BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 46, 3315—3316 (1973)

Synthesis of Bridged Bicycloferrocene: Participation of Anhydrous Aluminum Chloride in the Condensation Reaction

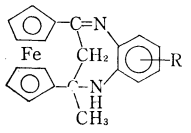
Yoshimori OMOTE, Ryuichiro KOBAYASHI, Yoshio NAKADA, and Noboru SUGIYAMA

Department of Chemistry, Faculty of Science, Tokyo Kyoiku University, Otsuka, Tokyo 112

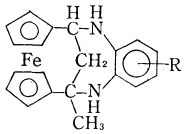
(Received July 3, 1973)

Only a few papers[1] are known on the synthesis of bridged bicycloferrocenes. We now wish to report a new method for one-step synthesis of bridged bicycloferrocenes from 1,1′-diacetylferrocene-aluminum chloride complex (I).[2] Anhydrous aluminum chloride is known to catalyze the condensation reaction of *o*-benzoylbenzophenone with *o*-phenylenediamine.[3] Two acetyl groups of the complex (I) are expected to be accessible to two amino groups in the reaction of (I) with aromatic diamines such as *o*-phenylenediamine, because of their orientation in the same direction by aluminum chloride participation.

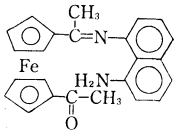
A mixture of (I) and *o*-phenylenediamine was heated in a molten state to give (IIa), whose structure was determined on the basis of the following evidences. The elemental analysis was in accord with (IIa). The mass spectrum of (IIa) indicated a peak at *m/e* 342 (M^+). The infrared spectrum showed a N–H absorption at 3340 cm^{-1} and a C=N absorption at 1610 cm^{-1}. The NMR spectrum is also consistent with (IIa), especially showing AB quartets at τ 6.96 (d, 1H, J= 11.4 Hz) and 7.51 (d, 1H, J=11.4 Hz) (methylene protons). In order to confirm the structure of (IIa), it was reduced with sodium borohydride in methanol to give (IIIa). In a similar manner, reaction of (I) with 4-methyl-1,2-diaminobenzene gave a product (IIb), which on reduction with sodium borohydride gave (IIIb). A nonbridged compound was obtained in the reaction of (I) and 1,8-diaminonaphthalene, which was determined to have structure (IV). The reason why no bridged ferrocene could be obtained in the reaction of (I) and 1,8-diaminonaphthalene can be considered to be that the distance between two amino groups of this diamine is too short to form a bridge with the complex (I). The formation of (II) can be explained by the condensation of carbonyl groups and aromatic amino groups, followed by intramolecular aldol type condensation.



(IIa): R=H
(IIb): R=CH_3



(IIIa): R=H
(IIIb): R=CH_3



(IV)

Experimental

Bridged Bicycloferrocene (IIa). 1,1′-Diacetylferrocene-aluminum chloride complex (I) was prepared according to the literature.[2] The complex (1.44 g) was mixed with *o*-phenylenediamine (1.94 g) in a stoppered flask and the mixture was heated in a molten state at 90—100 °C in an oil bath for 5 min. The reaction mixture was extracted three times with 10 ml of benzene each. The extract was evaporated *in vacuo* and chromatographed on a silica gel column in benzene–ethyl acetate (10: 1) to give the product (6%), which was recrystallized from benzene–*n*-hexane as orange needles, mp 274—280 °C (dec.).

1) R. L. Schaaf, P. T. Kan, and C. T. Lenk, *J. Org. Chem.*, **26**, 1790 (1961); T. H. Barr and W. E. Watts, *Tetrahedron*, **25**, 3219 (1968); R. A. Schnetter, J. T. Suh, and C. I. Judd, U.S. 3417118 (1968).

2) I. Pavlik and K. Handlir, *Collect. Czech. Chem. Commun.*, **31**, 1958 (1966).

3) H. D. Perlmutter, *Chem. Commun.*, **1968**, 1202.

Found: C, 70.44; H, 5.32; N, 7.98%. Calcd for $C_{20}H_{18}FeN_2$: C, 70.19; H, 5.30; N, 8.18%. IR (KBr) cm^{-1}: 3340, 1610. UV: λ_{max}^{EtOH} nm (ε) 237 (26000), 296 (4170), 344 (5040), 443 (658). NMR ($CDCl_3$): τ 2.66—3.16 (m, 4H), 5.21 (m, 4H), 5.57 (m, 3H), 5.90 (m, 2H), 6.96 (d, 1H, J=11.4 Hz), 7.52 (d, 1H, J=11.4 Hz), 8.50 (s, 3H). Mass *m/e* 342.

