348. *Tritylation of* ortho-*Disubstituted Benzenes. Systematic Differences of Activation of* ortho- *and* para-*Directing Groups.*

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As tritylation of aromatic compounds may involve direct attack of the triphenylmethylcarbonium ion on the benzene ring, this investigation was directed towards showing the differing directive influences of strongly activating substituents in disubstituted benzenes. In all cases only one trityl group entered the ring. The relative directing powers were: OH > NH_2 > NHAc > OMe > Me.

Since resonance would considerably stabilise the triphenylmethylcarbonium ion, its direct attack on the benzene ring should be rather slow and occur at a position of high electron density. The present work was directed to show that the trityl group may react only at one point where there is a difference of electron density due to a pair of activating groups which thus control the orientation control of this product. In a compound *o*-C_6H_4YZ a triphenylmethyl will enter *para* to whichever of Y or Z controls the reaction.

ortho-Disubstituted benzenes were chosen because the opposite side of each activator is free for substitution. Though adjacent substitution occurs in some cases with the *meta*- and *para*-disubstituted isomers,[1-3] this will not happen readily with the bulky trityl

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[1] Schorigin, *Ber.*, 1927, **60**, 2373.
[2] Boyd and Hardy, *J.*, 1928, 630.
[3] Hardy, *J.*, 1929, 1000.

group. Further, change in temperature changes the result.[1-4] It was also found that hydrochloric acid used as catalyst may convert the triphenylmethanol into 9-phenylfluorene without affecting the aromatic compound.

The Table shows that of the compounds studied only two, *o*-acetanisidide and *o*-aminoacetanilide, did not react with triphenylmethanol: however, electrophilic attack of triphenylmethyl chloride alone on aromatic compounds occurs under favourable conditions,[4,5] and the products to be expected from these two compounds were thus obtained in our work.

The only tritylated products previously reported were made from *o*-toluidine[3,6] and *o*-cresol[4] with hydrochloric acid, and from *o*-methylanisole[2] and *o*-cresol[1,2,7] with sulphuric acid as catalyst. The same products were obtained by us with both catalysts. Hardy[3] assumed, without proof, that the products on tritylation of guaiacol were 4- and 5-tritylguaiacol, but only 4-tritylguaiacol was isolated in our work. While our work was in

Tritylation of ortho-*disubstituted benzenes.*[c]

No.	Compound	Time	Temp.	M. p. Found	M. p. Lit.	Yield (%)	Posn. of CPh_3
1	*o*-Cresol *	3 days	B. p.	182—183°	182—183°[7]	87	4 (OH = 1)
2	*o*-Cresol	1 day	Room	182—183	,,	84	,,
3	*o*-Toluidine *	6 hours	B. p.	215—216	216[3]	79	4 (NH_2 = 1)
4	*o*-Toluidine	2 hours	B. p.	215—216	,,	76	,,
5	*o*-Acetotoluidide *	2 days	B. p.	215—216	,,	84	,,
6	*o*-Acetotoluidide	7 days	70—75°	261—262	—	51	4 (NHAc = 1)
7	*o*-Acetotoluidide	2 days	80°	93	93·0—93·5[4]	42	[a]
8	*o*-Methylanisole *	4 days	B. p.	165—166	165[2]	86	4 (OMe = 1)
9	*o*-Methylanisole	2 hours	80—85°	165—166	165[2]	92	,,
10	*o*-Acetanisidide *	3 days	B. p.	184—185	185—186[8]	83	4 (NH_2 = 1)
11	*o*-Acetanisidide	4 days	65°	93	93·0—93·5[4]	36	[a]
12	*o*-Anisidine *	3 days	B. p.	184—185	185—186[8]	80	4 (NH_2 = 1)
13	*o*-Anisidine	4 hours	B. p.	184—185	185—186[8]	65	,,
14	*o*-Anisidine HCl	4 days	B. p.	184—185	185—186[8]	74	,,
15	Guaiacol *	4 days	B. p.	188—189	—	76	4 (OH = 1)
16	Guaiacol	1 day	Room	188—189	—	81	,,
17	*o*-Aminoacetanilide *	4 days	B. p.	144—145	144[9]	47	[b]
18	*o*-Aminoacetanilide	2 days	65°	93	93·0—93·5[4]	33	[a]
19	*o*-Hydroxyacetanilide *	2 days	B. p.	286—288	—	82	4 (OH = 1)
20	*o*-Hydroxyacetanilide	4 days	65—72°	272—273	—	36	,,
21	*o*-Aminophenol *	3 days	B. p.	286—288	—	85	,,
22	*o*-Aminophenol	2 days	B. p.	286—288	—	71	,,
23	*o*-Aminophenol HCl †	4 days	B. p.	286—288	—	76	,,
24	*o*-Phenylenediamine	2 days	B. p.	256—257	—	77	4

* In cases thus marked, HCl was the catalyst; † indicates no catalyst; in the others, H_2SO_4. [a] Product was $CHPh_3$; Benkeser and Schroeder (*J. Org. Chem.*, 1958, **23**, 1059) reported also two other hydrocarbons. [b] Product was 9-phenylfluorene. [c] NHAc hydrolysed to NH_2, except Nos. 6 and 20.

