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SHORT COMMUNICATIONS

Reaction of 1,2,3,4-Tetrachloro-5,5-dimethoxycyclopentadiene with Sodium 2-Furylmethoxide in Tetrahydrofuran*

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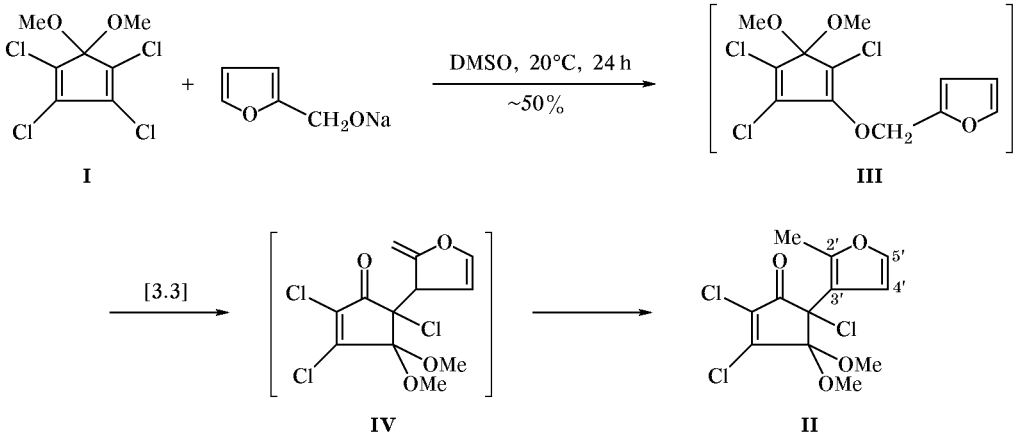
By reaction of sodium 2-furylmethoxide with 1,2,3,4-tetrachloro-5,5-dimethoxycyclopentadiene in DMSO we previously [1] obtained furyl-substituted cyclopentenone (**II**). The assumed reaction mechanism includes intermediate formation of furfuryl ether **III** (analogous ethers were isolated, e.g., in [2, 3]) and its subsequent Claisen [3.3]-rearrangement into *exo*-methylene derivative **IV** (Scheme 1). In the present work we made an attempt to isolate intermediate compound **IV**. We failed to achieve this goal under the conditions given in [1]. Therefore, in order to slow down the isomerization of methylenedihydrofuran **IV** into methylfuran **II** we carried out the reaction in THF at 20°C (24 h). After appropriate treatment of the reaction mixture and preliminary chromatographic separation of unchanged initial compounds and polymeric products, we isolated a viscous material which was subjected to column chromatography on silica gel. As a result, we isolated individual crystalline compound **V** and an oily substance which was sufficiently pure according to the TLC data. The spectral parameters of the latter product indicated that it was a mixture of several compounds. The oily residue was subjected to repeated chromatographic purification, and its ^{1}H NMR and ^{13}C NMR spectra were recorded. According to the spectral data, there were two compounds one of which was identical (according to the NMR and GLC data) to furylcyclopentenone **II** [1]. The other component was assigned the structure of 2,5-dichloro-3-(3-furylmethoxy)-5-(2-methyl-3-furyl)-4,4-dimethoxy-2-cyclopentenone (**VI**). The ratio of compounds **II** and **VI** was ~5:6 (according to the ^{1}H NMR data). Thus, unlike in DMSO, the reaction in THF is accompanied by further replacement of

Scheme 1.



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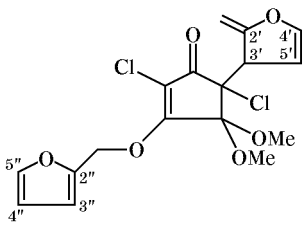
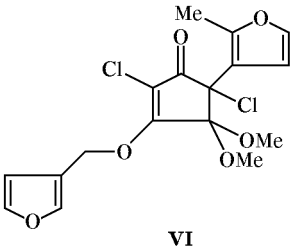
chlorine at C^3 in trichlorocyclopentenones **II** and **IV**, presumably due to higher nucleophilicity of the 2-furylmethoxide ion in THF than in DMSO where it is solvated more strongly. Nevertheless, the formation of compound **V** indirectly shows that methylfuran **II** is formed through intermediate *exo*-methylene derivative **IV**.



