35. *The Action of the Phenyl Radical on Anthracene and* meso-*Substituted Anthracenes.*

By R. O. C. Norman and William A. Waters.

Phenyl radicals can be prepared conveniently by the action of zinc powder on benzenediazonium salts suspended in acetone. These radicals can be substituted into anthracene in the *meso*-positions, but isolation of 9 : 9′ : 10 : 10′-tetrahydro-10 : 10′-diphenyl-9 : 9′-dianthryl indicates that the substitution occurs *via* phenyl-radical addition. 9-Methylanthracene reacts with phenyl radicals to give 9-methyl-10-phenylanthracene and not dianthrylethane. Both 9-methyl- and 9-phenyl-anthracene are more reactive towards phenyl radicals than is anthracene, but 9 : 10-dimethylanthracene is not reactive.

Whilst reactions between free phenyl radicals and organic liquids have been studied extensively, little attention has as yet been paid to reactions with solid organic compounds because of the difficulty of obtaining phenyl radicals uncontaminated with others in high enough concentration in organic solvents. Benzoyl peroxide produces phenyl radicals from benzoate radicals by the decomposition $Ph{\cdot}CO{\cdot}O{\cdot} \longrightarrow Ph{\cdot} + CO_2$, and reactive solutes, such as anthracene, interact with the benzoate radicals before this decomposition has taken place.[1] Tracer studies of reactions with olefins [2] have elaborated this fact. Other sources of phenyl radicals used by Hey and his colleagues [3-5] also give rise to radicals of two different types and are limited in their applicability. The decomposition of phenylmagnesium bromide in the presence of a cobaltous salt,[6] though it yields only phenyl radicals, is of little value because these radicals are so largely removed by interaction with the ether that is the necessary solvent,[7] that only small yields from interactions with added solutes are obtainable.

To surmount these difficulties we have examined the wider applicability of the reaction

---

[1] Roitt and Waters, *J.*, 1952, 2695.
[2] Bevington, *Proc. Roy. Soc.*, 1957, *A*, **239**, 420.
[3] Hey, Nechvatal, and Robinson, *J.*, 1951, 2892.
[4] Hey, Stirling, and Williams, *J.*, 1954, 2747.
[5] *Idem, J.*, 1955, 3963.
[6] Kharasch and Fields, *J. Amer. Chem. Soc.*, 1941, **63**, 2316.
[7] Norman and Waters, *J.*, 1957, 950.

between benzenediazonium salts and zinc powder in neutral acetone suspension, previously used by one of us for the phenylation of naphthalene,[8] and later for the rapid synthesis of triphenylarsine.[9] This reaction, which gives only phenyl radicals, can be conveniently carried out with the easily prepared solid benzenediazonium zincichloride, $(PhN_2)_2ZnCl_4$, or with the less reactive solid benzenediazonium fluoroborate. Though there is considerable interaction of phenyl radicals with acetone, this liquid is such a good solvent that high concentrations of solutes can be used, particularly since the reaction, being exothermic, mainly occurs at the boiling point.

Dr. J. I. G. Cadogan has informed us that in a similar reaction in which copper powder is used instead of zinc, the isomer ratios for the *p*-bromophenylation of nitrobenzene in nitrobenzene–acetone by the reactions

$$p\text{-Br}\cdot C_6H_4N_2,BF_4 \xrightarrow{\text{Cu}} BrC_6H_4\cdot; \qquad BrC_6H_4\cdot + PhNO_2; \qquad p\text{-}BrC_6H_4\cdot NO_2\ (o,\ m,\ p)$$

are identical with those obtained by using *p*-bromobenzoyl peroxide [5]*, consequently the liberation of free phenyl radicals by the reduction of diazonium salts by metals in acetone suspension cannot be questioned.

We ourselves have used only zinc powder as the reducing agent and have studied thereby the reaction of phenyl radicals with anthracene and *meso*-substituted anthracenes. From anthracene, 9 : 10-diphenylanthracene and 9 : 9′ : 10 : 10′-tetrahydro-10 : 10′-diphenyl-9 : 9′-dianthryl (I) were obtained in 11 and 12% yield, respectively.

