Tritylation of Aminophenols *

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o-Aminophenol gave, on tritylation under various sets of conditions, 2-amino-5-tritylphenol (I), this structure being different from the one assigned in an earlier report. *m*-Aminophenol and *m*-anisidine yielded 5-amino-2-tritylphenol (V) and 3-methoxy-4-tritylaniline (VIII), respectively. *p*-Aminophenol and *p*-anisidine were not tritylated under the same conditions. Deamination of (V) and (VIII) are probably the best methods of obtaining *o*-tritylphenol and *o*-tritylanisole, respectively.

m-TRITYLPHENOL[1] was obtained by deamination of the direct tritylation derivative (I) of *o*-aminophenol. This means that the trityl group went *para* to the amino-group and not to the hydroxy-group, contrary to the earlier report.[2] The possibility of the trityl group having entered in the position *ortho* to the amino-group was dismissed, as the infrared spectrum of (I) shows absorption bands in the 800—900-cm.$^{-1}$ region, typical of 1,2,4-trisubstituted benzenes.[3] A proof of this based strictly on chemical reactions can be deduced from the combined evidence of this Paper and those in ref. 2 and 4. Furthermore, the fact that 2-methoxy-4-tritylaniline[2] (II) yielded (I) on demethylation, also points to (I) being 5-trityl-*o*-aminophenol. Thus, other compounds previously described, namely the hydrolysis product (III) of the reported 2-acetamido-4-tritylphenol[2] and the reduction product[2] (IV) of the supposed 2-nitro-4-tritylphenol,[5] had to be re-examined. Compounds (I), (III), and (IV) had the same elemental analysis and showed little or no depression on mixed melting point determinations, and were considered to be identical. From the infrared spectra and deamination products of these compounds we have now found them to be different.

Acetyl cleavage of the reported[2] 2-acetamido-4-tritylphenol to (III), followed by deamination *via* the diazonium salt, gave *p*-tritylphenol. This confirmed the previously assigned structure[2] of the anilide and showed that (III) was indeed 2-amino-4-tritylphenol.

Infrared spectra indicate that reduction[2] of the supposed 2-nitro-4-tritylphenol,[5] does not give 2-amino-4-tritylphenol (III) but a mixture of materials which could not be separated by recrystallisation. On repeating the nitration of *p*-tritylphenol under the conditions reported by Zincke and Wugk[5] we could isolate only mixtures of varying infrared spectra. Moreover, no satisfactory result was obtained on attempting the synthesis of 2-nitro-4-tritylphenol either by tritylation of *o*-nitrophenol in various conditions or diazotisation followed by hydrolysis of 2-nitro-4-tritylaniline.

Tritylated *m*-aminophenol (V) gave on deamination a tritylphenol (VI) which was shown to be different from *m*- or *p*-tritylphenol. The tritylanisole (VII) obtained in the same fashion from tritylated *m*-anisidine (VIII) was different from both *m*- or *p*-tritylanisole. Compounds (VI) and (VII) must therefore be *o*-tritylphenol and *o*-tritylanisole, respectively. Tritylated *m*-aminophenol (V) yielded, on diazotisation followed by hydrolysis, the trityl derivative of resorcinol[4d] (IX). The infrared spectra of compounds (V), (VIII), and (IX) in the 800—900-cm.$^{-1}$ region point to structures with 1,2,4-trisubstitution in the benzene ring.[3] Therefore it can be concluded that (V) is 5-amino-2-tritylphenol and (VIII) is 3-methoxy-4-tritylaniline.

Attempts to obtain *o*-tritylphenol (VI) and *o*-tritylanisole (VII) by methods other than deamination of (V) and (VIII) were unsuccessful. (*a*) Compound (VI) did not react with methyl iodide, methyl sulphate, or diazomethane. (*b*) Treatment of (VII) with hot hydriodic acid yielded triphenylmethane, whereas refluxing

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[1] R. A. Benkeser and R. B. Gosnell, *J. Org. Chem.*, 1957, **22**, 327.

[2] G. Chuchani, *J. Chem. Soc.*, 1959, 1753.

[3] K. Nakanishi, "Infrared Absorption Spectroscopy," Holden-Day Inc., San Francisco, 1962, p. 27.

