

FORMATION OF ETHYNYL METALLOCENYL KETONE FROM
1,1,1-TRICHLORO-3-ALKOXY-3-METALLOCENYLPROPANE

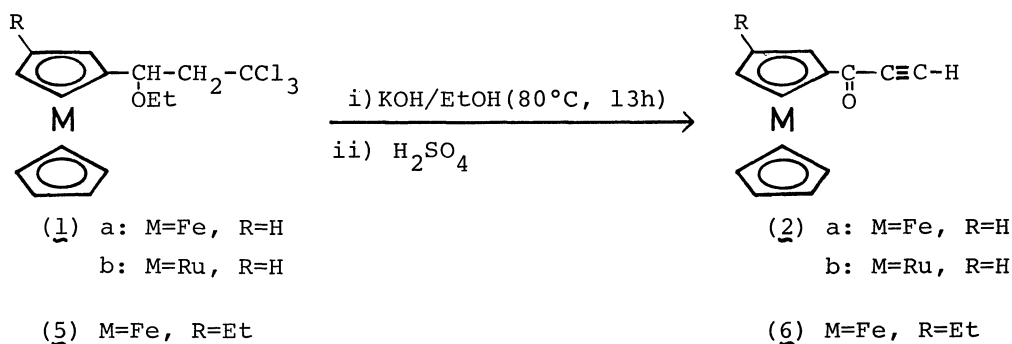
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1,1,1-Trichloro-3-ethoxy-3-ferrocenylpropane(1a) gives ethynyl ferrocenyl ketone(2a) via an unusual elimination of hydrogen chloride, when 1a is treated with alkali and then acid. The ruthenium analog(1b) also affords ethynyl ruthenocenyl ketone(2b). No migration of the side chain is involved in this process.

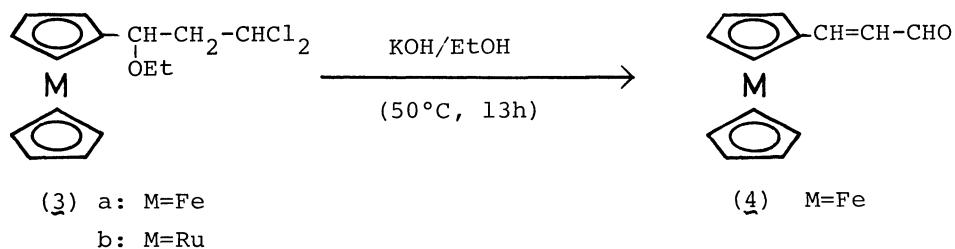
It has been well known that ferrocene shows some interesting reactivities owing to the participation of iron.¹⁾ The rearrangements characteristic of ferrocene have also been reported.²⁾

We wish to report here an unusual elimination of hydrogen chloride of 1,1,1-trichloro-3-ethoxy-3-ferrocenyl- and ruthenocenylpropane(1a),³⁾ (1b)⁴⁾ which were prepared in the photoreaction of vinylferrocene and of vinylruthenocene in carbon tetrachloride-ethanol solutions, respectively. Compound 1a was treated with ethanolic potassium hydroxide at 80°C for 13h. Then the solution was acidified with sulfuric acid, and the products were isolated with TLC. Ethynyl ferrocenyl ketone(2a)⁵⁾ was obtained as a red crystalline solid in a 78% yield. The ruthenium analog 1b also provided ethynyl ruthenocenyl ketone(2b)⁶⁾ in a 64% yield under the same reaction conditions as above.



The benzene analog, 1,1,1-trichloro-3-bromo-3-phenylpropane, gave the normal hydrolysis product, cinnamic acid.⁷⁾

In contrast with 1a, 1,1-dichloro-3-ethoxy-3-ferrocenylpropane(3a)⁸⁾ which was prepared in the photoreaction of vinylferrocene in a chloroform-ethanol solution, gave 3-ferrocenyl-2-propenal(4)⁹⁾ in a 39% yield after alkali treatment of 3a as described above. In the case of ruthenocene analog(3b),¹⁰⁾ however, the alkali treatment of 3b did not provide the corresponding α,β -unsaturated aldehyde.



