

## A Comparison of the 1,2- and 1,4-Addition of Some Grignard Reagents with Different Halogens and Methyl Cuprates to 2-Furanacrolein

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When  $i\text{-PrMgX}$  ( $X = \text{Cl, Br, I}$ ),  $t\text{-BuMgX}$  ( $X = \text{Cl, Br}$ ), and  $\text{PhCH}_2\text{MgX}$  ( $X = \text{Cl, Br, I}$ ) react with 2-furanacrolein, the corresponding 1,2- and 1,4-addition products are formed. A heavier halogen in the  $i\text{-Pr}$  and  $t\text{-Bu}$  reagents enhances the formation of the 1,4-adducts, while the effect is the reverse for  $\text{PhCH}_2$  reagents. A higher concentration of the Grignard reagent gives a higher yield of the 1,2-adduct, while the ratio of reagent to substrate does not affect the product distribution.

The methyl substituted 1,4-adduct is obtained with  $\text{MeMgI/CuI}$  and with  $\text{LiMe}_2\text{Cu}$ .

The initial complex, formed when the Grignard reagent is brought into contact with the substrate, is briefly discussed.

The influence of the halogen of the Grignard reagent on the distribution between 1,2- and 1,4-addition products has largely been neglected, although some different results have been published. In the reactions between 2-butyl crotonate and methyl-, propyl-, isopropyl-, and *tert*-butylmagnesium halide,<sup>1</sup> it was found that a heavier halogen in the reagent increased the yield of the 1,2-adduct. The same trend was also found in the reaction of butylmagnesium halide with acetals of acrylic aldehydes.<sup>2</sup> When the present work was already finished, an article which deals with the effect of the halogen in the reaction between  $\text{RMgX}$  and coumarin was published.<sup>3</sup> In that work a heavier halogen in isopropyl-, *sec*-butyl-, and *tert*-butylmagne-

sium halide was found to favour the 1,4-addition. The results were discussed on the basis of a theoretical model.

The Grignard reagent has been found to consist of the species  $\text{RMgX}$  and  $\text{R}_2\text{Mg}$  in equilibrium with each other (the Schlenk equilibrium<sup>4</sup>). It has also been established that  $\text{RMgX}$  predominates at equilibrium, but because  $\text{R}_2\text{Mg}$  is more reactive, a part of the reaction product is always formed by reaction between  $\text{R}_2\text{Mg}$  and the substrate.<sup>5</sup> Moreover, when the substrate is unreactive, most of the reaction product is formed by attack from  $\text{R}_2\text{Mg}$ .<sup>6</sup>

From these results, the conclusion can be drawn that a reactive substrate is needed in order to favour reaction with the  $\text{RMgX}$  part of the reagent and that a study of the effect of the halogen on the product distribution should be performed on a reactive substrate. Because aldehydes react fast with Grignard reagents, a conjugated aldehyde was considered suitable for this investigation.

Recent works on the furfurylidenemalonate ester system have shown that *tert*-butylmagnesium chloride and benzylmagnesium chloride can add in the 1,6- and 1,8-manners.<sup>7</sup> It therefore seemed interesting to choose 2-furanacrolein as the conjugated aldehyde.

It has been found in earlier studies of the reaction between conjugated aldehydes and Grignard reagents that the reagent, with the exception of tertiary reagents<sup>8</sup> and especially benzylmagnesium chloride,<sup>9,10</sup> adds almost exclusively in the 1,2-manner. With benzylmagnesium chloride the yield of 1,2-addition

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product varied between 7.5 and 78 % and the yield of 1,4-addition product between 28 and 0 %.

Large quantities of unidentified polymeric products have often been reported in the reaction of Grignard reagents with conjugated aldehydes. In these studies the composition of the reaction mixture has been analysed by chemical means or by distillation. Such analyses can affect the sensitive substances in the product mixture and lead to larger quantities of secondarily formed substances. In the present work the analysis was performed by GLC, and the ratios between the reaction products were calculated by measuring the peak areas.

