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MECHANISMS OF FREE-RADICAL AROMATIC SUBSTITUTION

D.H. Hey and M.J. Perkins
Department of Chemistry, King's College, London, W.C.2.
and Gareth H. Williams
Department of Chemistry, Birkbeck College, London, W.C.1.

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In a recent communication, Eliel, Eberhardt, Simamura and Meyerson,[1] while recognising a common homolytic substitution pattern in the arylation of aromatic compounds with three sources of aryl radicals, namely diaroyl peroxides, acylarylnitrosamines, and arylazotriarylmethanes, regarded the first of these sources as unique among them in that arylcyclohexadienyl radicals (II) (see below) were thought to exist in the free state as intermediates in the arylation process with diaroyl peroxides. This conclusion was reached by the application of three stated criteria for the existence of these radicals, namely (a) the formation of dihydrobiaryls as by-products of these reactions; (b) an apparent isotope effect in the arylation of benzene-d as computed from the deuterium content of the biaryl formed, due, at least in part, to isotopic discrimination in the

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[1] E.L. Eliel, M. Eberhardt, O. Simamura and S. Meyerson, Tetrahedron Letters, 749 (1962).

disproportionation of arylcyclohexadienyl radicals; and (c) the appearance of biaryl-$\underline{d}_2$ in the arylation of benzene-$\underline{d}$, as a result of oxidation of dideuterated dihydrobiaryls. Since these criteria were satisfied by reactions with diaroyl peroxides, but not by those with acylarylnitrosamines or arylazotriarylmethanes, it was concluded that arylation with the second and third sources occurred by way of very rapid formation and subsequent dehydrogenation of the radicals II within a solvent-cage, and that the species II never had a free existence in solution. However, closer examination of the criteria detailed above reveals that they all diagnose, not the existence of free arylcyclohexadienyl radicals, but their disproportionation, and are valid only if it can be assumed that some disproportionation is a necessary consequence of their existence.

It has long been recognised that the reactions of acylarylnitrosamines are anomalous in respect of the very small quantities of carbon dioxide which are liberated, since appreciable yields of this product would be predicted from the known instability of the acetyloxy-radical. This was recognised by Huisgen and Horeld[2] and led to their "krypto-radical" theory for the substitution reactions with acylarylnitrosamines. More recently, nitrosoacetanilide has

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[2] R. Huisgen and G. Horeld, Liebigs Ann. **562**, 137 (1949).

been found to be out of step with benzoyl peroxide and with phenylazotriphenylmethane in its reaction with chloroform. While in reactions with benzoyl peroxide and with phenylazotriphenylmethane, the only monocyclic product formed is benzene, the corresponding reaction with nitrosoacetanilide gives both benzene and chlorobenzene, by abstraction of both hydrogen and chlorine from chloroform.[3] Analogous results have been obtained in other closely-related reactions.[4] It therefore appears probable that acylarylnitrosamines are anomalous in not giving rise to free phenyl, acetyloxy- and arylcyclohexadienyl radicals in their reactions with aromatic compounds, but that the radicals are formed, and subsequently react, within a solvent-cage, probably as a result of the high reactivity of the radicals which result from simultaneous homolysis of the weak bonds, as suggested by Eliel, Eberhardt, Simamura and Meyerson.[1] The necessary requirement for the operation of such a mechanism, namely high reactivity on the part of both homolysis fragments, is not satisfied by diaroyl peroxides, as benzoyloxy-radicals are sufficiently stable to diffuse apart, and react as true free radicals, and hence the cage-mechanism does not operate with this source. On these grounds, however, arylazotriarylmethanes must be classified with diaroyl peroxides on account of

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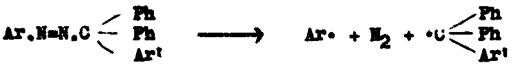
[3] D.H. Hey and J. Peters, J. Chem. Soc. 79 (1960).

[4] J.I.G. Cadogan, D.H. Hey and P.G. Hibbert, unpublished work.

the great stability of triarylmethyl radicals, rather than with acylarylnitrosamines, as suggested by Eliel, Eberhardt, Simamura and Meyerson, on the basis of their non-fulfilment of the "criteria for the existence of free arylcyclohexadienyl radicals".

The work now reported establishes that such free radicals are present in solutions of decomposing arylazotriarylmethanes in aromatic solvents, and it thus follows that their reactions do not share a common mechanistic path with those of the acylarylnitrosamines.

