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THE CROSS-MIGRATION OF THE TRITYL GROUP IN COMPETITIVE ORIENTATIONAL CONTROL IN AROMATIC SUBSTITUTION

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Abstract—The cross-migration of the trityl (triphenylmethyl) group from N-tritylaniline and from tritylphenyl ether to mono-substituted benzenes containing strong activating substituents showed the systematic sequence $NMe_2 > NH_2 > OH > OMe$ in directive power. The experimental results appear to indicate that both intramolecular and intermolecular migration are involved.

THE literature cites evidences[2] that tritylation of aromatic compounds with triphenylmethanol in the presence of sulphuric–acetic acid (the Baeyer-Villiger reaction)[3] or hydrochloric–acetic acid solutions[2d,4] involves direct attack of the trityl cation on the benzene ring, rather than lateral condensation in *o*-cresol[5] or the formation of ethers on phenols and N-substituted anilines,[6] with the corresponding migration of the trityl group on the aromatic nucleus. The use of chlorotriphenylmethane without solvent[2bd,7] is also known to give, by electrophilic substitution, the corresponding C-trityl derivatives. On the other hand, the only known methods producing the tritylphenyl ethers and N-trityl anilines, which were believed to be the intermediates occurring under the above reaction conditions, are by condensation of the chlorotriphenylmethane with phenolate salts or with phenols and anilines in basic and nonpolar solvents.[4,6,8]

Although migration of the trityl group to the *para*-position occurs in the interaction of tritylphenyl ether and N-trityl aniline in acid media, it was suggested[2d,9] that, under the conditions employed, the compounds are cleaved and then recombined by subsequent electrophilic attack of the trityl cation to the activated *para*-position of the aromatic nucleus. In view of this assumption, it was considered in the present work to give further evidence of an inter- or intramolecular rearrangements for the conversion

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[2a] D. R. Boyd and D. V. N. Hardy, *J. Chem. Soc.* 630 (1928); [b] W. J. Hickinbottom, *Ibid.* 1700 (1934); [c] H. Hart and F. A. Cassis, *J. Amer. Chem. Soc.* **76**, 1634 (1954); [d] C. A. MacKenzie and G. Chuchani, *J. Org. Chem.* **20**, 336 (1955); [e] T. G. Bonner, J. M. Clayton and G. Williams, *J. Chem. Soc.* 2867 (1957).

[3] A. Baeyer and V. Villiger, *Ber. Dtsch. Chem. Ges.* **35**, 3013 (1902).

[4] M. Gomberg and O. Kamm, *J. Amer. Chem. Soc.* **39**, 2009 (1917).

[5] P. Schorigin, *Ber. Dtsch. Chem. Ges.* **59**, 2502 (1926); **60**, 2373 (1927).

[6a] J. van Alphen, *Rec. Trav. Chim.* **46**, 287 (1927); [b] **46**, 501 (1927).

[7] A. Baeyer, *Ber. Dtsch. Chem. Ges.* **42**, 2624 (1909); E. von Maeyer, *J. Prak. Chem.* **82**, 521 (1911).

[8a] B. Helferich, L. Moog and A. Jünger, *Ber. Dtsch. Chem. Ges.* **58**, 882 (1925); [b] G. S. Parson and C. W. Porter, *J. Amer. Chem. Soc.* **54**, 363 (1932); [c] J. van Alphen, *Ber. Dtsch. Chem. Ges.* **61**, 276 (1928); [d] G. Gardner Swain, *J. Amer. Chem. Soc.* **70**, 1119 (1948); [e] P. E. Verkade, H. Nijon, F. D. Tellenaar, J. H. van Rij and M. Leeuwen, *Rec. Trav. Chim.* **71**, 1007 (1952).

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of O-trityl and N-trityl compounds into the corresponding C-trityl derivatives by cross-migrating the trityl group produced from the former compounds with several monosubstituted benzenes containing strong *ortho-* and *para*-directing groups.

TABLE 1. CROSS-MIGRATION USING N-TRITYLANILINE

Product[a]	Reaction of $C_6H_5NHC(C_6H_5)_3$ with Anisole	 Phenol	 N,N'-Dimethylaniline
p-Tritylanisole	0·3		
p-Tritylphenol		6·2	
p-Tritylaniline	77·6	86·9	26·9
p-Trityl-N,N'-dimethylaniline			57·9
Difference of Activation	$NH_2 > OCH_3$	$NH_2 > OH$	$N(CH_3)_2 > NH_2$

[a] Average yield of two runs.

