Competition in Intramolecular Arylation of Triphenylmethanols

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Six new unsymmetrically substituted derivatives of 2-aminotriphenylmethanol (**1**) have been synthesised. The direction of ring closure following diazotisation and loss of nitrogen is determined by the nature of the intermediates formed. Where aryl radical intermediates are formed, the selectivity parallels that found in intermolecular competition by phenyl radicals, whereas copper-catalysed decomposition of the diazonium ion leads to intermediates which seem, from their selectivity, to possess considerable cationic nature. The slower thermal decomposition of the diazonium ions unexpectedly shows very little selectivity, suggesting that electrostatic interactions predominate in determining a very short lifetime of the crucial intermediate.

The relative rates of arylation of substituted benzene derivatives,[1,2] and even some absolute rate constants,[3] have been measured by making use of some form of competition process. The assumptions inherent in this method have been criticised; in homolytic aromatic arylation the rates both of phenylation of derivatives of pentafluorobenzene[4] and of pentafluorophenylation of simple derivatives of benzene[5] show some anomalies, evidenced by deviation from additivity of the observed substituent effect upon the reactivity of the substrate, and thought to arise from selective interactions between reactants. More recently,[6] the apparent selectivity of phenylation of a number of polyfluorobenzenes was altered by the presence of hexafluorobenzene, and this was interpreted in terms of complexes between this arene and some arylating agent, possibly phenyl radical itself.

Many of the complicating contributions may be removed by studying competitive *intra*molecular processes. Whilst in a number of classical studies of the mechanism of the Pschorr reaction competition has been observed between nucleophiles (usually water) and aromatic sites, or between heterolytic and homolytic mechanisms of ring closure,[7-9] the construction of a system in which two dissimilarly substituted aryl rings are equally disposed towards an aryl radical generated within the same molecule does not seem to have been attempted. We therefore began a study of the orientation of cyclisation of some derivatives of 2-aminotriphenylmethanol (**1**) containing substituents upon either or both of the aryl rings which do not have the amino-group attached; diazotisation appeared to be a suitable route to the aryl radical, and the relative yields of the possible cyclisation products could be determined spectroscopically. The various ways in which reaction intermediates can be formed from such diazonium ions suggested a variety of degrees of selectivity depending upon the demands of the particular reagent, and we intended to study both reactions in which the aryl radical was the attacking agent and those in which the aryl carbocation was important. Such a study could confirm the correctness of conclusions based upon intermolecular competition.

The yields of cyclisation products are greater when derivatives of triphenylmethanol are used, rather than those of the corresponding triphenylmethane.[8] The 9-(2-aminophenyl)-fluorene system, although attractive, was rejected on two counts; (a) greater synthetic difficulty and (b) the preference for phenol formation (69%) over cyclisation to indeno[1,2,3-*jk*]-fluorene (23%).[10,11]

Discussion

The uncatalysed decomposition of arenediazonium ions in aqueous media proceeds by the formation of a carbocation,[12-17] and such an intermediate is usually[8] invoked in the corresponding cyclisation mechanism. In Me_2SO and similar solvent systems, arylation by Ar^+ is characterised by a reduction in rate by electron-withdrawing groups in the substrate,[18a] and by changes in the orientation of attack, although the selectivity between sites in naphthalene and anthracene is less than when Ph· is held to be the reactive intermediate.[18b] Some (but not all[19-21]) studies of the relative yields of biaryl and phenol have confirmed the presence of a cationic intermediate in these intramolecular reactions.

Earlier studies of the cyclisation process could not readily distinguish between cationic and radical intermediates. The present results offer more definitive evidence, because they show a selection between alternative sites in aromatic substitution, whereas deduction from the earlier work requires the comparison of yields of cyclised products and those of phenolic materials, which may not be formed by similar mechanisms. The total yields of cyclised products were high whether copper powder was present or not (Table). In contrast, the pentyl nitrite–benzene system did not give such high yields. The decomposition of diazo-ethers to form aryl radicals only proceeds well with the *cis*-isomer,[14,22] and the highly constrained reaction site might well favour the formation of the *trans*-isomer. Certainly azo-dyes were formed as well as cyclisation products, and under these reaction conditions, unlike those in aqueous acid, a covalent arylazo derivative is a necessary precursor.[23]

