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Synthesis of Organometallic Complexes. I. Synthesis of Ferrocenylpyrazolone Derivatives

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The reactivity of 3-ferrocenyl-pyrazolones was studied. Alkylation of 3-ferrocenyl-2-pyrazolin-5-one (**2b**) occurred on the pyrazolone ring to give **2** or **4** alkyl or **5** alkoxy derivatives. Vilsmeyer–Haack formylation of 3-ferrocenyl-3-pyrazolin-5-one (**5a**) occurred on the pyrazolone ring at 4 position. Diazocoupling reaction to 3-ferrocenyl-2-pyrazolin-5-ones (**2a, b**) occurred on the pyrazolone ring at 4 position as well.

Keywords——ferrocenyl-pyrazolone; ferrocene derivatives; alkylation; Vilsmeyer–Haack reaction; diazocoupling

Rosenblum, *et al.*[2] and Yamakawa, *et al.*[3] have reported that the acetylation reactivity of biferrocenyl and phenyl ferrocene decreases than that of ferrocene itself due to intraannular electronic effects. It was felt that more extensive investigation of the reactivity of ferrocenes having heterocycles might be of interest.

This paper deals with the synthesis and reactivity of some pyrazolones having ferrocenyl substituent at 3 position of pyrazolone ring. The starting compounds, 3-ferrocenylpyrazolones (**2a, b**) were synthesized from ethyl ferrocenoylacetate (**1**) by the method of Hauser, *et al.*[4] Alkylation of 3-ferrocenyl-2-pyrazolin-5-one (**2b**) was studied. When methyl iodide was allowed to react with **2b**, in the presence of sodium alkoxide, four kinds of methylated compounds; 4,4-dimethyl-2-pyrazolin-5-one (**3a**), 2,4-dimethyl-3-pyrazolin-5-one (**4a**), 2-methyl-3-pyrazolin-5-one (**5a**) and 4-methyl-3-pyrazolin-5-one- (**6a**) were obtained, which were separated by column chromatography on alumina. The structures of **3a** and **6a** were confirmed by alternative synthesis from ethyl 2-ferrocenoyl-2-methylpropionate (**1c**) and ethyl 2-ferrocenoylpropionate (**1b**) respectively. The structures of **4a** and **5a** were assigned by the spectral and analytical data. The infrared (IR) spectra of **4a** and **5a** have carbonyl absorption bands at 1660 and 1670 cm^{-1} respectively. The nuclear magnetic resonance (NMR) spectrum of **4a** showed C–CH_3 signal at δ 2.18 and N–CH_3 signal at δ 2.90, **5a** showed N–CH_3 signal at δ 3.12. In the similar manner, analogous alkylation such as ethylation, isopropylation, allylation and benzylation of **2b** were carried out to give several alkyl substituted pyrazolones. Treatment of **2b** with dimethylsulfate resulted in the formation of **5a** and 5-methoxypyrazole (**7a**). The alkylated pyrazolones thus prepared are shown in Chart 1.

The all alkylation took place on the pyrazolone ring and not on the cyclopentadienyl(Cp) ring, which showed the decrease of the reactivity of Cp ring. And the positions alkylated were 2, 4 or O atom of 5 position of the pyrazolone ring. This fact accords with the discussions of Wiley, *et al.*[5] and Sonn, *et al.*[6] that the alkylation of 2-pyrazolin-5-ones occurs readily at these positions.

1) Location: *Tanabe-dori, Mizuho-ku, Nagoya.*
2) M. Rosenblum, J.O. Santer, and W.G. Howells, *J. Am. Chem. Soc.*, **85**, 1450 (1963).
3) K. Yamakawa, N. Ishibashi, and K. Arakawa, *Chem. Pharm. Bull.* (Tokyo), **12**, 119 (1964).
4) C.R. Hauser and J.K. Kindsay, *J. Org. Chem.*, **22**, 482 (1957).
5) R.H. Wiley and P. Wiley, "Pyrazolones, Pyrazolidones, and Derivatives," Interscience Publishers, Inc., New York, 1964, pp. 19—29.
6) A. Sonn and W. Litten, *Chem. Ber.*, **66**, 1582 (1933).

