Acta Chemica Scandinavica B 34 (1980) 435–441

Reactions between Furyl Ketones and Grignard Reagents. II. Steric Effects in the Reactions of 2-Furyl Ketones with Alkylmagnesium Halides*,**

RAINER SJÖHOLM and KRISTER WÖRLUND

Institutionen för organisk kemi, Åbo Akademi, SF-20500 Åbo 50, Finland

The effect of steric crowding at the carbonyl carbon of some alkyl 2-furyl ketones, 2-Fur-CO-R (R = Et, i-Pr, and *t*-Bu), on the reaction with alkyl Grignard reagents, R′MgX (R′ = Me, i-Pr and *t*-Bu), has been studied. The effect of the size of the alkyl group of the Grignard reagent was also considered.

When MeMgI reacts with the ketones only 1,2-addition products are formed. Reactions with i-PrMgCl and *t*-BuMgCl give considerable amounts of 1,4- and 1,6-addition products besides 1,2-addition. The primary conjugate addition products are easily oxidized to alkyl substituted alkyl 2-furyl ketones and 2-(5*H*)-furanones when exposed to air. Further, the i-Pr reagent gives reaction products formed by reduction of the carbonyl group.

An increase in the amounts of conjugate addition products is observed when the size of the alkyl group in the substrate or that of the alkyl group of the reagent is increased.

Possible reaction mechanisms are discussed.

Previous studies on reactions of Grignard reagents with α,β-unsaturated carbonyl compounds in which the unsaturation is part of a furan ring, have shown that 2-furanaldehyde and 2-acetylfuran give reaction products formed by 1,2- and conjugate additions of the reagent to the substrate.[2–5]

Although the results reveal that a bulky substituent at the carbonyl carbon does not necessarily cause conjugate addition, steric crowding at the carbonyl group cannot be completely outruled as a directing factor for the course of the reaction. It is well known that saturated ketones, heavily substituted at the carbonyl carbon, undergo enolization and reduction when they are treated with alkylmagnesium halides and that reduction becomes the main reaction when the reagent contains a bulky alkyl group.[6] For α,β-unsaturated ketones, 1,4-addition is the expected alternative to 1,2-addition when the carbonyl group is sterically hindered, provided that the β-carbon is not heavily substituted. In compounds, such as 2-furyl ketones, containing two double bonds conjugated with the carbonyl group, 1,6-addition is also possible.

The present investigation was undertaken in order to study how a bulky substituent at the carbonyl carbon affects the formation of 1,2-, 1,4- and 1,6-addition products in reactions of alkyl 2-furyl ketones with various alkylmagnesium halides. The effect of the size of the alkyl group in the reagent is also considered.

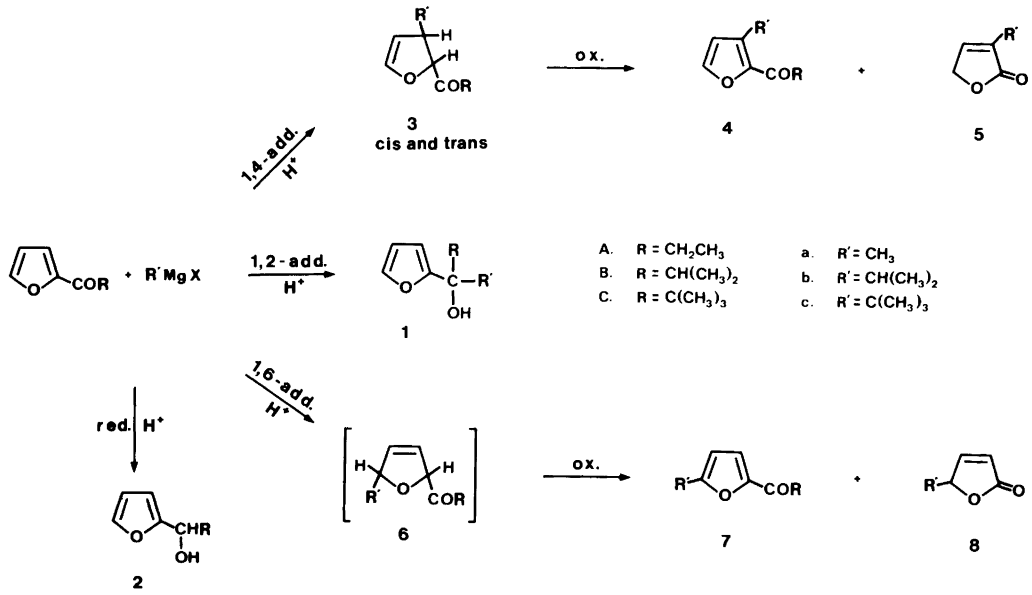
RESULTS AND DISCUSSION

The Grignard reagents (excess 5:1), R′MgX (R′ = Me, i-Pr or *t*-Bu), were allowed to react with the furyl ketones, 2-Fur-CO-R (R = Et, i-Pr or *t*-Bu), and the worked-up reaction mixtures were quantitatively and qualitatively analyzed by GLC and spectroscopic methods. The reactions are described in Scheme 1 and the yields of the different reaction products are given in Table 1.

