183. *The Detection, by Means of Anthracene, of Free Radicals formed in "Abnormal" Reactions of Grignard Reagents.*

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Free alkyl and aryl radicals are produced from Grignard reagents under the catalytic action of cobaltous chloride in the presence of an organic halide, or on reaction with azobenzene. In both reactions, addition of radicals to anthracene has been observed. In ether, benzyl radicals add to give 9 : 10-dibenzyl-9 : 10-dihydroanthracene and three stereoisomers of 10 : 10′-dibenzyl-9 : 9′ : 10 : 10′-tetrahydro-9 : 9′-dianthryl; both phenyl and methyl radicals abstract hydrogen from the ether to give the radical •CHMe•OEt which then adds to anthracene in a similar manner. In the reaction with azobenzene in benzene, addition of a methyl radical occurs to give one of the stereoisomers of 9 : 9′ : 10 : 10′-tetrahydro-10 : 10′-dimethyl-9 : 9′-dianthryl.

Although the majority of the reactions of Grignard reagents are heterolytic, many abnormal reactions are known in which fission of R•MgHal bonds is homolytic.[1,2] In their critical review Kharasch and Reinmuth [2] point out that the actual liberation of free radicals may not occur in all stages of these homolytic processes, and indeed diagnostic evidence of the liberation of free radicals from Grignard reagents is very scanty.

Since recent work in this laboratory [3,4,5] has shown how easily free radicals combine, even in dilute solution, with anthracene to give identifiable products, we have used this hydrocarbon to trap the free radicals that are liberated in two of the "abnormal" Grignard reactions, *viz.*, (*A*) their catalysed reactions with organic halides in the presence of a small percentage of a cobalt salt,[6] and (*B*) their reactions with azobenzene.[7,8,9]

Reaction *A* can now be represented as involving:

$$(1)\quad \mathrm{R{\cdot}MgHal + CoCl_2 \longrightarrow R{\cdot}CoCl + MgClHal}$$

$$(2)\quad \mathrm{R{\cdot}CoCl \longrightarrow R{\cdot} + {\cdot}CoCl}$$

$$(3)\quad \mathrm{{\cdot}CoCl + R'Hal \longrightarrow R'{\cdot} + CoClHal}$$

and leads to the formation, in excellent yield, of dimers or disproportionation products of the organic radicals R• and R′•. There has however been much doubt whether reaction (2) really yielded *free* radicals R• and was not a bimolecular process (2*a* or *b*)

$$(2a)\quad \mathrm{2R{\cdot}CoCl \longrightarrow R{\cdot}R + 2{\cdot}CoCl}$$

$$(2b)\quad \mathrm{2R{\cdot}CoCl \longrightarrow R_{(+H)} + R_{(-H)} + 2{\cdot}CoCl}$$

that gave only dimers or disproportionation products of the radical R•, for the early work of Kharasch and Fields [6,10] indicated that mixed dimers R•R′ did not seem to be formed in appreciable quantities. Thus the cobalt-catalysed reaction of phenylmagnesium bromide with *p*-tolyl bromide was reported to yield diphenyl and no methyldiphenyl, whilst the reaction of butylmagnesium bromide with bromobenzene gave only 3% of butylbenzene. It is now clear that with radicals of long life, such as benzyl, products R•R′ can be formed, for the cobalt bromide-catalysed reaction of benzylmagnesium

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[1] Waters, "The Chemistry of Free Radicals," Clarendon Press, Oxford, 1946, pp. 211—214.

[2] Kharasch and Reinmuth, "Grignard Reactions of Non-metallic Substances," Prentice-Hall, New York, 1954, Chapter 5.

[3] Roitt and Waters, *J.*, 1952, 2695.

[4] Turner and Waters, *J.*, 1956, 879.

[5] Beckwith and Waters, *J.*, 1956, 1108.

[6] Kharasch and Fields, *J. Amer. Chem. Soc.*, 1941, **63**, 2316.

[7] Ref. 2, pp. 1249—1251.

[8] Gilman and Pickens, *J. Amer. Chem. Soc.*, 1925, **47**, 2407.

[9] Rheinboldt and Kirberg, *J. prakt. Chem.*, 1928, **118**, 1.