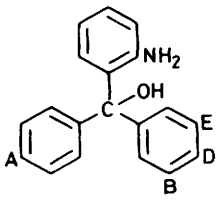
The significance of the results in the Table is not invalidated by the observation that the relative yields of biaryls formed in the thermolysis of benzoyl peroxide depend upon the temperature of the reaction[24] unless the derived partial rate factors change from > 1 to < 1; nor does the suggestion that arylation is reversible impede analysis of our results, although if it were true the ultimate yields of the various biaryls would be determined by thermodynamic and not kinetic considerations. However, the evidence for reversibility of phenylation of arenes supports the reversible dimerisation of the derived intermediate radicals equally as well.[24] Reversible dimerisation allows the intermediate radical further opportunities to be oxidised to the biaryl, differences in the amount of which have been taken as evidence supporting reversible phenylation. It only remains for different dimers, formed from the coupling of isomeric radicals, to show different susceptibilities towards such homolysis, and crowding around the formal centre of electron density in the radical intermediate offers an explanation.[25]

Our results suggest that there is very little differentiation by Ar^+ between sites with quite different electron densities, if we assume the uncatalysed cyclisation to proceed through such an intermediate cation. The copper-catalysed cyclisation, however, shows a discrimination between the available sites of attack

Table. Product yields[a] of dediazoniation of some substituted 2-aminotriphenylmethanols

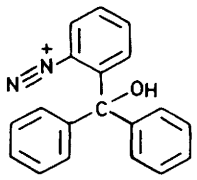
Substituents	Thermal (3M-H_2SO_4; 50 °C)	Cu-catalysed (3M-H_2SO_4; 50 °C)	$C_5H_{11}ONO$–C_6H_6(reflux)
None (**1a**)	(**5a**), 0.79; phenols, 0.18; Ph_3COH, 0.03	(**5a**), 0.86; phenols, 0.07	(**5a**), 0.32; phenols 0.06; Ph_3COH, 0.37
4′-Cl (**1b**)	(**5b**), 0.39; (**5c**), 0.35; phenols, 0.39	(**5b**), 0.41; (**5c**), 0.26; phenols, 0.03	(**5b**), 0.14; (**5c**), 0.14; phenols, 0.02
4′-Me (**1c**)	(**5d**), 0.47; (**5e**), 0.38; phenols, 0.14	(**5d**), 0.57; (**5e**), 0.40; phenols, 0.03	(**5d**), 0.18; (**5e**), 0.23; phenols, 0.08
3′,5′-Me_2 (**1d**)	(**5f**), 0.48; (**5g**), 0.46; phenols, 0.08	(**5f**), 0.40; (**5g**), 0.58; phenols, 0.03	(**5f**), 0.08; (**5g**), 0.18; phenols, 0.10
3′,5′-Cl_2 (**1e**)	(**5h**), 0.47; (**5i**), 0.43; phenols, 0.09	(**5h**), 0.53; (**5i**), 0.19; phenols, 0.05	(**5h**), 0.07; (**5i**), 0.22; phenols, 0.09
4′-Cl,4″-Me (**1f**)	(**5j**), 0.40; (**5k**), 0.39; phenols, 0.17	(**5j**), 0.26; (**5k**), 0.40; phenols, 0.02	(**5j**), 0.12; (**5k**), 0.16; phenols, 0.09
4′-OMe (**1g**)	(**5l**), 0.45; (**5m**), 0.43; phenols, 0.10	—	(**5l**), 0.17; (**5m**), 0.08; phenols, 0.09

[a] Yields of alcohols are quoted in moles per mole of starting material; yields of phenols are quoted in g per g of starting material.

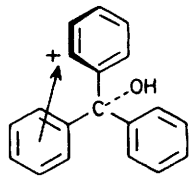


(1)

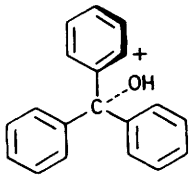
a; A = B = D = E = H
b; A = Cl, B = D = E = H
c; A = Me, B = D = E = H
d; A = D = H, B = E = Me
e; A = D = H, B = E = Cl
f; A = Cl, B = E = H, D = Me
g; A = OMe, B = D = E = H



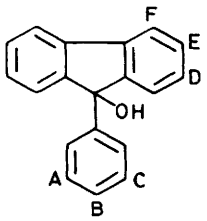
(2)



(3)



(4)