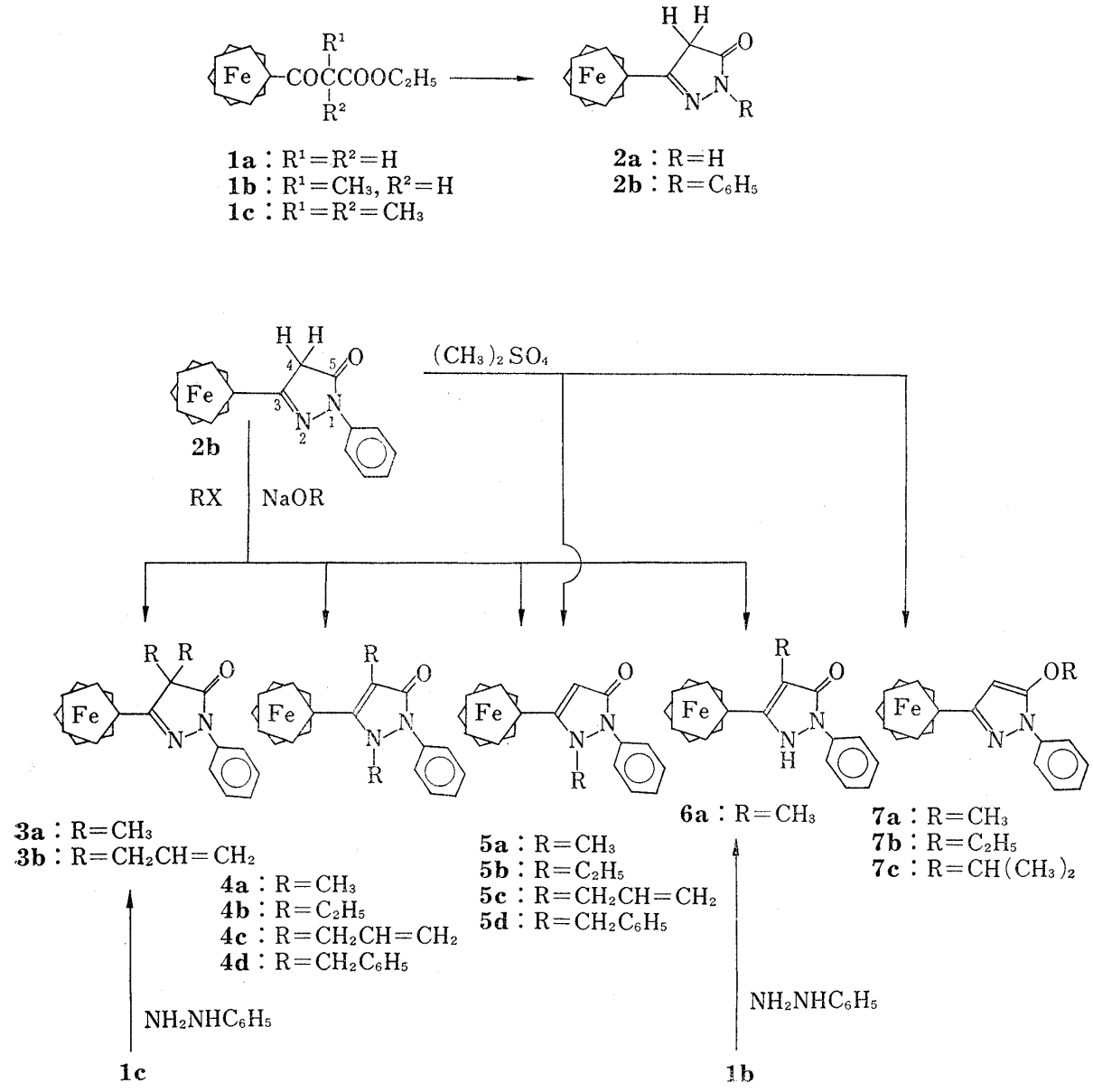


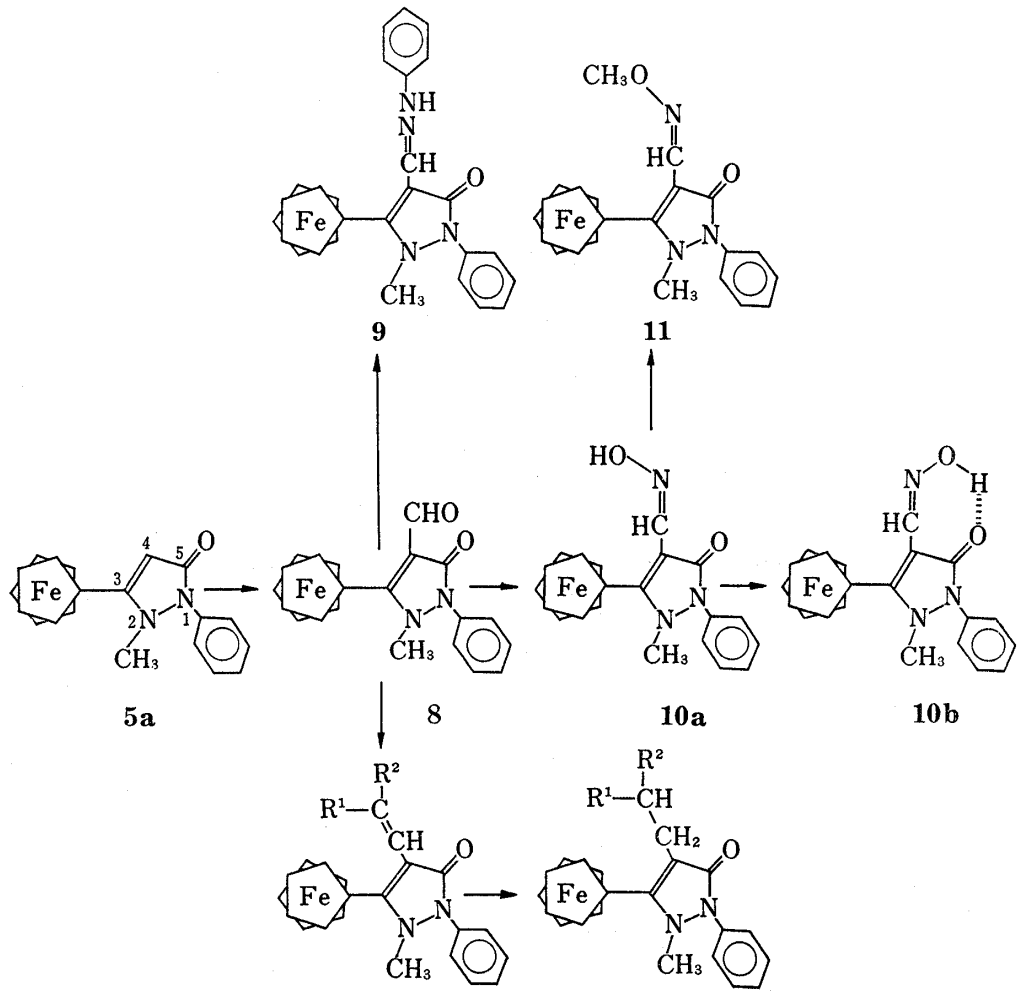
Chart 1

Rosenblum, *et al.*[7] have applied the Vilsmeyer-Haack reaction to ferrocene to get formyl ferrocene. We tried an analogous reaction to 2-methyl-3-ferrocenyl-3-pyrazolin-5-one(**5a**). In this case as well as alkylation, formylation did not occur on Cp ring but occurred on pyrazolone ring to give 4-formyl-3-pyrazolin-5-one (**8**). Reaction of the formyl compound (**8**) with phenylhydrazine or hydroxylamine produced Shiff base (**9**) and oxime (**10a**) respectively. **10a** was obtained as *syn*-oxime form, which was converted to *anti*-oxime form (**10b**) by heating in acidic medium. *anti*-Oxime form (**10b**) has a carbonyl absorption band at 1625 cm^{-1} shifted from 1680 cm^{-1} of *syn*-oxime form (**10a**), and showed OH signal at δ 12.56 shifted from δ 11.00 of that of *syn*-oxime form (**10a**), indicating the formation of chelate bonding. **10a** was methylated with methyl iodide to give methoxyiminomethyl-3-pyrazolin-5-one (**11**).

Some active methylene compounds such as malonic acid, ethyl malonate, malononitril and ethyl cyanoacetate were allowed to react with the formyl compound (**8**) to give the corre-

7) M. Rosenblum, A.K. Banerjee, N. Danieli, R.W. Fish, and V. Schlatter, *J. Am. Chem. Soc.*, **85**, 316 (1963).

sponding ethylene compounds (**12a—e**). **12a—c** were catalytically hydrogenated in the presence of paradium on charcoal to give the corresponding ethyl compounds (**13a—c**).



12a: R^1=H, R^2=COOH
