Reaction of α,β-Unsaturated Imidates with Grignard Reagents Leading to 2-Alkyl 1,3-Diimines

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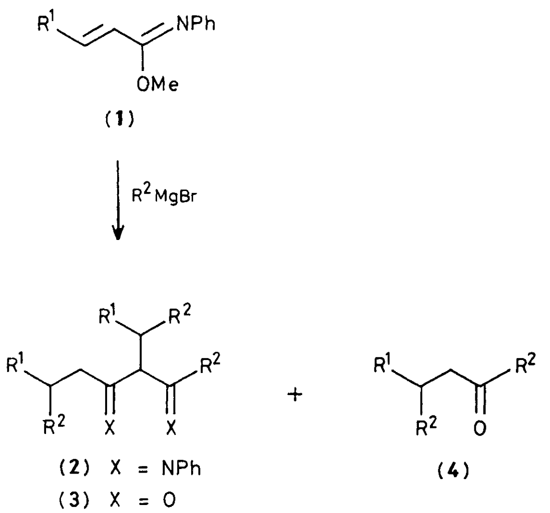
Methyl *N*-phenylacrylimidate (**1a**) reacted with alkyl- and aryl-magnesium bromides in ether at 0 °C to give 2-alkyl 1,3-diketones (**3a**) in a good yield after aqueous work-up; methyl *N*-phenylcrotonimidate (**1b**) and *N*-phenylcinnamimidate (**1c**) with alkylmagnesium bromides furnished analogous 1,3-diketones (**3**) as the major products after hydrolysis of the corresponding stable diimines (**2**).

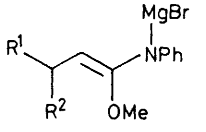
There has been increasing recent attention on the chemistry of imidates (imino ethers) and related compounds from the synthetic and mechanistic points of view.[1] Imino ethers have been shown to be reactive toward electrophiles and nucleophiles at the imino nitrogen and imino carbon atoms, respectively.[2,3] Based on our recent observation on the reaction of α,β-unsaturated imidates with benzenesulphenyl chloride,[4] we expect that Grignard reagents would undergo initial 1,4-addition to acrylimidates to produce very reactive 1-methoxy magnesio enamines, which could be intercepted by an appropriate acylating agent to give dicarbonyl compounds. To our surprise, the reaction in question took place in an



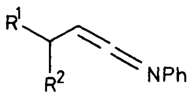
(**2**) X = NPh

(**3**) X = O

(**4**)



(**5**)



(**6**)

a; R^1 = H
b; R^1 = Me
c; R^1 = Ph

R^2 = Et, $PhCH_2CH_2$, or Ph

intermolecular fashion without addition of the acylating agent.

Treatment of methyl *N*-phenylacrylimidate (**1a**)[5] with ethylmagnesium bromide (6 mol. equiv.) in ether at 0 °C for 3 h, followed by work-up with dilute hydrochloric acid for 1 h at 0 °C, afforded a pale yellow liquid which was subjected to column chromatography to give 4-propylnonane-3,5-dione† (**3a**; R^2 = Et) as a colourless liquid in 70% yield, b.p. 129—130 °C (bath temp.) at 11 mmHg. The product gave a positive enol test (aq. $FeCl_3$), but the presence of the enol tautomer was barely discernable in the ^1H n.m.r. and i.r. spectra. It is noteworthy that the enolizable proton of the diketone resonated at δ 3.67 as a clear triplet in the ^1H n.m.r. spectrum. Similar treatment of (**1a**) with 2-phenylethyl- and phenyl-magnesium bromide afforded the diones† (**3a**; R^2 = $PhCH_2CH_2$) (64%) and (**3a**; R^2 = Ph) (74%): m.p. 66—67 °C, respectively.

Reaction of the crotonimidate (**1b**)[5] and cinnamimidate (**1c**)[5] with alkyl Grignard reagents afforded the 1,3-diimines (**2b**)† (75% yield for R^2 = Et; 69% for R^2 = $PhCH_2CH_2$) and (**2c**)† (72% yield for R^2 = Et; 26% for R^2 = $PhCH_2CH_2$), respectively, as stable liquids along with minor amounts of the monoketones (**4**). The diimines (**2b**) and (**2c**) could be hydrolysed with 1 M HCl at room temperature for 1—4 days to give the 1,3-diketones (**3b**)† and (**3c**)† (72—85% yield).

These results clearly suggest that the reaction of the acrylimidates (**1a**) with the Grignard reagents leads initially to the formation of the diimines (**2a**) which are susceptible to hydrolysis during the work-up. Several interpretations can be offered as to the mechanism of formation of (**2**). The most plausible pathway seems to involve initial conjugate addition of a Grignard reagent to the imidate affording the very reactive 1-methoxy-*N*-magnesio-enamine (**5**), which leads to the unstable ketenimine (**6**) upon β-elimination of metal methoxide. The ketenimine (**6**) is selectively alkylated by the strongly nucleophilic (**5**) to yield a diimine precursor which is then alkylated at the imidate carbon by the Grignard reagent. Although possible precursors could not be detected even by the use of limited quantities of the Grignard reagent, the intermediacy of (**6**) was strongly suggested by the fact that treatment of a mixture of (**1a**) and (**6**; R^1 = R^2 = H), prepared by the reaction of triethylamine with *N*-phenylpropionimidoyl chloride,[6] with ethylmagnesium bromide afforded (**3a**; R^2 = Et) (43%) and 4-propylheptane-3,5-dione (15%).

The most unusual feature of the reaction of the α,β-unsaturated imidates with the Grignard reagents is the ready formation of 2-branched 1,3-diimines by the exclusive coupling of two moles of the imidate associated with double alkylation by the Grignard reagents. In marked contrast the reaction of the imidates (**1**) with alkyl-lithium reagents took place even more rapidly to produce monoketones (**4**) exclusively (73% yield for R^1 = H, R^2 = Bu^n).

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† Satisfactory analytical data have been obtained for all new compounds.

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