A mechanism in which the side chain migrates to the other cyclopentadienyl ring may be conceivable. However, the ethyl substituted derivative of 1a, namely 1,1,1-trichloro-3-ethoxy-3-(3-ethylferrocenyl)propane(5),¹¹⁾ gave only 3-ethylferrocenyl ethynyl ketone(6).¹²⁾

This result indicates that the reaction does not involve the side chain migration process neither to the substituted cyclopentadienyl ring nor to the unsubstituted ring of the metallocene.¹⁴⁾

The detailed reaction mechanism of the formation of 2a, 2b from 1a, 1b is now under investigation.

References and Notes

- 1) a) M.Rosenblum, "Chemistry of the Iron Group Metallocenes", Part I, Interscience Publishers, New York, N.Y., (1965), p. 129. b) R.Hermann and I.Ugi, *Angew. Chem.*, **90**, 734 (1978). c) D.Kaufman, R.Kupper, and T.Neal, *J. Org. Chem.*, **44**, 3076 (1979). d) T.S.Abram and W.E.Watts, *J. Chem. Soc., Perkin Trans. 1*, **1975**, 113.
- 2) a) M.Hisatome and K.Yamakawa, *J. Organomet. Chem.*, **133**, C9 (1977). b) A.Eisenstadt and M.Cais, *J. Chem. Soc., Chem. Commun.*, **1972**, 216. c) W.M.Horspool, R.G.Sutherland, and B.J.Thomson, *J. Chem. Soc., (C)*, **1971**, 1558. d) T.D.Turbitt and W.E.Watts, *J. Chem. Soc., Perkin Trans. 2*, **1974**, 177, 189. e) T.S.Abram and W.E.Watts, *ibid.*, *Perkin Trans. 1*, **1977**, 1522, 1527, 1532.
- 3) NMR(CCl₄) δ = 4.02(9H,s, C₅H₅ + C₅H₄-), 4.37(1H,q, a proton at 3-position of propane), 3.30(2H,m, protons at 2-position of propane), 3.30(2H,m, -CH₂- of -OEt), 1.09(3H,t, -CH₃ of -OEt). Methoxy derivative could also be obtained when methanol was used instead of ethanol.
- 4) NMR(CDCl₃) δ = 4.55(9H,s, C₅H₅ + C₅H₄-), 4.35(1H,q, a proton at 3-position of propane), 3.54(2H,q, -CH₂- of -OEt), 3.25(1H,d) and 3.23(1H,d) (protons at 2-position of propane), 1.15(3H,t, -CH₃ of -OEt).
- 5) mp 75-77°C (lit.¹³) 77-80°C; NMR(CCl₄) δ = 4.24(5H,s, C₅H₅), 4.89(2H,t, ring α -protons), 4.53(2H,t, ring β -protons), 3.13(1H,s, -C \equiv C-H); IR(KBr) 3230(ν_{C-H} of -C \equiv C-H), 2075($\nu_{C\equiv C}$), 1615($\nu_{C=O}$), 3100, 1100, and 1000 cm⁻¹ (mono substituted ferrocene); MS(70eV), M⁺(m/e) 238.
- 6) mp 96-100°C. NMR(CDCl₃) δ = 5.22(2H,t, ring β -protons), 4.86(2H,t, ring α -protons), 4.64(5H,s, C₅H₅), 3.25(1H,s, -C \equiv C-H); IR(KBr) 3240(ν_{C-H} of -C \equiv C-H), 2075($\nu_{C\equiv C}$), 1620($\nu_{C=O}$), 3100, 1100, and 1000 cm⁻¹ (mono substituted ruthenocene).
- 7) M.S.Kharasch, O.Reinmuth, and W.H.Urry, *J. Amer. Chem. Soc.*, **69**, 1105 (1947).
- 8) NMR(CCl₄) δ = 4.08(9H,s, C₅H₅ + C₅H₄-), 4.21(1H,m, a proton at 3-position of propane), 2.65(2H,m, protons at 2-position of propane), 5.88(1H,m, -CHCl₂), 3.32(2H,q, -CH₂- of -OEt), 1.09(3H,t, -CH₃ of -OEt).
- 9) mp 90-95°C (lit.¹³) 90-95°C; NMR(CCl₄) δ = 9.42(1H,d, -CHO), 7.22(1H,d) and 6.20(2H,q) (trans olefinic protons, J=16 Hz), 4.42(4H,m, C₅H₄-), 4.10(5H,s, C₅H₅); IR(KBr) 2800, 2730(ν_{C-H} of -CHO), 1660($\nu_{C=O}$), 1610($\nu_{C=C}$), 3090, 1100, and 1000 cm⁻¹ (mono substituted ferrocene); MS(70eV), M⁺(m/e) 240.
- 10) NMR(CDCl₃) δ = 5.91(1H,m, -CHCl₂), 4.57(9H,s, C₅H₅ + C₅H₄-), 4.11(1H,t, proton