TABLE 2. CROSS-MIGRATION USING TRITYLPHENYL ETHER

Product[a]	Reaction of $C_6H_5OC(C_6H_5)_3$ with Anisole	 Aniline	 N,N'-Dimethylaniline
p-Tritylanisole	8·6		
p-Tritylphenol	80·4	8·4	1·8
p-Tritylaniline		73·3	
p-Trityl-N,N'-dimethylaniline			79·9
Difference of Activation	$OH > OCH_3$	$NH_2 > OH$	$N(CH_3)_2 > OH$

[a] Average yield of two runs.

The systematic results obtained in the experimental part of this work is shown in Tables 1 and 2. The sequence of directive power among strong activators of the benzene ring is as follows:

$$NMe_2 > NH_2 > OH > OMe$$

It was recently shown by using the intermolecular nonkinetic "competition method" between monosubstituted benzenes containing strong activators for the trityl cation[10] to have a comparable orientation control, thus,

$$NMe_2 > NHMe > NH_2 > OH$$

An extensive search of the chemical literature revealed a great similarity between orientation in disubstituted benzenes for common electrophilic inorganic reagents and that for the trityl cation.[11] The relative strength of activation by intramolecular competition of two given substituents for inorganic electrophiles was shown to be:

$$NH_2 > OH > NHAc > OMe > Me$$

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[10] V. Kese and G. Chuchani, *J. Org. Chem.* **27**, 2032 (1962).

[11] Leading references: G. Chuchani, *Acta Cient. Venezolana* Supl. 1 **14**, 200 (1963); *J. Chem. Soc.* 1753 (1959); *Ibid.* 325 (1960).

This identical sequence was also obtained in the tritylation of *ortho*-disubstituted benzenes.[11,12]

There are no references of intramolecular competition between the substituted and unsubstituted amino groups in disubstituted benzenes and this may be due to the experimental difficulties involved when common inorganic electrophiles are used. It is probable that these disubstituted compounds are unstable during nitration, sulfonation, bromination, etc., and, furthermore, any formation of onium salts in such strong acid media could give a doubtful comparison. The few intermolecular partial comparisons which are reported[13] in the orientational control among strong activators of the benzene ring reveal a good correlation with the results obtained from the systematic intermolecular nonkinetic "competition method" of aromatic compounds containing these groups for the trityl cation[10] and is by no means in contradiction with the sequence of directive power found in the experimental part of this work.

An exclusive intermolecular mechanism for cross-tritylation does not appear to be indicated by cleavage and migration of the trityl group from N-tritylaniline to phenol and from tritylphenyl ether to aniline. In Table 1, it is seen that the ratio of *p*-tritylaniline to *p*-tritylphenol was 86·9 to 6·2. This is an argument in favour that $NH_2 >$ OH in directive power arising from a scheme involving a pre-equilibrium giving dissociated trityl cation and a low concentration of aniline and then subsequent direct electrophilic attack of this ion to the intermolecular competition of aniline with the phenol present in greater concentration. However, when the reagents are reversed where the trityl cation from tritylphenyl ether competes for phenol in low equilibrium concentration and aniline in considerably large excess (0·01 mole), the ratio of *p*-tritylaniline to *p*-tritylphenol shown in Table 2 was only 73·3 to 8·4. If the dissociated trityl cation formed from cleavage of the phenolic ether migrates intermolecularly, then one would expect that the ratio of *p*-tritylaniline to *p*-tritylphenol should be greater in the second experiment, since the aniline to phenol concentration ratio is greater than in the first experiments (Table 1). The somewhat smaller ratio of the second experiment indicates that an intramolecular migration must be occurring along with the intermolecular migration. Previous work in the intermolecular competition between aniline and phenol for a trityl cation[14] showed a close product ratio of *p*-tritylaniline to *p*-tritylphenol of 82 to 2 which implies that the results based on average yields are of only qualitative significance and may give rise to a doubtful mechanistic assumption proposed for cross-tritylation.