Whereas both methyl [10] and benzyl [11] radicals react with anthracene at moderate temperatures to give *meso*-radical adducts, *e.g.* 9 : 10-dibenzyl-9 : 10-dihydroanthracene, in higher yields than *meso*-substitution products, yet in the reaction with phenyl radicals no 9 : 10-dihydro-9 : 10-diphenylanthracene appears to be formed. However, isolation of the coupled dimer (I) indicates that the *meso*-phenylation of anthracene must follow the same additive mechanism as that already described for homolytic alkylation.[10,11] Evidently, phenyl radicals are much more effective than alkyl radicals in abstracting nuclear hydrogen atoms when necessary to regenerate a wholly aromatic system. 9 : 10-Dihydro-9 : 10-diphenylanthracene was not dehydrogenated by phenyl radicals under these conditions, so that of the two possible paths (*A*) and (*B*) for the phenylation process, (*B*) is the correct one; failure to isolate 9-phenylanthracene from the phenylation of anthracene is presumably due to 9-phenylanthracene's being much more reactive towards phenyl radicals than is anthracene (see below).

Another difference in reactivity between phenyl and methyl radicals is well examplified by the reaction of phenyl radicals with 9-methylanthracene. Nuclear attack at the *meso*-position seems to occur exclusively to give 9-methyl-10-phenylanthracene, whereas methyl radicals give only 1 : 2-di-9′-anthrylethane.[10] Phenylation gave neither 1 : 2-di-9′-anthrylethane nor 1 : 2-di-(10-phenyl-9-anthryl)ethane.

These latter observations are relevant to consideration of the mechanism of homolytic substitution of benzene derivatives, for the fact that phenyl radicals attack toluene to give mainly methyldiphenyls [12,13] whereas methyl radicals attack the side-chain to give benzyl radicals [11] exactly parallels these observations of phenyl and methyl radical attack on 9-methylanthracene.

Both 9-methyl- and 9-phenyl-anthracene reacted with phenyl radicals much more readily than did anthracene itself, no starting material being recovered in either case. This accords with the previously reported [14] higher reactivity of *meso*-substituted anthracenes

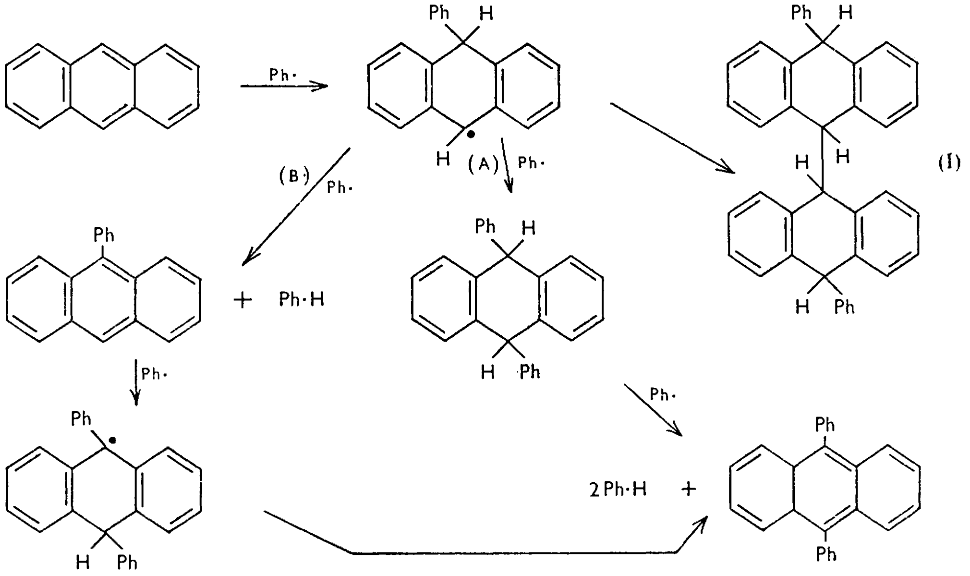
---

* We thank Dr. Cadogan for this significant information about his unpublished work.