[4] (*a*) F. Sachs and R. Thonet, *Ber.*, 1904, **37**, 3327; (*b*) M. Gomberg and G. C. Forrester, *J. Amer. Chem. Soc.*, 1925, **47**, 2373; (*c*) T. R. Lea and R. R. Robinson, *J. Chem. Soc.*, 1926, 2351; (*d*) D. V. N. Hardy, *ibid.*, 1929, 1000.

[5] T. Zincke and E. Wugk, *Annalen*, 1908, **363**, 284.

with hydrochloric acid left it unchanged. (*c*) *o*-Methoxytriphenylcarbinol[6] with aniline in acetic acid and in the presence of hydrochloric acid, yielded only *o*-methoxytriphenylmethane.[7] (*d*) The Grignard reagents of *o*-bromoanisole and *o*-bromophenetole did not condense with trityl chloride. (*e*) The attempted tritylation of *m*-phenetidine yielded 9-phenylfluorene and triphenylmethane. All these failures are probably due to the large steric hindrance produced by the bulky trityl group.

Tritylation attempts of *p*-aminophenol with triphenylcarbinol in the presence of hydrochloric acid catalyst resulted in the formation of 9-phenylfluorene and triphenylmethane. When sulphuric acid was used and the mixture heated above 65° triphenylmethane was the main product. *p*-Aminophenol did not react with trityl perchlorate in nitromethane at 30°. Similar behaviour was also observed for *p*-anisidine under the same conditions.

The intramolecular competition for orientational control between the amino- and the hydroxy-groups in *o*-aminophenol, as indicated by the results of the present work, and the lack of reactivity of *o*-nitrophenol as compared with *o*-nitroaniline towards tritylation,[8] suggest that $NH_2 > OH$ in activation, and the sequence proposed before [2,9] should be changed to the general one: $NH_2 > OH > NHAc > OMe > Me$. This is in accordance with the generalisation N > O found in electrophilic aromatic substitution.[10]

EXPERIMENTAL

2-*Amino*-5-*tritylphenol* (I). This *tritylated aminophenol* was prepared by the reaction of *o*-aminophenol with triphenylmethanol,[2,11] triphenylmethyl perchlorate,[11] or chlorotriphenylmethane,[9] and was previously described [2,9,11] as 2-amino-4-tritylphenol.

2-*Methoxy*-4-*tritylaniline* (II). This was prepared as previously reported.[2,9]

5-*Amino*-2-*tritylphenol* (V). Triphenylmethanol (2·6 g.) and *m*-aminophenol (1·5 g.) were mixed in glacial acetic acid (30 ml.) and concentrated hydrochloric acid (4 ml.). After 3 days under reflux the mixture was poured into water and treated with 20% sodium hydroxide solution until no more precipitate was formed. The resulting *product* (2·9 g., 83%) when recrystallised from ethanol had m. p. 247—249° (Found: C, 86·2; H, 5·95; N, 3·7; O, 4·4. $C_{25}H_{21}NO$ requires C, 85·5; H, 6·0; N, 4·0; O, 4·6%).

3-*Methoxy*-4-*tritylaniline* (VIII). Triphenylmethanol (2·6 g.), *m*-anisidine (1·35 g.), glacial acetic acid (30 ml.), and concentrated hydrochloric acid (4 ml.) were heated under reflux for 3 days, then poured into water (200 ml.), and treated with 20% sodium hydroxide solution until no more precipitate was formed. The *product* (2·3 g., 63%) was recrystallised from ethanol (m. p. 189—191°) and then sublimed (m. p. 191—193°) [Found: C, 85·0; H, 6·5; N, 4·1%; *M* (Rast), 363. $C_{26}H_{23}NO$ requires C, 85·45; H, 6·25; N, 3·8%; *M*, 365%].

Proofs of Structures.—m-*Tritylphenol by deamination of* 2-*amino*-5-*tritylphenol* (I). The latter compound (1 g.) was dissolved in dimethyl sulphoxide (50 ml.) and 50% hypophosphorous acid (50 ml.). Concentrated hydrochloric acid (4 ml.) was slowly added and then sodium nitrite (1 g. in 10 ml. of water) at 0—2°. The mixture was stirred for 2 hr. and kept overnight at 0°. The solution was diluted with water and the solid product (0·6 g., 66%) recrystallised from ethanol and after sublimation had m. p. 277—279°. It was shown to be *m*-tritylphenol by mixed m. p., infrared spectrum and elemental analysis (Found: C, 89·3; H, 6·0; O, 4·5. Calc. for $C_{25}H_{20}O$: C, 89·2; H, 6·0; O, 4·8%).

