18. *Homolytic Aromatic Substitution. Part XXXIII.* Reactions with Arylazotriarylmethanes.*

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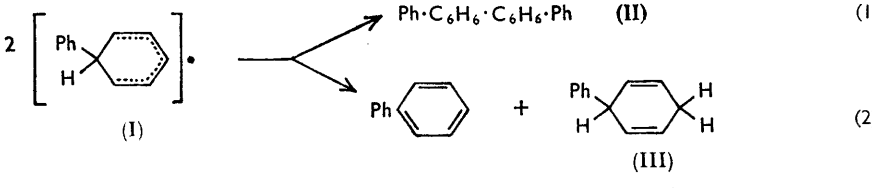
Products of radical coupling reactions have been found from the reaction of phenylazotriphenylmethane with benzene. By means of a cross-over experiment with two substituted azo-compounds, it has been possible to establish the participation of *free* radical intermediates in the formation of these products.

Aromatic phenylation, brought about by the decomposition of dibenzoyl peroxide in an aromatic solvent, is considered to involve free phenyl radicals as intermediates. If the solvent is benzene, addition of a phenyl radical to a solvent molecule gives a phenylcyclohexadienyl radical (I), which, in very dilute solution, reacts mainly by dimerisation to give tetrahydroquaterphenyls (II) (reaction 1) or by disproportionation to give biphenyl and dihydrobiphenyls (III) (reaction 2).



When homolytic aromatic substitution is effected by the use of reagents other than diaroyl peroxides, there is evidence of the occurrence of concerted or cage processes, in which truly free radicals are not involved. Such is believed to be the case in the phenylation of benzene with nitrosoacetanilide as illustrated in reactions (3) and (4).

$$\mathrm{Ph{\cdot}N(NO){\cdot}CO{\cdot}CH_3} \rightleftharpoons \mathrm{Ph{\cdot}N{=}N{\cdot}O{\cdot}CO{\cdot}CH_3} \qquad (3)$$

$$\mathrm{Ph{\cdot}N{=}N{\cdot}O{\cdot}CO{\cdot}CH_3} \longrightarrow [\mathrm{Ph}\cdot + \mathrm{N_2} + \mathrm{CH_3{\cdot}CO{\cdot}O}\cdot] \xrightarrow{\mathrm{C_6H_6}} \mathrm{Ph_2} + \mathrm{N_2} + \mathrm{CH_3{\cdot}CO_2H} \qquad (4)$$

This concerted or cage mechanism is strongly supported by the fact that little carbon dioxide is liberated in the reaction, which gives acetic acid in high yield. This observation

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* Part XXXII, preceding Paper.

led to the " Krypto-radical " theory of Huisgen and Horeld,[1] which postulates concerted homolysis and bond formation. It has also been observed that nitrosoacetanilide reacts with polyhalogenomethanes to give results which are frequently significantly different from those obtained when other aryl-radical sources are employed.[2,3]

Further support for a concerted, or diffusion-controlled cage, mechanism in the decomposition of nitrosoacetanilide in benzene has recently been claimed.[4] It was held that, if free phenylcyclohexadienyl radicals (I) participate in the reaction, it should be possible to demonstrate their formation by identifying one of the products of disproportionation, namely, dihydrobiphenyl (III) (reaction 2), or certain transformation products of the dihydrobiphenyl. No evidence, however, could be found for the disproportionation.

The same criterion was also applied to the phenylation of benzene with phenylazotriphenylmethane, with the same result. Thus, Eliel *et al.*[4] argued that this reaction must also involve a concerted or cage process (these authors favoured the latter), although indications to the contrary had been obtained in earlier work [5,6] using iodine as a radical scavenger. It may also be noted that other aspects of the reactions of this reagent, such as that with chloroform, indicate a resemblance to reactions with benzoyl peroxide rather than to those with nitrosoacetanilide.[2,3]

As a result of detailed studies of the reactions of phenylazotriphenylmethane and related compounds with benzene, evidence is now provided which indicates the participation of free radicals in these reactions.