The methyl reagent gave only 1,2-addition products, whereas the i-propyl and *t*-butyl reagents gave also 1,4- and 1,6-addition products. Moreover, in the reactions between the ketones and the i-propyl

* *Cf.* Ref. 1.
** For Part I, see Ref. 4.

0302-4369/80/060435-07$02.50



Scheme 1.

Grignard reagent reduction of the carbonyl group took place.

As no attempts to exclude air during the work-up procedure were made, oxidations of the primary conjugate addition products were expected in analogy with previously made observations.[3-5,7] In fact, compounds formed by oxidation of primarily formed adducts were detected in the reaction mixtures. The presence of compounds *7* and *8* is the only indication of 1,6-additions as no primary 1,6-addition products (*6*) were detected. Table 1 shows the compositions of the reaction mixtures immediately after work-up. On standing, the compositions changed, and the amounts of compounds

Table 1. Yields of products (as determined by GLC) formed in the reactions between Grignard reagents (R'MgX) and alkyl 2-furyl ketones (2-Fur−CO−R). Yields are given in mol-% of reacted substrate.

Ketone R	Reagent R'	Products 1	2	3 *trans*	3 *cis*	4	5	7	8	Tot.
Et	Me	69	–	–	–	–	–	–	–	69
	i-Pr	45	6	5	–	2	2	3	–	63
	t-Bu	24	–	10[a]	1	5	7	2	5	54
i-Pr	Me	65	–	–	–	–	–	–	–	65
	i-Pr	40	4	1	–	5	6	1	2	59
	t-Bu	14	–	5[a]	–	10	11	3	5	48
t-Bu	Me	71	–	–	–	–	–	–	–	71
	i-Pr	24	12	2	1	13	6	3	6	67
	t-Bu	11	–	5[a]	–	21	3	3	2	45

[a] *trans*-Configuration confirmed by ^{1}H NMR spectroscopy.

Table 2. Normalized[a] yields of products from the reactions of Grignard reagents (R'MgX) with alkyl 2-furyl ketones (2-Fur – CO – R).

Substrate R	Reagent R'	Products			
		% 1.2-redn	% 1.2-addn	% 1.4-addn[b]	% 1.6-addn[b]
Et	Me	–	100	–	–
	i-Pr	10	71	14	5
	t-Bu	–	45	42	13
i-Pr	Me	–	100	–	–
	i-Pr	7	68	20	5
	t-Bu	–	29	54	17
t-Bu	Me	–	100	–	–
	i-Pr	18	36	33	13
	t-Bu	–	24	64	12

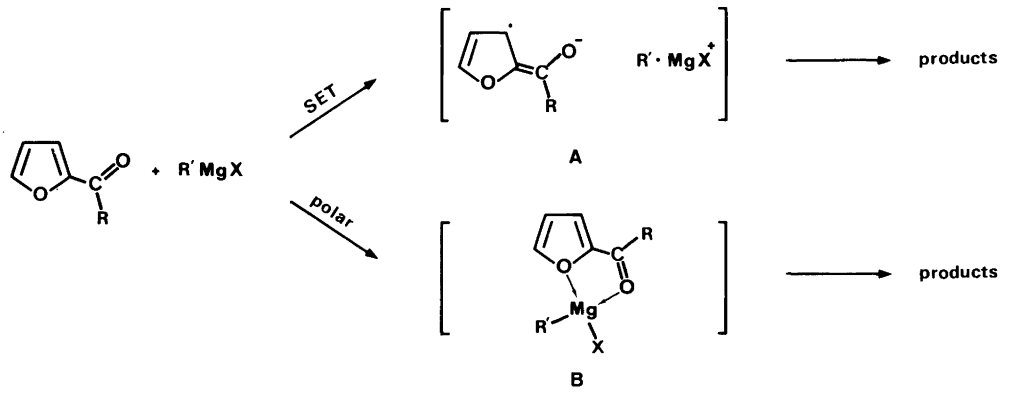
[a] 100 % = % 1,2-redn + % 1,2-addn + % 1,4-addn + % 1,6-addn. [b] Oxidation products are included.

4 and *5* increased at the expense of compound *3* (*cis* and *trans*).

Normalized yields of addition and reduction products are presented in Table 2. The data in Table 2 show that conjugate addition is favoured by bulky substituents at the carbonyl carbon and by voluminous Grignard reagents and that 1,4-addition dominates over 1,6-addition. The results show also that i-propylmagnesium chloride was the only reagent used which caused reduction of the carbonyl group.

Preliminary results from studies of the reactions between benzylmagnesium chloride and alkyl 2-furyl ketones have shown that the amount of 1,4-addition decreases when the size of the alkyl group of the ketone is increased.[1] This indicates that the steric hindrance of the alkyl group is mainly exerted on the "*ortho*" position in the furan ring. This can be rationalized so that the initial step is polar and involves the coordination of the Mg-atom to both oxygen atoms of the substrate (Scheme 2). In the chelate so formed, the substrate would be forced to occupy the *syn* conformation (I in Fig. 1) in which C-3 of the furan ring is shielded by voluminous groups at the carbonyl carbon.

In the present study no suppression of 1,4-addition due to voluminous alkyl groups at the carbonyl carbon was observed. This indicates that no chelation of the Mg-atom by the substrate takes place and that the more stable *anti* conformation (II in



Scheme 2.

I II

Fig. 1. Anti (I) and *syn* (II) conformations of alkyl 2-furyl ketones.