It has been established that alkylmagnesium chlorides are best described as dimers throughout the whole concentration range, while bromides and iodides consist of associated and unassociated species in an equilibrium which depends on the concentration.<sup>11</sup> It therefore seemed meaningful to vary the concentration of the Grignard reagent in order to find out if a change in the composition of the reagent is followed by a change in distribution of the 1,2- and 1,4-adducts.

It is also known that different complexes are formed between reacted substrate molecules and unreacted reagent molecules,<sup>12</sup> and therefore the ratio of reagent to substrate was varied to find out if the appearance of these kinds of complexes affects the product distribution.

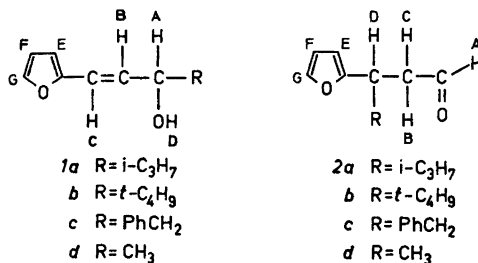
2-Furanacrolein has earlier been reacted with methylmagnesium iodide, ethylmagnesium bromide, and butylmagnesium chloride,<sup>13</sup> but only 1,2-addition was reported.

The methyl substituted 1,4-adduct was considered most easily obtainable with the aid of a copper reagent. The addition of copper(I) chloride to Grignard reagents has been shown to increase the yield of the conjugate addition product,<sup>14</sup> and the lithium diorganocuprates in particular are known to give high yields of the 1,4-adduct.<sup>15</sup>

## RESULTS

When 2-furanacrolein reacts with Grignard reagents, a complex is immediately formed, which reacts further with more reagent. If less than one equivalent of the Grignard reagent is added to the aldehyde, the complex gives a

yellow-brown precipitate. If the reaction is quenched at this stage, the aldehyde can be recovered quantitatively. The complex is probably formed from one molecule of the aldehyde by displacement of two ether molecules from the solvated Grignard reagent. If so, one ether molecule is displaced by the carbonyl oxygen, and the other by the furan oxygen. The second molecule of the Grignard reagent, which is needed to complete the reaction, is believed to react on the surface of the complex particle by a nucleophilic attack.



When isopropylmagnesium halide ( $\text{RMgX}$ ;  $\text{X} = \text{Cl}, \text{Br}, \text{and I}$ ) reacts with 2-furanacrolein, the corresponding 1,2-adduct 1-(2-furanyl)-4-methylpent-1-en-3-ol ( $1a$ ) and 1,4-adduct 3-(2-furanyl)-4-methylpentanal ( $2a$ ) are formed as the only products (GLC and NMR analysis). The products were separated by distillation and identified by spectroscopic means. Variation of the halogen and the concentration of the reagent resulted in the product distributions in Fig. 1. The chloride gives considerably more 1,2-

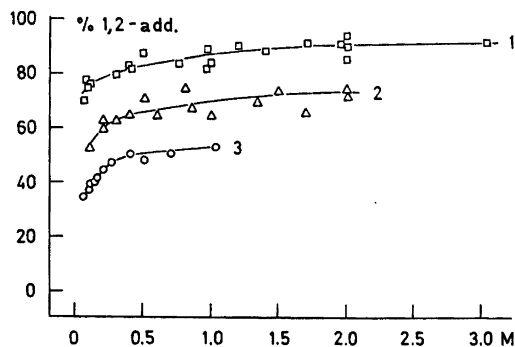


Fig. 1. Yield of 1,2-adduct versus the molarity of isopropylmagnesium halide (1,2- + 1,4-adduct = 100 %). 1, isopropylmagnesium chloride; 2, isopropylmagnesium bromide; 3, isopropylmagnesium iodide.