[8] Waters, *J.*, 1939, 864.
[9] Hanby and Waters, *J.*, 1946, 1029.
[10] Beckwith and Waters, *J.*, 1956, 1108.
[11] *Idem, J.*, 1957, 1001.
[12] Dannley and Zaremsky, *J. Amer. Chem. Soc.*, 1955, **77**, 1588.
[13] Hey, Pengilly, and Williams, *J.*, 1956, 1463.
[14] Farenhorst and Kooyman, *Nature*, 1955, **175**, 598.

towards free radicals. 9 : 10-Dimethylanthracene, however, proved unreactive; this agrees with its low inhibitory power in the radical-catalysed autoxidation of benzaldehyde.[15]

An improved method for the preparation of 9-substituted anthracenes is described.



EXPERIMENTAL

Materials.—Anthracene was purified by two distillations from ethylene glycol, followed by recrystallisation from toluene; it had m. p. 218°.

9-*Methylanthracene* (cf. ref. 16). A solution of anthrone in hot benzene (80 ml.) was added slowly to a stirred solution of methylmagnesium iodide [from methyl iodide (36·0 g.) and magnesium (6·0 g.) in ether (50 ml.)]. After addition was complete, the solvent was removed through a small fractionating column until the reflux temperature was 79—80°, the solution then refluxed for ½ hr., and an excess of 50% hydrochloric acid added. The organic layer was washed and dried ($CaCl_2$), the solvent was removed, and the material, in light petroleum, was filtered through alumina. 9-Methylanthracene gave yellow plates (13·0 g.; 83%), m. p. 79—80°, from methanol.

9-Phenylanthracene was prepared similarly from the Grignard compound from bromobenzene (38·0 g.). The crude product in light petroleum–benzene (1 : 1) was filtered through alumina and crystallised from ethanol–benzene, giving 9-phenylanthracene (17·6 g.; 85%), m. p. 154—155°.

9 : 10-Dimethylanthracene, prepared from 9-methylanthracene by formylation followed by reduction,[17] had m. p. 180—181° after chromatography and crystallisation from ethanol.

" AnalaR " acetone was dried over potassium carbonate, then refluxed over anhydrous copper sulphate, and finally fractionated; it had b. p. 56°. Zinc powder was " AnalaR " material.

9 : 10-Dihydro-9 : 10-diphenylanthracene was prepared by the reduction of 9 : 10-diphenylanthracene with sodium and pentanol,[18] and crystallised from light petroleum–benzene; it had m. p. 227°.

Phenylation.—This was always carried out under the same conditions. A typical experiment was as follows: to a solution of anthracene (2·95 g.; 1/60 mole) in acetone (250 ml.), in a 500-ml. flask fitted with a Hershberg stirrer, nitrogen inlet, and condenser ($CaCl_2$ tube),

---

[15] Turner and Waters, *J.*, 1956, 879.
[16] Krollpfeiffer and Bronscheid, *Ber.*, 1923, **56**, 1617.
[17] Buu-Hoï and Hoán, *J. Org. Chem.*, 1951, **16**, 874.
[18] Willemart, *Bull. Soc. chim. France*, 1942, **9**, 83.

were added benzenediazonium zincichloride (28·0 g.; 1/15 mole) and a small quantity of chalk (to ensure neutrality). While the suspension was stirred, zinc powder (5 g.) was added in small portions. When the initial reaction had subsided, the mixture was heated until a test with " H " acid showed no unchanged diazonium compound, then filtered hot. The acetone was evaporated from the filtrate and the viscous residue repeatedly extracted with hot petroleum. This solution was concentrated and cooled, material crystallising was removed, and the mother-liquor was chromatographed. The results were as follows:

Anthracene. The solution, on cooling, deposited unchanged anthracene. Elution of the chromatogram with light petroleum yielded diphenyl (20 mg.), m. p. 72°, and a mixture of anthracene and 9 : 10-diphenylanthracene which were separated by fractional crystallisation. The yields were: anthracene, in all 39%; 9 : 10-diphenylanthracene, m. p. 248—250°, 11%. Further elution with light petroleum–benzene (6 : 1) gave 9 : 9′ : 10 : 10′-tetrahydro-10 : 10′-diphenyl-9 : 9′-dianthryl (12%), m. p. 255—258° after crystallisation from ethanol.

