Insertion and Fragmentation of 2-Ferrocenylmethylidene-1, 3-diketones upon Their Reactions with *N*-Methylhydrazine

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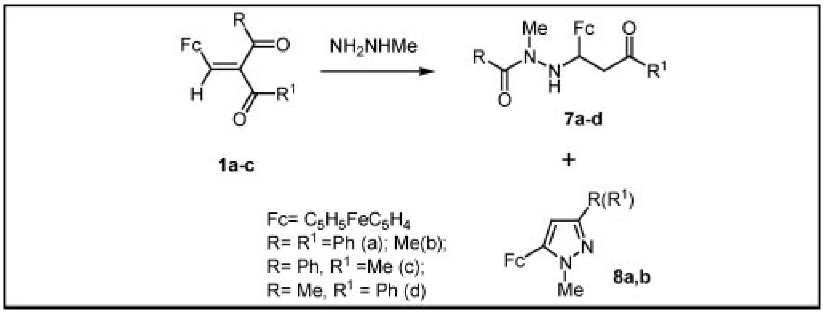
Received July 1, 2008
DOI 10.1002/jhet.94
Published online 26 May 2009 in Wiley InterScience (www.interscience.wiley.com).



Reactions of 2-ferrocenylmethylidene-1,3-diketones (**1a–c**) with methylhydrazine afford mainly insertion products (~40–58%), *viz*., 1-(*N*′-acyl-*N*′-methylhydrazino)-1-ferrocenyl-2-acylethanes (**7a–d**), together with lesser amounts of pyrazoles (**8a,b**) and dihydropyrazoles (**9a,b**).

J. Heterocyclic Chem., **46**, 484 (2009).

INTRODUCTION

Syntheses of pyrazoles are mainly based on reactions of 1,3-diketones or 2,3-ynones with hydrazines or on the oxidation of 2-pyrazolines [1–3]. Both these methods are virtually inapplicable as approaches to ferrocenylpyrazoles, because 1,3-diketones with ferrocenyl substituents are usually accessible with difficulty, while oxidative methods may result in destruction of the metallocene substituent. Earlier [4,5], we have proposed a method for the preparation of ferrocenylpyrazole derivatives by condensation of 3- and 5-ferrocenyl-4,5-dihydropyrazoles with aromatic aldehydes (Scheme 1).

Biological assays of the thus obtained compounds have shown that the majority of them possessed high antiviral and anti-inflammatory activities [6–11]. The low solubility of the ferrocenylpyrazoles in water, alcohols, and in acidic solutions is their substantial drawback precluding their manifestation in full pharmacological potential.

In view of the aforesaid, the quest for the approaches to introduce new functional groups to increase the solubility of ferrocenyl-containing pyrazoles is topical. One of such approaches might be based on the use of easily accessible ferrocenylmethylidene-1,3-diketones as precursors of ferrocenylpyrazoles with retention of one of the functional groups in the reaction products.

Data on the features of reactions of these compounds with hydrazines are absent in the chemical literature. Here, we describe the results of investigations of the reactions of methylhydrazine with 2-ferrocenylmethylidene-1,3-dicarbonyl compounds.

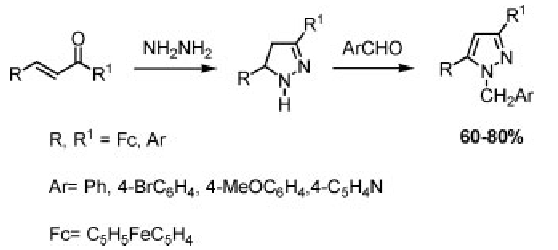
RESULTS AND DISCUSSION

The starting 2-ferrocenylmethylidene-1,3-diketones **1a–c** were obtained by the Knoevenagel condensation of β-dicarbonyl compounds **2a–c** with ferrocenecarbaldehyde in the presence of piperidinium y pyridinium acetates [12–14] (Scheme 2).