Fig. 1)[8] of the ketone is retained in the intermediate. A single-electron transfer (SET) mechanism according to Holm *et al.*[9] seems quite probable in the initial step of the 1,4-addition since it should proceed with retention of the *anti* conformation in the intermediate radical pair (A in Scheme 2). Possibly a SET also initiates the 1,6-addition. This hypothesis is supported by the fact that no 1,6-additions were observed in reactions with benzylmagnesium chloride,[1] known to react relatively slowly in SET reactions.[10]

In their studies of the reaction between *t*-butylmagnesium chloride and 2,2,6,6-tetramethylhept-4-en-3-one Ashby and Wiesemann[11] observed that 1,2-reduction is the main reaction. This fact indicates that the addition reactions are slow (relatively) probably due to steric hindrance by the *t*-butyl groups in the substrate. In the present study, however, no reductions by *t*-butylmagnesium chloride were observed, although i-propylmagnesium chloride reduced all substrates to some extent. The reason for this difference might be steric as the carbonyl carbon is shielded, at least to some extent, in all three ketones while the furan ring carbons should be accessible to attack even by a bulky alkyl group provided the substrate occupies the *anti* conformation.

EXPERIMENTAL

1-(2-Furyl)-propan-1-one was prepared in 50 % yield (b.p. 77.0–77.5 °C/2.3 kPa) by a method described in Ref. 12.

1-(2-Furyl)-2-methylpropan-1-one was prepared in 83 % yield (b.p. 77.5–80.0 °C/2.7 kPa) by a method described in Ref. 13.

1-(2-Furyl)-2,2-dimethylpropan-1-one was prepared in 44 % yield (b.p. 85.5–86.0 °C/2.9 kPa) by a method described in Ref. 13.

The reactions between the ketones and the Grignard reagents were performed as described previously.[4] The reaction mixtures were analyzed by GLC immediately after work-up on a Varian 2400 gas chromatograph equipped with a 0.2 by 150 cm 3 % OV-225 on 100/120 Gas Chrom Q glass column. Dibenzyl was used as an internal standard in the quantitative analyses. Mass spectra were taken on a combined GC-MS instrument (LKB 9000). The isolations of the reaction products were performed on a Varian Aerograph A – 700 preparative gas chromatograph equipped with a 0.95 by 600 cm 30 % SE-30 on 45/60 Chromosorb W steel column and their ^{1}H NMR spectra recorded on a JEOL FX-60 FT NMR spectrometer at 60 MHz.

The ^{1}H NMR spectra of the furfuryl alcohols (*1* and *2*) displayed ABX systems for the furan ring protons, the shifts ranging from approx. δ 6.00 to 6.35 ppm for H_3 and H_4 and from approx. δ 7.15 to 7.40 ppm for H_5. The ABX systems were, however, not completely analyzed in this work and the exact shifts and couplings are omitted. In the mass spectra of the furfurylalcohols, hydrocarbon fragments (*m/e* 79, 77, 65 and 39) were detected. The formations of these fragments from alkyl substituted furans have been described in the literature.[14]

2-(2-Furyl)-butan-2-ol (1 Aa). ^{1}H NMR (60 MHz, $CDCl_3$): δ 0.82 (CH_3CH_2-, t, *J* 7.5 Hz), 1.48 ($CH_3-C\leftarrow$, s), 1.85 (CH_3CH_2-, q, *J* 7.5 Hz). MS [IP 70 eV; *m/e* (% rel. int.)]: 140 (9, M), 125 (6, M – CH_3), 122 (45, M – H_2O), 107 (19, M – H_2O – CH_3), 111 (100, M – CH_3CH_2), 95 (10, Fur – CO), 93 (15, M – H_2O – CH_3CH_2), 79 (23), 77 (16), 65 (10), 57 (5, CH_3CH_2CO), 43 (62, CH_3CO), 39 (19), 29 (8, CH_3CH_2).

3-(2-Furyl)-2-methylpentan-3-ol (1 Ab). ^{1}H NMR (60 MHz, $CDCl_3$): δ 0.78 (CH_3CH_2-, t, *J* 7.2 Hz), 0.82 and 0.91 [$(CH_3)_2CH-$, dd, *J* 6.6 Hz], 1.84 (CH_3CH_2-, q, *J* 7.2 Hz), 2.04 [$(CH_3)_2CH-$, sept, *J* 6.6 Hz]. MS [IP 70 eV; *m/e* (% rel.int.)]: 168 (4, M), 150 (4, M – H_2O), 139 (5, M – CH_3CH_2), 135 (2, M – H_2O – CH_3), 125 [100, M – $(CH_3)_2CH$], 107 [2, M – H_2O – $(CH_3)_2CH$], 97 (7, Fur-CHOH), 95 (9, Fur-CO), 79 (3), 77 (3), 57 (17, CH_3CH_2CO), 43 [30, $(CH_3)_2CH$], 39 (7), 29 (11, CH_3CH_2).