12b: R^1=R^2=COOH
12c: R^1=R^2=$COOC_2H_5$
12d: R^1=R^2=CN
12e: R^1=$COOC_2H_5$, R^2=CN

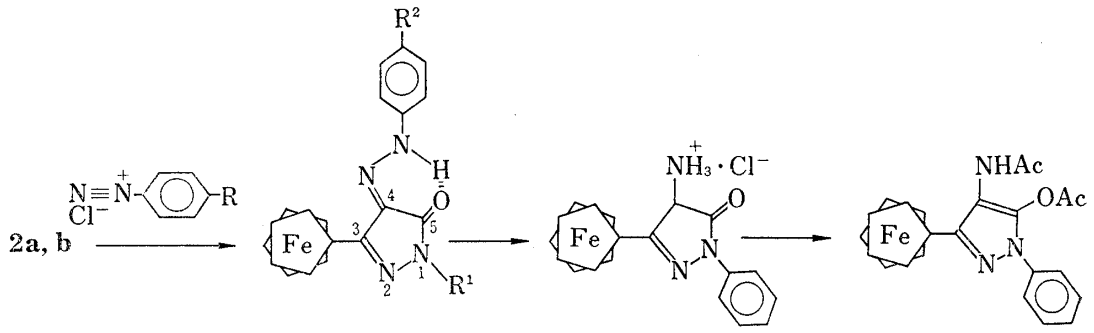
13a: R^1=H, R^2=COOH
13b: R^1=R^2=COOH
13c: R^1=R^2=$COOC_2H_5$

Chart 2

Diazocoup ing reaction was subjected to the 3-ferrocenyl-2-pyrazolones (**2a, b**), and in this case as well the reaction did not occur on Cp ring, but occurred on pyrazolone ring at 4 position to give 3-ferrocenyl-4-arylazo-2-pyrazolin-5-ones (**14a—d**). **14a—d** have carbonyl absorption bands at 1645—1662 cm^{-1}, and showed N–H signals at δ 13.54—14.00. These low wave numbers of the carbonyl absorptions and low field shifts of N–H signals reveal the existence of an internal hydrogen bonding between these two groups. Such a bonding has been reported by Jones, *et al.*[8] on some 4-arylazo-5-pyrazolone derivatives.

14c was reduced with tin and hydrochloric acid to give amine hydrochloride (**15**), which was derived to acetyl compound (**16**).

8) R. Jones, A.J. Ryan, S. Sternhell, and S.E. Wright, *Tetrahedron*, **1963**, 1497.



14a: $R^1=R^2=H$
14b: $R^1=C_6H_5$, $R^2=N(C_2H_5)_2$
14c: $R^1=C_6H_5$, $R^2=H$
14d: $R^1=C_6H_5$, $R^2=NO_2$

15 **16**

Chart 3

Experimental

All melting points were measured on a Yanagimoto Melting Point Apparatus and are uncorrected. Ultraviolet (UV) spectra were taken on a HITACHI EPS-3TS Spectrophotometer and IR spectra on a JASCO IR-A2 Infrared spectrophotometer. NMR spectra were recorded on a JEOL JNM-MH-100 Spectrometer using tetramethylsilane as an internal standard.