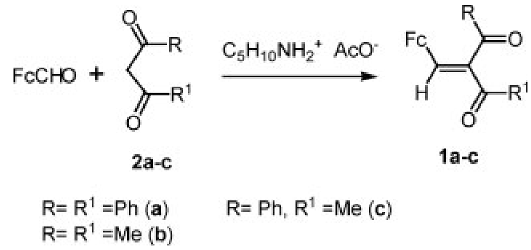
The structure of **1c** was elucidated based on the data from mass spectrometry, elemental analysis, and ^{1}H NMR spectroscopy (see Experimental section). According to the NMR data, compound **1c** is formed as single geometric isomers. The ^{1}H NMR spectrum of compound **1c** contains characteristic signals for one ferrocenyl, one phenyl, and one methyl entities, as well as one signal for the olefinic proton.

The spatial structure of compound **1c** as (*Z*)-2-ferrocenylmethylidene-1-phenylbutane-1,3-dione was determined by X-ray analysis of a single crystal obtained by crystallization from chloroform. The general view of the molecule of **1c** and its principal characteristics are given

Scheme 1



Scheme 2



in Figure 1(a), and the crystal packing is shown in Figure 1(b).

It was anticipated that compounds **1a–c** would react with methylhydrazine to form 4-acyl-5-ferrocenyl-4,5-dihydropyrazoles **3a**,**b** and **4a,b** or 4-acyl-3-ferrocenyl-2,3-dihydropyrazoles **5a**,**b** and **6a,b** [15], respectively (Scheme 3).

However, the results of these reactions turned out to be unexpected. In neither case did the coupling of *N*-methylhydrazine with compounds **1a–c** yield 4-acyl-4,5-dihydropyrazoles **3a,b**, **4a,b**, **5a,b**, and **6a,b**.

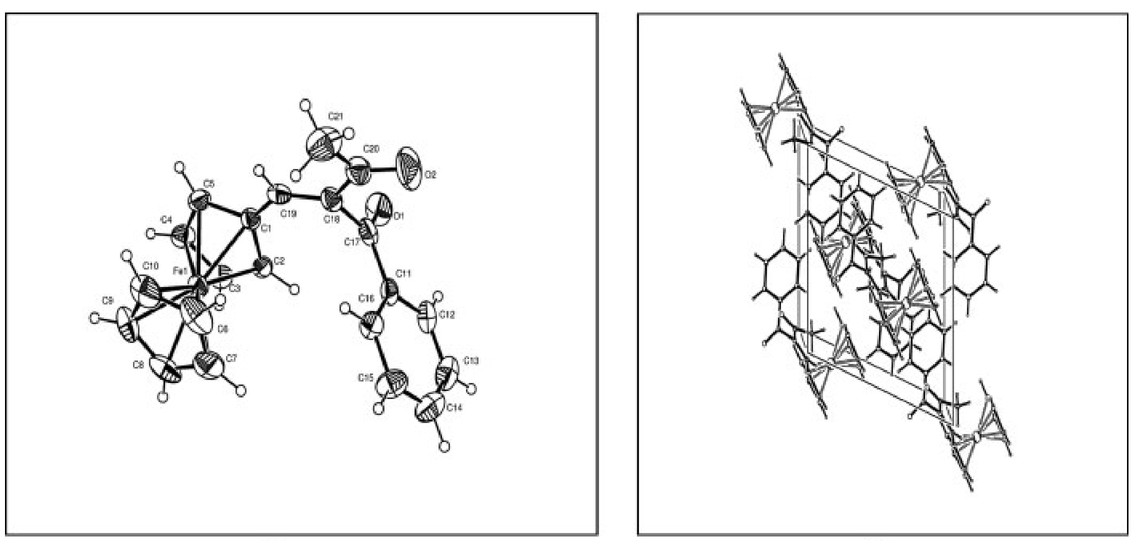
We have found that 1,3-diketones **1a** and **1b** react with *N*-methylhydrazine at 20°C to give mainly (~50%) the insertion products, *viz*., 1-benzoyl-2-(*N*′-benzoyl-*N*′-methylhydrazino)-2-ferrocenylethane **7a** and 4-(*N*′-acetyl-*N*′-methylhydrazino)-4-ferrocenylbutan-2-one **7b** (Scheme 4).