3-(2-Furyl)-2,2-dimethylpentan-3-ol (1 Ac). ^{1}H NMR (60 MHz, $CDCl_3$): δ 0.69 (CH_3CH_2-, t, *J* 6.8 Hz), 0.94 [$(CH_3)_3C-$, s], 1.86 (CH_3CH_2-, q, *J* 6.8 Hz). MS [IP 70 eV; *m/e* (% rel. int.)]: 182 (2, M), 167 (1, M – CH_3), 164 (2, M – H_2O), 153 (1, M – CH_3CH_2), 149 (2, M – H_2O – CH_3), 125 [100, M – $(CH_3)_3C$], 107 [M – H_2O – $(CH_3)_3C$], 95 (8, Fur-CO), 79 (3), 77(2), 57 [21, CH_3CO and $(CH_3)_3C$], 39 (8), 29 (13, CH_3CH_2).

2-(2-Furyl)-3-methylbutan-2-ol (1 Ba). ^{1}H NMR (60 MHz, $CDCl_3$): δ 0.78 and 0.88 [$(CH_3)_2CH-$, dd, *J* 6.6 Hz], 1.32 (CH_3-, s), 2.00 [$(CH_3)_2CH-$, sept, *J* 6.6 Hz]. MS [IP 70 eV; *m/e* (% rel. int.)]: 154 (5, M), 136 (3, M – H_2O), 121 (3, M – H_2O – CH_3), 111 [100, M – $(CH_3)_2CH$], 97 (2, Fur-CHOH), 95 (5, Fur-CO), 77 (2), 65 (2), 56 [43, CH_3CO and $(CH_3)_2CH$], 39 (8).

3-(2-Furyl)-2,4-dimethylpentan-3-ol (1 Bb). ^{1}H NMR (60 MHz, $CDCl_3$): δ 0.80 and 0.88 [$(CH_3)_2$-CH−, dd, J 6.7 Hz], 2.23 [$(CH_3)_2CH-$, sept, J 6.7 Hz]. MS [IP 70 eV; *m/e* (% rel. int.)]: 182 (4, M), 164 (1, M−H_2O), 139 [100, M−$(CH_3)_2CH$], 121 [1, M−H_2O−$(CH_3)_2CH$], 97 (59, Fur-CHOH), 95 (17, Fur-CO), 79 (3), 77 (3), 71 [3, $(CH_3)_2CHCO$], 43 [84, $(CH_3)_2CH$], 39 (9).

3-(2-Furyl)-2,2,4-trimethylpentan-3-ol (1 Bc and 1 Cb). ^{1}H NMR (60 MHz, $CDCl_3$): δ 0.75 and 1.01 [$(CH_3)_2$CH−, dd, J 6.8 Hz], 0.99 [$(CH_3)_3C-$, s], 2.38 [$(CH_3)_2CH-$, sept, J 6.8 Hz]. MS [IP 70 eV; *m/e* (% rel. int.)]: 196 (2, M), 181 (1, M−CH_3), 153 [13, M−$(CH_3)_2CH$], 139 [100, M−$(CH_3)_3C$], 121 [1, M−H_2O−$(CH_3)_3C$], 97 (50, Fur-CHOH), 95 (14, Fur-CO), 85 [2, $(CH_3)_3CCO$], 79 (2), 77 (3), 71 [7, $(CH_3)_2CHCO$], 57 [10, $(CH_3)_3C$], 43 [73, $(CH_3)_2CH$], 39 (8).

2-(2-Furyl)-3,3-dimethylbutan-2-ol (1 Ca). ^{1}H NMR (60 MHz, $CDCl_3$): δ 0.94 [$(CH_3)_3C-$, s], 1.48 (CH_3-, s). MS [IP 70 eV; *m/e* (% rel. int.)]: 168 (3, M), 153 (1, M−CH_3), 150 (3, M−H_2O), 135 (3, M−H_2O−CH_3), 111 [100, M−$(CH_3)_3C$], 95 (5, Fur-CO), 93 [3, M−H_2O−$(CH_3)_3C$], 79 (1), 77 (1), 65 (2), 57 [7, $(CH_3)_3C$], 43 (43, CH_3CO), 39 (7).

3-(2-Furyl)-2,2,4,4-tetramethylpentan-3-ol (1 Cc). ^{1}H NMR (60 MHz, $CDCl_3$): δ 1.07 [$(CH_3)_3C-$, s]. MS [IP 70 eV; *m/e* (% rel. int.)]: 210 (2, M), 153 [100, M−$(CH_3)_3C$], 111 (58, C_8H_{15}), 97 (4, Fur-CHOH), 95 (9, Fur-CO), 85 [8, $(CH_3)_3C$], 79 (2), 77 (2), 65 (3), 57 [40, $(CH_3)_3C$], 39 (8).

1-(2-Furyl)-propan-1-ol (2 A). ^{1}H NMR (60 MHz, $CDCl_3$): δ 0.96 (CH_3CH_2-, t, J 7.0 Hz), 1.90 (CH_3CH_2-, m), 4.61 (Fur-$CH<$, t, J 6.0 Hz). MS [IP 70 eV; *m/e* (% rel. int.)]: 126 (17, M), 124 (4, M−2), 109 (6, M−2−CH_3), 108 (1, M−H_2O), 97 (100, M−CH_3CH_2), 95 (19, M−2−CH_3CH_2), 79 (5), 77 (3), 65 (1), 39 (14), 29 (6, CH_3CH_2).