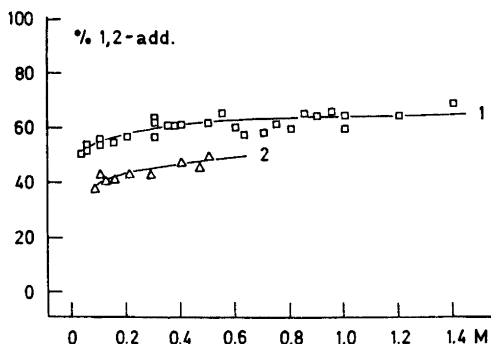


Fig. 2. Yield of 1,2-adduct versus the molarity of *tert*-butylmagnesium halide (1,2- + 1,4-adduct = 100 %). 1, *tert*-butylmagnesium chloride; 2, *tert*-butylmagnesium bromide.

addition product than the bromide and iodide, and the bromide in its turn more than the iodide.

When *tert*-butylmagnesium halide ( $\text{RMgX}$ ;  $\text{X} = \text{Cl}$  and  $\text{Br}$ ) reacts with 2-furanacrolein, the corresponding 1,2-adduct 1-(2-furanyl)-4,4-dimethylpent-1-en-3-ol (*1b*) and 1,4-adduct 3-(2-furanyl)-4,4-dimethylpentanal (*2b*) are the only products. These products were separated either by distillation or by preparative GLC, and identified as above. Variation of the halogen and the concentration of the Grignard reagent resulted in the distributions in Fig. 2. Also this chloride gives more of the 1,2-adduct.

Variation of the halogen and the concentration of the benzylmagnesium halide ( $\text{RMgX}$ ;

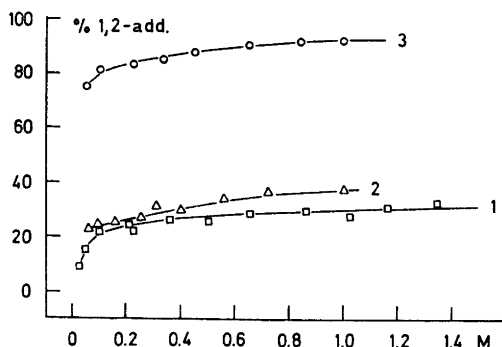


Fig. 3. Yield of 1,2-adduct versus the molarity of benzylmagnesium halide (1,2- + 1,4-adduct = 100 %). 1, benzylmagnesium chloride; 2, benzylmagnesium bromide; 3, benzylmagnesium iodide.

$\text{X} = \text{Cl}$ ,  $\text{Br}$ , and  $\text{I}$ ) resulted in the product distributions in Fig. 3. The only reaction products formed are the 1,2-adduct 4-(2-furanyl)-1-phenylbut-3-en-2-ol (*1c*) and the 1,4-adduct 3-(2-furanyl)-4-phenylbutanal (*2c*). The chloride and the bromide give good yields of the 1,4-adduct, while the iodide almost exclusively gives the 1,2-adduct. The products were isolated by preparative GLC (the saturated aldehyde) and by steam distillation (the unsaturated alcohol).

When methylmagnesium iodide reacts with 2-furanacrolein, the 1,2-adduct 4-(2-furanyl)but-3-en-2-ol (*1d*) is the only observed reaction product. A catalytic amount of copper(I) iodide added to the Grignard reagent in small portions during addition of the substrate failed to affect the fast reaction. When an equimolar amount of the copper salt was added to the Grignard reagent before the addition of the substrate, 16 % of the 1,4-adduct 3-(2-furanyl)butanal (*2d*) could be obtained. With lithium dimethylcuprate 85 % of the 1,4-adduct was formed. The separation of this product is simplified because no 1,2-adduct is formed in this reaction.

The reaction temperature ( $-15$  to  $+25^\circ\text{C}$ ) or the ratio of reagent to substrate (100:1–1.5:1) did not affect the observed product distribution in any of the Grignard reactions.

The first striking fact to be observed is the large proportion of 1,4-addition that can be achieved. Even with isopropyl reagent the conjugate addition product can become the main substance of the reaction mixture. Secondly, by combining the effect of the halogen with the effect of diluting the reagent, one obtains changes that can be of synthetic value, particularly in the case of benzylmagnesium halides.