Ethyl 2-Ferrocenoylpropionate (1b) and Ethyl 2-Ferrocenoyl-2-methylpropionate (1c)——A solution of ethyl ferrocenoylacetate (**1a**)[9] (450 mg) in 15 ml of anhyd. ether was added dropwise to a stirred suspension of NaH (70 mg) in 5 ml of anhyd. ether. The mixture was refluxed for 30 min under an atmosphere of nitrogen. After cooling, 1.14 g of CH_3I was added to the mixture and was refluxed for 30 min. The mixture was washed with 5% H_2SO_4, 5% $NaHCO_3$ and water successively then dried over Na_2SO_4. After evaporation of the solvent, the residue was dissolved in benzene–ethyl acetate (10: 1) and chromatographed on alumina (Merck, Art. 1097). The first fraction was evaporated and the residue was crystallized from EtOH to give 65 mg (13.2%) of **1c** as red needles, mp 85—86°. *Anal.* Calcd. for $C_{17}H_{20}FeO_3$: C, 62.22; H, 6.14. Found: C, 62.14; H, 6.03. IR ν_{max}^{KBr} cm^{-1}: 1735, 1210 (COOEt), 1670 (CO). The second fraction gave **1b** as red needles, mp 71—72°, yield 210 mg (44.6%). *Anal.* Calcd. for $C_{16}H_{18}FeO_3$: C, 61.17; H, 5.78. Found: C, 60.88; H, 5.67. IR ν_{max}^{KBr} cm^{-1}: 1736, 1190 (COOEt), 1661 (CO). NMR ($CDCl_3$) δ: 1.46 (3H, d, $J=8$ Hz, CH_3–CH–CO), 4.00 (1H, q, $J=8$ Hz, CH_3–CH–CO).

3-Ferrocenyl-2-pyrazolin-5-one (2a)——A mixture of **1a**[9] (300 mg) and hydrazine hydrate (0.3 g) in 4 ml of EtOH–AcOH (1: 1) was refluxed for 2 hr. The mixture was allowed to cool and the crystals were filtered and recrystallized from EtOH to give 140 mg (52.2%) of yellow needles, mp 211—212°. *Anal.* Calcd. for $C_{13}H_{12}FeN_2O$: C, 58.20; H, 4.51; N, 10.45. Found: C, 58.05; H, 4.46; N, 10.47.

Methylation of 3-Ferrocenyl-1-phenyl-2-pyrazoiln-5-one (2b)——a) A mixture of **2b** (700 mg) and CH_3I (4 g) in 15 ml of anhyd. MeOH containing NaOMe (2.3 mmol) was stirred for 24 hr at room temperature. The crystals were filtered and dissolved in $CHCl_3$. The solution was washed with water and the solvent was evaporated under reduced pressure. The residue was dissolved in benzene–ethyl acetate (10: 1) and chromatographed on alumina (Merck, Art. 1097). The first fraction was evaporated and the residue was crystallized from EtOH to give **3a** (yield, 23%). The second fraction, the third fraction, and the fourth fraction gave **4a** (yield, 8%), **5a** (yield, 11%) and **6a** (yield, 6%) respectively. Physical and analytical data are listed in Table I.

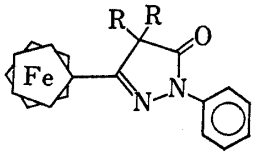
b) To a stirred mixture of **2b** (520 mg) and NaOH (180 mg) in 30 ml of 60% EtOH was added $(CH_3)_2SO_4$ (1 g) dropwise. The mixture was stirred for 1.5 hr at room temperature, and then heated at 60—70° for 30 min. The mixture was basified with 10% NaOH and extracted with $CHCl_3$, washed with water. After evaporation of the solvent, the residue was dissolved in benzene–ethyl acetate (10: 1) and chromatographed on alumina (Merck, Art. 1097). The first fraction was evaporated and the residue was crystallized from EtOH to give **7a** (yield, 13.1%). The second fraction was evapolated and the residue was crystallized from EtOH to give **5a** (yield, 47.3%). Physical and analytical data are listed in Table I.

Ethylation of 3-Ferrocenyl-1-phenyl-2-pyrazolin-5-one (2b)——A mixture of **2b** (650 mg), NaOEt (200 mg) and EtBr (4.3 g) in 30 ml of anhyd. EtOH was stirred for 18 hr at room temperature. The mixture was treated in the same manner as the above analog. The first fraction gave **7b** (yield, 17%). The second fraction gave **4b** (yield, 6.6%), the third fraction gave **5b** (yield, 5.5%). Physical and analytical data are listed in Table I.

9) D.T. Roberts Jr., W.F. Little, and M.M. Bursey, *J. Am. Chem. Soc.*, **89**, 6156 (1967).