1-(2-Furyl)-2-methylpropan-1-ol (2 B). ^{1}H NMR (60 MHz, $CDCl_3$): δ 0.85 and 1.00 [$(CH_3)_2CH-$, dd, J 6.7 Hz], 1.94 [$(CH_3)_2CH-$, m], 4.35 (Fur-$CH<$, d, J 6.8 Hz). MS [IP 70 eV; *m/e* (% rel. int.)]: 140 (10, M), 122 (2, M−H_2O), 107 (2, M−H_2O−CH_3), 97 [100, M−$(CH_3)_2CH$], 95 (4, Fur-CO), 79 (2), 77 (2), 65 (5), 43 [6, $(CH_3)_2CH$], 39 (10).

1-(2-Furyl)-2,2-dimethylpropan-1-ol (2 C). ^{1}H NMR (60 MHz, $CDCl_3$): δ 0.96 [$(CH_3)_3C-$, s], 4.37 (Fur-$CH<$, s). MS [IP 70 eV; *m/e* (% rel. int.)]: 154 (8, M), 139 (1, M−CH_3), 136 (1, M−H_2O), 97 [100, M−$(CH_3)_3C$], 95 (3, Fur-CO), 79 (1), 77 (1), 65 (3), 57 [17, $(CH_3)_3C$], 39 (10).

The gas chromatograms of those reaction mixtures containing 2,3-dihydro-2-furyl ketones formed by 1,4-addition of the reagents, revealed two isomers (probably *cis* and *trans*) of the dihydrofurans. The mass spectra of the two isomers were very similar and only the MS data of the more abundant isomer (believed to be *trans*) are given below. Formations of some of the fragments characteristic of 2,3-dihydro-2-furyl ketones have been described earlier.[5] The *trans*-structure of the more abundant isomers was confirmed only in the cases in which isolation, followed by ^{1}H NMR analysis, was successful (*3 Ac*, *3 Bc* and *3 Cc*). The couplings between H_2 and H_3 ranged in magnitude from J = 4.7 Hz to J = 5.4 Hz which is expected for *trans*-isomers.[4]

1-(3-i-Propyl-2,3-dihydro-2-furyl)-propan-1-one (3 Ab). MS [IP 70 eV; *m/e* (% rel. int.)]: 168 (10, M), 139 (9, M−CH_3CH_2), 125 [18, M−$(CH_3)_2CH$], 111 (39, M−CH_3CH_2CO), 97 (4, 2,3-dih.Fur-CO), 95 (5, Fur-CO), 69 (34, 2,3-dih.Fur), 57 (100, CH_3CH_2CO), 43 [57, $(CH_3)_2CH$], 39 (13).

trans-*1-(3-t-Butyl-2,3-dihydro-2-furyl)-propan-1-one* (3 Ac). ^{1}H NMR (60 MHz, $CDCl_3$): δ 0.88 [$(CH_3)_3C-$, s], 0.8−1.2 (CH_3CH_2-, poorly res. m.), 2.4−2.8 (CH_3CH_2- and H'_3, overlapping), 4.56 (H'_2, d, J 4.8 Hz), 4.93 (H'_4, dd, J 2.7 and 2.8 Hz), 6.41 (H'_5, dd, J 2.3 and 2.8 Hz). MS [IP 70 eV; *m/e* (% rel. int.)]: 182 (1, M), 153 (4, M−CH_3CH_2), 125 [4, M−$(CH_3)_3C$ and M−CH_3CH_2CO], 97 (2), 95 (1), 69 (2), 57 [100, $(CH_3)_3C$ and CH_3CH_2CO], 39 (5).

1-(3-i-Propyl-2,3-dihydro-2-furyl)-2-methylpropan-1-one (3 Bb). MS [IP 70 eV; *m/e* (% rel. int.)]: 182 (2, M), 139 [26, M−$(CH_3)_2CH$], 111 [26, M−$(CH_3)_2CHCO$], 97 (1), 95 (1), 71 [26, $(CH_3)_2CHCO$], 69 (25), 43 [100, $(CH_3)_2CH$], 39 (13).

trans-*1-(3-t-Butyl-2,3-dihyro-2-furyl)-2-methylpropan-1-one* (3 Bc). ^{1}H NMR (60 MHz, $CDCl_3$): δ 0.87 [$(CH_3)_3C-$, s], 1.05 and 1.13 [$(CH_3)_2CH-$, dd, J 7.0 Hz)], 2.77 (H'_3, ddd, J 1.9, 2.7 and 4.7 Hz), 3.10 [$(CH_3)_2CH-$, sept, J 7.0 Hz], 4.63 (H'_2, d, J 4.7 Hz), 4.93 (H'_4, dd, J 2.7 and 2.8 Hz), 6.41 (H'_5, dd, J 1.9 and 2.8 Hz). MS [IP 70 eV; *m/e* (% rel. int.)]: 196 (1, M), 153 [33, M−$(CH_3)_2CH$], 125 [2, M−$(CH_3)_2$-CHCO], 97 (5), 95 (3), 71 [98, $(CH_3)_2CHCO$], 69 (4), 57 [100, $(CH_3)_3C$], 43 [95, $(CH_3)_2CH$], 39 (10).