In addition, the fragmentation products, *viz*., 5-ferrocenyl-1-methylpyrazoles **8a,b**, 4,5-dihydropyrazoles **9a,b**, hydrazones **10a**,**b**, and hydrazides **11a**,**b** were isolated in lesser amounts.

Compounds **7a** and **7b** are yellow crystalline substances that precipitated from the reaction mixtures. They are storage-stable in the crystalline state, whereas in solution they gradually decompose. Pyrazole derivatives **8a,b** and **9a,b** were isolated by chromatography from the mother liquors following separation of the insertion products **7a** and **7b**.

The structures of compounds **7a** and **7b** were established based on data from ^{1}H and ^{13}C NMR spectroscopy. Their ^{1}H NMR spectra contain characteristic signals for the protons of the ABM system of the —CH_2—CH— fragments, singlets for protons of the CH_3— and NH groups, and the signals for the protons of the ferrocenyl and phenyl (for **7a**) substituents (Table 1).

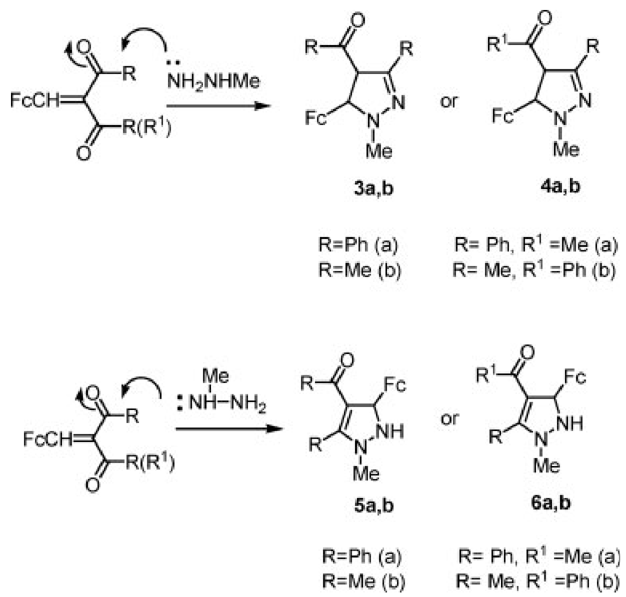
The ^{13}C NMR spectra of compounds **7a** and **7b** contain signals for the carbon atoms of two carbonyl



(a) (b)

Figure 1. (a) Crystal structure of **1c**. Selected bond lengths (Å): C(11)-C(17) = 1.478(7); C(17)-O(1) = 1.223(7); C(17)-C(18) = 1.510(7); C(18)-C(19) = 1.338(7); C(19)-C(1) = 1.439(7); C(18)-C(20) = 1.459(8); C(20)-C(21) = 1.503(9); C(20)-O(2) = 1.215(7). Selected bond angles (°): O(1)-C(17)-C(11) = 121.5(5); C(18)-C(17)-O(1) = 119.8(5); C(17)-C(18)-C(19) = 122.6(5); C(19)-C(18)-C(20) = 122.7(5); C17)-C(18)-C(20) = 114.6(5). (b) Crystal packing of **1c**.

Scheme 3



groups, of one ferrocenyl fragment with one signal for C_{ipso}Fc, and the appropriate number of signals for Me, Ph with two signals for C_{ipso} (**7a**), CH_2, and CH groups (Table 2).

X-ray diffraction analysis of a single crystal of the insertion product **7a** obtained upon crystallization from a 10:1 ethanol–methylhydrazine mixture proves unambiguously its structure. The general view of the molecule **7a** and its main geometric parameters are presented in Figure 2; these require no special comments.