In studies of the reaction of benzoyl peroxide with benzene it was found that treatment of the product with *o*-chloranil resulted in the formation of the sparingly soluble *p*-quaterphenyl (together with isomeric quaterphenyls) by dehydrogenation of the C_{24} dimers (II) (reaction 1).[7] In the belief that *p*-quaterphenyl formation in this way might also provide a further criterion for the existence of the intermediate (I), a search for *p*-quaterphenyl was made after dehydrogenating the reaction product from the decomposition of phenylazotriphenylmethane in dilute solution in boiling benzene. Instead of the expected quaterphenyl, 4-tritylbiphenyl was isolated in 30% yield, in addition to biphenyl and triphenylmethane. The latter compounds are the normal products of the reaction, which is represented in reactions (5)—(7). In contrast to the peroxide arylation, kinetic measurements have eliminated the possibility of any radical-induced decomposition of the azo-compound.[5,6]

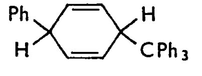
$$\mathrm{Ph{\cdot}N{=}N{\cdot}CPh_3} \longrightarrow \mathrm{Ph\cdot} + \mathrm{N_2} + \mathrm{\cdot CPh_3} \qquad (5)$$

$$\mathrm{Ph\cdot} + \mathrm{C_6H_6} \longrightarrow (\mathrm{I}) \qquad (6)$$

$$(\mathrm{I}) + \mathrm{\cdot CPh_3} \longrightarrow \mathrm{Ph_2} + \mathrm{HCPh_3} \qquad (7)$$

The formation of tritylbiphenyl, which was identified by comparison with a specimen prepared independently, requires the addition of the further radical-coupling reaction (8), the dihydrotritylbiphenyl (IV) thus formed being subsequently dehydrogenated to give 4-tritylbiphenyl.

$$(\mathrm{I}) + \mathrm{\cdot CPh_3} \longrightarrow$$



(IV) (8)

Confirmation of this mechanism was obtained by repetition of the reaction and examination of the products, without dehydrogenation, by chromatography. In this way it was possible to show that biphenyl and triphenylmethane were obtained in equivalent yields and together accounted for 59% of the azo-compound. A trace of tetraphenylmethane was also found, as well as two further products (" P " and " Q ") which are regarded as

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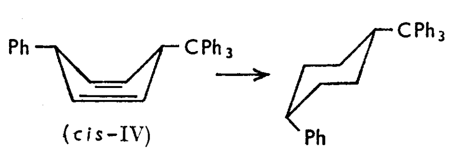
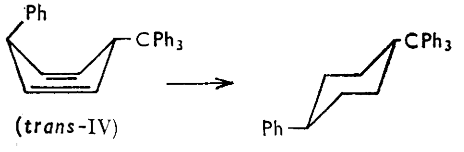
[1] Huisgen and Horeld, *Annalen*, 1949, **562**, 137.
[2] Hey and Peters, *J.*, 1960, 79.
[3] Cadogan, Hey, and Hibbert, unpublished work.
[4] Eliel, Eberhardt, Simamura, and Meyerson, *Tetrahedron Letters*, 1962, 749.
[5] Huisgen and Nakaten, *Annalen*, 1954, **586**, 70.
[6] Davies, Hey, and Williams, *J.*, 1956, 4397.
[7] Hey, Perkins, and Williams, *J.*, 1963, 5604.

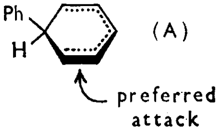
geometrical isomers of (IV). Each was dehydrogenated by *o*-chloranil to 4-tritylbiphenyl, and each, on catalytic hydrogenation, gave a tetrahydro-derivative. On heating above their melting points, each gave biphenyl and triphenylmethane. This last reaction presumably involves the cleavage of a weak carbon–carbon bond, the reverse of reaction (8), above, followed by reaction (7). A tentative configurational assignment is based on the assumption that the cyclohexadienyl radical is planar (A), and therefore the attack by the triphenylmethyl radical should be less hindered on the side remote from the phenyl substituent. Hence the *trans*-product should be formed in higher yield. The assignment of the *trans*-structure to the major product is also supported by conformational considerations. On the basis that a triphenylmethyl rather than a phenyl substituent would preferentially take up an equatorial position in a cyclohexane ring, the conformations of compounds "P" and "Q," and of their tetrahydro-derivatives, may be written as shown. The *cis*-isomer of (IV), m. p. 169—171° (decomp.), has a more elongated structure than the *trans*-isomer, m. p. 151—152° (decomp.), and it might therefore be anticipated that the former would have the higher melting point. The reverse is true for the tetrahydro-derivatives (*cis*, m. p. 151—152°; *trans*, m. p. 193°) All three criteria lead to the same configurational assignments for compounds "P" and "Q."