V



VI

Reaction of 1,2,3,4-tetrachloro-5,5-dimethoxycyclopentadiene (I) with sodium 2-furylmethoxide. A solution of 2.3 ml of furfuryl alcohol in 5 ml of THF was added dropwise with stirring to a mixture of 0.27 g of NaH and THF, cooled with an ice bath. The mixture was stirred for 30 min, a solution of 0.8 g (3.02 mmol) of compound **I** in 4 ml of THF was added dropwise at 0°C, and the mixture was stirred for 24 h at room temperature. It was then diluted with 10 ml of water and extracted with $CHCl_3$ (3×50 ml), the extract was dried over $MgSO_4$ and evaporated, and the residue was subjected to column chromatography on silica gel using ethyl acetate–petroleum ether (1 : 9) as eluent. An oily substance, 0.49 g, was thus isolated. It was treated with petroleum ether, and 0.1 g (~8.5%) of colorless crystalline product **V** precipitated. It was purified by recrystallization from ethyl acetate–petroleum ether. The residue was subjected to repeated chromatographic purification on silica gel to isolate 0.35 g (overall yield ~32%) of a mixture of compounds **II** and **VI** at a ratio of 5 : 6 (^{1}H NMR).

2,3,5-Trichloro-4,4-dimethoxy-5-(2-methyl-3-furyl)-2-cyclopentenone (II). mp 89–90°C. IR spectrum, ν, cm^{-1}: 1615 (C=C), 1755 (C=O). ^{1}H NMR spectrum, δ, ppm: 2.13 s (3H, CH_3), 3.30 s and 3.35 s (6H, OCH_3), 6.47 d (1H, 4′-H, J = 1.9 Hz), 7.21 d (1H, 5′-H, J = 1.91 Hz). ^{13}C NMR spectrum, δ_C, ppm: 13.95 (CH_3), 51.89 and 52.41 (OCH_3), 72.28 (C^5), 102.35 (C^4), 112.29 ($C^{4'}$), 112.84 ($C^{3'}$), 132.57 (C^2), 139.12 ($C^{5'}$), 151.54 ($C^{2'}$), 157.41 (C^3), 186.01 (C=O).

2,5-Dichloro-3-furfuryloxy-4,4-dimethoxy-5-(2-methylene-2,3-dihydro-3-furyl)-2-cyclopentenone (V). mp 97–99°C. IR spectrum, ν, cm^{-1}: 1610 (C=C), 1755 (C=O). ^{1}H NMR spectrum, δ, ppm: 3.36 s and 3.38 s (6H, OCH_3), 4.08 s (1H, 3′-H), 4.48 s (2H, $=CH_2$), 4.46 d (1H, J = 13.0 Hz), 4.55 d (1H, OCH_2, J = 13.0 Hz), 6.23 s (1H) and 6.34 s (2H, 4″-H, 4′-H), 7.37 s and 7.41 s (2H, 5′-H, 5″-H). ^{13}C NMR spectrum, δ_C, ppm: 51.44 (OCH_3, $C^{3'}$); 53.81 (OCH_3); 61.84 (OCH_2); 63.54 (C^5); 102.27 (C^4); 109.82, 110.25, 111.69 ($C^{4'}$, $C^{3''}$, $C^{4''}$); 115.9 ($=CH_2$), 134.58 (C^2); 142.05 and 142.91 ($C^{5'}$, $C^{5''}$); 149.73 ($C^{2'}$); 150.97 ($C^{2''}$); 158.75 (C^3), 191.78 (C=O). Found, %: C 53.17; H 4.07; Cl 18.86. $C_{17}H_{16}Cl_2O_6$. Calculated, %: C 52.71; H 4.13; Cl 18.35.

2,5-Dichloro-3-(3-furylmethoxy)-4,4-dimethoxy-5-(2-methyl-3-furyl)-2-cyclopentenone (VI). ^{1}H NMR spectrum, δ, ppm: 2.08 s (3H, CH_3), 3.39 s and 3.42 s (6H, OCH_3), 5.33 d (1H, J = 13.0 Hz), 5.41 d (1H, OCH_2, J = 13.0 Hz), 6.23 m and 6.30 m (2H, 3″-H, 4″-H), 6.44 d (1H, 4′-H, J = 1.90 Hz), 7.17 d (1H, 5′-H, J = 1.90 Hz), 7.37 d (1H, 5″-H, J = 1.0 Hz). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 14.16 (CH_3); 50.90 and 51.14 (OCH_3); 63.65 (OCH_2); 72.67 (C^5); 100.62 (C^4); 111.25 ($C^{4''}$); 111.56 ($C^{3''}$); 112.38 ($C^{4'}$); 113.54 ($C^{3'}$); 139.35 ($C^{5'}$); 139.68 (C^2); 143.57 ($C^{5''}$); 148.95 ($C^{2''}$); 150.29 (C^3); 151.64 ($C^{2'}$); 187.80 (C=O).

The IR spectra were recorded on Specord M-80 and UR-20 spectrometers from samples prepared as thin films or Nujol mulls. The NMR spectra were obtained on a Bruker AM-300 instrument at 300 MHz for ^{1}H and 75.47 MHz for ^{13}C; $CDCl_3$ was used as solvent, and TMS, as internal reference.

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