

## Short Communications

### The Reactions of Ethyl 2-Furanacrylate with Grignard Reagents

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The action of Grignard reagents on diethyl furfurylidene malonate has previously been studied in this laboratory.<sup>1</sup> Against this background, it seemed justified to allow Grignard reagents to react with the corresponding monocarboxylic ester, ethyl 2-furanacrylate. Our results considerably diverge from those reported by Maxim and Georgescu who have studied the reactions of this ester with some Grignard reagents and invariably found only double 1,2-addition products, *i.e.* unsaturated alcohols (2 in Scheme 1).<sup>2</sup> It has, however, been shown that the purity of the magnesium used for the preparation of the Grignard reagent highly influences the course of the additions.<sup>3</sup> Because the commercial magnesium may be expected to be purer nowadays than 41 years ago, the discrepancies might be explained by this fact.

Our results show that the competing reactions in Scheme 1 occur. The observation that an  $\alpha,\beta$ -unsaturated ester gives 1,4-, 1,2+1,4-, and/or double 1,2-addition in the same reaction is not new.<sup>4,5</sup>

The primary 1,4-addition products are enolates that can scarcely react with another molecule of the Grignard reagent. The reaction sequence in the formation of the combined 1,2- and 1,4-adducts must therefore be that in the scheme. Munch-Petersen has previously come to the same result in connection with similar reactions.<sup>6</sup>

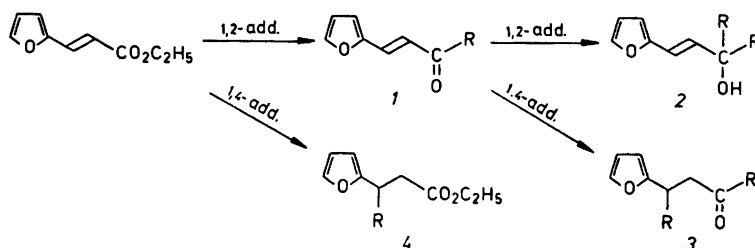
The principal course of the reactions depends on the alkyl group of the Grignard reagent. Methylmagnesium iodide gives 1 that reacts further to 2 and 3, the ratio of which is 7:3. Any 1,4-addition is not observed. Isopropylmagnesium bromide gives 4 and 3 in the ratio 3:1. Isobutylmagnesium chloride reacts in the same way but gives more of 3 (the ratio of 4 and 3 is 1:4). The predominant product of *tert*-butylmagnesium chloride is 4 although small amounts of ethyl (5-*tert*-butyl-2-furan)propionate (1,8-addition product) and ethyl (3-*tert*-butyl-2,3-dihydro-2-furylidene)propionate (1,6-addition product) are observed. The 1,6-addi-

tion product easily rearranges to ethyl (3-*tert*-butyl-2-furan)propionate in acid ethereal solution. The three last-mentioned Grignard reagents do not give rise to any double 1,2-addition product (2).

Because the substrate is not varied and the Grignard reagents that have been studied are saturated and aliphatic, steric effects can explain the differences. In the first competition between 1,2- and 1,4-addition (to 2 and 4), the 1,4-addition is more favoured the more branched the alkyl group is at the carbon atom that is bonded to the magnesium atom. Methylmagnesium iodide gives only 1,2-addition, the primary Grignard reagent (isobutyl) causes the formation of a small amount of 1,4-addition product, the secondary Grignard reagent (isopropyl) gives more 1,4-addition product than 1,2-addition, and if the alkyl group is tertiary the 1,2-addition is totally suppressed. In the second competition (from 1 to 2 and 3), only the smallest alkyl group causes 1,2-addition in addition to 1,4-addition.

Another case (dialkyl isopropylidenemalonates) in which methylmagnesium iodide also gives double 1,2-addition in competition with 1,4-addition while other Grignard reagents react to give 1,4-addition and/or reduction of the carbon-to-carbon double bond has previously been reported.<sup>7</sup> The observation that methylmagnesium iodide gives double 1,2-addition to methyl cinnamate and that phenylmagnesium bromide predominantly reacts to give 1,4-addition might also be cited.<sup>4</sup>

If the present reactions are compared with those of diethyl furfurylidene malonate<sup>1</sup> which has two ethoxycarbonyl groups in the  $\alpha$  position instead of one in the present substrate, it is observed that ethyl 2-furanacrylate is not reduced by branched Grignard reagents as the malonate is under the same conditions. A reduction of the carbon-to-carbon double bond by branched Grignard reagents seems to require a stronger polarisation than that which one ethoxycarbonyl group induces. Another result of the weaker polarisation caused by only one ethoxycarbonyl group is the weakened tendency towards extension of the conjugated double bond system into the furan nucleus. In the present study, the 1,6- and 1,8-addition products of *tert*-butylmagnesium chloride were obtained in very small amounts while the proportions of these products are much greater when diethyl furfurylidene malonate is allowed to react with the same Grignard reagent.