The dilution of a Grignard reagent favours the 1,4-addition equally in the studied reactions, in spite of the dependence of the reagent association on the halogen of the reagent. This indicates a somewhat different molecularity in the transition state for the 1,2- and 1,4-reactions.

## EXPERIMENTAL

The reactions between 2-furanacrolein and Grignard reagents were performed by adding 2-furanacrolein<sup>16</sup> dissolved in a minimal amount

of dry diethyl ether (1.0 g/10.0 ml) to a solution of a freshly prepared and titrated Grignard reagent. The reaction mixtures were worked up after about 5 min in the usual way using  $\text{NH}_4\text{Cl}$ -solution.

**Analysis.** After the reaction mixtures had been worked up, they were analysed by GLC using a 3 m (i.d. 1.7 mm) glass column packed with pretested 1% XE-60 on 100–120 mesh Gas-Chrom Q supplied by Applied Science Laboratories Inc. The peaks were integrated by a Varian Integrator model 481. The mass spectra were taken on a combined GLC/MS instrument (LKB 9000). The preparative GLC separation was performed by using 5% XE-60 on 60–80 mesh Chromosorb G in a 2 m (i.d. 4 mm) glass column. The fractionated distillation was done on a Todd distillation assembly. The NMR spectra were recorded on Bruker WH-270 and Perkin-Elmer R 12 spectrometers and the IR spectra on a Perkin-Elmer 257 spectrometer.

**3-(2-Furanyl)-4-methylpentanal (2a)**, from the reaction between 2-furanacrolein and isopropylmagnesium bromide, was separated by fractionated distillation from a mixture containing 25% of the aldehyde. The crude product (5.0 ml) was distilled, giving 0.5 ml of pure aldehyde, b.p. 66°C/0.4 kPa. MS [IP 70 eV;  $m/e$  (% rel. int.)]: 166 (8, M), 137 (5, [M-CHO]), 123 (33, [M-C<sub>3</sub>H<sub>7</sub>]), 95 (100, C<sub>6</sub>H<sub>7</sub>O), 81 (25, C<sub>5</sub>H<sub>5</sub>O), 67 (91, C<sub>4</sub>H<sub>3</sub>O), 43 (37, C<sub>3</sub>H<sub>7</sub>), 41 (94, C<sub>3</sub>H<sub>5</sub>), 39 (73, C<sub>3</sub>H<sub>3</sub>). <sup>1</sup>H NMR (270 MHz, CDCl<sub>3</sub>):  $\delta$  9.44 (1 H, dd,  $J_{AB}$  2.4 Hz,  $J_{AC}$  1.9 Hz, H<sub>A</sub>), 7.29 (1 H, dd,  $J_{GF}$  1.9 Hz, H<sub>G</sub>), 6.26 (1 H, dd,  $J_{FE}$  3.4 Hz, H<sub>F</sub>), 6.01 (1 H, ddd,  $J_{EG}$  0.7 Hz,  $J_{ED}$  0.8 Hz, H<sub>E</sub>), 3.14 (1 H, m,  $J$  5.7 Hz, H<sub>D</sub>), 2.74 (1 H, ddd,  $J_{BD}$  9.3 Hz,  $J_{BC}$  16.6 Hz, H<sub>B</sub>), 2.63 (1 H, ddd,  $J_{CD}$  5.2 Hz, H<sub>C</sub>), 1.96 (1 H, m), 0.90 (3 H, d,  $J$  6.7 Hz), 0.84 (3 H, d,  $J$  6.7 Hz). IR (CCl<sub>4</sub>): Aliphatic CH 2980–2880, aldehyde CH 2820 and 2720, aldehyde C=O 1735 cm<sup>-1</sup>.