The structures of pyrazole derivatives **8a**,**b** and **9a**,**b**, compounds **10a**,**b** and **11a**,b were unambiguously established based on the data from elemental analysis (Table 3), ^{1}H and ^{13}C NMR spectroscopy (Tables 1 and 2), and mass spectrometry (Table 3). Data from ^{1}H and ^{13}C NMR spectra of compounds **8a**,**b** and **9a**,**b** corroborate their structures. The number of signals for the CH=, C_5H_5, C_5H_4, Ph, Me **8a**,**b** and CH_2, CH, Fc, Ph, and Me **9a**,**b** groups and their chemical shifts correspond completely to the structures **8** and **9**.

The reaction of benzoyl(ferrocenylmethylidene)acetone **1c** with *N*-methylhydrazine affords mainly the insertion products, *viz*., 4-(*N*′-benzoyl-*N*′-methylhydrazino)-4-ferrocenylbutan-2-one **7c** and 3-(*N*′-acetyl-*N*′-methylhydrazino)-3-ferrocenyl-1-phenylpropan-1-one **7d** (~1:1) and lesser amounts of pyrazole derivatives **8a**,**b**, **9a**,**b**, hydrazones **10a**,**b,** and hydrazides **11a**,**b** (Scheme 5).

Data from elemental analysis, mass spectrometry, and ^{1}H and ^{13}C NMR spectroscopy including 1D NOE experiments, which have demonstrated the CH_3CO fragment either to be, or not to be, adjacent to the CH_2 group, prove the structure of compounds **7c** and **7d**.

Thus, the results obtained in this study demonstrate that the following processes take place in the reactions of *N*-methylhydrazine with 2-ferrocenylmethylidene-1,3-dicarbonyl compounds: (i) insertion of *N*-methylhydrazine into the molecules of the starting compounds **1a–c**; (ii) fragmentation of 1,3-diones **1a–c** under the action of *N*-methylhydrazine with, apparently, intramolecular redox process with formation of pyrazoles **8a,b**; and (iii) fragmentation of the same 1,3-diones **1a–c** under the action of *N*-methylhydrazine with formation of 4,5-dihydropyrazoles **9a,b** from α,β-unsaturated ketones.

The following putative reaction schemes seem to rationalize the formation of compounds **7a–d**, **8a**,**b**, **9a**,**b**, **10a**,**b,** and **11a**,**b**:

1. The addition of the NH_2 group of *N*-methylhydrazine to the activated double bond of the fragment FcCH=C of β-dicarbonyl compounds **1a–c** (the Michael addition) results in intermediates **12a–d** [Scheme 6(a)]. Subsequent nucleophilic attack by the CH_3NH fragment on the carbon atom of the carbonyl group with higher positive charge (δ+) is accompanied by migration of the carbon–carbon σ bond to the adjacent position with formation of the enol forms of the insertion products (**13a–d**), which are transformed into final compounds **7a–d**.
2. The initial nucleophilic addition of the —$NHCH_3$ group of *N*-methylhydrazine to the carbon atom of a carbonyl group of the starting compounds **1a–c** [Scheme 6(b)] resulting in intermediates **12e–h**, **13e–h**, which are transformed into final compounds **7a–d**.
3. 5-Ferrocenylpyrazoles **8a,b** are formed apparently upon initial nucleophilic attack by the NH_2 group of *N*-methylhydrazine on the carbon atom of a carbonyl

Scheme 4

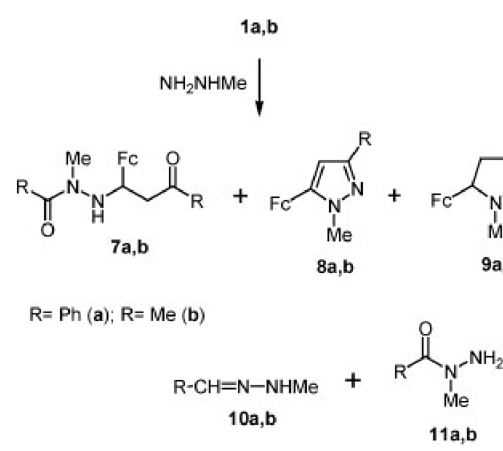


Table 1

^{1}H NMR spectral data of compounds **1c, 7a–d, 8a,b, 9a,b, 10a,b, and 11a,b** (δ, *J*/Hz).

