

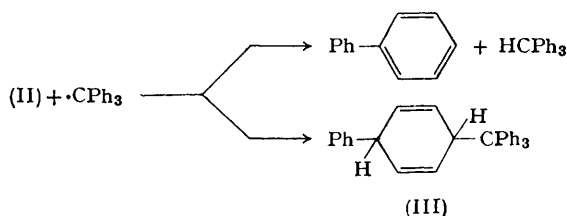
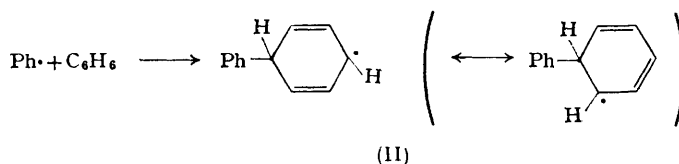
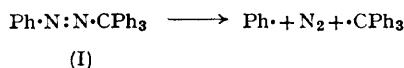
1145. The Thermal Decomposition of Phenylazotriphenylmethane in *p*-Xylene.

By M. J. PERKINS.

The major products of the title reaction are 2,5-dimethylbiphenyl, triphenylmethane, benzene, and 1,1,1-triphenyl-2-*p*-tolylethane. Their formation is accommodated by a scheme of free-radical reactions which is dominated by the stability of the triphenylmethyl radical.

In work described in an earlier Paper,¹ it was shown that the major products of the thermal decomposition of phenylazotriphenylmethane (I), in benzene, included *cis*- and *trans*-1,4-dihydro-4-tritylbiphenyl (III), in addition to the previously reported biphenyl and triphenylmethane.² The formation of these products was explained by means of a scheme (A) of free-radical reactions. A feature of this scheme is the absence of dimerisation and disproportionation of the phenylcyclohexadienyl radical (II), as both of these processes are

SCHEME A



known to occur in other systems.³ This is particularly surprising because phenylcyclohexadienyl radicals (believed to be formed by the *rapid* interaction of phenyl radicals with benzene) and triphenylmethyl radicals are apparently being formed and destroyed at the same rate.

It has now been found that the decomposition of phenylazotriphenylmethane, in dilute solution in *p*-xylene, proceeds by a scheme of reactions which is again dominated by processes involving the selective removal of radicals by their interaction with triphenylmethyl radicals.

¹ D. H. Hey, M. J. Perkins, and G. H. Williams, *Tetrahedron Letters*, 1963, 445; *J.*, 1965, 110.

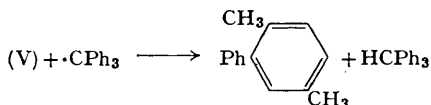
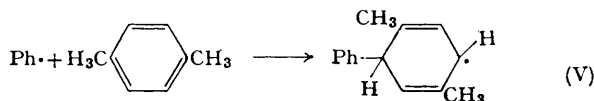
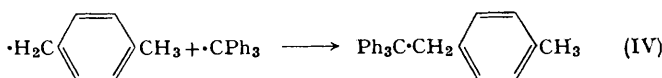
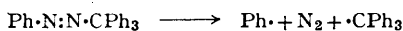
² D. H. Hey, *J.*, 1934, 1966.

³ D. F. DeFar and R. A. J. Long, *J. Amer. Chem. Soc.*, 1958, 80, 4742.

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The products of the reaction (at 50°) were found to be benzene and 1,1,1-triphenyl-2-*p*-tolylethane (IV) (which together accounted for 58—59% of the phenylazotriphenylmethane) and 2,5-dimethylbiphenyl and triphenylmethane (together, *ca.* 36%). Traces of tetraphenylmethane and triphenylmethyl peroxide were also observed. Thus, Scheme B accounts for the formation of the major products. The apparent absence of products analogous to the dihydro-compounds (III) may be ascribed to a steric effect of the methyl group *ortho* to the radical centre shown in the intermediate (V).

SCHEME B



Alternative reactions may be formulated from which the same products would result. For example, it is known that the ethane (IV) may be obtained from triphenylmethyl radicals and *p*-xylene.⁴ However, this reaction would also give triphenylmethane, and it seems improbable that a number of these alternatives should operate together in such a way as to give equivalent yields of products which arise by different reaction paths.

In Scheme B, as in Scheme A, the radical-destroying steps both involve triphenylmethyl radicals. 4,4'-Dimethylbibenzyl, the familiar product of dimerisation of 4-methylbenzyl radicals,⁵ was not detected among the products of the reaction of phenylazotriphenylmethane with *p*-xylene.

The exceptional stability of triphenylmethyl radicals is probably responsible for the observed discrimination between possible product-forming steps in reactions of phenylazo-triphenylmethane. (It is well known that hexaphenylethane partially dissociates in solution to triphenylmethyl radicals.) This is because any trace occurrence of radical-destroying processes which do not involve triphenylmethyl radicals must give rise to a high stationary-state concentration of this stable species. The relatively high concentration of triphenylmethyl radicals can subsequently scavenge other radicals which are formed (with the exception of the very short-lived phenyl radical). Under stationary-state conditions, triphenylmethyl radicals are being formed at the same rate as that at which they are being

⁴ R. A. Benkeser, J. L. Bach, and R. G. St. Clair, *J. Org. Chem.*, 1961, **26**, 1404.

⁵ W. R. Foster and G. H. Williams, *J.*, 1962, 2862.

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converted into products. Hence, the relatively high concentration is maintained, and the scavenging effect continues throughout the reaction.