at 3-position of propane), 3.75-3.22(2H,m, $-\text{CH}_2-$ of $-\text{OEt}$), 2.60(2H,m, protons at 2-position of propane), 1.13(3H,t, $-\text{CH}_3$ of $-\text{OEt}$).

The alkali treatment of **3b** gave an unidentified compound as a main product and no **3b** was recovered. The IR and NMR spectra of this compound indicate that this compound is a mono substituted ruthenocene with C=C double bond and ketonic C=O. No aldehyde proton could be observed in the NMR spectra.

- 11) The compound (**5**) was obtained in the photoreaction of 3-ethyl vinylferrocene in CCl_4 -EtOH(1:1,v/v) solution. NMR(CCl_4) δ = 4.17(8H,s, $\text{C}_5\text{H}_5 + \text{C}_5\text{H}_3^-$), 4.52(1H,q, a proton at 3-position of propane), 3.40(2H,m, protons at 2-position of propane), 3.40(2H,q, $-\text{CH}_2-$ of $-\text{OEt}$), 2.34(2H,q, $-\text{CH}_2-$ of $-\text{Et}$), 1.17(6H,t, two sets of $-\text{CH}_3$); Found: C, 50.6, H, 5.4%. Calcd for $\text{C}_{17}\text{H}_{21}\text{Cl}_3\text{OFe}$: C, 50.6, H, 5.2%. MS(70eV), M^+ (m/e) 404, 406.
- 12) The compound (**6**) was obtained in a 49% yield. mp 73-77°C. NMR(CDCl_3) δ = 4.23(5H,s, C_5H_5), 4.87(2H,t, ring α -protons), 4.58(1H,t, ring β -proton), 3.22(1H,s, $-\text{C}\equiv\text{C}-\text{H}$), 2.42(2H,q, $-\text{CH}_2-$ of $-\text{Et}$), 1.25(3H,t, $-\text{CH}_3$ of $-\text{Et}$); IR(KBr) 3250($\nu_{\text{C}-\text{H}}$ of $-\text{C}\equiv\text{C}-\text{H}$), 2080($\nu_{\text{C}\equiv\text{C}}$), 1610($\nu_{\text{C}=\text{O}}$), 2960, and 2920 cm^{-1} ($\nu_{\text{C}-\text{H}}$ of $-\text{Et}$). Found: C, 67.2, H, 5.7%. Calcd for $\text{C}_{15}\text{H}_{14}\text{OFe}$: C, 67.7, H, 5.3%. MS(70eV), M^+ (m/e) 266.
- 13) K.Schlögl and A.Mohar, Monatsh. Chem., 93, 861 (1962).
- 14) No other ethylferrocene derivative with ethynyl ketone group was obtained from the fractions separated with TLC.

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