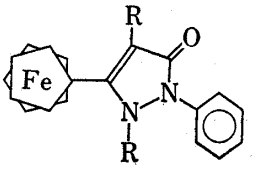
TABLE I. Alkylated Products of 3-Ferrocenyl-1-phenyl-2-pyrazolin-5-one (**2b**)

a) 4,4-Dialkyl-3-ferrocenyl-1-phenyl-2-pyrazolin-5-ones (**3a,b**)



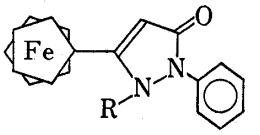
Compd. No.	R	mp (°C)	Appearance	Formula	Analysis (%) Calcd. C	H	N	Found C	H	N
3a	CH_3	169—170	Red prisms	$C_{21}H_{20}FeN_2O$	67.81	5.42	7.53	67.62	5.37	7.73
3b	$CH_2CH=CH_2$		Red oil	$C_{25}H_{24}FeN_2O$	70.76	5.70	6.60	70.58	5.47	6.87

b) 2,4-Dialkyl-3-ferrocenyl-1-phenyl-3-pyrazolin-5-ones (**4a—d**)



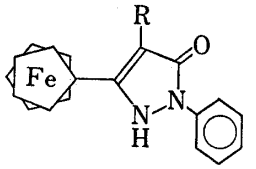
4a	CH_3	101—103.5	Yellow needles	$C_{21}H_{20}FeN_2O$	67.81	5.42	7.53	67.60	5.51	7.52
4b	C_2H_5	140—141	Yellow needles	$C_{23}H_{24}FeN_2O$	69.01	6.04	7.00	68.81	6.11	6.92
4c	$CH_2CH=CH_2$		Red oil	$C_{25}H_{24}FeN_2O$	70.76	5.70	6.60	70.89	5.67	6.38
4d	$CH_2C_6H_5$	201—202	Red prisms	$C_{33}H_{28}FeN_2O$	75.58	5.38	5.34	75.57	5.09	5.54

c) 2-Alkyl-3-ferrocenyl-1-phenyl-3-pyrazolin-5-ones (**5a—d**)



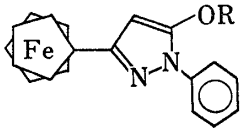
5a	CH_3	140—141.5	Yellow needles	$C_{20}H_{18}FeN_2O$	67.06	5.06	7.82	66.93	5.05	7.81
5b	C_2H_5		Red oil	$C_{21}H_{20}FeN_2O$	67.76	5.42	7.53	67.49	5.71	7.76
5c	$CH_2CH=CH_2$		Red oil	$C_{22}H_{20}FeN_2O$	68.77	5.25	7.29	68.58	5.37	7.12
5d	$CH_2C_6H_5$	135—136	Red prisms	$C_{26}H_{22}FeN_2O$	71.90	5.11	6.45	71.78	4.94	6.43

d) 3-Ferrocenyl-4-methyl-1-phenyl-3-pyrazolin-5-one (**6a**)



6a	CH_3	211—212	Red needles	$C_{20}H_{18}FeN_2O$	67.06	5.06	7.82	67.18	5.02	7.98

e) 5-Alkoxy-3-ferrocenyl-1-phenyl-pyrazoles (**7a—c**)



7a	CH_3	127—128.5	Yellow needles	$C_{20}H_{18}FeN_2O$	67.05	5.06	7.82	66.99	5.01	7.84
7b	C_2H_5	142—143	Yellow needles	$C_{21}H_{20}FeN_2O$	67.76	5.42	7.53	67.92	5.44	7.82
7c	$CH(CH_3)_2$	105—106.5	Yellow needles	$C_{22}H_{22}FeN_2O$	64.20	5.15	6.51	63.93	5.12	6.38

Isopropylation of 3-Ferrocenyl-1-phenyl-2-pyrazolin-5-one (2b)——A mixture of **2b** (520 mg), NaOMe (160 mg) and isopropyl bromide (2.6 g) in 30 ml of anhyd. MeOH was refluxed for 7 hr. The mixture was treated in the same manner as the above analog giving **7c** (yield, 13.6%). Physical and analytical data are listed in Table I.

Allylation of 3-Ferrocenyl-1-phenyl-2-pyrazolin-2-one (2b)——A mixture of **2b** (520 mg), NaOMe (160 mg) and allyl bromide (700 mg) in 30 ml of anhyd. MeOH was stirred for 24 hr at room temperature. The mixture was treated in the same manner as the above analog. The first fraction gave **3b** (yield, 15%), the second fraction gave **4c** (yield, 25%), the third fraction gave **5c** (yield, 12.8%). Physical and analytical data are listed in Table I.

Benzylation of 3-Ferrocenyl-1-phenyl-2-pyrazolin-5-one (2b)——A mixture of **2b** (520 mg), NaOMe (90 mg) and benzyl bromide (500 mg) in 15 ml of anhyd. MeOH was stirred for 24 hr at room temperature. The mixture was treated in the same manner as the above analog. The first fraction gave **4d** (yield, 24.2%), the second fraction gave **5d** (yield, 10.3%). Physical and analytical data are listed in Table I.

3-Ferrocenyl-4-formyl-2-methyl-1-phenyl-3-pyrazolin-5-one (8)——To a stirred mixture of **5a** (1.07 g) and N-methylformanilide (0.5 g) was added 0.5 g of $POCl_3$ in small portions under atmosphere of nitrogen. The mixture was then gradually warmed to 70° and maintained at the temperature for 1.5 hr. The mixture was poured onto ice water and basified with 10% NaOH. The crystals which appeared were dissolved in $CHCl_3$–ethyl acetate (3: 1) and chromatographed on silica gel (Wako gel C-200). After evaporation of the effluent, the residue was crystallized from EtOH to give 0.85 g (73.7%) of red prisms, mp 166.5—168°. *Anal.* Calcd. for $C_{12}H_{18}FeN_2O_2$: C, 65.30; H, 4.70; N, 7.25. Found: C, 65.46; H, 4.42; N, 7.11. IR ν_{max}^{KBr} cm^{-1}: 1650 (CHO). NMR ($CDCl_3$) δ: 10.09 (1H, s, CHO).

