1,6-Addition of a Grignard Reagent to Anthraquinone

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ADDITION of excess of Grignard reagents (RMgX) to anthraquinone generally occurs at the two carbonyl groups to form diols.[1] With t-butylmagnesium chloride, however, the reaction under nitrogen takes an unexpected course and the major addition product (25%) is formulated as compound (I; R = Bu^t, $R^1 = R^2 = H$). Two t-butyl groups (τ 8·65, 9·25) in different environment are evident from its n.m.r. spectrum, while in the infrared, sharp absorption bands representing hydroxyl and carbonyl groups (3450, 1652 cm.$^{-1}$ respectively) are observed. On chromic oxidation it yields the quinone (II; R = Bu^t, $R^1 = R^2 = H$), identical with an independently synthesised specimen.[2] An alternative formulation (I; $R^1 = Bu^t$, $R = R^2 = H$) cannot be excluded at present but is considered less likely on mechanistic grounds. Experiments to clarify this point formally are in progress.

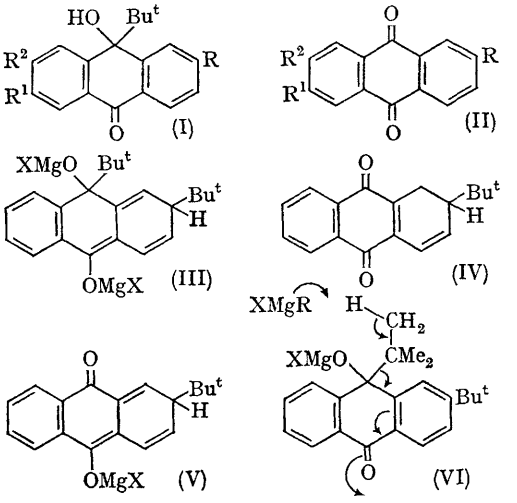
Formation of this di-adduct presumably involves nucleophilic 1,6-addition, giving an intermediate

such as (III) which is then oxidised at the expense of unchanged anthraquinone. Indeed 9,10-anthraquinol (40%) is also obtained from the reaction, though its formation may be attributed in part to direct reduction of the quinone by the Grignard reagent. The addition process appears to have no direct analogy in the anthraquinone series, although 1,6-addition of Grignard reagents to aryl ketones, *e.g.*, to hindered benzophenone derivatives,[3] has been observed. 1,2-Addition of t-butylmagnesium chloride to anthrone has recently been reported[4] but no other products were obtained from the reaction. The apparent absence of 1,4-addition to anthraquinone presumably reflects steric considerations.

The reaction also yields smaller quantities of mono-adducts (I; R = R^1, R^2 = H; 3%) and (IV; 8%). Compound (IV) is smoothly converted into 2-t-butylanthraquinone on oxidation with dichlorodicyano-1,4-benzoquinone, while catalytic hydrogenation results in saturation of its olefinic bond. Its formation possibly involves reduction of an intermediate adduct (V), forming the quinol corresponding to compound (IV), which is stable to further addition and oxidised during work-up.

Addition of t-butylmagnesium chloride to the di-adduct (I; R = Bu^t, R^1 = R^2 = H) yields the symmetrical tri-adduct (I; R = R^2 = Bu^t, R^1 = H; 50%) as the major product. This compound (5%) and its unsymmetrical isomer (I; R = R^1 = Bu^t, R^2 = H; 7%) are also obtained by addition to 2-t-butylanthraquinone. The anthraquinones (II; R = R^2 = Bu^t, R^1 = H), (II; R = R^1 = Bu^t, R^2 = H) derived from them by oxidation are symmetrically substituted and their n.m.r. spectra may be analysed completely. These and other compounds described here have been characterised and identified by methods similar to those described for the di-adduct above; the yields quoted refer to purified products.

Addition to the carbonyl group of the di-adduct (I; R = Bu^t, R^1 = R^2 = H) is not observed even with the sterically less demanding methylmagnesium iodide. On work-up, this reaction remarkably yields 2-t-butylanthraquinone (49%) which is also formed to some extent in the other addition reactions described above. The same process is catalysed by ethereal sodium triphenylmethide, suggesting that a further rôle of the Grignard reagent is to act as a base, *e.g.*, (VI). This process would lead to the quinol level of oxidation and the product would thereby be protected from further addition.



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