**1-(2-Furanyl)-4-methylpent-1-en-3-ol (1a)** was purified by distilling the crude product from the reaction of 2-furanacrolein with isopropylmagnesium chloride. By this simple method a 95% pure product could be obtained, b.p. 87.5–88°C/0.8 kPa. MS [IP 70 eV;  $m/e$  (% rel. int.)]: 166 (12, M), 149 (1, [M-OH]), 148 (2, [M-H<sub>2</sub>O]), 123 (92, [M-C<sub>3</sub>H<sub>7</sub>]), 95 (34, C<sub>6</sub>H<sub>7</sub>O), 81 (36, C<sub>5</sub>H<sub>5</sub>O), 67 (50, C<sub>4</sub>H<sub>3</sub>O), 55 (100, C<sub>4</sub>H<sub>7</sub>), 43 (59, C<sub>3</sub>H<sub>7</sub>), 41 (97, C<sub>3</sub>H<sub>5</sub>), 39 (93, C<sub>3</sub>H<sub>3</sub>). <sup>1</sup>H NMR (270 MHz, CDCl<sub>3</sub>):  $\delta$  7.33 (1 H, dd,  $J_{GF}$  1.9 Hz, H<sub>G</sub>), 6.40 (1 H, dd,  $J_{CA}$  1.0 Hz, H<sub>C</sub>), 6.36 (1 H, dd,  $J_{FE}$  3.5 Hz, H<sub>F</sub>), 6.22 (1 H, dd,  $J_{EG}$  1.0 Hz, H<sub>E</sub>), 6.18 (1 H, dd,  $J_{BC}$  16.0 Hz, H<sub>B</sub>), 4.00 (1 H, m,  $J_{AB}$  6.5 Hz,  $J$  1.0 Hz, H<sub>A</sub>), 1.81 (1 H, m), 1.57 (1 H, s, H<sub>D</sub>), 0.97 (3 H, d,  $J$  6.9 Hz), 0.95 (3 H, d,  $J$  6.9 Hz). IR (CCl<sub>4</sub>): Alcohol OH 3620 and 3490, aliphatic CH 2980–2880, olefinic C=C 1670 cm<sup>-1</sup>.

**3-(2-Furanyl)-4,4-dimethylpentanal (2b)**, from the reaction of 2-furanacrolein with *tert*-butylmagnesium chloride, was separated by

fractionated distillation. The crude product (7.2 g), containing 35% of the aldehyde, was distilled, giving 1.3 g (51%) of 98% pure aldehyde, b.p. 94°C/1.3 kPa. MS [IP 70 eV;  $m/e$  (% rel. int.)]: 180 (18, M), 165 (4, [M-CH<sub>3</sub>]), 151 (4, [M-CHO]), 124 (44, [M-C<sub>4</sub>H<sub>9</sub>]), 123 (13, [M-C<sub>4</sub>H<sub>9</sub>]), 95 (41, C<sub>6</sub>H<sub>7</sub>O), 81 (15, C<sub>5</sub>H<sub>5</sub>O), 57 (100, C<sub>4</sub>H<sub>9</sub>), 41 (24, C<sub>3</sub>H<sub>5</sub>). <sup>1</sup>H NMR (270 MHz, CDCl<sub>3</sub>):  $\delta$  9.58 (1 H, dd,  $J_{AB}$  2.5 Hz,  $J_{AC}$  1.8 Hz, H<sub>A</sub>), 7.30 (1 H, dd,  $J_{GF}$  2.0 Hz, H<sub>G</sub>), 6.28 (1 H, dd,  $J_{FE}$  3.1 Hz, H<sub>F</sub>), 6.04 (1 H, ddd,  $J_{EG}$  1.0 Hz,  $J_{ED}$  0.5 Hz, H<sub>E</sub>), 3.09 (1 H, dd, H<sub>D</sub>), 2.82 (1 H, ddd,  $J_{BD}$  10.9 Hz,  $J_{BC}$  16.5 Hz, H<sub>B</sub>), 2.66 (1 H, ddd,  $J_{CD}$  3.9 Hz, H<sub>C</sub>), 0.93 (9 H, s). IR (CCl<sub>4</sub>): Aliphatic CH 2960–2870, aldehyde CH 2820 and 2720, aldehyde C=O 1735 cm<sup>-1</sup>.