In similar experiments there is strong support for a reaction pathway taking place by other than the simple intermolecular scheme. The competition of equivalent amounts of aniline and N,N′-dimethylaniline for the trityl group gave a ratio of product from the latter to the former of 2:1. In the experiment of Table 1 the ratio is also 2:1 even though there is a great excess of the N,N′-dimethylaniline compared to aniline. These observations suggest that a simultaneous intramolecular mechanism

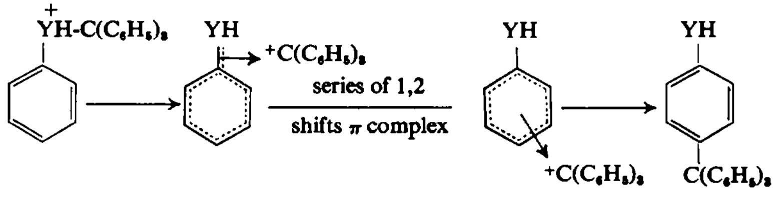
[12] The intramolecular competition for orientational control between the amino and the hydroxy group in the tritylation of *o*-aminophenol suggested that $NH_2 >$ OH in activation and the sequence proposed before[11] OH $> NH_2$ should be changed. See G. Chuchani and J. Zabicky, *J. Chem. Soc.* c, 297 (1966).

[13] See Ref. 10.

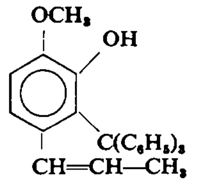
[14] G. Chuchani, *J. Chem. Soc.* 575 (1961).

may occur with the additional evidence that the intermolecular competition of aniline and N,N′-dimethylaniline for triphenylmethyl perchlorate gave only the *para*-tritylated product of the latter compound.[10]

The above argument may indicate that both intramolecular and intermolecular mechanisms are involved, most likely through intimate ion-pairs and/or aromatic π complex for the former and dissociated ions for the latter. The ion-pair intramolecular rearrangement is rather unlikely to be operative in good ionizing media,[15] such as the one used in this work, and this could well favour the series of 1,2- shifts via π complex mechanism.[16] Thus, the intermediacy of ion-pairs described by Cram[17] was limited to the thermal rearrangements of alkyl aryl ethers[15,18] and in this connection it was not possible in a previous investigation[2d] to convert tritylphenyl ether and N-tritylaniline to the *para*-tritylated product by the action of heat alone, up to 200°. Therefore, the acidic media must suggest the π complex mechanism proposed above. Although, the bulky trityl group was hardly found to migrate intramolecularly at the *ortho*-position of the benzene ring, even in those cases when the *para*-position is occupied by another substituents,[6,19] the literature reports the migration of the trityl group from the ethers of isochavibetol (I) and isoeugenol (II)[20] to the adjacent position of the OH group. This is the only example indicating a probable intramolecular rearrangement. However, the authors do not present unequivocal proof of structure of the final compounds.



Where Y = O or NH group



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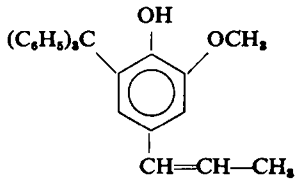

II

Several objections may be raised to the results of this competitive type of reaction. The rearrangement of benzylphenyl ether[21] in the presence of an equivalent amount of

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[15] H. Hart and J. R. Kosak, *J. Org. Chem.* **23**, 2019 (1958).

[16] M. J. S. Dewar, *Molecular Rearrangements* (Edited by P. de Mayo) Part I; p. 295. Interscience, N.Y. (1963).

[17] D. J. Cram, *Steric Effects in Organic Chemistry* (Edited by M. S. Newman) p. 298. Wiley, New York (1965).

[18] H. Hart and H. S. Eleuterio, *J. Amer. Chem. Soc.* **76**, 519 (1954).

[19] H. A. Iddles, W. H. Miller and W. H. Powers, *J. Amer. Chem. Soc.* **62**, 71 (1940).

[20] E. Funakubo and T. Hirotani, *Ber. Dtsch. Chem. Ges.* **69**, 2123 (1936); E. Funakubo, *Ibid.* **70** 1981 (1937).