The reaction of phenylazotriphenylmethane (IA) with benzene can be rationalised in terms of equations (i)-(iii), the major products being biphenyl, triphenylmethane and nitrogen. We have now also isolated products of a radical combination process (iv), which accompanies the hydrogen transfer process (iii). The possibility that these products are formed in a radical-induced decomposition of the azo-compound is excluded by kinetic measurements.[5]



$$\mathrm{Ar.N{=}N.C}\left\langle\begin{matrix}\mathrm{Ph}\\ \mathrm{Ph}\\ \mathrm{Ar'}\end{matrix}\right. \longrightarrow \mathrm{Ar}\cdot + \mathrm{N_2} + \cdot\mathrm{C}\left\langle\begin{matrix}\mathrm{Ph}\\ \mathrm{Ph}\\ \mathrm{Ar'}\end{matrix}\right. \qquad ....(i)$$

(I)
A: Ar = Ar' = Ph
B: Ar = Ph, Ar' = $\underline{p}.\mathrm{ClC_6H_4}$
C: Ar = $\underline{p}.\mathrm{CH_3C_6H_4}$, Ar' = Ph
D: Ar = $\underline{p}.\mathrm{CH_3C_6H_4}$, Ar' = $\underline{p}.\mathrm{ClC_6H_4}$

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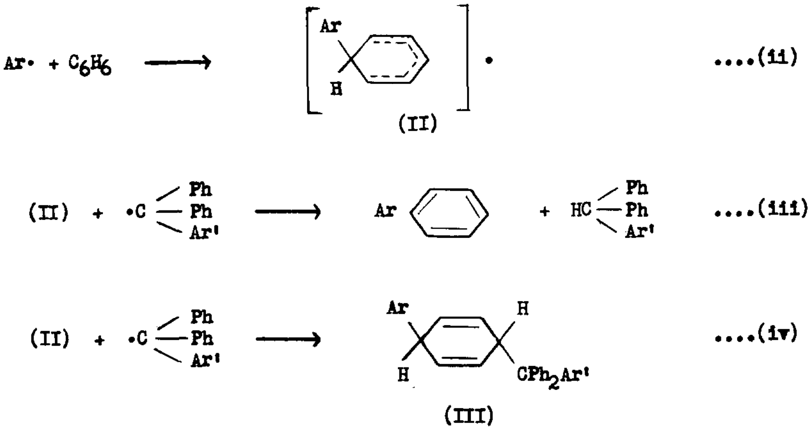
[5] R. Huisgen and H. Nakaten, Liebigs Ann. **586**, 70 (1954)



$$(III) \xrightarrow{-2H} Ar.C_6H_4.CPh_2Ar'$$

(IV) (A-D as for I)

The existence of reaction (iv) was brought to light when the reaction product from the decomposition of phenylazotriphenylmethane in dilute solution in boiling benzene (approx. 0.02 molar) was heated *in situ* with *o*-chloranil to effect dehydrogenation. Surprisingly, no *p*-quaterphenyl, which could arise from the dimerisation and dehydrogenation of II (Ar = Ph) was isolated, but instead 4-tritylbiphenyl (IVA; m.p. 201°) was obtained in approximately 30% yield based on phenylazotriphenylmethane. The structure of this compound was confirmed by independent synthesis. Its formation recalls the isolation of 2-phenyl-5-tritylpyridine from the decomposition of phenylazotriphenylmethane in pyridine reported by Grashey and Huisgen[6].

When the product from the decomposition of phenylazotriphenylmethane in dilute solution in benzene was subjected to chromatography on basic alumina, employing the gradient elution technique with increasing concentration of benzene in light petroleum, biphenyl and

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[6] R. Grashey and R. Huisgen, *Chem. Ber.* **92**, 2641 (1959).

triphenylmethane (from reaction iii) were isolated in equivalent amounts, together accounting for 59% of the azo-compound. A trace of tetraphenylmethane was detected (∼3%), and also two new products which, on the supposed mechanism of their formation and the following evidence, were formulated as geometrical isomers of III (Ar = Ar' = Ph) (*trans* [?] m.p. 151°; 26% : *cis* [?] m.p. 170°; 8%). Each was dehydrogenated with *o*-chloranil to give IVA in good yield (> 80%); each was readily hydrogenated to a tetrahydro-derivative (*trans* [?] m.p. 192°; *cis* [?] m.p. 151°), and each, on heating above its melting-point, decomposed almost quantitatively into biphenyl and triphenylmethane. This last reaction, which presumably occurs by the cleavage of a weak carbon-carbon bond to give two resonance stabilized free-radicals, probably explains previous failures to isolate these products. Slow decomposition of one isomer was noted when the solid was heated *in vacuo* at 125°. The tentative configurational assignment for the two isomers is based on relative yields, melting-points, and melting-points of the tetrahydro-derivatives.

