The synthesis of new dienes of the ferrocene series

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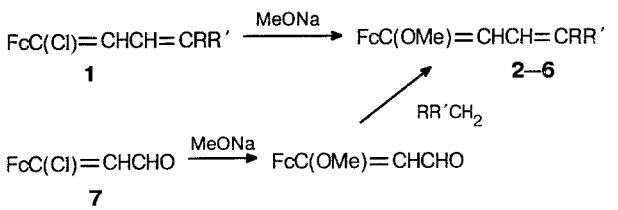
The dienes FcC(OMe)=CHCH=CRR' have been synthesized by the reaction of dienes FcC(Cl)=CHCH=CRR' with sodium methoxide or by the interaction of aldehyde FcC(OMe)=CHCHO with compounds CH_2RR' having mobile hydrogen atoms.

Key words: 4-mono- and 4,4-disubstituted 1-ferrocenyl-1-methoxy-1,3-butadienes, synthesis.

Previously[1] we obtained ferrocenyl-containing nitrodienes FcC(Cl)=CHCH=CRR' (**1**) with R, R' = H, NO_2; Me, NO_2; Et, NO_2. It was found that these compounds, as well as the previously described[2] dienes **1** with R, R' = CN, COOEt or R = R' = CN, interact with sodium methoxide to form the corresponding dienes FcC(OMe)=CHCH=CRR' (**2—6**).

These compounds are obtained as the result of the condensation of 3-methoxy-3-ferrocenylpropenal (**7**) (we were the first to synthesize **7** by the reaction of 3-chloro-3-ferrocenylpropenal with sodium methoxide) with nitroalkanes RCH_2NO_2 (R = H, Me, Et) as well as with cyanoacetic ester or malonodinitrile.



R,R' = H, NO_2 (**2**); Me, NO_2 (**3**); Et, NO_2 (**4**); COOEt, CN (**5**); CN, CN (**6**)

Experimental

The spectra of all of the compounds synthesized for the first time were recorded on a Varian device (60 MHz) in acetone-d_6, TMS served as the internal standard.

3-Ferrocenyl-3-methoxypropenal (7). A solution of 1 mmol of 3-chloro-3-ferrocenylpropenal in 15 mL of dry MeOH was added at 30—40 °C to a solution of 30 mmol of Na in 15 mL of dry methanol and stirred for 10 min; then the solution was stirred for 20 min more, poured into 100 mL of water, and extracted with ether. The ether extracts were washed with water and dried with $MgSO_4$, and the solvent was removed. Obtained 0.245 g (90 %) of aldehyde **7**, m.p. 74—76 °C (from petroleum ether). Found (%): C, 62.0; H, 5.3. $C_{14}H_{14}FeO_2$. Calculated (%): C, 62.2; H, 5.12. ^{1}H NMR, δ: 4.70 (m, 2 H, C_6H_4); 4.48 (m, 2 H, C_5H_4); 4.23 (s, 5 H, C_5H_5); 3.90 (s, 3 H, OCH_3); 5.56 (d, 1 H, =CH); 9.66 (d, 1 H, CHO).

1-Ferrocenyl-1-methoxy-4-nitrobuta-1,3-diene (2).

A. A solution of 0.5 mmol of diene **1** (R = H, R' = NO_2) in 20 mL of dry MeOH was added dropwise to a solution of 15 mmol of sodium in 7.5 mL of dry MeOH. The mixture was held for 12 h at ~20 °C, poured into 30 mL of 10% HCl, and extracted with ether. After drying with $MgSO_4$ the ether extracts were evaporated in the vacuum of a water-jet pump. The residue was chromatographed on a column with silica gel, benzene was used as the eluent. Obtained: 0.051 g (33 %) of the compound **2**, m.p. 124—126 °C (from alcohol). Found (%): C, 57.8; H, 4.9; N, 4.6. $C_{15}H_{15}FeNO_3$. Calculated (%): C, 57.5; H, 4.8; N, 4.5. ^{1}H NMR, δ: 4.66 and 4.48 (both m, 2 H, C_5H_4); 4.26 (s, 5 H, C_5H_5); 3.90 (s, 3 H, OCH_3); 5.87 and 7.30 (both d, 1 H, =CH); 8.53 (q, 1 H, =CH).

B. A solution of 1 mmol of aldehyde **7**, 2 mmol of nitromethane, and 0.1 g of ammonium acetate in 20 mL of EtOH was stirred for 5 min and held for 11 days at ~20 °C. The mixture was poured into water, extracted with ether, and the ether extracts were dried with $MgSO_4$ and evaporated in a vacuum. The residue was chromatographed on a column with silica gel, benzene served as the eluent. Obtained 0.038 g (11 %) of the compound **2**, m.p. 124—126 °C.

The following compounds were synthesized similarly:

1-Ferrocenyl-1-methoxy-4-nitropenta-1,3-diene (3). M.p. 125—126 °C (from alcohol). Found (%): C, 58.5; H, 5.2; N, 4.4. $C_{16}H_{17}FeNO_3$. Calculated (%): C, 58.7; H, 5.2; N, 4.3. ^{1}H NMR, δ: 4.52 and 4.40 (both m, 2 H, C_5H_4); 4.16 (s, 5 H, C_5H_5); 3.84 (s, 3 H, OCH_3); 5.63 and 8.43 (both d, 1 H, =CH). Yields: 46 % by method ***A***, 14 % by method ***B***.

1-Ferrocenyl-1-methoxy-4-nitrohexa-1,3-diene (4). M.p. 101—102 °C (from alcohol). Found (%): C, 59.9; H, 5.5; N, 3.9. $C_{17}H_{19}FeNO_3$. Calculated (%): C, 60.0; H, 5.6; N, 4.1. ^{1}H NMR, δ: 4.79 and 4.59 (both m, 2 H, C_5H_4); 4.33 (s, 5 H, C_5H_5); 4.06 (s, 3 H, OCH_3); 2.94 (q, 2 H, CH_2); 1.23 (t, 3 H, CH_3); 5.90 and 8.70 (both d, 1 H, =CH). Yields: 47 % by method ***A***, 16 % by method ***B***.

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4-Ethoxycarbonyl-1-ferrocenyl-1-methoxy-4-nitrobuta-1,3-diene (5). M.p. 113—115 °C (from alcohol). Found (%): C, 62.2; H, 5.2; N, 3.7. $C_{19}H_{19}FeNO_3$. Calculated (%): C, 62.5; H, 5.2; N, 3.8. ^{1}H NMR, δ: 4.66 and 4.50 (both m, 2 H, C_5H_4); 4.23 (s, 5 H, C_5H_5); 3.95 (s, 3 H, OCH_3); 4.25 (q, 2 H, CH_2); 1.30 (t, 3 H, CH_3); 5.94 and 8.74 (both d, 1 H, =CH). Yields: 38 % by method *A*, 55 % by method *B*.

4,4-Dicyano-1-ferrocenyl-1-methoxybuta-1,3-diene (6). M.p. 146—148 °C (from alcohol). Found (%): C, 64.5; H, 4.5; N, 8.6. $C_{17}H_{14}FeN_2O$. Calculated (%): C, 64.2; H, 4.4; N, 8.8. ^{1}H NMR, δ: 5.17 and 4.63 (both m, 2 H, C_5H_4); 4.20 (s, 5 H, C_5H_5); 4.17 (s, 3 H, OCH_3); 7.33 and 8.67 (both d, 1 H, =CH). Yield 47 % (by method *A*).

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