With ethyl acetate as solvent instead of acetone, the course of the reaction and the products were the same. With fluoroborate instead of zincichloride, the yields dropped sharply, possibly because zinc fluoroborate formed an insoluble coating round the diazonium salt.

9-*Phenylanthracene.* No unchanged material was obtained; the products were diphenyl (25 mg.) and 9 : 10-diphenylanthracene (40%).

9 : 10-*Dihydro*-9 : 10-*diphenylanthracene.* From 9 : 10-dihydro-9 : 10-diphenylanthracene (1 g.) the starting material was recovered in 72% yield.

9-*Methylanthracene.* No unchanged material was obtained. Diphenyl (25 mg.), m. p. 72°, 9-methyl-10-phenylanthracene (44%), m. p. 113°, and its photo-oxide, m. p. 180°, were isolated. The quantity of the photo-oxide could be reduced to 3% but not eliminated by carrying out all operations in the dark.

9 : 10-*Dimethylanthracene.* Starting material was obtained in 71% yield; no products were obtained.

Reference Materials.—9 : 10-Diphenylanthracene [18] had m. p. 248° (from benzene).

9 : 9′ : 10 : 10′-*Tetrahydro*-10 : 10′-*diphenyl*-9 : 9′-*dianthryl.* This was prepared by reducing 10 : 10′-diphenyl-9 : 9′-dianthryl [19] (0·5 g.) with sodium (0·5 g.) in a boiling mixture of pentanol (5 ml.) and toluene (15 ml.); crystallised from benzene it had m. p. 257—258° (yield 50%) (Found: C, 93·9; H, 6·1. $C_{40}H_{30}$ requires C, 94·1; H, 5·9%).

9-*Methyl*-10-*phenylanthracene.* The method involving the conversion of anthrone into 10-phenylanthrone, followed by methylation and dehydration [20] was inferior to the following: A solution of 9-phenylanthracene (1·1 g.) and *N*-methylformanilide (1·75 g.) in *o*-dichlorobenzene (2·5 ml.) was treated carefully with phosphorus oxychloride (1·75 g.). Hydrogen chloride was evolved; the dark red solution was heated at 95° for 20 min. and then cooled, and aqueous sodium acetate (5 g. in 25 ml.) added. The solvent was removed (steam distillation), and the residue was rubbed with 6N-hydrochloric acid to remove methylaniline. 9-*Formyl*-10-*phenylanthracene* formed yellow cubes (0·90 g., 74%), m. p. 165—166° (from benzene) (Found: C, 88·7; H, 5·0. $C_{21}H_{14}O$ requires C, 88·7; H, 5·0%). Infrared absorption: intense band at 5·99 μ. The formyl compound was reduced by the Huang-Minlon procedure to 9-methyl-10-phenylanthracene, m. p. 113°, in 85% yield.

9-Methyl-10-phenylanthracene photo-oxide was prepared [21] by keeping a solution of the hydrocarbon in carbon disulphide in bright sunlight for 2 hr.; it had m. p. 180°.

1 : 2-*Di*-(10-*phenyl*-9-*anthryl*)*ethane* (*cf. ref.* 22). A mixture of 9-bromomethyl-10-phenylanthracene [20] (0·15 g.) and phenyl-lithium [from bromobenzene (1 ml.) and lithium (0·1 g.) in ether (5 ml.)] was refluxed for 1 hr. Ice and water were added to the cooled solution, the ethereal layer was dried ($CaCl_2$), and the solvent removed. 1 : 2-*Di*-(10-*phenyl*-9-*anthryl*)*ethane* (60% yield) formed yellow needles, m. p. 322—323°, from ethanol–benzene (Found: C, 94·1; H, 5·8. $C_{42}H_{30}$ requires C, 94·4; H, 5·6%).

One of us (R. O. C. N.) thanks the Governing Body of Merton College for a Research Fellowship.

THE DYSON PERRINS LABORATORY, OXFORD UNIVERSITY. [*Received, July* 16*th*, 1957.]

---

[19] Barnett and Cook, *J.*, 1923, 2631.
[20] Barnett and Matthews, *Ber.*, 1926, **59**, 1429.
[21] Willemart, *Compt. rend.*, 1936, **203**, 1372.
[22] Hall, Lesslie, and Turner, *J.*, 1950, 711.