The failure by Eliel *et al.*[1] to observe the disproportionation of phenylcyclohexadienyl radicals derived from the decomposition of phenylazotriphenylmethane in benzene was advanced as evidence that reactions (i)-(iii) occur within a solvent cage, *free* radicals not being involved. The present failure to isolate *p*-quaterphenyl might be held to support this conclusion. The absence of dihydrobiphenyl and p-quaterphenyl could, on the other hand, be due to the incidence of reactions (iii) and (iv) between unlike radicals, if these are faster than the disproportionation and dimerization of the arylcyclohexadienyl radical (ii). In order to test this alternative a reaction was carried out with two azo-compounds, IB and Ic, which were expected to decompose at approximately the same rate. When decomposed separately in dilute solution in boiling benzene, followed by dehydrogenation with o-chloranil, IB and IC yielded the substituted tritylbiphenyls IVB (m.p. 182°) and IVC (m.p. 221-224°) in yields of about 15% and 25% respectively. The corresponding reaction with an equimolar mixture of IB and IC gave, after dehydrogenation, a product which was subjected to gradient elution chromatography as described above. Clean separation of the tritylbiphenyls was not achieved, but fortunately the crossed-products IVA and IVD (m.p. 185°; dechlorinated to IVC) moved at the tail and head, respectively, of the total tritylbiphenyl fraction, and were isolated in a pure state (IVA; ~2%, based on total azo-compound decomposed: IVD; ~3.5%). A small quantity of impure IVC (m.p. 217-220°) was also isolated, and the infra-red spectrum of a solid fraction (m.p. ~160-170°) was closely reproduced by that of a mixture of roughly equal proportions of IVB and IVD.

Under the most favourable conditions for such a mixed reaction, and with clean separation of the products, only 7-8% of each crossed-product would be anticipated (based on a total yield of tritylbiphenyls of about 30%; cf. decomposition of IA). We consider that the isolation of the crossed-products IVA and IVD provides compelling evidence for the participation of free arylcyclohexadienyl and triarylmethyl radicals in this reaction. Further, it seems likely that the products of reaction (iv) are produced predominantly, if not entirely, by combination of such species, rather than by reaction within the solvent cage.

The only available rationalisation of these observations appears to involve the preference for reaction between unlike radicals mentioned above. This then suggests that a reappraisal may be necessary, of the "criteria for existence of free arylcyclohexadienyl radicals" which were proposed by Eliel *et al.*[1] and which, as pointed out above, depend upon disproportionation of arylcyclohexadienyl radicals to give dihydrobiaryls. Dihydrobiaryls should be observed among the reaction products only if removal of arylcyclohexadienyl radicals by disproportionation is not superseded by some faster reaction.

In view of these considerations, and of recent arguments favouring closely similar transition states for the dimerisation and disproportionation of free radicals,[7] it is also possible that the products of reaction (iii) may be formed *via free*-radical intermediates, as the preferred combination of unlike radicals might well be paralleled by a preference for hydrogen transfer between unlike radicals. This accords with the results of previous workers who have succeeded in trapping, almost quantitatively, the radicals from the decomposition of phenylazotriphenylmethane in pyridine[5] and in toluene,[8] and have therefore inferred that *free* radicals are formed.

Direct evidence for discrimination between radicals in their reactivity as hydrogen acceptors from arylcyclohexadienyl radicals has recently been provided by a study of the reaction of benzoyl peroxide with bromobenzene.[9] In this system, both failure to detect any dihydrobiaryl among the products, and an analysis of the reaction kinetics, argue against the removal of arylcyclohexadienyl radicals by disproportionation.

Satisfactory elementary analyses were obtained for all new compounds.

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[7] J.N. Bradley, *J. Chem. Phys.* **35**, 748 (1961); J.N. Bradley and B.S. Rabinovitch, *J. Chem. Phys.* **36**, 3498 (1962); J.A. Kerr and A.F. Trotman-Dickenson, *Progress in Reaction Kinetics* Pergamon Press, London (1961), Vol. I, p. 113.

[8] G.L. Davies, D.H. Hey and G.H. Williams, *J. Chem. Soc.* 4397 (1956).

[9] G.B. Gill and G.H. Williams, unpublished work.