No.	Found (%) C	Found (%) H	Found (%) N	Formula	Required (%) C	Required (%) H	Required (%) N	Solvent for crystn
15	85·1	6·0	—	$C_{26}H_{22}O_2$	85·2	6·05	—	AcOH
16	85·1	6·1	—	,,	,,	,,	—	,,
19	84·7	6·5	4·1	$C_{25}H_{21}ON$	84·95	6·6	4·0	Xylene
20	82·2	6·1	3·7	$C_{27}H_{23}O_2N$	82·4	5·9	3·6	C_6H_6
21	85·2	6·7	3·85	$C_{25}H_{21}ON$	84·95	6·6	4·0	Xylene
22	84·8	6·5	3·9	,,	,,	,,	,,	,,
23	84·6	6·7	3·9	,,	,,	,,	,,	,,
24	86·9	6·4	6·3	$C_{25}H_{22}N_2$	87·2	6·4	6·4	EtOH

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[4] MacKenzie and Chuchani, *J. Org. Chem.*, 1955, **20**, 336.
[5] Hart and Cassis, *J. Amer. Chem. Soc.*, 1954, **76**, 1634.
[6] van Alphen, *Rec. Trav. chim.*, 1927, **46**, 501.
[7] Iddles, French, and Mellon, *J. Amer. Chem. Soc.*, 1939, **61**, 3192.

progress, tritylation of *o*-anisidine was reported,[8] with slight variations of isolation and structural proof of the product.

The relative directive influences for tritylation were: $OH > NH_2 > NHAc > OMe > Me$. This is the same as in inorganic electrophilic substitution into aromatic compounds, except that there $NH_2 > OH$. The anomaly may result from the circumstance that the concentration of free amine available for reaction is reduced by salt formation.

EXPERIMENTAL

General Procedure.—Triphenylmethanol (1 mol.) was mixed with slightly more than 1 mol. of the compound to be tritylated. For 0·01 mole of the alcohol, about 2 ml. of concentrated sulphuric acid or 4 ml. of concentrated hydrochloric acid and 50 ml. of glacial acetic acid were added. Products were isolated by pouring the mixture into a large amount of cold water. When the compound contained an amino-group, the aqueous mixture was treated with 20% sodium hydroxide solution until no more precipitate was formed. Results are in the Table.

4-*Trityl*-o-*acetanisidide.*—Triphenylmethyl chloride (2·8 g.) was heated with *o*-acetanisidide (1·8 g.) at 135—140° for 8 hr., without solvent. The resulting solid mass, recrystallised from acetic acid, had m. p. 206—207° (3·1 g., 76%) (Found: C, 82·2; H, 6·1; N, 3·4. Calc. for $C_{28}H_{25}O_2N$: C, 82·5; H, 6·2; N, 3·4%).

2-*Amino*-5-*tritylacetanilide.*—Triphenylmethyl chloride (2·8 g.) and *o*-aminoacetanilide (1·7 g.) were heated at 155—160° for 22 hr. The resulting solid was treated with 10 ml. of 20% sodium carbonate solution and crystallised from toluene; it had m. p. 297—299° (1·9 g., 48%) (Found: C, 82·3; H, 6·2; N, 7·0. Calc. for $C_{27}H_{24}ON_2$: C, 82·6; H, 6·2; N, 7·1%).

9-*Phenylfluorene.* Acetic acid (50 ml.) containing concentrated hydrochloric acid (4 ml.) and triphenylmethanol (2·7 g.) was refluxed for 4 days, then poured into water; the resulting solid (1·2 g., 44%), recrystallised from ethanol, had m. p. 144—145° alone or mixed with the product obtained by Kliegl's method.[9]

Proof of Structures.—*Acetylation of* 4-*trityl*-o-*toluidine.* 4-Trityl-*o*-toluidine (2·0 g.), acetic acid (20 ml.), and acetic anhydride (10 ml.) were refluxed for 6 hr., then poured into water (100 ml.). The solid (1·8 g., 82%), recrystallised from xylene, had m. p. 261—262° alone or mixed with the compound obtained by tritylation of *o*-acetotoluidide.

Hydrolysis of 4-*trityl*-o-*acetotoluidide.* 4-Trityl-*o*-acetotoluidide (2 g.), acetic acid (20 ml.), and concentrated hydrochloric acid (4 ml.) were refluxed for 8 hr., then poured into water (100 ml.). The solid (1·3 g., 72%), recrystallised from ethanol, had m. p. 215—216° alone or mixed with the product formed by tritylating *o*-toluidine.

