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ALKYLATION AND ARYLATION OF NAPHTHALENE AND BIPHENYL BY ORGANOMAGNESIUM COMPOUNDS. "NASCENT" METAL ALKYLS.

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The alkylation of benzene by alkali metal alkyls has been reported (1) and has been classified as a nucleophilic substitution, involving attack on carbon by the carbanionic part of the reagent (2a); it is the only known example of nucleophilic substitution in benzene. Metallation occurs concurrently by nucleophilic attack on hydrogen (protophilic substitution) (2). The alkylation reaction has recently been the subject of a more detailed study by Dixon and his co-workers, using alkyl-lithium compounds. They have obtained evidence that the intermediate formed by nucleophilic attack on the aromatic ring can be obtained as a dihydro derivative following hydrolysis (3).

We now report that Grignard reagents can be used for the direct alkylation and arylation of certain aromatic hydrocarbons; in general, we have used ether-free reagents (prepared in dekahydronaphthalene (4) or in the aromatic hydrocarbon), but reagents prepared in ether also undergo the reactions. Thus, 1-phenylnaphthalene has been obtained from the reaction of phenylmagnesium bromide and naphthalene at 200°, in a yield of 34% based on bromobenzene; the crude product was dehydrogenated with chloranil (see below). Similarly, n-butylmagnesium bromide and

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naphthalene gave 1-n-butylnaphthalene (9%), and phenylmagnesium bromide and biphenyl gave a mixture (6% yield) of o- and p- terphenyls. These yields could probably be substantially improved.

The first stage in the reaction seems to involve addition of the Grignard reagent to the aromatic ring, as with alkyl-lithium compounds (3). Hydrolysis of the product of the reaction of phenylmagnesium bromide and naphthalene at 200° gave a mixture of 1-phenylnaphthalene and a dihdro-derivative (presumably 1-phenyl-1,2-dihydronaphthalene and/or 1-phenyl-1,4-dihydronaphthalene); the mixture was readily dehydrogenated to 1-phenylnaphthalene by chloranil. The elemental analysis and infra-red spectrum of the product indicated that the dihydro-derivative formed approximately half the product. On the other hand, the product from a reaction performed at 150° was apparently largely the dihydro-derivative. (Found: C, 93.3; H,6.65%. Calc. for $C_{16}H_{14}$: C, 93.2; H, 6.8%. Calc. for $C_{16}H_{12}$: C, 94.1; H, 5.9%).

Comparison with the results of Dixon *et al.* (3) suggests that the thermal elimination of hydride occurs much less readily with the magnesium than with the lithium reagents. Our reactions may thus have applications in the synthesis of cyclohexadiene derivatives.

We have considered, and rejected, the possibilities (a) that the reactions are electrophilic substitutions of the Friedel-Crafts type catalysed by magnesium bromide, and (b) that substitution by free alkyl and aryl radicals is involved. It is known that forms of magnesium halides active as Friedel-Crafts catalysts can be obtained by reactions of unsolvated Grignard reagents with alkyl and certain other halides, but they lose most of their activity at the temperatures used in the present work (5). Moreover, Friedel-Crafts substitution with aryl halides is difficult even under favourable conditions (6). Free radical phenylation of naphthalene, using benzoyl peroxide, has been reported to give mixtures of 1- and 2- phenylnaphthalenes containing ca. 17% and 20% of the 2- isomer from reactions at 85° and 100° respectively (7). The much lower proportion ($<$ 5%, from infra-red spectra) of the 2- isomer obtained in the present work seems to exclude a free radical mechanism.

It was observed that the yields of alkylated and arylated products from these reactions tended to be higher when the organomagnesium reagents were prepared in situ than when they were pre-formed in ether or dekahydronaphthalene; and a similar effect has been noted in the alkylation of benzene with n-buty-lithium. Recently it was reported that, whereas pre-formed alkyl-lithium reagents and Grignard reagents attack the 2-position of pyridine, in situ reactions of the metal and alkyl halide in pyridine lead to attack of the 4-position (8). We suggest that these "in situ" phenomena may involve "nascent" organometallic compounds, i.e. that when the monomeric species formed in situ can react with the substrate faster than it associates, enhanced reactivity or even a different reaction course may be observed in comparison with the pre-formed associated reagent. It is relevant to note that monomeric n-butyllithium, in equilibrium with the normal hexamer, appears to be the active species in initiating the anionic polymerisation of olefins (9). These phenomena are being studied further.

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