[10] Cf. Kharasch, Sayles, and Fields, *J. Amer. Chem. Soc.*, 1944, **66**, 482.

bromide with ethyl bromide gives 20% of propylbenzene and 10% of dibenzyl.[11] Again Kharasch, Mulley, and Nudenberg,[12] investigating the addition of isoprene to the catalysed reaction between *iso*propylmagnesium bromide and 2-phenoxyethyl bromide, have isolated the coupled dimers $(PhO{\cdot}C_2H_4{\cdot}C_5H_8{\cdot})_2$ and $PhO{\cdot}C_2H_4{\cdot}[C_5H_8]_2{\cdot}CHMe_2$ in which the free radicals $Me_2CH{\cdot}$ and $PhO{\cdot}C_2H_4{\cdot}$ must have added independently to isoprene molecules.

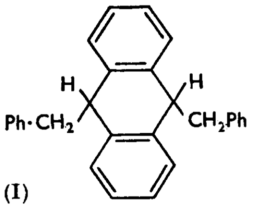
Undoubtedly ether, the customary solvent for Grignard reactions, is a very poor medium in which to attempt to detect an active radical such as methyl, butyl, or phenyl, for it is so easily dehydrogenated :

$$(4a)\quad Ph{\cdot} + CH_3{\cdot}CH_2{\cdot}OEt \longrightarrow PhH + {\cdot}CHMe{\cdot}OEt$$

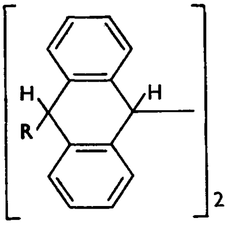
$$(4b)\quad Alk{\cdot} + CH_3{\cdot}CH_2{\cdot}OEt \longrightarrow AlkH + {\cdot}CHMe{\cdot}OEt$$

and since highly reactive Grignard reagents R·MgHal have usually been selected for effecting the conversion of halides R′Hal into dimers R′·R′ the radical–solvent reactions (4), for which we have now obtained further diagnostic evidence (see below), probably account for failures to establish the independent existence of *free* radicals R· derived from the initial Grignard reagents.

In the present work the independent existence of the free benzyl radical has been established by isolating after reaction, from solutions that originally contained anthracene, a small but significant yield of 9 : 10-dibenzyl-9 : 10-dihydroanthracene (I), a trace of 9 : 10-dibenzylanthracene, and three forms of 10 : 10′-dibenzyl-9 : 9′ : 10 : 10′-tetrahydro-9 : 9′-dianthryl (II ; R = $Ph{\cdot}CH_2$) which are probably geometrical isomers differing in their configurations at the *meso*-carbon atoms.



(I)



(II)

Two of these isomers have been synthesised by independent methods. Small quantities of anthraquinone were always isolated, but this may arise by photo-oxidation during the chromatographic separations. Compounds of type (I) are so easily dehydrogenated [13] that we suggest that the trace of dibenzylanthracene arises from compound (I) by dehydrogenation by the primary radicals, R·, R′·, present in the system and not by a direct substitution. The isolation of isomeric compounds of type (II) indicates that radicals such as benzyl must add individually to anthracene, and that at the low temperature of boiling ether their dimerisation to (II ; R = $Ph{\cdot}CH_2$) is not stereospecific. At the higher temperature of boiling toluene Beckwith and Waters [13] had isolated only the isomer (II), that of greatest thermal stability ; into this each of the other isomers is converted when heated above its melting point.

All the anthracene derivatives mentioned above have been isolated after reaction in ether under nitrogen in presence of cobalt chloride between (i) benzylmagnesium chloride and benzyl chloride, (ii) benzylmagnesium chloride and butyl bromide (*i.e.*, R = $Ph{\cdot}CH_2$, R′ = Bu), and (iii) butylmagnesium bromide and benzyl chloride (*i.e.*, R = Bu, R′ = $Ph{\cdot}CH_2$). No such derivatives were obtained in ether solution in the absence of cobalt chloride. Reaction between anthracene, benzyl chloride, benzylmagnesium chloride, and cobalt chloride in boiling benzene gave 30% of 9 : 10-dibenzylanthracene

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[11] Kharasch, Hancock, Nudenberg, and Tawney, *J. Org. Chem.*, 1956, **21**, 324.

[12] Kharasch, Mulley, and Nudenberg, *ibid.*, 1954, **19**, 1477.

[13] Beckwith and Waters, *J.*, 1956, in the press.

and 14% of 9-benzylanthracene, as well as dibenzyl: from its entirely different character we suggest that this is mainly an aromatic substitution of the Friedel–Crafts type.