Compound	C_5H_5 (s)	C_4H_4 (m)	CH_3, CH=	CH_AH_B (dd), CH_X (dd)	Ph, NH, NH_2
Z-**1c**	4.13 (5H)	4.24 (2H), 4.35 (2H)	2.31 s (3H), 7.64 s (1H)	–	7.46 m (2H), 7.58 m (1H), 7.94 m (2H)
7a	4.18 (5H)	3.94 (2H), 4.16 (2H)	2.93 s (3H)	3.17 (1H, *J* = 6.9, 16.5 Hz), 3.23 (1H, *J* = 4.5, 16.5 Hz), 3.59 (1H, *J* = 4.5, 6.9 Hz)	7.20–8.00 m (10H), 6.63 bs (1H)
7b	4.10 (5H)	3.89 (1H), 4.06 (1H), 4.17 (1H), 4.21 (1H)	1,79 s (3H), 2.94 s (3H), 3.12 s (3H)	2.60 (1H, *J* = 6.6, 16.8 Hz), 2.85 (1H, *J* = 3.9, 16.8 Hz), 3.41 (1H, *J* = 3.9, 6.6 Hz)	6.39 bs (1H)
7c	4.10 (5H)	4.14 (2H), 4.37 (1H), 4.44 (1H)	2.91 s (3H), 3.16 s (3H)	3.09 (1H, *J* = 6.3, 16.8 Hz), 3.31 (1H, *J* = 9.0, 16.8 Hz), 3.68 (1H, *J* = 6.3, 9.0 Hz)	7.37–7.56 m (3H), 7.95 m (2H), 5.92 bs (1H)
7d	4.19 (5H)	4.13 (1H), 4.15 (2H), 4.50 (1H)	2.18 s (3H), 2.96 s (3H)	3.03 (1H, *J* = 6.7, 16.3 Hz), 3.25 (1H, *J* = 4.8, 16.3 Hz), 3.75 (1H, *J* = 4.8, 6.7 Hz)	7.20–7.40 m (5H), 6.06 bs (1H)
8a	4.14 (5H)	4.33 (2H), 4.64 (2H)	3.78 s (3H), 5.86 s (1H)	–	7.34–7.68 m (5H)
8b	4.08 (5H)	4.24 (2H), 4.63 (2H)	2.27 s (3H), 3.75 s (3H), 6.04 s (1H)	–	–
9a	4.18 (5H)	4.21 (3H), 4.28 (1H)	2.83 s (3H)	3.26 (1H, *J* =13.5, 15.6 Hz), 3.47 (1H, *J* =9.6, 15.6 Hz), 3.97 (1H, *J* = 9.6, 13.5, Hz)	7.32–7.42 m (3H), 7.68–7.71 m (2H)
9b	4.14 (5H)	4.20 (1H), 4.26 (1H), 4.32 (1H), 4.47 (1H)	2.01 s (3H), 2.68 s (3H)	2.92 (1H, *J* = 13.2, 16.2 Hz), 2.97 (1H, *J* = 9.0, 16.2 Hz), 3.75 (1H, *J* = 9.0, 13.2 Hz)	–
10a	–	–	2.98 s (3H), 7,43 s (1H)	–	7.40 m (3H), 7.60 m (2H), 8.72 bs (1H)
10b	–	–	1.92 d (3H, *J* = 7.5 Hz), 3.14 s (3H), 6.87 q (1H, *J* = 7.5 Hz)	–	6.48 bs (1H)
11a	–	–	2.95 s (3H)	–	5.02 bs (2H), 7.50 m (3H), 7.89 m (2H)
11b	–	–	2.19 s (3H), 3.22 s (3H)	–	4.67 bs (2H)

group (preferably, of the C=O group linked with the Ph substituent) of the starting compounds **1a–c** (Scheme 7) resulting in hydrazones **14a–c**.