**1-(2-Furanyl)-4,4-dimethylpent-1-en-3-ol (1b)**. The residue from the distillation above was distilled over a short column. By this method 1.9 ml (40%) of the unsaturated alcohol could be obtained. B.p. 127°C/2.3 kPa. MS [IP 70 eV;  $m/e$  (% rel. int.)]: 180 (11, M), 165 (1, [M-CH<sub>3</sub>]), 163 (1, [M-OH]), 123 (100, [M-C<sub>4</sub>H<sub>9</sub>]), 95 (16, C<sub>5</sub>H<sub>7</sub>O), 81 (9, C<sub>5</sub>H<sub>5</sub>O), 67 (14, C<sub>4</sub>H<sub>3</sub>O), 57 (23, C<sub>4</sub>H<sub>9</sub>). <sup>1</sup>H NMR (270 MHz, CDCl<sub>3</sub>):  $\delta$  7.33 (1 H, dd,  $J_{GF}$  1.9 Hz, H<sub>G</sub>), 6.41 (1 H, dd,  $J_{CA}$  0.7 Hz, H<sub>C</sub>), 6.36 (1 H, dd,  $J_{FE}$  3.3 Hz, H<sub>F</sub>), 6.24 (1 H, dd,  $J_{BC}$  16.0 Hz, H<sub>B</sub>), 6.22 (1 H, d, H<sub>E</sub>), 3.89 (1 H, dd,  $J_{AB}$  6.7 Hz, H<sub>A</sub>), 1.26 (1 H, s, H<sub>D</sub>), 0.97 (9 H, s). IR (CCl<sub>4</sub>): Alcohol OH 3620, aliphatic CH 2960–2870, olefinic C=C 1670 cm<sup>-1</sup>.

**3-(2-Furanyl)-4-phenylbutanal (2c)**, from the reaction of benzylmagnesium chloride with 2-furanacrolein, was purified by preparative GLC. MS [IP 70 eV;  $m/e$  (% rel. int.)]: 214 (5, M), 185 (7, [M-CHO]), 123 (62, [M-C<sub>6</sub>H<sub>5</sub>]), 95 (100, C<sub>6</sub>H<sub>7</sub>O), 91 (64, C<sub>7</sub>H<sub>7</sub>), 67 (73, C<sub>4</sub>H<sub>3</sub>O). <sup>1</sup>H NMR (270 MHz, CDCl<sub>3</sub>):  $\delta$  9.57 (1 H, dd,  $J_{AB}$  2.0 Hz,  $J_{AC}$  1.7 Hz, H<sub>A</sub>), 7.3–7.0 (5 H, m), 7.28 (1 H, dd,  $J_{GF}$  1.8 Hz, H<sub>G</sub>), 6.20 (1 H, dd,  $J_{FE}$  3.2 Hz, H<sub>F</sub>), 5.90 (1 H, ddd,  $J_{EG}$  1.0 Hz,  $J_{ED}$  0.6 Hz, H<sub>E</sub>), 3.56 (1 H, m,  $J$  7.0 Hz,  $J$  7.5 Hz, H<sub>D</sub>), 3.03 (1 H, dd,  $J$  13.7 Hz), 2.83 (1 H, dd), 2.65 (1 H, ddd,  $J_{BD}$  7.8 Hz,  $J_{BC}$  16.8 Hz, H<sub>B</sub>), 2.58 (1 H, ddd,  $J_{CD}$  6.1 Hz, H<sub>C</sub>).