Deamination of 4-*trityl*-o-*anisidine.* To 4-trityl-*o*-anisidine (2 g.) in acetone (100 ml.), 50% hypophosphorous acid (100 ml.), and concentrated hydrochloric acid (4 ml.) at 0—2°, a slight excess of sodium nitrite was added. The mixture was stirred for 4 hr. and kept overnight at 0°. The product, *m*-tritylanisole, was filtered off after dilution with water and crystallised from acetic acid; it had m. p. 168—169° (1·1 g., 58%) (Found: C, 89·0; H, 6·5. Calc. for $C_{26}H_{22}O$: C, 89·1; H, 6·3%).

m-*Tritylanisole.* The Grignard reagent from *m*-bromoanisole was condensed with triphenylmethyl chloride in the conventional manner under nitrogen. The product, *m*-tritylanisole, crystallised from acetic acid and had m. p. 168—169° (46%), not depressed on admixture with the deamination product of 4-trityl-*o*-anisidine.

Acetylation of 4-*trityl*-o-*anisidine.* 4-Trityl-*o*-anisidine gave, as above, the acetyl derivative (77%), m. p. 206—207° (from acetic acid) alone or mixed with the product obtained from triphenylmethyl chloride and *o*-acetanisidide.

Hydrolysis of 4-*trityl*-o-*acetanisidide.* This material was hydrolysed as described above. The mixture was poured into water and treated with 20% sodium hydroxide solution (~10 ml.). The solid (83%), recrystallised from benzene, had m. p. 184—185° alone or mixed with that obtained by tritylation of *o*-anisidine.

4-*Tritylguaiacol from* 4-*trityl*-o-*anisidine.* 4-Trityl-*o*-anisidine (3 g.) was dissolved in acetone (200 ml.) and water (50 ml.). Concentrated sulphuric acid (5 ml.) was slowly added,

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[8] Benkeser and Gosnell, *J. Org. Chem.*, 1957, **22**, 327.

[9] Kliegl, *Ber.*, 1905, **38**, 284.

then at 0—2° sodium nitrite in slight excess. The mixture was stirred for 2 hr. and kept for 6 hr. at 0°. The diazonium salt solution was diluted with water (100 ml.), and the acetone evaporated on a water-bath. Concentrated sulphuric acid (10 ml.) was added and the whole boiled for 1 hr. The resulting gum solidified, and gradually recrystallised from acetic acid–water. Sublimation gave 0·9 g. (30%) of 4-tritylguaiacol, m. p. 188—189° alone or mixed with the product obtained by tritylation of guaiacol.

m-*Tritylaniline.* This was prepared as described by Benkeser and Gosnell.[10]

m-*Tritylacetanilide.* Prepared by acetylation of *m*-tritylaniline as described above and recrystallised from toluene, this product (86%) melted at 167—168° (Found: C, 85·6; H, 6·1; N, 3·8. Calc. for $C_{27}H_{23}ON$: C, 85·9; H, 6·1; N, 3·7%).

Deamination of 2-*Amino*-5-*tritylacetanilide.* This compound was deaminated as described for the 4-trityl-*o*-anisidine. The solid (54%) crystallised from toluene had m. p. 167—168° alone or mixed with *m*-tritylacetanilide.

Hydrolysis of 2-*amino*-5-*tritylacetanilide.* The acetyl group was cleaved as described above. Recrystallisation from ethanol gave the 4-trityl-*o*-phenylenediamine (64%), m. p. of 256—257° alone or mixed with the substance obtained by tritylation of *o*-phenylenediamine.

4-*Trityl*-o-*phenylenediamine.* 2-Nitro-4-tritylaniline[10] (0·01 mole) was heated in ethanol (50 ml.) and 20% sodium hydroxide solution (4 ml.) for 4 hr. while zinc dust (6 g.) was added with stirring. The mixture was filtered while hot, and most of the solvent removed in a vacuum. Cooling and recrystallisation from ethanol gave the product (79%), m. p. 256—257° alone or mixed with the product obtained by tritylation of *o*-phenylenediamine and by hydrolysis of 2-amino-5-tritylacetanilide.

2-*Amino*-4-*tritylphenol.* Ethanol (200 ml.), concentrated hydrochloric acid (30 ml.), and 2-nitro-4-tritylphenol[11] were heated, while tin (6 g.) was added during 0·5 hr. Refluxing with stirring was continued for 8 hr.; the solution was filtered and two-thirds of the solvent removed by distillation. Water (200 ml.) was added and then 20% sodium hydroxide solution until no more precipitation occurred. The crystals were filtered off and after recrystallisation from xylene, had m. p. of 286—288° (2·6 g., 70%) alone or mixed with the product resulting from tritylation of *o*-aminophenol or *o*-aminophenol hydrochloride.

Hydrolysis of 2-*hydroxy*-5-*tritylacetanilide.* The acetyl group of this material (0·01 mole) was cleaved as described above. The acetic acid solution was diluted with water (200 ml.), and 20% sodium hydroxide solution (~10 ml.) was added. The solid, crystallised from xylene, had m. p. 286—288° (79%) alone or mixed with 2-amino-4-tritylphenol obtained by tritylation of *o*-aminophenol or its hydrochloride and or by reduction of 2-nitro-4-tritylphenol.

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[10] Benkeser and Gosnell, *J. Amer. Chem. Soc.*, 1956, **78**, 4914.
[11] von Zincke and Wugk, *Annalen*, 1908, **363**, 284.