The subsequent nucleophilic attack by the CH_3NH fragment of hydrazones **14a–c** on the carbon atom of the second carbonyl group is accompanied, in our opinion, by an intramolecular redox process (see Scheme 7) resulting in intermediates **15a–c**, which are transformed into pyrazoles **8a,b** and hydrazones **10a**,**b**.

4. The formation of 4,5-dihydropyrazoles **9a,b** and hydrazides **11a**,**b** from 2-ferrocenylmethylidene-1,3-diones **1a–c** and *N*-methylhydrazine can be explained by the fragmentation of the starting dicarbonyl compounds to yield hydrazones **17a**,**b** according to a tentative Scheme 8.

The insertion products of *N*-methylhydrazine to 2-ferrocenylmethylidene-1,3-diketones have been isolated for the first time. This novel reaction may be regarded as a version of the Michael reaction, which allows preparation of (i) β-ferrocenyl-β-hydrazinoketones and (ii) 1-hydrazinoalkyl-substituted ferrocene derivatives. The synthetic potential of this type of reactions deserves undoubtedly more detailed studies.

Table 2

^{13}C NMR spectral data of compounds **7a–d**, **8a,b**, **9a,b**, **10a,** and **11a** (**δ**, ppm).

Compound	C_5H_5	C_5H_4	$C_{ipso}Fc$	CH_3	CH, CH=	Ph	CH_2	C, C=O
7a	68.91	67.30, 67.74, 68.09, 68.23	85.84	38.03	53.04	128.42, 128.51, 128.78, 129.78, 132.99	43.77	137.63, 137.77, 187. 01, 197.90
7b	68.15	66.42, 67.29, 67.64, 68.33	86.63	20.49 23.11, 31.58	52.89	–	41.29	170.23,176.15
7c	68.27	66.38, 67.41, 67.73, 67.82	87.47	20.60, 32.93	51.39	127.45, 127.78, 128.34	41.97	132.98, 174.19, 198.50
7d	68.33	66.19, 67.58, 67.64, 67.87	87.80	13.96, 39.46	60.43	127.30, 127.97, 129.88	40.65, 53.35	134.95, 170.91, 171.78
8a	69.49	68.19, 68.86	78.68	37.76	102.68	125.43, 127.48, 128.48	–	134.28, 142.83, 148.03
8b	69.38	66.30, 68.18	78.97	15.21, 35.88	103.03	–	–	139.02, 148.94
9a	69.04	67.87, 69.02	79.86	41.13	55.01	126.84, 128.66, 129.98	42.81	132.17, 134.13
9b	68.48	65.62, 68.14, 68.35, 70.19	79.17	16.57, 42.07	54.44	–	43.31	130.72
10a	–	–	–	34.37	138.21	125.64, 129.63, 136.38	–	130.50
11a	–	–	–	33.80	–	125.91, 130.59, 132. 51	–	134.89, 172.85

EXPERIMENTAL

The ^{1}H and ^{13}C NMR spectra were recorded on a Unity Inova Varian spectrometer (300 and 75 MHz) for solutions in $CDCl_3$with Me_4Si as the internal standard. The NMR spectroscopic data are listed in Tables 1 and 2. The mass spectra were obtained on a Varian MAT CH-6 instrument (EI MS, 70 eV).