**4-(2-Furanyl)-1-phenylbut-3-en-2-ol (1c)**, from the reaction of benzylmagnesium iodide with 2-furanacrolein, was purified by steam distillation. The crude product (5 g) was purified by the steam from 250 ml of water, giving 3.7 g of 94% pure aldehyde. MS [IP 70 eV;  $m/e$  (% rel. int.)]: 214 (4, M), 196 (12, [M-H<sub>2</sub>O]), 123 (100, [M-C<sub>6</sub>H<sub>5</sub>]), 95 (18, C<sub>6</sub>H<sub>7</sub>O), 91 (25, C<sub>7</sub>H<sub>7</sub>), 81 (20, C<sub>5</sub>H<sub>5</sub>O), 77 (18, C<sub>6</sub>H<sub>5</sub>), 67 (23, C<sub>4</sub>H<sub>3</sub>O), 55 (44, C<sub>3</sub>H<sub>3</sub>O). <sup>1</sup>H NMR (60 MHz, CCl<sub>4</sub>):  $\delta$  7 (5 H, m), 7.05 (1 H, d,  $J_{GF}$  2.0 Hz, H<sub>G</sub>), 6.15 (1 H, d, H<sub>C</sub>), 6.08 (1 H, dd,  $J_{FE}$  3.2 Hz, H<sub>F</sub>), 5.97 (1 H, dd,  $J_{BC}$  15.3 Hz, H<sub>B</sub>), 5.92 (1 H, d, H<sub>E</sub>), 4.20 (1 H, dt,  $J_{AB}$  4.0 Hz, H<sub>A</sub>), 2.69 (2 H, d,  $J$  6.2 Hz), 2.33 (1 H, s, H<sub>D</sub>). IR (CCl<sub>4</sub>): Alcohol OH 3620 and 3480, Ar CH 3100–3000, aliphatic CH 2960–2860, olefinic C=C 1665 cm<sup>-1</sup>.

3-(2-Furanyl)butanal (2d), from the reaction of lithium dimethylcuprate with 2-furana-crolein. The reagent was prepared under N<sub>2</sub>-atmosphere from methyl lithium (59.6 mmol) and copper(I) iodide (5.2 g, 30 mmol) in absolute diethyl ether (distilled from sodium benzo-phenone ketyl) at 0 °C. After 15 min the reagent showed a negative Gilman Test I.<sup>17</sup> The reagent was cooled to about -35 °C in an acetone bath cooled with dry ice and 1.83 g (15 mmol) of 2-furana-crolein in ether was added *via* a hypodermic syringe. The reaction was worked up after 20 min. The GLC yield of the 1,4-adduct was 85 %. The crude product was distilled over a short column giving *ca* 1 ml of pure product; B.p. 85 °C/2.7 kPa. MS [IP 70 eV; *m/e* (% rel. int.)]: 138 (29, M), 123 (10, [M - CH<sub>3</sub>]), 109 (12, [M - CHO]), 95 (100, C<sub>8</sub>H<sub>8</sub>O), 81 (15, C<sub>8</sub>H<sub>8</sub>O), 68 (40, C<sub>4</sub>H<sub>4</sub>O), 67 (38, C<sub>4</sub>H<sub>3</sub>O), 41 (48, C<sub>3</sub>H<sub>3</sub>), 39 (44, C<sub>3</sub>H<sub>3</sub>). <sup>1</sup>H NMR (270 MHz, CDCl<sub>3</sub>): δ 9.72 (1 H, t, *J*<sub>AB</sub> 2.0 Hz, *J*<sub>AC</sub> 2.0 Hz, H<sub>A</sub>), 7.29 (1 H, dd, *J*<sub>CF</sub> 2.0 Hz, H<sub>C</sub>), 6.26 (1 H, dd, *J*<sub>FF</sub> 3.4 Hz, H<sub>F</sub>), 6.00 (1 H, ddd, *J*<sub>EG</sub> 1.0 Hz, *J*<sub>ED</sub> 1.0 Hz, H<sub>E</sub>), 3.41 (1 H, m, *J* 6.5 Hz, H<sub>D</sub>), 2.76 (1 H, ddd, *J*<sub>BD</sub> 6.5 Hz, *J*<sub>BC</sub> 16.8 Hz, H<sub>B</sub>), 2.56 (1 H, ddd, *J*<sub>CD</sub> 7.2 Hz, H<sub>C</sub>), 1.30 (3 H, d).

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