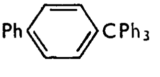

(*cis*-IV)

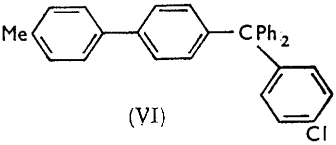

(*trans*-IV)

The isomers of (IV) had presumably remained undetected in previous work owing to their thermal instability, although 2-phenyl-5-tritylpyridine had been identified as a product of the decomposition of phenylazotriphenylmethane in pyridine.[8]

The isolation of the isomeric radical-coupling products (IV), and of tritylbiphenyl, rather than the expected quaterphenyl could be construed as further evidence for a cage or concerted mechanism. However, alternative explanations of this result cannot be ruled out (see below), and in order to test for participation of free radicals in the system, a crossed reaction was carried out between two chemically labelled azo-compounds. In one case the phenyl group was replaced by *p*-tolyl, in the other the triphenylmethyl group was replaced by *p*-chlorophenyldiphenylmethyl. It was expected that the compounds chosen would decompose at approximately the same rate. They were allowed to decompose together in boiling benzene and, after treatment with *o*-chloranil, the tritylbiphenyl derivatives formed were examined for evidence of the crossed reaction. Gas–liquid chromatography (g.l.c.) revealed the presence of four products in approximately equal proportions, and pure specimens of the crossed products (V) and (VI) were isolated by chromatography on alumina. A successful crossing experiment was also carried out at 50°, under nitrogen in a sealed tube, and the ratio of crossed to non-crossed products in this experiment was found by g.l.c. to be 0·95 ± 0·15.




(V)


(VI)

Before concluding with certainty that crossing between free radicals had occurred in the above reactions, two control experiments were necessary. Firstly, it was necessary to demonstrate that no exchange of trityl groups occurred during dehydrogenation. This was established by conducting separate experiments with the substituted azo-compounds,

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[8] Grashey and Huisgen, *Ber.*, 1959, **92**, 2641.

and combining the reaction mixtures before dehydrogenation, when only a trace (~1%) of one crossed product (V) was found after dehydrogenation. This product may well have arisen from a slight impurity in one of the azo-compounds. The second possibility to be eliminated was that crossing occurred prior to the homolytic decomposition. This possibility was suggested by the recent conclusions of Miles and Suschitsky [9] that arylazotriarylmethanes are in equilibrium with small concentrations of ion-pairs, interaction of which could cause the crossing observed in the present work. A mixture of the two azo-compounds

$$\mathrm{Ar'{-}N{=}N{-}CAr_3} \rightleftharpoons (\mathrm{Ar'{-}N_2^{+}{-}{-}{-}CAr_3^{-}})$$

was therefore allowed to decompose in benzene solution for one hour (~1 half-life [6]) at 50°, and then the undecomposed azo-compounds were examined for evidence of such an exchange process. The results indicated that a maximum of 6—7% of exchange might have occurred in the azo-compounds, although all of this may have been due to experimental difficulties. The figure is certainly insufficient to account for the almost complete exchange found in the tritylbiphenyls. The results of these control experiments do not necessarily discredit the ion-pair hypothesis of Miles and Suschitsky,[9] but they satisfactorarily uphold the validity of the main conclusions reached in this Paper, which are that both phenylcyclohexadienyl and triphenylmethyl free radicals are formed in the decomposition of phenylazotriphenylmethane in benzene at least insofar as the radical coupling products are concerned.

Since the preliminary report of this work,[10] the concept of caged radical reactions in the decomposition of phenylazotriphenylmethane in aromatic solvents has been discounted in two additional communications,[11,12] in both of which it is concluded that probably no more than 10% of the decomposition in aromatic solvents can involve caged radicals.

It therefore seems reasonable that the biphenyl and triphenylmethane produced in the reaction of phenylazotriphenylmethane with benzene are also produced *via* free-radical intermediates. The failure to observe dihydrobiphenyl and *p*-quaterphenyl in the reaction may well be due to a build-up in stationary-state concentration of the stable triphenylmethyl radical, which consequently acts as a trap for other radical species formed.[13,14]

It is unlikely that this type of phenomenon could account for the results reported by Eliel *et al.*[4] for the reaction of nitrosoacetanilide with benzene. Furthermore, as noted above, several other features distinguish the reactions of nitrosoacetanilide from those of benzoyl peroxide and phenylazotriphenylmethane.