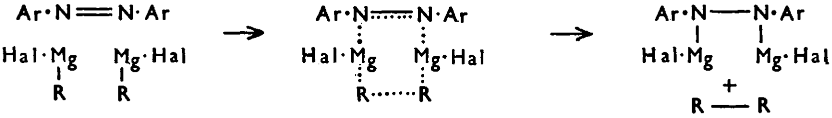
From the cobalt chloride-catalysed reactions, both of methylmagnesium iodide with methyl iodide and of phenylmagnesium bromide with phenyl bromide, there has been isolated a small amount of a dihydroanthracene derivative $(C_{18}H_{19}O)_2$ which we consider to be the dimer (II; R = ·CHMe·OEt) in which a 1-ethoxyethyl radical arising from reactions (4*a* and 4*b*) has been added at a *meso*-position in anthracene.

Butylmagnesium bromide, cobalt chloride, and butyl bromide, however, gave disproportionation products and only a trace of an unidentified dihydroanthracene derivative.

The same technique has been used to detect the transient formation of free radicals in reactions between azobenzene and Grignard reagents:

$$(5)\quad \mathrm{Ph{\cdot}N{=}N{\cdot}Ph} + 2\mathrm{R{\cdot}MgHal} \longrightarrow \mathrm{HalMg{\cdot}NPh{\cdot}NPh{\cdot}MgHal} + 2\mathrm{R{\cdot}}$$

Here again Kharasch and Reinmuth [7] doubted whether *free* hydrocarbon radicals are involved and wrote the following reaction scheme to suggest that homolytic changes may be occurring within an addition complex:



When conducted under nitrogen in the presence of anthracene the reaction between azobenzene and benzylmagnesium chloride again yielded, besides hydrazobenzene and dibenzyl, compounds (I) and (II; R = $Ph{\cdot}CH_2{\cdot}$), so that free benzyl radicals had undoubtedly been generated. Similarly after reaction in benzene between azobenzene and methylmagnesium iodide one of the stereoisomers of 9 : 9′ : 10 : 10′-tetrahydro-10 : 10′-dimethyl-9 : 9′-dianthryl (II; R = Me) was isolated, but an attempt to isolate a corresponding product from the reaction between azobenzene and phenylmagnesium bromide failed.

EXPERIMENTAL

Materials.—Anthracene was purified by two distillations from ethylene glycol and had m. p. 217°.

Anhydrous cobaltous chloride was prepared from the hydrated material by distilling acetic anhydride over it and was dried at 130° in a vacuum.

Benzyl chloride, b. p. 178—179°, was purified by bubbling nitrogen through it to remove hydrogen chloride and then dried (K_2CO_3).

9-Benzylanthracene, prepared by Cook's method [14] from benzylideneanthrone and crystallised from ethanol, had m. p. 135°.

Chromatographic alumina used in the hydrocarbon separations was prepared by heating commercial alumina (Spence's alumina, type "H") at 700° for 4 hr., cooling it to 200°, and allowing it to cool to room temperature in a vacuum-desiccator. The light petroleum used in these separations had b. p. 60—80°.

Reactions were carried out in a steady stream of dry nitrogen, purified by passage through Fieser's solution.

(A) *Reactions of Grignard Reagents with an Organic Halide in the Presence of Cobaltous Chloride and Anthracene.*—The Grignard reagents were prepared from an excess of magnesium, and unchanged halide was destroyed by refluxing the solution for 2 hr. after visible reaction had ceased. The efficiency of the reaction was assumed to be 80% (cf. Kharasch and Reinmuth [15]). The ethereal solution of the reagent (1 equiv.), filtered under nitrogen from excess magnesium, was added dropwise during 8 hr. to a stirred refluxing solution of anthracene (0·25 equiv.) and an organic halide (1 equiv.) in ether in which was suspended a small amount (0·06 equiv.) of

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[14] Cook, *J.*, 1926, 2160.
[15] Ref. 2, p. 30.

cobaltous chloride. After a further 8 hr. under reflux, the solution was cooled and the complex was decomposed with aqueous ammonium chloride. The product was washed with water and, when a benzyl or phenyl Grignard reagent or halide had been used, it was distilled in steam to remove dibenzyl or diphenyl. The product was extracted in ether, dried, and crystallised from light petroleum: unchanged anthracene was deposited and the mother-liquor was chromatographed.

In each case the structure of the product was proved by mixed m. p. and by infrared and ultraviolet spectra.