Bridged Bicycloferrocene (IIb). The complex (1.44 g) was mixed with 4-methyl-1,2-diaminobenzene (2.18 g) and the mixture was heated in a molten state at 100 °C for 3 min. The reaction mixture was worked up as described above to give the product (11%), which was recrystallized from benzene–*n*-hexane as yellowish organge needles, mp 280.5—282.0 °C.

Found: C, 70.86; H, 5.70; N, 8.03%. Calcd for $C_{21}H_{20}FeN_2$: C, 70.60; H, 5.64; N, 7.86%. IR (KBr) cm^{-1}: 3345, 1615. UV: λ_{max}^{EtOH} nm (ε) 237 (26000), 266 (8700), 306 (4100), 346 (4870), 438 (673). NMR ($CDCl_3$): τ 2.78—3.41 (m, 3H), 5.21 (m, 4H), 5.57 (m, 3H), 5.91 (m, 2H), 6.97 (d, 1H, J=11.4 Hz), 7.52 (d, 1H, J=11.4 Hz), 7.68 (s, 3H), 8.50 (s, 3H).

Reduction of Bridged Bicycloferrocene (IIa). Sodium borohydride (100 mg) was added to bridged bicycloferrocene (IIa) (60 mg) in 50 ml of methanol in portions and the mixture was stirred for 30 min at room temperature. After addition of 10 ml of water, the reaction mixture was extracted with 100 ml of ethyl ether and the organic layer was washed with water, dried over anhydrous sodium sulfate, evaporated *in vacuo*, and recrystallized from benzene–*n*-hexane as yellow rods (IIIa) (78%), mp 225—227.5 °C.

Found: C, 69.71; H, 5.88; N, 7.91%. Calcd. for $C_{20}H_{20}FeN_2$: C, 69.80; H, 5.85; N, 8.15%. IR (KBr) cm^{-1}: 3360. UV λ_{max}^{EtOH} nm (ε) 222 (28400), 308 (2880), 441 (180). NMR ($CDCl_3$): τ 3.22 (s, 4H), 5.67 (m, 2H), 5.77—6.18 (m, 7H), 6.72 (bs, 2H), 7.46—8.10 (m, 2H), 8.46 (s, 3H).

Reduction of Bridged Bicycloferrocene (IIb). Sodium borohydride (140 mg) was added to bridged bicycloferrocene (IIb) (40 mg) in 60 ml of methanol in portions and the mixture was stirred for 30 min at room temperature. The reaction mixture was worked up as described above to give the product (85%), which was recrystallized from benzene–*n*-hexane as yellow prisms (IIIb), mp 195—197 °C.

Found: C, 70.38; H, 6.32; N, 7.88%. Calcd. for $C_{21}H_{22}FeN_2$: C, 70.40; H, 6.18; N, 7.81%. IR (KBr) cm^{-1}: 3365. UV: λ_{max}^{EtOH} nm (ε) 222 (30600), 312 (2960), 444 (193). NMR ($CDCl_3$): τ 3.35 (s, 3H), 5.62 (m, 2H), 5.77—6.16 (m, 7H), 6.98 (bs, 2H), 7.45—7.75 (b, 2H), 7.75 (s, 3H), 8.47 (s, 3H).

The Compound (IV). The complex (2.09 g) was mixed with 1,8-diaminonaphthalene (4.10 g) and the mixture was heated in a molten state at 90—95 °C for 1.5 hr. The reaction mixture was worked up as described above to give the product (12%), which was recrystallized from benzene–*n*-hexane as orange plates, mp 218.5—220.5 °C.

Found: C, 70.26; H, 5.38; N, 6.99%. Calcd. for $C_{24}H_{22}FeN_2O$: C, 70.26; H, 5.40; N, 6.83%. IR (KBr) cm^{-1}: 3380, 3350, 1642, 1601. UV: λ_{max}^{EtOH} nm (ε) 235 (48600), 269 (7000), 350 (13000), 463 (475). NMR ($CDCl_3$): τ 2.53—2.90 (m, 5H), 3.37—3.53 (m, 1H), 5.24 (t, 2H), 5.48 (t, 2H), 5.80 (m, 4H), 5.95 (m, 2H), 7.62 (s, 3H), 8.17 (s, 3H).