A general consequence of the above argument is that, when phenylazotriphenylmethane is used as a source of phenyl radicals, simple product-mixtures may be anticipated. This has been exploited recently in a study of environmental influences on the reactivity of carbon-hydrogen bonds towards attack by free phenyl radicals.^{6,7} Other examples of reactions in which the build-up in concentration of a stable radical intermediate is important include the decomposition of pentaphenylethane⁸ and the photolysis of organic nitrites.⁹ In the latter instance, nitric oxide is the stable intermediate.

An alternative explanation, invoking a cage or concerted mechanism to explain the simple product-mixtures obtained from phenylazotriphenylmethane decompositions, has been excluded for reactions in a wide range of solvents.^{1,6,7,10-12}

EXPERIMENTAL

Materials.—*p*-Xylene was purified as described by Foster and Williams,⁵ and had b. p. 138°. Phenylazotriphenylmethane was prepared as reported previously.¹ It was uncontaminated with 1-phenyl-2-triphenylmethylhydrazine, as shown by absence of a precipitate when its solution in ether was treated with dry hydrogen chloride.¹² All the reference compounds used in gas-chromatographic analyses were at least 99% pure, and for all such analyses a linear detector response was established.

The Decomposition of Phenylazotriphenylmethane in p-Xylene.—A solution of phenylazotriphenylmethane (2 g.) in *p*-xylene (250 ml.) was heated at 50° under reflux, in an atmosphere of nitrogen, for 48 hr. (≥ 10 half-lives). The reaction mixture was cooled, and a small portion (*ca.* 50 μ l.) was removed for gas-chromatographic analysis for benzene. The analysis was effected by comparison with standard solutions of benzene in *p*-xylene, using the xylene as an internal standard. The yield of benzene was $58 \pm 4\%$ per mole of azo-compound decomposed. Solvent was then distilled from the remaining solution, under reduced pressure, the temperature being kept below 80° in order to avoid decomposition¹ of possible hydroaromatic products. The residue (*ca.* 6 ml.) was diluted with light petroleum (b. p. 60–80°; 15 ml.) and cooled to 0°. The 1,1,1-triphenyl-2-*p*-tolylethane which separated (0.814 g.; m. p. 155–157°) was washed with ice-cold light petroleum, and then crystallised from ethanol as prisms, m. p. 159–161° (*lit.*,⁴ 159–160°) (Found: C, 93.5; H, 6.85. Calc. for C₂₇H₂₄: C, 93.05; H, 6.95%). [The proton-resonance spectrum of this compound (in CDCl₃) was in accord with the assigned structure, showing peaks at τ 2.82 (15 protons), 3.22 and 3.50 (two doublets, 2 protons each), 6.13 (2 protons), and 7.85 (3 protons). Chemical shifts are in p.p.m. relative to tetramethylsilane, $\tau = 10$.] The combined filtrate and light-petroleum washings, from the initial isolation of this solid product, were concentrated under reduced pressure, and then chromatographed on basic alumina, employing a gradient-elution technique with light petroleum and benzene. This afforded *p*-xylene, 2,5-dimethylbiphenyl [n_D^{20} 1.581 (*lit.*,¹³ n_D^{20} 1.5819); 0.300 g., 29%; the product showed no impurities when examined by gas chromatography, and was used as reference for subsequent analyses], triphenylmethane (m. p. and mixed m. p. 89–92°; 0.523 g., 37%), and 1,1,1-triphenyl-2-*p*-tolylethane (m. p. 157–160°; 0.337 g.). In addition, traces of tetraphenylmethane (m. p. 285°; 6 mg. after crystallization from benzene-light petroleum) and triphenylmethyl peroxide [m. p. 185° (*decomp.*); *ca.* 30 mg.] were isolated. The total yield of 1,1,1-triphenyl-2-*p*-tolylethane was 57.5%.

In view of possible loss of dimethylbiphenyl by evaporation during the above work-up procedure, the experiment was repeated, in duplicate, though on a reduced scale, and the products were analysed gas-chromatographically for benzene and for 2,5-dimethylbiphenyl. Weighed quantities of toluene and bibenzyl were used as internal standards for the analyses, which were performed by comparison with calibration mixtures of known composition. The yields (per mole

⁶ G. A. Russell and R. F. Bridger, *Tetrahedron Letters*, 1963, 737.

⁷ R. F. Bridger and G. A. Russell, *J. Amer. Chem. Soc.*, 1963, **85**, 3754.

⁸ W. E. Bachmann and F. Y. Wiselogle, *J. Org. Chem.*, 1936, **1**, 354.

⁹ M. Akhtar and M. M. Pechet, *J. Amer. Chem. Soc.*, 1964, **86**, 265.

¹⁰ R. Huisgen and H. Nakaten, *Annalen*, 1954, **586**, 70.

¹¹ G. L. Davies, D. H. Hey, and G. H. Williams, *J.*, 1956, 4397.

¹² J. F. Garst and R. S. Cole, *Tetrahedron Letters*, 1963, 679.

¹³ E. A. Johnson, *J.*, 1957, 4155.

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of azo-compound) were: benzene, $60.5 \pm 3\%$, $59 \pm 3\%$; 2,5-dimethylbiphenyl, $36.5 \pm 3\%$, $35.5 \pm 3\%$. No evidence was obtained for the formation of 4,4'-dimethylbibenzyl (an authentic specimen of which was kindly provided by Dr. G. H. Williams).

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