Regioselective Reactions of *ortho*-Quinone Methides with Magnesium Phenolates

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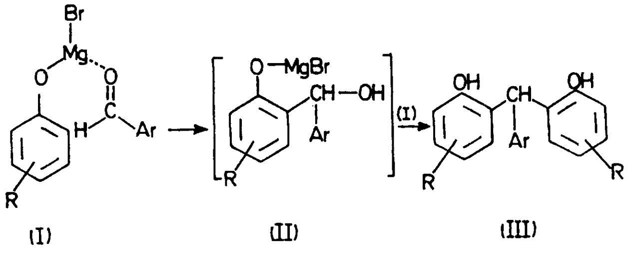
Summary *ortho*-Regioselective alkylation of aryloxy-magnesium bromides with diphenyl methanols in benzene is achieved only with reagents capable of generating *o*-quinone methides; regioselectivity is explained in terms of co-ordination of these intermediates with the magnesium.

The reaction between aryloxymagnesium bromides and aromatic aldehydes in benzene is characterized by high *ortho*-regioselectivity giving 2,2′-dihydroxytriphenylmethane derivatives.[1] The formation of these products has been explained in terms of a substrate–reagent complex (see Scheme) in which *ortho*-regiospecific attack on the aromatic nucleus of the phenol occurs, followed by a regiospecific reaction of the 'intermediate' (II) with another molecule of the phenol to give compounds of type (III).



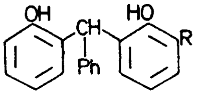
Scheme

Table. Reaction of PhOMgBr with o-$RC_6H_4CH(OH)Ph$[a]

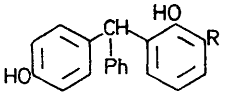
R	% PhOMgBr consumed	Ratio (III) : (IV) in product
H	70	20 : 80
OMe	75	20 : 80
OH	65	55 : 45
OMgBr	70	100 : 0

[a] 24 h in refluxing benzene.

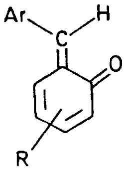
By analogy with the chemistry of *o*-hydroxybenzyl derivatives,[2] *o*-quinone methide intermediates may be involved in the second stage of this reaction, and an indication of the presence of such intermediates (VI) was obtained from a study of the reactions of the diphenylmethanols, o-RC_6H_4-CH(OH)Ph, with PhOMgBr (Table). *ortho*-Attack to give compounds (IV) predominated over *para*-attack to give (V) only for the *o*-hydroxy-compound, and was exclusive for its MgBr salt. The *o*-hydroxy-compound o-HOC_6H_4CH-(OH)Ph is capable of forming an *o*-quinone methide, but such species are unstable and can be detected by spectroscopic techniques only at low temperatures.[3] Their presence is normally deduced by trapping with suitable reagents,[4] and accordingly we investigated the reaction between the *ortho*-compound (II; R = H, Ar = Ph) and PhOMgBr in refluxing benzene in the presence of ethyl vinyl ether. The chroman (VII) together with the triphenylmethane (IV; R = H) were obtained.



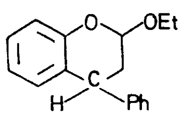
(IV)



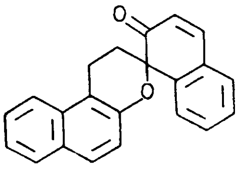
(V)



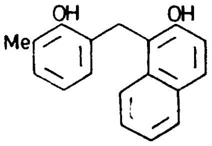
(VI)



(VII)



(VIII)



(IX)

Further evidence supporting the intermediacy of *o*-quinone methides in these reactions is the fact that these, when generated by a different procedure, undergo selective alkylation with aryloxymagnesium bromides in benzene or other hydrocarbon solvents, analogous to that which is observed with several carbonyl reagents.[1,5] The reaction of 1,2-naphthoquinone 1-methide, generated by thermal depolymerization of its dimer (VIII) in mesitylene at 160 °C,[6] with o-MeC_6H_4OMgBr for 15 min gave the 2,2′-dihydroxydiaryl derivative (IX). Products of attack at the position *para* to the OMgBr group were not observed, in spite of the rather high temperature.

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