(a) *Reactions yielding benzyl radicals.* (i) The Grignard reagent formed from magnesium (5·0 g.) and benzyl chloride (21·0 g.) in ether (150 ml.) was added to anthracene (5·9 g., 1/30 mole) and benzyl chloride (16·7 g., 4/30 mole) in ether (500 ml.) in which was suspended cobaltous chloride (1·0 g.).

After reaction as described above, distillation in steam gave dibenzyl (3·90 g.), m. p. 52°. Crystallisation of the remainder of the product from light petroleum gave anthracene (1·87 g.). The mother-liquor was chromatographed: elution with light petroleum gave dibenzyl (0·15 g.) and then anthracene (1·85 g.); further elution with light petroleum–benzene (9 : 1) gave 9 : 10-dibenzyl-9 : 10-dihydroanthracene (0·67 g.), m. p. and mixed m. p. 119°. Elution with a 2 : 1 mixture of these solvents gave three isomers of 10 : 10'-dibenzyl-9 : 9' : 10 : 10'-tetrahydro-9 : 9'-dianthryl which were separated by fractional crystallisation; the decreasing solubility of these compounds in methanol and ethanol corresponded with increasing m. p. [Found, (*a*) cpd. m. p. 238—240° (0·40 g,) : C, 93·4; H, 6·5; (*b*) cpd. m. p. 227—229° (0·03 g.) : C, 93·6; H, 6·3; (*c*) cpd. m. p. 182—183° (0·05 g.) : C, 93·6; H, 6·4. $C_{42}H_{34}$ requires C, 93·7; H, 6·3%]. Substances (*a*) and (*c*) were synthesised by Beckwith and Waters,[13] but (*b*) is new. When (*b*) or (*c*) was heated in a sealed and evacuated tube above its m. p., it was converted into (*a*). The infrared spectra of these isomers show slight but significant differences.

Further elution gave 9 : 10-dibenzylanthracene (0·03 g.), m. p. 248°, and finally a small quantity of anthraquinone (10 mg.), m. p. 284°. Total significant recoveries were: anthracene, 63%; 9 : 10-dibenzyl-9 : 10-dihydroanthracene, 5·7%; 10 : 10'-dibenzyl-9 : 9' : 10 : 10'-tetrahydro-9 : 9'-dianthryls, 5·5%; 9 : 10-dibenzylanthracene, 0·3%.

(ii) The reaction was repeated with *n*-butyl bromide (20·0 g.) in place of benzyl chloride. The products isolated were the same as those in (i) and in approximately the same proportions [unchanged anthracene 54·2%; (I) 5·4%; (II) 4·9%]. During the reaction a gas was evolved which decolorised bromine water and dilute alkaline permanganate solution.

(iii) Reaction (i) was repeated, with the Grignard reagent from *n*-butyl bromide (23·0 g.) and magnesium (5·0 g.) in ether (150 ml.) in place of benzylmagnesium chloride. The course of the reaction and the products were as in expt. (ii).

(iv) Reaction (i) was repeated, but the ethereal solution of the Grignard reagent was added to the other reactants in boiling benzene (500 ml.). Recrystallisation of the product from light petroleum gave 9 : 10-dibenzylanthracene (2·03 g.), m. p. 248°. Chromatography of the mother-liquor gave, successively in order, dibenzyl (3·01 g.), m. p. 52°, 9-benzylanthracene (1·26 g., 14·5%), m. p. 134°, anthracene (1·01 g., 17·1%), and 9 : 10-dibenzylanthracene (1·59 g.). The total yield of the last compound was 3·62 g. (30·7%).

(v) When the conditions of expt. (i) were applied in the absence of cobaltous chloride, no products from anthracene were obtained. Dibenzyl (45 mg.) was obtained by steam-distillation. Anthracene was recovered in 89% yield.

(b) *Reaction of butylmagnesium bromide with* n-*butyl bromide.* The conditions of expt. (i) above were applied to butylmagnesium bromide (from butyl bromide, 23·0 g., and magnesium, 5·0 g., in ether, 150 ml.) and butyl bromide (18·3 g.). A gas was evolved which contained ethylenic compounds. Anthracene was recovered in 72% yield and the only other product obtained by chromatography was a white compound (<10 mg.), m. p. 174—175°, whose ultraviolet spectrum was characteristic of dihydroanthracenes.