3-Ferrocenyl-2-methyl-1-phenyl-4-phenylhydrazonomethyl-3-pyrazolin-5-one (9)——A mixture of **8** (0.2 g), phenylhydrazine (0.55 g), and AcOH (2 ml) in 15 ml of 70% EtOH was heated on a water bath for 30 min. The mixture was diluted with water, and the crystals which appeared were filtered and dissolved in benzene–ethyl acetate (1: 1) and chromatographed on alumina (Merck, Art 1097). After evaporation of the effluent, the residue was crystallized from EtOH to give 0.15 g (60.8%) of orange plates, mp 229—230°. *Anal.* Calcd. for $C_{27}H_{24}FeN_4O$: C, 68.08; H, 5.08; N, 11.76. Found: C, 67.80; H, 5.04; N, 11.86. IR ν_{max}^{KBr} cm^{-1}: 1640 (CO). NMR ($CDCl_3$–DMSO-d_6) δ: 6.74 (1H, s, –CH=), 11.73 (1H, s, NH).

3-Ferrocenyl-4-*syn*-hydroxyiminomethyl-2-methyl-1-phenyl-3-pyrazolin-5-one (10a)——To a stirred mixture of **8** (0.5 g) and $NH_2OH \cdot HCl$ (0.5 g) in 20 ml of EtOH was added NaOAc (0.6 g) in 5 ml of water in small portions and stirring was continued for additional 1 hr. The crystals were filtered, washed with water and recrystallized from EtOH to give 0.44 g (84.7%) of red prisms, mp 197—198°. *Anal.* Calcd. for $C_{21}H_{19}FeN_3O_2$: C, 62.86; H, 4.77; N, 10.47. Found: C, 62.61; H, 4.53; N, 10.44. IR ν_{max}^{KBr} cm^{-1}: 3290 (OH), 1680 (CO). NMR ($CDCl_3$–DMSO-d_6) δ: 8.31 (1H, s, CH=N), 11.00 (1H, s, OH).

3-Ferrocenyl-4-*anti*-hydroxyiminomethyl-2-methyl-1-phenyl-3-pyrazolin-5-one (10b)——A solution of **11a** (0.18 g) in 4 ml of conc. HCl–AcOH (1: 1) was heated on a water bath for 1 hr. The mixture was extracted with $CHCl_3$. The extracts were washed with 5% $NaHCO_3$ and dried over Na_2SO_4. After evaporation of the solvent, the residue was dissolved in benzene–EtOH (30: 1) and chromatographed on alumina (Merck, Art. 1097). The effluent was evaporated and the residue was crystallized from EtOH to give 0.065 g (36.1%) of yellow needles, mp 206—207°. *Anal.* Calcd. for $C_{21}H_{19}FeN_3O_2$: C, 62.86; H, 4.77; N, 10.47. Found: C, 62.99; H, 4.81; N, 10.45. IR ν_{max}^{KBr} cm^{-1}: 1625 (CO). NMR ($CDCl_3$–DMSO-d_6) δ 8.06 (1H, s, –CH=N–), 12.50 (1H, s, OH).

3-Ferrocenyl-4-methoxyiminomethyl-2-methyl-1-phenyl-3-pyrazolin-5-one (11)——A mixture of **10a** (0.25 g), MeI (3 g) and NaOMe (40 mg) in 7 ml of anhyd. EtOH was refluxed for 4 hr. The mixture was diluted with $CHCl_3$ and washed with water. After evaporation of the solvent, the residue was dissolved in benzene–ethyl acetate (15: 1) and chromatographed on alumina (Merck, Art. 1097). The effluent was evaporated and the residue was crystallized from EtOH to give 0.12 g (58.0%) of red prisms, mp 139—140°. *Anal.* Calcd. for $C_{22}H_{21}FeN_3O_2$: C, 63.63; H, 5.10; N, 10.12. Found: C, 63.73; H, 5.24; N, 10.25. IR ν_{max}^{KBr} cm^{-1}: 1678 (CO), 1140 (C–O–C). NMR ($CDCl_3$) δ: 4.00 (3H, s, OCH_3).