1-(3-i-Propyl-2,3-dihydro-2-furyl)-2,2-dimethylpropan-1-one (3 Cb). MS [IP 70 eV; *m/e* (% rel. int.)]: 196 (8, M), 153 [2, M−$(CH_3)_2CH$], 139 [21, M−$(CH_3)_3C$], 111 [85, M−$(CH_3)_3CCO$], 97 (4), 95 (7), 85 [8, $(CH_3)_3CCO$], 69 (66), 57 [87, $(CH_3)_3C$], 43 [100, $(CH_3)_2CH$], 39 (19).

trans-*1-(3-t-Butyl-2,3-dihydro-2-furyl)-2,2-dimethylpropan-1-one* (3 Cc). ^{1}H NMR (60 MHz, $CDCl_3$): δ 0.86 [$(CH_3)_3C-$, s], 1.23 [$(CH_3)_3CCO-$, s], 3.10 (H'_3, ddd, J 1.9, 2.7 and 5.4 Hz), 4.85 (H'_2, d, J 5.4 Hz), 4.95 (H'_4, dd, J 2.7 and 2.8 Hz), 6.30 (H'_5, dd, J 1.9 and 2.8 Hz). MS [IP 70 eV; *m/e* (% rel. int.)]: 210 (1, M), 154 [14, M−$(CH_3)_2C=CH_2$], 125 [1, M−$(CH_3)_3CCO$], 97 (1), 95 (1), 85 [7, $(CH_3)_3$-CCO], 69 (1), 57 [100, $(CH_3)_3C$], 39 (4).

In all reactions with i-propyl- and *t*-butylmag-

nesium Grignard reagents, 3- and 5-alkyl substituted 2-furyl ketones were formed, probably by oxidation of the primary 1,4- and 1,6-addition products, respectively. All, except one (*4 Ab*), of these compounds (*4* and *7*) could be isolated by preparative GLC and their ^{1}H NMR and mass spectral data are given below. The ^{1}H NMR spectra displayed weak couplings between the ring protons and α-protons of the alkyl substituents. The couplings were, however, not resolved in the signals of the alkyl protons, the multiplicities of which are therefore indicated by m.

1-(3-i-Propyl-2-furyl)-propan-1-one (4 Ab). MS [IP 70 eV; *m/e* (% rel. int.)]: 166 (47, M), 151 (28, M−CH_3), 137 (100, M−CH_3CH_3), 123 [2, M−$(CH_3)_2CH$], 109 (16, M−CH_3CH_2CO), 95 (8, Fur-CO), 79 (7), 77 (7), 57 (17), CH_3CH_2CO), 43 [20, $(CH_3)_2CH$], 39 (17).

1-(3-t-Butyl-2-furyl)-propan-1-one (4 Ac). ^{1}H NMR (60 MHz, $CDCl_3$): δ 1.16 (CH_3CH_2-, t, *J* 7.8 Hz), 1.31 [$(CH_3)_3C-$, s], 2.90 (CH_3CH_2, q, *J* 7.8 Hz), 6.50 (H′$_4$, d, *J* 1.9 Hz), 7.40 (H′$_5$, d, *J* 1.9 Hz). MS [IP 70 eV; *m/e* (% rel. int.)]: 180 (54, M), 165 (100, M−CH_3), 151 (98, M−CH_3CH_2), 123 [9, M−CH_3CH_2CO and M−$(CH_3)_3C$], 95 (9, Fur-CO), 79 (22), 77 (20), 57 [54, CH_3CH_2CO and $(CH_3)_3C$], 39 (38).

1-(3-i-Propyl-2-furyl)-2-methylpropan-1-one (4 Bb). ^{1}H NMR (60 MHz, $CDCl_3$): δ 1.17 and 1.18 [$(CH_3)_2CH-$ and $(CH_3)_2CHCO-$, dd, *J* 6.8 Hz], 3.35 [$(CH_3)_2CH-$, m], 3.50 [$(CH_3)_2CHCO-$, sept, *J* 6.8 Hz], 6.50 (H′$_4$, dd, *J* 0.5 and 1.8 Hz), 7.39 (H′$_5$, dd, *J* 0.6 and 1.8 Hz). MS [IP 70 eV; *m/e* (% rel. int.)]: 180 (23, M), 165 (5, M−CH_3), 137 [100, M−$(CH_3)_2CH$], 109 [11, M−$(CH_3)_2CHCO$], 95 (17, Fur-CO), 79 (9), 77 (10), 71 [29, $(CH_3)_2CHCO$], 43 [3, $(CH_3)_2CH$], 39 (37).

1-(3-t-Butyl-2-furyl)-2-methylpropan-1-one (4 Bc). ^{1}H NMR (60 MHz, $CDCl_3$): δ 1.16 [$(CH_3)_2$-CH−, d, *J* 6.8 Hz], 1.36 [$(CH_3)_3C-$, s], 3.52 [$(CH_3)_2CH-$, sept, *J* 6.8 Hz], 6.50 (H′$_4$, d, *J* 1.7 Hz), 7.38 (H′$_5$, d, *J* 1.7 Hz). MS [IP 70 eV; *m/e* (% rel. int.)]: 194 (23, M), 179 (12, M−CH_3), 151 [100, M−$(CH_3)_2CH$], 137 [2, M−$(CH_3)_3C$], 123 [2, M−$(CH_3)_2CHCO$], 95 (2, Fur-CO), 79 (7), 77 (5), 57 [2, $(CH_3)_3C$], 43 [9, $(CH_3)_2CH$], 39 (6).