(5)

a; A = B = C = D = E = F = H
b; B = Cl, A = C = D = E = F = H
c; E = Cl, A = B = C = D = F = H
d; B = Me, A = C = D = E = F = H
e; E = Me, A = B = C = D = F = H
f; A = C = Me, B = D = E = F = H
g; D = F = Me, A = B = C = E = H
h; A = C = Cl, B = D = E = F = H
i; D = F = Cl, A = B = C = E = H
j; B = Me, E = Cl, A = C = D = F = H
k; B = Cl, E = Me, A = C = D = F = H
l; B = OMe, A = C = D = E = F = H
m; E = OMe, A = B = C = D = F = H

which is generally consistent with an electrophilic reagent (ρ *ca.* −0.5). Thus, the cyclisation of (**1d**) gives rather more (**5g**) than (**5f**), suggesting that a site *ortho*- and *para*- to methyl substituents is preferred to one without these substituents; the situation is exactly reversed in (**1e**). The mechanism of copper catalysis in this reaction has been keenly argued[26] but our own evidence suggests that Ar^+ is too unstable to be selective, [(**2**) ⟶ (**4**), not (**3**)] whereas the intermediate in the copper-catalysed decomposition is cationic but more stabilised; the rate at which nitrogen is lost from the arenediazonium ion is irrelevant in determining the relative rate of the subsequent arylation process.[14,20,21,27]

Phenyl radicals show intermolecular rates of arylation of arenes[28] (k_2 0.4—1.7 × 10^7 l mol^{-1} s^{-1}) which are rather less than those expected of a diffusion-controlled process (k_2 *ca.* 2 × 10^9 l mol^{-1} s^{-1}). The fair degree of selectivity shown in intermolecular attack is also apparent in intramolecular cyclisation. While it is hard to be certain of the nature and spatial requirements of the various intermediates, the similarity in the selectivity of aryl radicals towards intra- and intermolecular attack suggests that cyclisation, at least in this instance, is not precipitated by the relief of steric strain.

If we assume similar spatial properties for Ar^+ and $Ar^\bullet$, the aryl carbocation seems to be much less selective than the corresponding radical, although this selectivity is improved by the presence of copper, presumably through some polarisation of the diazonium ion which does not result in C–N bond fission.

Experimental

2-Aminotriphenylmethanol Derivatives.—2-Aminotriphenylmethanol (m.p. 121 °C; lit.,[11] 121.5 °C) was obtained in 31% yield from the reaction of methyl anthranilate (0.24 mol) with phenylmagnesium bromide (0.78 mol).[11] Derivatives of 2-aminotriphenylmethanol were obtained by the following general procedure. To an ice-cold, well stirred solution of 2-aminobenzophenone (or an appropriately substituted derivative) in benzene–ether (1:20 v/v) was slowly added an ethereal solution of the appropriate arylmagnesium bromide (3 molecular proportions, based on the amino ketone). After the addition the mixture was allowed to reach room temperature and was boiled for 1 h; the cooled mixture was then decomposed (ice–NH_4Cl). The residue from the removal of volatile material from the organic layer was digested with hydrochloric acid (3M). In most instances a sparingly soluble hydrochloride was formed. The suspension was filtered, and the residue was thoroughly

leached with benzene. The benzene solutions were then concentrated and the residue was further extracted until no more amine hydrochloride was isolated. The combined ionic products were made alkaline with aqueous ammonia, and the liberated base was dissolved in a large volume of benzene. The benzene layer was washed with water and concentrated under reduced pressure after drying (Na_2SO_4). Many recrystallisations from benzene or toluene were needed to obtain material with a constant and sharp m.p. In the few cases where the amine hydrochloride was soluble in the mixture, it was extracted from the benzene–ether solution with dilute hydrochloric acid and was liberated from this aqueous solution by the addition of an excess of ammonia.