EXPERIMENTAL

Materials.—Benzene was purified as described previously.[15] Biphenyl and triphenylmethane were crystallised to constant m. p. from light petroleum (b. p. 40—60°). Preparation of *o*-chloranil has been reported previously.[7] Phenyl- and *p*-tolyl-azotriphenylmethane were prepared by the method of Wieland, Popper, and Seefried.[16] The azo-compounds were purified by precipitation from chloroform with methanol, and had correct m. p.s.[6] *Phenylazo-*p*-chlorophenyldiphenylmethane*, prepared in 33% yield in similar manner, was purified by chromatography on basic alumina and precipitation from chloroform solution. It had m. p. 97° (decomp.) (Found: C, 78·4; H, 5·25; Cl, 9·3. $C_{25}H_{19}ClN_2$ requires C, 78·5; H, 5·0; Cl, 9·3%).

The Reaction of Phenylazotriphenylmethane with Benzene.—(*a*) Phenylazotriphenylmethane (1·5 g.) was allowed to decompose in boiling benzene (200 ml.) for 24 hr. *o*-Chloranil (1·275 g., ~1·2 mole) was added, and the solution boiled under reflux for 15 hr. The products were chromatographed on alumina, and the benzene eluate distilled to give biphenyl (b. p. 75—80°/0·1 mm) and triphenylmethane (b. p. 130—140°/0·1 mm.), identified by comparison with authentic specimens. The residue (0·608 g.) from the distillation was crystallised from benzene–methanol to give

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[9] Miles and Suschitzky, *Tetrahedron*, 1963, **19**, 385.

[10] Hey, Perkins, and Williams, *Tetrahedron Letters*, 1963, 445.

[11] Garst and Cole, *Tetrahedron Letters*, 1963, 679.

[12] Russell and Bridger, *Tetrahedron Letters*, 1963, 737.

[13] Bachmann and Wiselogle, *J. Org. Chem.*, 1939, **1**, 354.

[14] Russell and Bridger, *J. Amer. Chem. Soc.*, 1963, **85**, 3754.

[15] Augood, Hey, and Williams, *J.*, 1952, 2094.

[16] Wieland, Popper, and Seefried, *Ber.*, 1922, **55**, 1816.

4-tritylbiphenyl (0·53 g.), m. p. and mixed m. p. 198—201° (lit.,[17] 197—198°) (Found: C, 93·6; H, 6·35. Calc. for $C_{31}H_{24}$: C, 93·9; H, 6·1%). The infrared spectrum of this product was identical with that of a specimen prepared from 4-aminotetraphenylmethane (1 g.) by reaction with amyl nitrite (3 ml.) in benzene (50 ml.) by the general procedure described by Cadogan.[18] The mixture was boiled under reflux for 1·5 hr., the solvent removed, and the involatile product chromatographed on basic alumina. Elution with light petroleum (b. p. 60—80°)–benzene (3 : 1) gave 4-tritylbiphenyl (10%), m. p. 197—199° (from methanol–benzene), together with a little tetraphenylmethane.

(*b*) Phenylazotriphenylmethane (1·5 g.) was allowed to decompose in boiling benzene (200 ml.) for 24 hr. Most of the solvent was then removed, and the residue chromatographed on a column of basic alumina (85 × 1·5 cm.) equipped for gradient elution. The eluent was initially light petroleum (b. p. 40—60°), but as the chromatography progressed a steadily increasing proportion of benzene was added. This procedure greatly reduces "tailing," and gives excellent separations of hydrocarbon mixtures. The eluate was collected in 20 ml. portions whose contents were estimated by evaporation on a water-bath to constant weight. Biphenyl was eluted first, followed closely by triphenylmethane in 57 ± 3 and 60 ± 3% yield, respectively. A little tetraphenylmethane (~30 mg.) closely followed the triphenylmethane. This had m. p. and mixed m. p. 285° [from benzene–light petroleum (b. p. 60—80°)]. Two further compounds followed, each of which was crystallised from light petroleum (b. p. 60—80°). The first, compound "P" (crude yield 0·45 g., 26%), had m. p. 151—152° (decomp.) (Found: C, 92·9; H, 6·55%; *M*, 417. Calc. for $C_{31}H_{26}$: C, 93·4; H, 6·6%; *M*, 398). The second, compound "Q" (crude yield 0·135 g., 8%), had m. p. 169—171° (decomp.) (Found: C, 93·7; H, 6·6. Calc. for $C_{31}H_{26}$: C, 93·4; H, 6·6%).