1-(3-Ferrocenyl-2-methyl-1-phenyl-3-pyrazolin-5-one-4-yl)ethylene-2-carboxylic Acid (12a) and 1-(3-Ferrocenyl-2-methyl-1-phenyl-3-pyrazolin-5-one-4-yl)ethylene-2,2-dicarboxylic Acid (12b)——A mixture of **8** (1.5 g) and malonic acid (1 g) in 15 ml of pyridine was heated at 80—90° for 3 hr under an atmosphere of nitrogen. The mixture was poured onto ice, and acidified with 10% HCl. The crystals were filtered, washed with water and dissolved in $CHCl_3$–ethyl acetate (3: 1) and chromatographed on silica gel (Wako gel C-200). The first fraction was evaporated and crystallized from EtOH to give **12a**, red prisms, mp>250°. Yield, 0.6 g (36.1%). *Anal.* Calcd. for $C_{23}H_{20}FeN_2O_3$: C, 64.50; H, 4.71; N, 6.54. Found: C, 64.36; H, 4.54; N, 6.68. IR ν_{max}^{KBr} cm^{-1}: 3200—2400 (COOH dimer), 1670 (COOH). NMR ($CDCl_3$–DMSO-d_6) δ: 7.12 (1H, d, J=16 Hz, –CH=C<u>H</u>–CO_2), 8.41 (1H, d, J=16 Hz, –C<u>H</u>=CH–CO_2). Elution was continued with $CHCl_3$–EtOH (20: 1). After evaporation of the effluent, the residue was crystallized from EtOH to give **12b** as red prisms, mp 224—226°. Yield, 0.49 g (26.7%). *Anal.* Calcd. for $C_{24}H_{20}FeN_2O_5$: C, 61.04; H, 4.27; N, 5.93. Found: C, 60.87; H, 4.21; N, 5.75. IR ν_{max}^{KBr} cm^{-1}: 3200—2400 (COOH dimer), 1710 (COOH). NMR ($CDCl_3$–DMSO-d_6) δ: 8.26 (1H, s, –CH=C<).

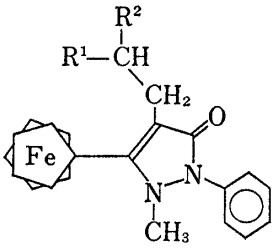
Diethyl 1-(3-Ferrocenyl-2-methyl-1-phenyl-3-pyrazolin-5-one-4-yl)ethylene-2,2-dicarboxylate (12c)——A mixture of **8** (0.5 g), diethyl malonate (0.48 g) and 3 drops of piperidine in 10 ml of anhyd. EtOH was refluxed for 8 hr under an atmosphere of nitrogen. The mixture was evaporated and the residue was dissolved in $CHCl_3$ and chromatographed on silica gel (Wako gel C-200). The effluent was evaporated to give 0.64 g (78.7%) of red oil. *Anal.* Calcd. for $C_{28}H_{28}FeN_2O_5$: C, 63.65; H, 5.34; N, 5.30. Found: C, 63.59; H, 5.46; N, 5.23. IR ν_{max}^{KBr} cm^{-1}: 1700, 1250 (COOEt). NMR ($CDCl_3$) δ: 1.33 (6H, t, $J=7$ Hz, $2\times CH_2\underline{CH_3}$), 4.42 (4H, q, $J=7$ Hz, $2\times \underline{CH_2}CH_3$), 8.76 (1H, s, -CH=C).

1-(3-Ferrocenyl-2-methyl-1-phenyl-3-pyrazolin-5-one-4-yl)ethylene-2,2-dicarbonitrile (12d)——A mixture of **8** (0.38 g), malononitrile (0.08 g) and 3 drops of piperidine in 10 ml of anhyd. EtOH was stirred for 30 min at room temperature. 50 ml of ether was added to the mixture and the crystals which appeared were recrystallized from EtOH to give 0.28 g (65.4%) of dark red prisms, mp 199—201°. *Anal.* Calcd. for $C_{24}H_{19}FeN_4O$: C, 66.38; H, 4.18; N, 12.90. Found: C, 66.41; H, 4.32; N, 13.09. IR ν_{max}^{KBr} cm^{-1}: 2310 (CN), 1680 (CO). NMR ($CDCl_3$) δ: 8.24 (1H, s, -CH=C<).

Ethyl 2-Cyano-1-(3-ferrocenyl-2-methyl-1-phenyl-3-pyrazolin-5-one-4-yl)ethylene-2-carboxylate (12e)——A mixture of **8** (0.38 g), ethyl cyanoacetate (0.14 g) and 3 drops of piperidine in 15 ml of anhyd. EtOH was stirred for 2 hr at room temperature. After evaporation of the solvent, the residue was dissolved in $CHCl_3$–ethyl acetate (5: 1) and chromatographed on silica gel (Wako gel C-200). The effluent was evaporated to give 0.22 g (46.4%) of red oil. *Anal.* Calcd. for $C_{26}H_{24}FeN_3O_3$: C, 64.88; H, 4.82; N, 5.73. Found: C, 64.80; H, 4.88; N, 5.68. IR ν_{max}^{KBr} cm^{-1}: 2300 (CN), 1700, 1245 (COOEt). NMR ($CDCl_3$) δ: 1.39 (3H, t, $J=8$ Hz, $CH_2\underline{CH_3}$), 4.38 (2H, q, $J=8$ Hz, $\underline{CH_2}CH_3$), 8.79 (1H, s, -CH=C<).