In this way were obtained *2-amino-4′-methyltriphenylmethanol* (**1c**) (25%); m.p. 88—89 °C (Found: C, 83.0; H, 6.6; N, 4.8. $C_{20}H_{19}NO$ requires C, 83.0; H, 6.6; N, 4.9%); *2-amino-4′-chlorotriphenylmethanol* (**1b**) (22%); m.p. 94—96 °C (Found: C, 74.0; H, 5.5; N, 4.4. $C_{19}H_{16}ClNO$ requires C, 73.7; H, 5.2; N, 4.4%); *2-amino-4′-chloro-4″-methyltriphenylmethanol* (**1f**) (13%); m.p. 90—92 °C (Found: C, 73.8; H, 5.9; N, 4.1. $C_{20}H_{18}ClNO$ requires C, 74.2; H, 5.6; N, 4.3%) (from 2-amino-4′-methylbenzophenone); *2-amino-3′,5′-dimethyltriphenylmethanol* (**1d**) (27%); m.p. 130—132 °C (Found: C, 83.3; H, 7.1; N, 4.6. $C_{21}H_{21}NO$ requires C, 83.2; H, 6.9; N, 4.6%); *2-amino-3′,5′-dichlorotriphenylmethanol* (**1e**) (43%); m.p. 125—126 °C (Found: C, 66.1; H, 4.4; N, 4.1. $C_{19}H_{15}Cl_2NO$ requires C, 66.3; H, 4.4; N, 4.1%); and *2-amino-4′-methoxytriphenylmethanol* (**1g**) (9%); m.p. 116—118 °C (Found: C, 78.7; H, 6.3; N, 4.6. $C_{20}H_{19}NO_2$ requires C, 78.7; H, 6.2; N, 4.6%) (from 2-amino-4′-methoxybenzophenone). 2-Amino-4′-methylbenzophenone [72%; m.p. 92—93 °C (lit.,[29] 92—93 °C)], 2-amino-4′-chlorobenzophenone [40%; m.p. 101—102 °C (lit.,[30] 102 °C)], and 2-amino-4′-methoxybenzophenone [34%; m.p. 78—79 °C (lit.,[31] 78—80 °C)] were obtained by Friedel–Crafts acylation of the appropriately monosubstituted benzene by *p*-tolylsulphonylanthranilic acid chloride.

2-Amino-3′,5′-dimethylbenzophenone [8%; m.p. 68—70 °C (lit.,[32] 68—70 °C)] was prepared by inverse addition of the Grignard reagent from 1-bromo-3,5-dimethylbenzene to a suspension of 2-methyl-3,1-benzoxazin-4-one by Lothrop and Goodwin's method.[33] 2-Amino-3,5-dichlorobenzophenone [m.p. 85—88 °C (lit.,[32] 93—94 °C) was prepared by chlorination of 2-aminobenzophenone with four molecular proportions of sulphuryl chloride in nitromethane.

Ring-closure of these derivatives of 2-aminobenzophenone by the general method of DeTar and Whiteley[34] gave the following ketones: 3-methylfluorenone [72%; m.p. 67 °C (lit.,[34] 66.0—66.5 °C)]; 3-chlorofluorenone [75%; m.p. 160 °C (lit.,[35a] 159 °C)]; 3-methoxyfluorenone [77%; m.p. 99 °C (lit.,[35] 99.5—100 °C)]; 2,4-dimethylfluorenone [82%; m.p. 149 °C (lit.,[36] 149—150 °C)]; and *2,4-dichlorofluorenone* [20%; m.p. 114—146 °C (Found: C, 62.7; H, 2.5%. $C_{13}H_6Cl_2O$ requires C, 62.7; H, 2.4%)]. The further reaction of these derivatives of fluorenone and either the appropriate arylmagnesium bromide (2.5 molecular proportions) or the aryl-lithium gave the following derivatives of 9-phenylfluorenol: 9-phenylfluoren-9-ol [86%; m.p. 85 °C (lit.,[37–40] 84—86, 85, 109 °C; 9-(4-methylphenyl)fluoren-9-ol [81%; m.p. 84—86 °C (lit.,[38] 85.5—86.5 °C)]; 9-(4-methoxyphenyl)fluoren-9-ol [70%; m.p. 86—88 °C (lit.,[39] 87—88 °C)]; *3-methyl-9-phenylfluoroen-9-ol* [71%; m.p. 87 °C (Found: C, 87.8; H, 5.9. $C_{20}H_{16}O$ requires C, 88.0; H, 5.9%)]; *3-chloro-9-phenylfluoren-9-ol* [70%; m.p. 87—89 °C (Found: C, 77.6; H, 4.7. $C_{19}H_{13}ClO$ requires C, 78.0; H, 4.4%)]; *3-methoxy-9-phenylfluoren-9-ol* [65%; m.p. 124—126 °C (Found: C, 83.0; H, 5.6. $C_{20}H_{16}O_2$ requires C, 83.3; H, 5.5%)]; *3-chloro-9-(4-methylphenyl)fluoren-9-ol* [40%; m.p. 64—66 °C (Found: C, 78.7; H, 5.3. $C_{20}H_{15}ClO$ requires C, 78.3; H, 4.9%)]; *9-(4-chlorophenyl)-3-methylfluoren-9-ol* [31%; m.p. 69—70 °C (Found: C, 78.2; H, 5.1. $C_{20}H_{15}ClO$ requires C, 78.3; H, 4.9%)]; *9-(3,5-dichlorophenyl)fluoren-9-ol* [23%; m.p. 107—110 °C (Found: C, 69.2; H, 4.1%. $C_{19}H_{12}Cl_2O$ requires C, 69.6; H, 3.8%)]; *2,4-dichloro-9-phenylfluoren-9-ol* [19%; m.p. 89—91 °C (Found: C, 69.4; H, 4.1. $C_{19}H_{12}Cl_2O$ requires C, 69.6; H, 3.8%)]; and, by the aryl-lithium method, *9-(3,5-dimethylphenyl-fluoren-9-ol* [68%; m.p. 117—119 °C (Found: C, 88.0; H, 6.6. $C_{21}H_{18}O$ requires C, 88.1; H, 6.3%)] and *2,4-dimethyl-9-phenylfluoren-9-ol* [64%; m.p. 199.5 °C (Found: C, 88.4; H, 6.3. $C_{21}H_{18}O$ requires C, 88.1; H, 6.3%)].