A solution of compound "P" (41·6 mg.) and *o*-chloranil (65 mg.) in benzene (6 ml.) was boiled under reflux overnight. Chromatography of the products on alumina, and elution with benzene, gave 4-tritylbiphenyl (37 mg.), m. p. and mixed m. p. 197—200° (from benzene–ethanol). Hydrogenation of compound "P" (52 mg.) in ethanol over 10% palladium–charcoal resulted in the uptake of 5·5 ml. of hydrogen (1·93 moles), and the formation of a product m. p. 193° (from methanol) (Found: C, 92·0; H, 7·4. Calc. for $C_{31}H_{30}$: C, 92·5; H, 7·5%). Pyrolysis of compound "P" (25 mg.) at 250° under nitrogen, followed by vacuum sublimation, gave two products, which were identified by m. p.s and mixed m. p.s as biphenyl and triphenylmethane. There was less than 1 mg. of residue unsublimed, and no evidence for the formation of tetraphenylmethane. Compound "P" slowly decomposed when heated *in vacuo* at 130°.

An examination of compound "Q" in the same manner gave the following results. Dehydrogenation gave 4-tritylbiphenyl, m. p. 201—202°, in 90% yield. On hydrogenation, 28 mg. of compound "Q" absorbed 2·7 ml. of hydrogen (1·74 moles) to give a product, m. p. 151—152° (from methanol) (Found: C, 92·7; H, 7·3. Calc. for $C_{31}H_{30}$: C, 92·5; H, 7·5%). Pyrolysis of compound "Q" followed by vacuum sublimation gave biphenyl and triphenylmethane, but no detectable tetraphenylmethane.

4-*Methyl*-4′-*tritylbiphenyl*.—A solution of *p*-tolylazotriphenylmethane (1·5 g.) in benzene (200 ml.) was boiled under reflux for 24 hr. *o*-Chloranil (1·3 g.) was added, and boiling continued for 15 hr. The solvent was removed by distillation, until the residual volume was about 30 ml., when methanol (40 ml.) was added, and the solution allowed to cool. The 4-*methyl*-4′-*tritylbiphenyl* which separated (0·375 g.) had m. p. 221—224° (from ethanol) (Found: C, 93·5; H, 6·5. $C_{32}H_{26}$ requires C, 93·6; H, 6·4%).

4-*Chloro*-4′-*phenyltetraphenylmethane*.—A solution of phenylazo-*p*-chlorophenyldiphenylmethane (0·75 g.) in benzene (100 ml.) was boiled under reflux for 24 hr. and the products dehydrogenated with *o*-chloranil (0·75 g.) as described above. The solvent was removed until the residual volume was about 10 ml., and this was diluted with methanol (20 ml.). 4-*Chloro*-4′-*phenyltetraphenylmethane* (100 mg.) separated on cooling as needles, m. p. 182° [from light petroleum (b. p. 60—80°)] (Found: C, 85·9; H, 5·4. $C_{31}H_{23}Cl$ requires C, 86·4; H, 5·4%). The structure of the product was confirmed by dechlorination to 4-tritylbiphenyl using hydrazine and palladium–charcoal.[19]

Crossed Reactions.—(*a*) A solution of *p*-tolylazotriphenylmethane (1·60 g.) and phenylazo-*p*-chlorophenyldiphenylmethane (1·56 g.), in a little cold benzene, was added to boiling benzene

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[17] Schoepfle and Trepp, *J. Amer. Chem. Soc.*, 1932, **54**, 4059.

[18] Cadogan, *J.*, 1962, 4257.

[19] Mosby, *Chem. and Ind.*, 1959, 1348.