1-(3-i-Propyl-2-furyl)-2,2-dimethylpropan-1-one (4 Cb). ^{1}H NMR (60 MHz, $CDCl_3$): δ 1.18 [$(CH_3)_2CH-$, d, *J* 6.8 Hz], 1.83 [$(CH_3)_3C-$, s], 3.68 [$(CH_3)_2CH-$, m], 6.47 (H′$_4$, dd, *J* 0.4 and 1.8 Hz), 7.38 (H′$_5$, dd, *J* 0.49 and 1.77 Hz). MS [IP 70 eV; *m/e* (% rel. int.)]: 194 (14, M), 179 (1, M−CH_3), 137 [100, M−$(CH_3)_3C$], 151 [1, M−$(CH_3)_2CH$], 109 [8, M−$(CH_3)_3CCO$], 95 (2, Fur-CO), 79 (4), 77 (3), 57 [29, $(CH_3)_3C$], 43 [9, $(CH_3)_2CH$], 39 (12).

1-(3-t-Butyl-2-furyl)-2,2-dimethylpropan-1-one (4 Cc). ^{1}H NMR (60 MHz, $CDCl_3$): δ 1.32 and 1.34 [$(CH_3)_3C-$ and $(CH_3)_3CCO-$, ss], 6.47 (H′$_4$, d, *J* 1.8 Hz), 7.35 (H′$_5$, d, *J* 1.8 Hz). MS [IP 70 eV; *m/e* (% rel. int.)]: 208 (9, M), 193 (2, M−CH_3), 151 [100, M−$(CH_3)_3C$], 123 [(2, M−$(CH_3)_3CCO$], 95 (1, Fur-CO), 85 [1, $(CH_3)_3CCO$], 79 (3), 77 (3), 57 [16, $(CH_3)_3C$], 39 (6).

1-(5-i-Propyl-2-furyl)-propan-1-one (7 Ab). ^{1}H NMR (60 MHz, $CDCl_3$): δ 1.19 (CH_3CH_2-, t, *J* 7.5 Hz), 1.31 [$(CH_3)_2CH-$, d, *J* 7.0 Hz], 2.78 (CH_3CH_2-, q, *J* 7.5 Hz), 3.02 [$(CH_3)_2CH-$, m], 6.09 (H′$_4$, dd, *J* 0.8 and 3.5 Hz), 7.04 (H′$_3$, d, *J* 3.5 Hz). MS [IP 70 eV; *m/e* (% rel. int.)]: 166 (26, M), 151 (25, M−CH_3), 137 (100, M−CH_3CH_2), 123 [2, M−$(CH_3)_2CH$], 109 (10, M−CH_3CH_2CO), 95 (9, Fur-CO), 79 (6), 77 (3), 43 [6, $(CH_3)_2CH$], 39 (11).

1-(5-t-Butyl-2-furyl)-propan-1-one (7 Ac). ^{1}H NMR (60 MHz, $CDCl_3$): δ 1.16 (CH_3CH_2-, t, *J* 7.8 Hz), 1.30 [$(CH_3)_3C-$, s], 2.80 (CH_3CH_2-, q, *J* 7.8 Hz), 6.10 (H′$_4$, d, *J* 3.7 Hz), 7.10 (H′$_3$, d, *J* 3.7 Hz). MS [IP 70 eV; *m/e* (% rel. int.)]: 180 (26, M), 165 (100, M−CH_3), 151 (29, M−CH_3CH_2), 123 [6, M−$(CH_3)_3C$ and M−CH_3CH_2CO], 95 (9, Fur-CO), 79 (6), 77 (3), 57 [17, $(CH_3)_3C$ and CH_3CH_2CO], 39 (5).

1-(5-i-Propyl-2-furyl)-2-methylpropan-1-one (7 Bb). ^{1}H NMR (60 MHz, $CDCl_3$): δ 1.19 and 1.30 [$(CH_3)_2CH-$ and $(CH_3)_2CHCO-$, dd, *J* 6.8 Hz], 3.04 [$(CH_3)_2CH-$, m], 3.29 [$(CH_3)_2CHCO-$, sept, *J* 6.8 Hz], 6.14 (H′$_4$, dd, *J* 1.0 and 3.5 Hz), 7.12 (H′$_3$, dd, *J* 0.37 and 3.54 Hz). MS [IP 70 eV; *m/e* (% rel. int.)]: 180 (13, M), 165 (4, M−CH_3), 137 [100, M−$(CH_3)_2CH$], 109 [2, M−$(CH_3)_2CHCO$], 95 (3, Fur-CO), 79 (3), 77 (2), 71 [1, $(CH_3)_2CHCO$], 43 [7, $(CH_3)_2CH$], 39 (6).