(c) *Reaction of methylmagnesium iodide with methyl iodide.* The conditions of expt. (i) were used in the reaction between methylmagnesium iodide (from methyl iodide, 23·0 g., and magnesium, 5 g., in ether, 150 ml.) and methyl iodide (18·5 g.). The total recovery of anthracene was 3·1 g. (52·5%). Elution of the alumina column with light petroleum–benzene (6 : 1) gave white cubic crystals (0·26 g.), m. p. 158° after recrystallisation from methanol [Found: C, 86·1; H, 7·9%; *M* (Cotterell's method in C_6H_6), 495. $(C_{18}H_{19}O)_2$ requires C, 86·1; H, 7·6%; *M*, 502]. Light absorption in EtOH: max. at 2650 Å (ε 1380). The infrared spectrum had strong bands at 8·92 and 9·25 μ (ether links) and in the 6—8 and 10—14 μ regions generally resembled dihydroanthracene derivatives. The compound was degraded to anthracene (i) by treatment of a solution in benzene with anhydrous aluminium chloride, (ii) by heating it with sulphur at 260° for 20 min., and (iii) by heating it with palladium–charcoal at 170° for 2 hr. This evidence is consistent with the formulation of this compound as 10 : 10′-*di*-(1-*ethoxyethyl*)-9 : 9′ : 10 : 10′-*tetrahydro*-9 : 9′-*dianthryl.*

Finally a small quantity of anthraquinone (15 mg.) was obtained.

(d) *Reaction of phenylmagnesium bromide with phenyl bromide.* When the conditions of expt. (i) were applied to phenylmagnesium bromide (from bromobenzene, 26·1 g., and magnesium, 5·0 g., in ether, 150 ml.) and bromobenzene (20·9 g.), there were isolated diphenyl (7·6 g.), m. p. 69°, and compound (II; R = CHMe·OEt) (0·30 g.), m. p. 158°.

(B) *Reaction of Grignard Reagents with Azobenzene.*—The technique was the same except that azobenzene (15·5 g.) was present in place of the organic halide and cobaltous chloride. Unchanged azobenzene was recovered by exhaustive distillation in steam, and hydrazobenzene was extracted in acid.

(a) *Reaction of benzylmagnesium chloride.* Unchanged azobenzene amounted to 40·6%, and hydrazobenzene, m. p. 130°, to 27%. Chromatography yielded (I) (4·7%) and (II) (R = Ph·CH$_2$) [isomers (*a*) and (*c*)] (4·2%), in addition to unchanged anthracene (60·5%).

(b) *Reaction of methylmagnesium iodide.* Benzene was added slowly to the ethereal Grignard reagent, and the solvent was distilled off until the reflux temperature was 79—80°. The resulting suspension of the Grignard reagent was added to the other components in benzene (500 ml.), and the reaction was carried out in the usual manner. Distillation in steam yielded azobenzene (43%), acid extraction gave hydrazobenzene (20%), and crystallisation and chromatography gave anthracene (70%) and one stereoisomer of 10 : 10′-*dimethyl*-9 : 9′ : 10 : 10′-*tetrahydro*-9 : 9′-*dianthryl* (1·5%), m. p. 213—214° after recrystallisation from ethanol (Found : C, 92·9; H, 6·8%; *M*, 310. $C_{30}H_{26}$ requires C, 93·3; H, 6·7%; *M*, 386). This was converted into the known isomer [5] by heating it in a sealed and evacuated tube above its m. p. Recrystallisation from ethanol gave the higher-melting isomer, m. p. and mixed m. p. 264°. Further elution gave anthraquinone (25 mg.) and left purple bands on the column which could not be eluted.

(C) *Reaction of phenylmagnesium bromide.* Reaction between phenylmagnesium bromide, azobenzene and anthracene in benzene, carried out as in the preceding case, gave no diphenyl. Unchanged anthracene was recovered in 41% and azobenzene in 24·3% yield. A considerable amount of tar was obtained, but after being boiled with concentrated hydrochloric acid this gave no material soluble in benzene. The organic material which was soluble in light petroleum–benzene was chromatographed, but apart from anthracene only oil was eluted, leaving intractable dark bands on the column.

We are grateful to Mr. A. L. J. Beckwith for specimens of 10 : 10′-dibenzyl-9 : 9′ : 10 : 10′-tetrahydro-9 : 9′-dianthryl, m. p. 252°, 9 : 10-dibenzyl-9 : 10-dihydroanthracene, m. p. 119°, 10 : 10′-dimethyl-9 : 9′ : 10 : 10′-tetrahydro-9 : 9′-dianthryl, m. p. 264°, and 9 : 10-dibenzylanthracene, m. p. 248°. One of us (R. O. C. N.) thanks the Department of Scientific and Industrial Research for a maintenance grant.

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