(400 ml.), and the solution boiled under reflux for 20 hr. The products were dehydrogenated with *o*-chloranil (2·6 g.) as before. Most of the solvent was removed, and the residual solution (~40 ml.) was chromatographed on basic alumina and eluted with benzene (400 ml.). Distillation of the eluate left (after removal of biaryls and most of the triarylmethanes) a high-boiling residue (1·549 g.), b. p. >160°/0·05 mm., which was dissolved in a minimum of light petroleum (b. p. 60—80°) and subjected to gradient elution chromatography as described previously. The four possible tritylbiphenyls were not completely separated on the column, but by careful crystallisation of the fractions collected from the head and tail of the total tritylbiphenyl fraction, it was possible to obtain pure specimens of 4-tritylbiphenyl (m. p. and mixed m. p. 199—201°; 2% based on total azo-compound decomposed) and *4-chloro-4'-*(p-*tolyl)tetraphenylmethane* (3·5%), m. p. 185° (Found: C, 86·4; H, 5·7. $C_{32}H_{25}Cl$ requires C, 86·5; H, 5·7%). The structure was confirmed by dechlorination [19] to 4-methyl-4'-tritylbiphenyl, m. p. and mixed m. p. 222—224%. Recrystallisation of the middle tritylbiphenyl fractions from the chromatography gave a specimen of impure 4-methyl-4'-tritylbiphenyl, m. p. 218—222° and mixed m. p. 219—224°. A further solid product was shown, by its infrared spectrum, to be a mixture of roughly equal parts of 4-chloro-4'-phenyl- and 4-chloro-4'-(*p*-tolyl)-tetraphenylmethane.

(*b*) (i) A second crossed reaction was carried out as in (*a*), but on a smaller scale (125 mg. of each azo-compound in 25 ml. of benzene). After dehydrogenation, the products were chromatographed on alumina and the benzene eluate was concentrated to 1 ml. and examined by g.l.c. for tritylbiphenyls. Four compounds, with retention times corresponding to those of the four possible products, were present in approximately equal amounts.

(ii) An experiment similar to (i) above was carried out under nitrogen in a sealed tube which was maintained at 50° for 24 hr. The products were dehydrogenated and worked up as before. Accurate analysis was not practicable owing to appreciable tailing on the gas chromatograms, and consequent overlap of the peaks corresponding to the four tritylbiphenyls. However, after comparison of the detector response to the four different compounds, it was estimated that the ratio of crossed to non-crossed products was 0·95 ± 0·15.

Control Experiments.—(*a*) The decomposition products of *p*-tolylazotriphenylmethane (125 mg.) in benzene (15 ml.) and phenylazo-*p*-chlorophenyldiphenylmethane (125 mg.) in benzene (15 ml.) were combined and dehydrogenated with *o*-chloranil as described above. G.l.c. analysis of the hydrocarbon products showed no 4-chloro-4'-(*p*-tolyl)tetraphenylmethane and only a trace (~1% of the total tritylbiphenyl derivatives) of 4-tritylbiphenyl, thus confirming that negligible crossing occurred during dehydrogenation.

(*b*) A solution of phenylazo-*p*-chlorophenyldiphenylmethane (125 mg.) and *p*-tolylazotriphenylmethane (125 mg.) in benzene (25 ml.) was heated under nitrogen in a sealed tube at 50° for 1 hr. The mixture was cooled and concentrated to 1 ml. by distillation under reduced pressure at 25°. The residual solution was examined for any exchange between the undecomposed azo-compounds. Thin-layer chromatography (t.l.c.) showed the presence of two yellow substances corresponding to the starting materials, but no conditions could be found under which separation of *p*-tolylazotriphenylmethane from phenylazotriphenylmethane could be achieved. To determine whether or not the latter compound had been formed, the t.l.c. was repeated on a preparative scale, and the yellow band whose behaviour was that of *p*-tolylazotriphenylmethane was extracted into boiling benzene, and the solution boiled under reflux for 2 hr. The resulting solution of azo-compound decomposition products was then examined by g.l.c., and the biaryls present were found to consist of 94% 4-methylbiphenyl and 6% biphenyl. This indicated that the yellow material from the t.l.c. was at least 94% *p*-tolylazotriphenylmethane. (The biaryls from the original reaction were well separated from the azo-compounds on t.l.c.). Similar treatment of the second azo-fraction, whose t.l.c. behaviour was that of phenylazo-*p*-chlorophenyldiphenylmethane, gave biaryls consisting of 93·5% biphenyl and 6·5% 4-methylbiphenyl.

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