1-(5-t-Butyl-2-furyl)-2-methylpropan-1-one (7 Bc). ^{1}H NMR (60 MHz, $CDCl_3$): δ 1.20 [$(CH_3)_2$-CH−, d, *J* 6.8 Hz], 1.30 [$(CH_3)_3C-$, s], 3.30 [$(CH_3)_2CH-$, sept, *J* 6.8 Hz], 6.13 (H′$_4$, d, *J* 3.5 Hz), 7.10 (H′$_5$, d, *J* 3.5 Hz). MS [IP 70 eV; *m/e* (% rel. int.)]: 194 (22, M), 179 (50, M−CH_3), 151 [100, M−$(CH_3)_2CH$], 137 [1, M−$(CH_3)_3C$], 123 [3, M−$(CH_3)_2CHCO$], 95 (10, Fur-CO), 79 (6), 77 (3), 71 [1, $(CH_3)_2CHCO$], 57 [2, $(CH_3)_3C$], 43 [11, $(CH_3)_2CH$], 39 (7).

1-(5-i-Propyl-2-furyl)-2,2-dimethylpropan-1-one (7 Cb). ^{1}H NMR (60 MHz, $CDCl_3$): δ 1.30 [$(CH_3)_2CH-$, d, *J* 6.8 Hz], 1.34 [$(CH_3)_3C-$, s], 2.91 [$(CH_3)_2CH-$, m], 6.11 (H′$_4$, dd, *J* 0.8 and 3.4 Hz), 7.13 (H′$_3$, dd, 0.2 and 3.4 Hz). MS [IP 70 eV; *m/e* (% rel. int.)]: 194 (10, M), 179 (1, M−CH_3), 151 [1, M−$(CH_3)_2CH$], 137 [100, M−$(CH_3)_3C$], 109 [6, M−$(CH_3)_3CCO$], 95 (2, Fur-CO), 79 (3), 77 (1), 57 [23, $(CH_3)_3C$], 43 [5, $(CH_3)_2CH$], 39 (9).

1-(5-t-Butyl-2-furyl)-2,2-dimethylpropan-1-one (7 Cc). ^{1}H NMR (60 MHz, $CDCl_3$): δ 1.42 and 1.43 [$(CH_3)_3C-$ and $(CH_3)_3CCO-$, ss], 6.18 (H′$_4$, d, *J* 3.5 Hz), 7.20 (H′$_3$, d, *J* 3.5 Hz). MS [IP 70 eV; *m/e* (% rel. int.)]: 208 (11, M), 193 (6, M−CH_3), 151 [100, M−$(CH_3)_3C$], 123 [2, M−$(CH_3)_3CCO$],

95 (7, Fur-CO), 85 [2, $(CH_3)_3CCO$], 79 (5), 77 (4), 57 [28, $(CH_3)_3C$], 39 (9).

The lactones *5c* and *8c* formed by oxidation of the primary 1,4- and 1,6-addition products respectively, were isolated and their ^1H NMR spectra found to be identical with those of compounds identified previously.[3] Attempts to isolate the i-propyl lactones *5b* and *8b* were, however, not successful and only the mass spectral data are presented below.

3-i-Propyl-2-(5H)-furanone (5b). MS [IP 70 eV; *m/e* (% rel. int.)]: 126(10, M), 111(3, $M-CH_3$), 84(100, $M-CH_3CH=CH_2$), 83[8, $M-(CH_3)_2CH$], 43[27, $(CH_3)_2CH$], 41(26).

5-i-Propyl-2-(5H)-furanone (8b). MS [IP 70 eV; *m/e* (% rel. int.)]: 126(2, M), 111(1, $M-CH_3$), 84(100, $M-CH_3CH=CH_2$), 83[4, $M-(CH_3)_2CH$], 43[23, $(CH_3)_2CH$], 41(20).

Acknowledgements. Financial support of this work by *Stiftelsens för Åbo Akademi Forskningsinstitut* and *Magnus Ehrnrooths stiftelse* is gratefully acknowledged.

REFERENCES

1. Results presented in part at *Ninth International Conference on Organometallic Chemistry*, Dijon, France 1979 and at *Third International Symposium of Furan Chemistry*, Smolenice, Czechoslovakia 1979.
2. Berreby, E., Morizur, J.-P. and Wiemann, J. *Bull. Soc. Chim. Fr.* (1967) 3529.
3. Sjöholm, R. *Acta Chem. Scand. B 31* (1977) 278.
4. Sjöholm, R. *Acta Chem. Scand. B 32* (1978) 105.
5. Sjöholm, R. and Aura, P.-E. *Acta Acad. Abo. Ser. B 38* (1978) No. 1.
6. Wright, G. F. In Newman, M. S., Ed., *Steric Effects in Organic Chemistry*, Wiley, New York 1956, pp. 394–424.
7. Fuson, R. C., Kaiser, E. W. and Speck, S. B. *J. Org. Chem. 6* (1941) 845.
8. Chadwick, D. J., Chambers, J., Meakins, G. D. and Snowden, R. L. *Chem. Commun.* (1971) 624.
9. Holm, T., Crossland, I. and Madsen, J. Ø. *Acta Chem. Scand. B 32* (1978) 754.
10. Holm, T. and Crossland, I. *Acta Chem. Scand. B 33* (1979) 421.
11. Ashby, E. C. and Wiesemann, T. L. *J. Am. Chem. Soc. 100* (1978) 3101.
12. Emling, B. L., Beatty, J. E. and Stevens, J. R. *J. Am. Chem. Soc. 71* (1949) 703.
13. Gruber, W. *Can. J. Chem. 31* (1953) 567.
14. Heyns, K., Stute, R. and Scharmann, H. *Tetrahedron 22* (1966) 2223.

Received February 13, 1980.