An Unusual Reaction of Methylmagnesium Iodide with Cyclohexadienones

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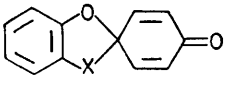
Summary Reaction of methylmagnesium iodide with the spirocyclohexadienones, (I), gives products consistent with 1,3-addition of the Grignard reagent to the enone system.

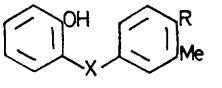
IT has recently been reported[1] that a minor product of the reaction of t-butylmagnesium chloride with ethyl cinnamate is ethyl 2-t-butylhydrocinnamate; a radical mechanism is proposed for this reaction. This appears to be the only example cited in the literature of a 1,3-addition of a Grignard reagent to an α,β-unsaturated carbonyl system. We now report that treatment of 1,3-benzodioxole-2-spirocyclohexadien-4′-one[2] (Ia) with an excess of methylmagnesium iodide, followed by acid hydrolysis of the reaction mixture gives the diphenyl ethers (IIa) and (IIb) as the only products. The identity of these compounds was established by chromatographic and spectroscopic comparison with authentic samples prepared by unambiguous Ullmann ether syntheses. Similarly the reaction of the spirosulphonamide (Ib) (obtained by oxidation of *N*-2-hydroxyphenyl-*N*-4-hydroxyphenyl-4-toluenesulphonamide) with an excess of methylmagnesium iodide gives in high yield (IIc), again available by an alternative route[3] for comparison.

The high specificity of attack by the Grignard at such an unusual reaction site may indicate that the reaction pro-



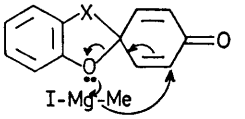
(I)

(a) X = O
(b) X = $NSO_2C_6H_4Me$-*p*



(II)

(a) X = O, R = OH
(b) X = O, R = Me
(c) X = $NSO_2C_6H_4Me$-*p*
R = Me



(III)

ceeds by a cyclic intermediate[4] of type (III) to give (IIa). Compounds (IIb) and (IIc) could arise by further 1,2-addition of the Grignard to (III), followed by dehydration of the resulting carbinol. Further studies are in progress to verify this mechanism, and to determine the scope of the reaction, especially the conditions under which a Grignard might add to an α,β-unsaturated acetal or ketal.

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