[21] W. F. Short and M. L. Stewart, *J. Chem. Soc.* 553 (1929).

anisole showed that the benzyl group migrated largely to the latter molecule, which is an indication that OMe > OH in directive power of the aromatic nucleus. However, it was presumed that the appropriation, by the anisole, was probably favoured by the smaller initial concentration of the phenol. This was confirmed by the competition experiments of equivalent amounts of phenol and anisole with benzyl chloride. Another view which may refute the present work is the transfer of the diphenylmethyl group from N-diphenylmethyl-*o*-toluidine to *o*-cresol,[22] but no yields were reported that would permit a deduction of the sequence in orientational control. An argument in favour of the largely intermolecular rearrangement in which the aromatic participants are nearly on equal terms for competition is as follows: the trityl cation formed from cleavage of the phenolic ether has a higher probability of colliding with aniline present in greater concentration and, thus, accounts for the predominance of the NH_2 group over the OH group in activation. However, when the reagents are reversed by interacting the N-tritylaniline in the presence of equimolecular amount of phenol, the acid fission should allow the trityl cation being formed to condense predominantly with phenol present in greater concentration. But the experimental result shows the NH_2 substituent favouring the electrophilic substitution. Moreover, tritylphenyl ether in the presence of anisole, as shown in Table 2, does not indicate the same difference of activation from the cross-migration experiments reported by Short and Stewart with benzyl phenyl ether,[21] but it does support their argument for the intermolecular benzylation of phenol and anisole that OH > OMe in directive power of the benzene ring.

Another objection may be raised for the cross-migration of N-tritylaniline to N,N′-dimethylaniline in which the NMe_2 group shows to be a more powerful *para*-directing group than the NH_2 group. To avoid any ambiguity in the observed results, these two groups as monosubstituted benzenes were competed in excess or acid catalyst with tritylphenyl ether. This experiment shows to reproduce the same sequence with that of Table 1 and with the intermolecular competition of these two aromatic amines for the trityl cation.[10]

From a qualitative point of view, the acid media should favour a relatively fast fission of the ether[20] or the N-substituted aniline[23] and the trityl cation being formed may then proceed to a greater extent with the intermolecular direct electrophilic attack of the detritylated aromatic compound competing with the mono-substituted benzene introduced in the same reaction. The stabilization by resonance of this cation can obviously be the cause for the slow formation of the C-trityl derivative and, in this way, permit both aromatic compounds to compete nearly equimolecularly. This sluggishness is also responsible for the selective substitution of highest electron density of the aromatic nucleus and a reason for allowing a long reaction time. Since all the acid cleavages were carried out for rather extended periods of time, this raises a possible objection as to whether there is any equilibrium of C-tritylated aromatics under these conditions. Accordingly, a recent work[24] showed almost no trityl group transferred to the other competing compound.

The results obtained in this work are in agreement with the idea[16] that cross migration is not necessarily strong evidence for an intermolecular migration and

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[22] H. A. Iddles and W. L. Hartop Jr., *J. Amer. Chem. Soc.* **72**, 4589 (1950).

[23] P. E. Verkade, H. van der Goot and F. D. Tollenaar, *Rec. Trav. Chim.* **83**, 696 (1964).

[24] M. L. Cortés and G. Chuchani, *J. Chem. Soc.* 4259 (1962).

therefore indicate that the rearrangement of tritylphenyl ether and N-trityl aniline takes place by two different mechanism largely by intermolecular route and partly by the intramolecular route.[15–18] The present finding also gives further support to the generalization[25] that N > O in orientational control.

EXPERIMENTAL

Tritylphenyl ether. The compound was prepared as described by Helferich *et al.*[8a]

N-*Tritylaniline*. This was prepared as reported,[6a] but with the modification that the reaction mixture is dissolved only in benzene and refluxed for 5 hr. The solvent is distilled and the syrup residue dissolved in ether–EtOH mixture and then treated with a few ml of 20% NaOHaq, warmed for 10 min, cooled and filtered. The crystals were recrystallized in a mixture of EtOH–ether (53%) had a m.p. 146°.