Reaction Conditions.—The amino alcohol (0.1—6.0 mmol) suspended in well stirred sulphuric acid (10% w/w; 25 cm^3 per mmol of amine), was heated to complete the formation of the amine salt, and then treated with a concentrated solution of sodium nitrite (1.05 mol per mol of amine) at 0—5 °C over 15 min. Stirring was continued at 0—10 °C for a further 30 min.

Decomposition in *acid* solution was brought about at room temperature after 4 h; separation of an oily layer was completed by heating to 50 °C for a few min. Organic products were removed by three extractions with ether; phenols were separated from this organic layer by treatment with sodium hydroxide (1M), followed by acidification (2M-HCl) and extraction with ether. Removal of the solvent from each of the dried (Na_2SO_4) extracts gave a neutral fraction, which was analysed, and a phenolic fraction which was weighed but not further investigated.

Copper-catalysed decomposition of the diazonium solution was brought about by adding copper powder and warming gently to 50 °C until a negative test for diazonium ions (2-naphthol) was obtained. Extraction and separation of phenolic products were carried out as above.

For *benzene* solution, the amino alcohol (0.1—8.0 mmol) was dissolved in the solvent (2—200 cm^3) and treated with pentyl nitrite (1.5 mol per mol of amine). The mixture was initially warmed until evolution of gas was perceptible; this was allowed to proceed until it slackened, and the mixture was then boiled until the diazonium ion test was negative (*ca.* 8 h). The solvent and other volatile materials were removed on a rotary evaporator, and the residue was separated as before.

Analysis.—Quantitative separation of the product mixture proved impossible, and the presence of azo derivatives hindered u.v. spectroscopic analysis of the alcohols. However, in strongly acidic media the formation of the corresponding carbocations, the protonation of the azo-dyes, and the resulting shifts in the absorption maxima allowed the expected reaction products to be differentiated clearly.

Accordingly, u.v. spectra were measured of the cyclisation products and of the neutral reaction product mixture in concentrated sulphuric acid, in which the formation of triarylmethyl or 9-arylfluoren-9-yl carbocations is essentially complete.[41] The spectroscopic results were analysed by a modification of Dewar and Urch's method.[42] If ε_A and ε_B are the extinction coefficients of the two components A and B which are the sole contributors to the absorption at a particular wavelength (selected for each mixture so as to maximise the difference in absorption by A and B and to be free from absorption by any other components), then equation (1) applies. This may be rearranged to equation (2), which has the

$$A = (\varepsilon_A[A] + \varepsilon_B[B])d \quad (1)$$

$$A/d\varepsilon_B = (\varepsilon_A/\varepsilon_B)[A] + [B] \quad (2)$$

form $y = mx + c$, from analysis of which values of [A] and [B], and hence (from the known total weight of product and of product dissolved in sulphuric acid) the weight and yield of

these two components, can be calculated. The goodness of fit of the line is taken to reflect the appropriateness of the selected region of the spectrum. In some cases where more than one suitable wavelength existed, each was used and gave independent but concordant measures of the yields of the cyclised products.

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