o-*Tritylphenol* (VI) *by deamination of* 5-*amino*-2-*tritylphenol* (V). To a solution of the latter compound (1 g.) in acetone (50 ml.), 50% hypophosphorous acid (50 ml.), and concentrated hydrochloric acid (4 ml.), an aqueous solution of sodium nitrite (1 g. in 10 ml. of water) was added at 0—2°. The solid o-*tritylphenol* (0·48 g., 53%) was filtered off and recrystallised from glacial acetic acid, m. p. 265—267°. On mixed m. p. and infrared spectral determination it was shown to be different from both *p*-tritylphenol[12] and *m*-tritylphenol[1] [Found: C, 89·1; H, 5·85; O, 5·05%; *M* (Rast), 356. $C_{25}H_{20}O$ requires C, 89·2; H, 5·95; O, 4·8%; *M*, 336].

2-*Amino*-4-*tritylphenol* (III) *by hydrolysis of* 2-*acetamido*-4-*tritylphenol*. The anilide was synthesised and cleaved as previously described.[2] The infrared spectrum of the hydrolysis product was different from that of the compound resulting from tritylating *o*-aminophenol (I) (see also next experiment).

p-*Tritylphenol by deamination of* 2-*amino*-4-*tritylphenol* (III). The latter compound was deaminated as described for 2-amino-5-tritylphenol. The solid (62%), after being recrystallised from glacial acetic acid, had m. p. 283—285° alone or mixed with an authentic sample of *p*-tritylphenol.[12] They had identical infrared spectra.

2-*Amino*-5-*tritylphenol* (I) *by demethylation of* 2-*methoxy*-4-*tritylaniline* (II). A solution of the latter (3·7 g.) in acetic acid (20 ml.) and concentrated hydriodic acid (4 ml.) was heated under reflux for 2 days, then poured into water (100 ml.) containing sodium hydrogen sulphite (1 g.). The solid (2·2 g., 63%), recrystallised from boiling toluene, had m. p. 285—287° alone or mixed with the product obtained by tritylating *o*-aminophenol. Their infrared spectra were identical.

m-*Tritylphenol by deamination of demethylated* 2-*methoxy*-4-*tritylaniline*. The foregoing product (I) deaminated as described for 2-amino-5-tritylphenol. The solid (48%), recrystallised from glacial acetic acid, had m. p. 278—280° alone or mixed with *m*-tritylphenol.[1] The infrared spectra were identical.

o-*Tritylanisole* (VII) *by deamination of* 3-*methoxy*-4-*tritylaniline* (VIII). This compound was deaminated as described for 6-trityl-*m*-aminophenol. The reaction mixture was diluted with water and the solid o-*tritylanisole* (41%) on sublimation had m. p. 146—147° (Found: C, 88·4; H, 6·5; O, 5·1; OCH_3, 8·3. $C_{26}H_{20}O$ requires C, 89·1; H, 6·3; O, 4·6; OCH_3, 8·9%).

4-*Tritylresorcinol* (IX) *from* 5-*amino*-2-*tritylphenol* (V). The latter compound (3·5 g.) was dissolved in glacial acetic

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[6] A. Baeyer, *Annalen*, 1907, **354**, 168.

[7] H. Kauffmann and P. Pannwitz, *Ber.*, 1912, **45**, 770.

[8] R. A. Benkeser and R. B. Gosnell, *J. Amer. Chem. Soc.*, 1956, **78**, 4914.

[9] G. Chuchani, *J. Chem. Soc.*, 1960, 325.

[10] C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, 1953, pp. 221—305.

[11] G. Chuchani, *J. Chem. Soc.*, 1961, 575.

[12] A. Baeyer and V. Villiger, *Ber.*, 1902, **35**, 1189.

acid (200 ml.) and water (50 ml.). Concentrated sulphuric acid (5 ml.) was slowly added, then at 0·2°, sodium nitrite (4 g.) in 10 ml. of water. The mixture was stirred for 1 hr. and kept for 4 hr. at 0°. The diazonium salt solution was added very slowly to a boiling solution of sulphuric acid (20 ml.) in water (200 ml.). The resulting gum solidified gradually and, after recrystallisation from acetone, gave 4-tritylresorcinol (2·1 g., 64%), m. p. 280—282° alone or mixed with the product obtained by tritylation of resorcinol.[4d] The infrared spectra of the compounds obtained by both methods were identical.

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