General Procedure of 3-Ferrocenyl-2-methyl-1-phenyl-4-(2-substituted ethyl)-3-pyrazolin-5-one (13a—c)——A solution of 1 mol of each **12a**, **12b**, or **12c** in 15 ml of anhyd. EtOH was hydrogenated over 0.3 g of 1% palladium on charcoal at 3 kg/cm^2 for 24 hr at room temperature. After removal of the catalyst the solvent was evaporated. The residue was dissolved in $CHCl_3$ and chromatographed on silica gel (Wako gel C-200). The effluent was evaporated and the residue was crystallized from EtOH to give the products. Physical and analytical data are listed in Table II. **13a**: IR ν_{max}^{KBr} cm^{-1}: 1708 (COOH), 1662 (CO). NMR ($CDCl_3$–DMSO-d_6) δ: 2.79 (2H, t, $J=8$ Hz, $-\underline{CH_2}-CH_2-COO$), 2.82 (2H, t, $J=8$ Hz, $-CH_2-\underline{CH_2}COO$). **13b**: IR ν_{max}^{KBr} cm^{-1}: 1730, 1700 (COOH). NMR ($CDCl_3$–DMSO-d_6) δ: 3.12 (2H, d, $J=7$ Hz, $-\underline{CH_2}-CH(COOH)_2$), 4.03 (1H, t, $J=7$ Hz, $-CH_2-\underline{CH}(COOH)_2$). **13c**: IR ν_{max}^{KBr} cm^{-1}: 1740, 1720, 1260 (COOEt), 1650 (CO). NMR ($CDCl_3$) δ: 3.32 (2H, d, $J=7$ Hz, $-\underline{CH_2}-CH(COOEt)_2$), 4.26 (1H, t, $J=7$ Hz, $-CH_2-\underline{CH}(COOEt)_2$).

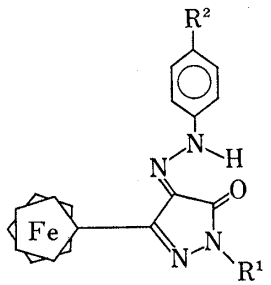
TABLE II. 3-Ferrocenyl-2-methyl-1-phenyl-4-(2-substituted ethyl)-3-pyrazolin-5-ones (**13a—c**)



Compd. No.	R^1	R^2	Yield (%)	mp (°C)	Appearance	Formula	Analysis (%) Calcd. (Found) C	H	N
13a	H	COOH	81.0	194—195	Yellow needles	$C_{23}H_{22}FeN_2O_3$	64.20 (64.47)	5.15 (5.20)	6.51 (6.70)
13b	COOH	COOH	74.5	172—173	Yellow prisms	$C_{24}H_{22}FeN_2O_5$	60.78 (60.76)	4.68 (4.66)	5.91 (6.06)
13c	COOEt	COOEt	49.0	119—121	Red prisms	$C_{28}H_{30}FeN_2O_5$	63.41 (63.62)	5.70 (5.88)	5.28 (5.41)

General Procedure of 3-Ferrocenyl-4-phenylhydrazino-2-pyrazolin-5-one (14a—d)——Benzene diazonium chloride solution (1.5 mmol) was added to a stirred mixture of **2a** or **2b** (1 mmol) and KOH (220 mg) in 30 ml of 20% EtOH with external cooling with ice-water. The mixture was stirred for 1 hr at room temperature, and acidified with AcOH. The crystals were filtered and washed with water. Recrystallization from EtOH gave the products. Physical and analytical data are listed in Table III.

Table III. 3-Ferrocenyl-4-phenylhydrazino-2-pyrazolin-5-ones (**14a—d**)



Compd. No.	R^1	R^2	Yield (%)	mp (°C)	Appearance	Formula	Analysis (%) Calcd. (Found) C	H	N
14a	H	H	56.5	172—173	Dark green needles	$C_{19}H_{16}FeN_4O$	61.31 (61.47)	4.33 (4.47)	15.05 (14.75)
14b	C_6H_5	NEt_2	59.7	170—171	Purple needles	$C_{29}H_{29}FeN_5O$	67.06 (66.85)	5.63 (5.68)	13.48 (13.44)
14c	C_6H_5	H	78.1	195—197	Dark red needles	$C_{25}H_{20}FeN_4O$	66.95 (66.78)	4.50 (4.61)	12.50 (12.51)
14d	C_6H_5	NO_2	72.0	251—253	Dark green needles	$C_{25}H_{19}FeN_5O_3$	60.87 (60.98)	3.88 (3.61)	14.20 (14.13)

4-Acetamido-5-acetoxy-3-ferrocenyl-1-phenyl-pyrazole (**16**)——A mixture of **14c** (0.5 g), granular Sn (1 g) and conc. HCl (5 ml) in 50 ml of EtOH was refluxed for 6 hr under stirring. The mixture was filtered and diluted with ice-water to give the hydrochloride (**15**) as crystals. The crude crystals (**15**) were acetylated without further purification. The crystals (**15**) were suspended in 7 ml of water. Ac_2O (1 ml) and NaOAc (1.1 g) were gradually added to the suspension under external cooling with ice water. The mixture was stirred for 1 hr and extracted with ether. The extract was washed with 5% $NaHCO_3$, dried over Na_2SO_4 and evaporated. The residue was dissolved in $CHCl_3$–EtOH (20: 1) and chromatographed on silica gel (Wako gel C-200). The effluent was evaporated and the residue was crystallized from EtOH to give 0.044 g (8.9%) of yellow needles, mp 142—144°. *Anal.* Calcd. for $C_{23}H_{21}FeN_3O_3$: C, 62.32; H, 4.78; N, 9.48. Found: C, 62.15; H, 4.64; N, 9.63. IR ν_{max}^{KBr} cm^{-1}: 3350 (NH), 1776, 1188 (–$OCOCH_3$), 1670 (NHCO). NMR ($CDCl_3$–DMSO-d_6) δ: 2.18 (3H, s, $NCOCH_3$ or $OCOCH_3$), 2.21 (3H, s, $OCOCH_3$ or $NCOCH_3$), 8.82 (1H, s, NH).

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