gave an 85% yields of *p*-trityl-*o*-chloroaniline after crystallization.

(b) The reaction was carried out with heating as above in (a) at 135–145° for 24 hr. Yields were *p*-trityl-*o*-chloroaniline 94, 93%, and no other product. Chromatography gave 91% of *p*-trityl-*o*-chloroaniline as the only product.

(c) With 24 hr. of heating under reflux, yields were 90, 92% by ethanolic potassium hydroxide separation and 95% by chromatography of *p*-trityl-*o*-chloroaniline as the only product.

(ii) *For triphenylmethyl perchlorate.* (a) A mixture of triphenylmethyl perchlorate (0.01 mole), *o*-chloroaniline (0.1 mole), and *o*-chlorophenol (0.1 mole) was heated at 90–100° for 24 hr. in darkness and under nitrogen. Working up the product as in (I, i, a) gave *p*-trityl-*o*-chloroaniline 95, 94%, and no other product. Chromatographic separation as in (III, i, a) gave *p*-trityl-*o*-chloroaniline in 91% yield as the only product.

(b) The reaction was carried out as in (a) but with 24 hr. of heating at 135–145° and gave *p*-trityl-*o*-chloroaniline, 92, 88%; while chromatography gave 83% yield of the same compound. No other product was isolated.

(c) With 24 hr. of refluxing yields were *p*-trityl-*o*-chloroaniline, 68, 52%; by chromatography, 57%. No other compound was obtained.

IV. *Competition between aniline and phenol.* (i) *For chlorotriphenylmethane.* (a) Aniline (0.1 mole), phenol (0.1 mole), and chlorotriphenylmethane (0.01 mole) were heated at 90–100° for 24 hr. under nitrogen. The reaction mixture, dissolved in glacial acetic acid, was diluted with water, and treated with 50% sodium hydroxide solution until no more solid precipitated. This product, in benzene, was chromatographed as in (I, i, a). Benzene and chloroform eluted the *p*-tritylaniline which was crystallized from ethanol-toluene mixtures, and identified[23] by melting point and mixed melting point. Yield of *p*-tritylaniline was 89%, and no other product.

(b) Reaction as in (a), with heating of the mixture for 24 hr. at 135–145°, gave by chromatography only *p*-tritylaniline in 79% yield.

(c) Reaction as in (a) with refluxing for 24 hr. gave an 89% yield of *p*-tritylaniline. *p*-Tritylphenol was eluted with acetone and obtained in 5% yield after crystallization with glacial acetic acid. It was identified[23] by melting point and mixed melting point.

(ii) *For triphenylmethyl perchlorate.* Aniline (0.1 mole), phenol (0.1 mole), and triphenylmethyl perchlorate (0 01 mole) were heated between 90–100° in darkness for 24 hr. under nitrogen. Working up and separating by chromatography as in (IV, i, a) gave only *p*-tritylaniline in 88% yield.

(b) With 24 hr. of heating at 135–145°, *p*-tritylaniline was obtained in 81% yield, and no other product.

(c) After 24 hr. of refluxing, *p*-tritylaniline was obtained as the only product in 83% yield.

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