The Reaction of 2-Methylfuran with Methyl Acrylate. Unusual Formation of 1,1′-Bis(5-methyl-2-furyl)ethane and Methyl 3,3′-Bis(5-methyl-2-furyl)propionate

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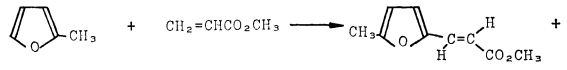
Synopsis. The reaction of 2-methylfuran with methyl acrylate in the presence of $Pd(OAc)_2$ gave unusual products such as 1,1′-bis(5-methyl-2-furyl)ethane (22%) and methyl 3,3′-bis(5-methyl-2-furyl)propionate (10%) along with the usual aromatic substitution product. This is a marked contrast to the reaction of furan with olefins.

In our previous paper we reported the palladium-assisted one-step alkenylation reactions of heterocycles.[1,2] These reactions afford both the 2-mono- and 2,5-dialkenylated products when the five-membered aromatic heterocycles such as furan, thiophene, or pyrrole are allowed to react with olefins. In subsequent related studies, we attempted 2-methylfuran to react with methyl acrylate, and obtained some unusual products such as 1,1′-bis(5-methyl-2-furyl)-ethane (**2**) and methyl 3,3′-bis(5-methyl-2-furyl)propionate (**3**).

The reaction of 2-methylfuran with methyl acrylate was carried out with stirring at 100 °C for 8 h. After the usual work-up, there were obtained 27%[3] of methyl 3-(5-methyl-2-furyl)acrylate (**1**), the usual aromatic substitution product, 22% of **2** of which identity was proved by comparison of NMR and IR spectra with those of an authentic sample prepared from 2-methylfuran and acetaldehyde,[4] 10% of **3**, and 5% of 5-methyl-2-furyl acetate (**4**). The formation of **2** and **3** in considerable amounts is of particular interest since no such products are obtained in the case of unsubstituted five-membered heterocycles.[1,2]



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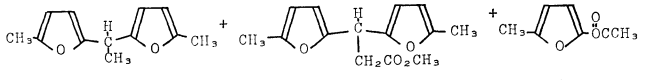
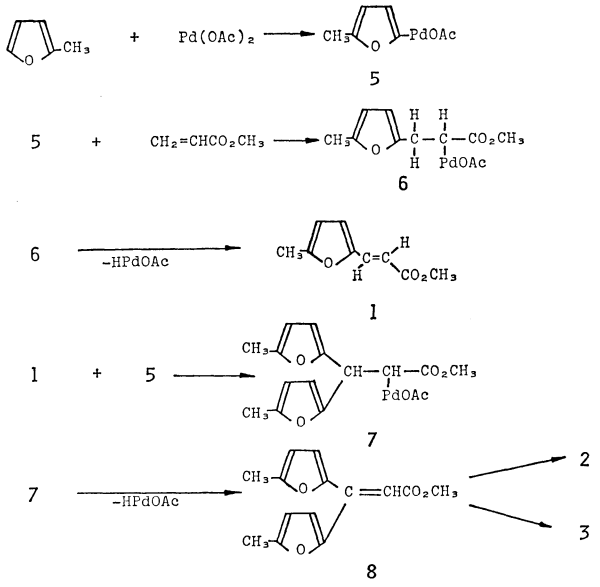
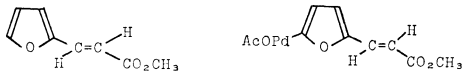


2 3 4

The formation of **2** and **3** may be explained in the following way (Scheme 1). First, palladium(II) attackes at the 5-position of 2-methylfuran electrophilically to give a furyl-Pd σ complex **5**. Then **5** adds to methyl acrylate affording a σ complex **6**. Elimination of a PdH species gives **1**. Then the furyl-Pd σ complex adds to **1** giving an intermediate complex **7**. Elimination of HPdOAc from **7** gives an olefin **8** which may be transformed into **2** and **3** by hydrogenation[5] and/or decarboxylation.[6] In the case of furan, Pd(II) can attack further at the 5-position of the furan ring of **9** to produce a furyl-Pd σ complex **10** which reacts with the olefin yielding the dialkenylated products.[1,2] However, in the present case, there is no reactive 5-position available since the 5-position is occupied with a methyl group.



Scheme 1.



9 10

Experimental

NMR spectra were obtained with a Hitachi R-24S spectrometer using Me_4Si as an internal standard. Materials used were prepared and purified as described already.[2]

Reaction of 2-Methylfuran with Methyl Acrylate. The reaction was performed with stirring at reflux for 8 h using 2-methylfuran (2 mmol), methyl acrylate (2 mmol), palladium(II) acetate (2 mmol), dioxane (20 ml), and acetic acid (5 ml). After work-up as described already,[2] the residue was chromatographed on a column of silica gel. Elution with hexane–ether (9:1) yielded **2** (22% yield) which was assigned by comparison of the IR and NMR spectra with those of an authentic sample prepared from 2-methylfuran and acetaldehyde.[4] **2**: bp 130 °C/15 mmHg†; IR (neat) 2960, 1562, 1015, and 790 cm^{-1}; NMR (CCl_4) δ 1.50 (d, 3H, J=7 Hz), 2.23 (s, 6H), 3.84 (q, 1H, J=7 Hz), and 5.69 (4H). Further elution gave a 1:5 mixture of **3** and **1**. The products were isolated by preparative glc (OV-17, 0.5 m, 118 °C). **1**: 27% yield; IR (Nujol) 1724 and 974 cm^{-1}; NMR ($CDCl_3$) δ 2.36 (s, 3H), 3.81 (s, 3H), 6.0—6.7 (3H), and 7.44 (d, 1H, J=17 Hz). **3**: 10% yield; IR (neat) 1725 cm^{-1}; NMR ($CDCl_3$) δ 2.22 (s, 6H), 2.91 (d, 2H, J=8 Hz), 3.60 (s, 3H), 4.48 (t, 1H, J=9 Hz), and 5.7—6.0 (m, 4H). Further elution with hexane–ether (3:2)

† 1 mmHg≈133.322 Pa

gave 5-methyl-2-furyl acetate (**4**). **4**: 5% yield; IR (neat) 1770 cm^{-1}; NMR ($CDCl_3$) δ 1.84 (s, 3H), 2.07 (s, 3H), 6.20 (d, 1H, J=6 Hz), and 7.17 (d, 1H, J=6 Hz).

References

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