I. *Rearrangement of* N-*tritylaniline*

(a) *In presence of anisole*. N-Tritylaniline (0·01 mole), anisole (0·01 mole), glacial AcOH (30 ml) and conc HCl (4 ml) were heated to reflux for 3 days. The mixture was poured into cold water (400 ml) and treated with 20% NaOHaq (40 ml). The solid was dried and chromatographed on a column of neutral alumina (75 g, Woelm, grade 1). Elution with benzene and benzene–chloroform gave *p*-tritylaniline, m.p. 257–258°, not depressed and identical IR spectra with an authentic sample[2d] and *p*-tritylanisole, m.p. 194–195°, unchanged on admixture and similar IR spectra with the pure compound.[2d] The yield from the average of two runs were: *p*-tritylaniline, 77·6%; and *p*-tritylanisole, 0·3%.

(b) *In presence of phenol*. Reaction as in I, a but replacing the anisole for phenol (0·01 mole) and refluxed for 3 days. The reaction mixture was diluted with water and treated with 20% NaOHaq. The resulting solid was gently refluxed with ethanolic KOH (5 g in 50 ml) and the mixture diluted 3 times its volume with water and filtered. The precipitate was crystallized from toluene (A), and the filtrate acidified with conc HCl (B). The crystals (A), m.p. 257–258°, proved to be *p*-tritylaniline. The compound, from (B) was crystallized from glacial AcOH, m.p. 284–286°, and showed to be *p*-tritylphenol with admixture and IR spectra with an authentic sample.[2d] Yields from duplicate runs were: *p*-tritylaniline, 86·9%; and *p*-tritylphenol, 6·2%.

(c) *In presence of* N,N′-*dimethylaniline*. Reaction as in I, a but replacing the anisole for N,N′-dimethylaniline (0·01 mole) and refluxed for 3 days. The reaction mixture was poured into cold water (400 ml), treated with conc HCl (15 ml) and warmed to dissolve any unreacted amine for 10 min. The solid was chromatographed as in I, a. The benzene–chloroform eluted the *p*-trityl-N,N′-dimethylaniline, m.p. 210–211°, not depressed and identical IR spectra with the pure compound.[2d] The other fraction obtained was *p*-tritylaniline. Yields from the average of two runs were: *p*-trityl-N,N′-dimethylaniline, 57·9%; and *p*-tritylaniline, 26·9%.

II. *Rearrangement of tritylphenyl ether*

(a) *In presence of anisole*. A mixture of tritylphenyl ether (0·01 mole), anisole (0·01 mole), glacial AcOH (30 ml) and conc HCl (4 ml) was refluxed for 3 days. Working up the ethanolic KOH procedure (I, b) gave an insoluble product *p*-tritylanisole, while the product from acidification of the ethanolic filtrate gave *p*-tritylphenol. Yields from duplicate runs were: *p*-tritylphenol, 80·4%; and *p*-tritylanisole 8·6%.

(b) *In presence of aniline*. The reaction was carried out as in II, a but replacing the anisole for aniline (0·01 mole). Following the procedure (I, b) the products separated and identified were: *p*-tritylaniline, 73·3%; and *p*-tritylphenol, 8·4%.

(c) *In presence of* N,N′-*dimethylaniline*. Reaction as in II, a but replacing the anisole for N,N′-dimethylaniline (0·01 mole). The chromatographic procedure described in I, b gave from duplicate runs: *p*-trityl-N,N′-dimethylaniline, 79·9%; and *p*-tritylphenol, 1·8%.

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[25] C. K. Ingold, *Structure and Mechanism in Organic Chemistry* p. 238. Cornell University Press, Ithaca, N.Y. (1953).

III. *Rearrangement of tritylphenyl ether in the presence of aniline and* N,N′*-dimethylaniline*

Tritylphenyl ether (0·01 mole), aniline (0·01 mole), N,N′-dimethylaniline (0·01 mole), glacial AcOH (30 ml) and conc HCl (8 ml) were refluxed for 4 days. The reaction mixture was poured into cold water (400 ml) and then treated with 20% NaOHaq (40 ml). The solid was refluxed in ethanolic KOH (5 g in 50 ml) and diluted 3 times its volume with water. The solid was chromatographed (A), and the filtrate acidified with conc HCl (B). The crude solid (A) on chromatography as in I, c gave: *p*-trityl-N,N′-dimethylaniline, 41·3%; *p*-tritylaniline, 20·3%; and triphenylmethane, 11·4%. The solid from (B) gave only *p*-tritylphenol, 0·3%.