Scheme 1.

**Experimental.** Ethyl 2-furanacrylate was prepared in a good yield according to Galat.<sup>8</sup> The coupling constant (16 Hz) of the AB quartet in the  $^1\text{H}$  NMR spectrum revealed that the *trans* isomer had formed.

The reactions between ethyl 2-furanacrylate and the Grignard reagents were performed as previously described for similar reactions with diethyl furfurylidene-malonate.<sup>1</sup> A fivefold excess of the Grignard reagents was used in all experiments. The reaction mixtures were analysed by GLC (stationary phase 3% SE-30) and by combined GLC-MS. When it was possible, the components were isolated by preparative GLC and the  $^1\text{H}$  NMR spectra taken on each separated substance.

**Methylmagnesium iodide** gave two compounds, 1,1-dimethyl-3-(2-furyl)-2-propenol (2; R = Me) and 4-(2-furyl)-2-pentanone (3; R = Me). The former compound was isolated. Both the NMR spectrum of this substance and the mass spectra contained the expected peaks. The ratio of the compounds (by GLC peak area) was about 70:30.

**Isopropylmagnesium bromide** gave two compounds, ethyl 3-(2-furyl)-4-methylpentanoate (4; R = Pr<sup>1</sup>) and 2,6-dimethyl-5-(2-furyl)-3-heptanone (3; R = Pr<sup>1</sup>). Both compounds were isolated. The NMR and mass spectra contained the expected peaks. The ratio of the compounds (by GLC peak areas) was 75:25.

**Isobutylmagnesium chloride** also gave two compounds, ethyl 3-(2-furyl)-5-methylhexanoate (4; R = Bu<sup>1</sup>) and 2,8-dimethyl-3-(2-furyl)-4-nonanone (3; R = Bu<sup>1</sup>). Both compounds, the ratio of which was 20:80, were isolated. The NMR and mass spectra of them contained the expected peaks.

**tert-Butylmagnesium chloride** gave one main product, ethyl 4,4-dimethyl-3-(2-furyl)pentanoate (4; R = Bu<sup>t</sup>), which was isolated. Because two by-products were identified by comparison of their mass spectra with those of the corresponding products of diethyl furfurylidene-malonate,<sup>1</sup> the mass spectrum of the isolated substance is given. MS [IP 70 eV;  $m/e$  (% rel. int.)]: 224 (5, M), 209 (1.5, M-Me), 179 (1.2, M-OEt), 167 (47, M-Bu<sup>t</sup>), 137 (23, M-CH<sub>2</sub>CO<sub>2</sub>Et), 94 (100, M-Bu<sup>t</sup>-CO<sub>2</sub>Et), 81 (23, Furyl-CH<sub>2</sub>), 57 (44, Bu<sup>t</sup>), 19 (27, Et).

The gas chromatogram of the reaction products showed several smaller peaks. Two of the

compounds due to these peaks were easily identified by MS. The compound that gave the peak next to the main peak was ethyl (5-*tert*-butyl-2-furan)propionate (1,8-addition product). MS [IP 70 eV;  $m/e$  (% rel. int.)]: 224 (23, M), 209 (100, M-Me), 179 (1.5, M-OEt), 150 (3, M-H-CO<sub>2</sub>Et), 137 (41, M-CH<sub>2</sub>CO<sub>2</sub>Et), 135 (74, M-H-CO<sub>2</sub>Et-Me), 121 (50), 43 (22, propen).

Ethyl (3-*tert*-butyl-2,3-dihydro-2-furylidene)-propionate (1,6-addition product) gave rise to peak No. 3. MS [IP 70 eV;  $m/e$  (% rel. int.)]: 224 (5, M), 222 (3, M-2H), 209 (8, M-Me), 168 (43, M-C<sub>4</sub>H<sub>9</sub>), 139 (7), 137 (10, M-CH<sub>2</sub>CO<sub>2</sub>Et), 135 (10), 121 (32), 94 (100), 81 (19), 57 (64, Bu<sup>t</sup>), 41 (19, propen), 29 (39, Et). In acid ether solution, the compound rearranged to ethyl (3-*tert*-butyl-2-furan)propionate. MS [IP 70 eV;  $m/e$  (% rel. int.)]: 224 (20, M), 209 (37, M-Me), 163 (34), 150 (26, M-H-CO<sub>2</sub>Et), 137 (47, M-CH<sub>2</sub>CO<sub>2</sub>Et), 135 (28), 121 (100), 29 (20, Et.).

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