


# Ferrocenes. V. Difunctional Ferrocenes from 1,1'-Ferrocenedicarboxylic Acid

ROBERT L. SCHAAF and CARL T. LENK  
Wyandotte Chemicals Corp., Wyandotte, Mich.

CERTAIN DIFUNCTIONAL ferrocenes were prepared for eventual incorporation into polymers from 1,1'-ferrocenedicarboxylic acid. For preparation of the diacid, lithiation of ferrocene in tetrahydrofuran (4) was employed with butyllithium in hexane as the lithiating agent at a mole ratio of 1 to 4.2. After carbonation, addition of water, and acidification, the monoacid was removed from the diacid by extraction with boiling toluene. By this method, the diacid, m.p. 250–260° (dec.), was obtained in 28 to 30% yields, and ferrocenoic acid, m.p. 215–220° (slow dec.), in 39 to 40%

*N*-methyl-*p*-nitroaniline (mole ratio 1 to 4) and refluxed in tetrahydrofuran for 40 hours to give a dinitro compound. It was isolated by cooling the reaction mixture to –70°, filtering, and washing the solid successively with ethyl acetate, water, methanol, and again ethyl acetate. Hydrogenation of the dinitro compound (7 grams) in warm ethanol (150 ml.) with platinum oxide as catalyst at 50 p.s.i. yielded the desired 1,1'-bis[*N*-methyl-*N*-(*p*-aminophenyl)-carboxamide]ferrocene. This diamine was insoluble in ethanol and benzene.

Table I. Disubstituted Ferrocenes, Fe(C<sub>5</sub>H<sub>4</sub>-R)<sub>2</sub>

R	Molecular Formula	Yield, %	M.P., °C. <sup>a</sup>	Crystn. Solvent	Carbon, %		Hydrogen, %		Nitrogen, %	
					Calcd.	Found	Calcd.	Found	Calcd.	Found
CON <sub>2</sub>	C <sub>12</sub> H <sub>8</sub> FeN <sub>6</sub> O <sub>2</sub>	100	115 <sup>b</sup>	Methanol	44.47	44.22	2.49	2.66	25.94	25.79
NCO	C <sub>12</sub> H <sub>8</sub> FeN <sub>2</sub> O <sub>2</sub>	77	81–82.5	Hexane	53.77	54.11	3.01	3.12	10.45	10.48
NHCOOCH <sub>3</sub>	C <sub>14</sub> H <sub>16</sub> FeN <sub>2</sub> O <sub>4</sub>	77	86.5–87.5 <sup>c,d</sup> 177–177.5		50.62	50.75	4.86	4.70	8.44	8.48
NHCOOCH <sub>2</sub> CH <sub>3</sub>	C <sub>16</sub> H <sub>20</sub> FeN <sub>2</sub> O <sub>4</sub>	72	119.5–120	1:1 Hexane-toluene	53.35	53.49	5.60	5.77	16.81 <sup>e</sup>	17.00 <sup>e</sup>
	C <sub>18</sub> H <sub>18</sub> FeO <sub>6</sub>	57	52–53 <sup>f</sup>		55.98	55.87	4.70	4.70	14.46 <sup>e</sup>	14.31 <sup>e</sup>
CON(CH <sub>3</sub> )C <sub>6</sub> H <sub>4</sub> NO <sub>2</sub> - <i>p</i>	C <sub>26</sub> H <sub>22</sub> FeN <sub>4</sub> O <sub>6</sub>	80	230–232 <sup>b</sup>	Toluene	57.58	57.50	4.09	4.27	10.33	10.11
CON(CH <sub>3</sub> )C <sub>6</sub> H <sub>4</sub> NH <sub>2</sub> - <i>p</i>	C <sub>26</sub> H <sub>26</sub> FeN <sub>2</sub> O <sub>2</sub>	85	228–230 <sup>b,g</sup>	Ethanol	64.74	64.47	5.43	5.35	11.62	11.45

<sup>a</sup> Under nitrogen. <sup>b</sup> Dec. <sup>c</sup> Two modifications. <sup>d</sup> λ<sub>max</sub>(log ε) 440 (2.25) and 213 mμ (4.54) in cyclohexane. <sup>e</sup> Iron, %. <sup>f</sup> λ<sub>max</sub>(log ε) 450

(2.41, 255 (3.95), and 219 mμ (4.52) in cyclohexane. <sup>g</sup> λ<sub>max</sub>(log ε) 450 (2.49) and 250 mμ (4.54) in ethanol.

yields. From a number of melting point determinations on the pure diacid, very close observation suggested that decomposition occurred at 250–260°, although there was no obvious melting or decomposition up to 350° under nitrogen. Treatment of the diacid with oxalyl chloride (6, 2) gave 1,1'-bis(chlorocarbonyl)ferrocene in 60 to 70% yields, m.p. 93–95°; reported m.p. 98–100° (2).

Addition of the diacid chloride in dioxane to sodium azide in 80% ethanol or methanol at 8–10° furnished quantitatively 1,1'-dicarbazidoferrrocene, which was previously described as prepared from 1,1'-dicarbydrazinoferrocene in undisclosed yield (5). Careful refluxing of the diazide (70 grams) in dry toluene (500 ml.) for 40 minutes gave 1,1'-ferrocene diisocyanate without difficulty. Diurethanes prepared by dissolving the diisocyanate in methanol and in ethanol were not unusually stable but decomposed near 250°.

A ferrocene-containing diepoxide was prepared from the diacid chloride and glycidol by a procedure patterned after that for diglycidyl terephthalate (1). The product was satisfactorily purified by chromatography on Florisil, which has been reported to be useful for partial purification of certain other diepoxides (3). Although diglycidyl 1,1'-ferrocenedicarboxylate contains two asymmetric centers, the product melted sharply (see Table I).

The diacid chloride was also treated with excess

## ACKNOWLEDGMENT

We are grateful to A.J. Sicree and H. Rosenberg of Aeronautical Systems Division for a procedure for the preparation of 1,1'-bis(chlorocarbonyl)ferrocene and to Calvin Kobayashi for a suggestion concerning the preparation of 1,1'-ferrocene diisocyanate. Ultraviolet absorption maxima were provided by J.M. Vandenbelt of Parke Davis and Co.

## LITERATURE CITED

- (1) Henkel & Cie. G. m.b.H., Brit. Patent 735,001 (August 10, 1953).
- (2) Knobloch, F.W., Rauscher, W.H., *J. Polymer Sci.* **54**, 651 (1961).
- (3) Maerker, G., Carmichael, J.F., Port, W.S., *J. Org. Chem.* **26**, 2681.
- (4) Mayo, D.W., Shaw, P.D., Rausch, M., *Chem. and Ind. (London)* 1957, p. 1388.
- (5) Rosenblum, M., Ph. D. thesis, Harvard University, 1953.
- (6) Sicree, A.J., Rosenberg, H., Wright Peterson Air Force Base, Ohio, unpublished work.

RECEIVED for review May, 8, 1963. Accepted August 8, 1963. Conducted under Air Force Contract AF 33(616)-7214, monitored by the Aeronautical Systems Division, Wright-Patterson Air Force Base, Ohio.