Elemental analyses were performed by Galbraith Laboratories, Knoxville. The mass spectrometric data, data from

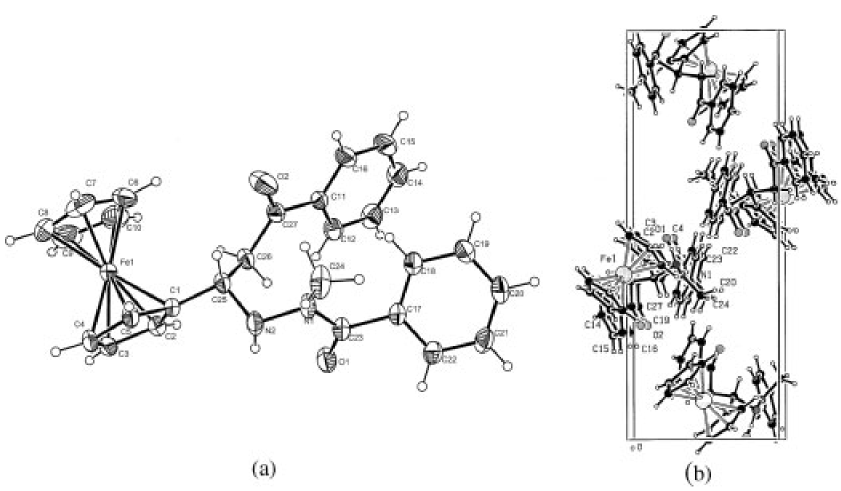


Figure 2. (a) Crystal structure of **7a**. Selected bond lengths (Å): N(1)-N(2)= 1.435(3); C(23)-O(1) = 1.233(3); N(1)-C(24) = 1.462(4); N(1)-C(23) = 1.350(3); N(2)-C(25) = 1.483(3); C(25)-C(26) = 1.535(3); C(26)-C(27) = 1.510(3); C(27)-O(2) = 1.211(3). Selected bond angles (°): O(1)-C(23)-N(1) = 121.0(2); C(23)-N(1)-N(2) = 116.5(2); N(1)-N(2)-C(25) = 111.4(2); C(25)-C(26)-C(27) = 112.1(2); C(26)-C(27)-O(2) = 120.2(2). (b) Crystal packing of **7a**.

Table 3

Elemental analysis data for the compounds **1c**, **7a–d, 8a,b, and 9a,b**.

Compound	Yield (%)	M.p. (°C)	Found (%), calculated (%) C	H	Fe	N	MS, *m/z* (M^+)	Molecular formula
1c	76	168–169	70.27	5.13	15.46	–	358	$C_{21}H_{18}FeO_2$
			70.41	5.06	15.60			
7a	51	208–210	69.39	5.54	12.07	6.05	466	$C_{27}H_{26}FeN_2O_2$
			69.54	5.62	11.98	6.00		
7b	50	170–171	59.51	6.53	16.43	8.11	342	$C_{17}H_{22}$ FeN_2O_2
			59.66	6.48	16.32	8.19		
7c	25	Oil	65.45	6.02	13.74	6.77	404	$C_{22}H_{24}FeN_2O_2$
			65.36	5.98	13.82	6.92		
7d	27	Oil	65.22	5.82	13.91	6.99	404	$C_{22}H_{24}FeN_2O_2$
			65.36	5.98	13.82	6.92		
8a	15	168–169	70.31	5.22	16.40	8.06	342	$C_{20}H_{18}FeN_2$
			70.20	5.30	16.32	8.18		
8b	16	137–138	64.19	5.83	20.02	9.86	280	$C_{15}H_{16}FeN_2$
			64.31	5.76	19.93	10.00		
9a	16	145–146	69.63	5.91	16.42	8.02	344	$C_{20}H_{20}FeN_2$
			69.78	5.86	16.23	8.13		
9b	14	124–125	63.94	6.26	19.71	9.79	282	$C_{15}H_{18}FeN_2$
			63.85	6.43	19.80	9.92		

elemental analyses, yields, and melting points of the compounds obtained are given in Table 3. Column chromatography was carried out on alumina (Brockmann activity III).

The following reagents were purchased from Aldrich: ferrocenecarbaldehyde, 99%; dibenzoylmethane, 98%; 2,4-pentanedione, 99+%; 1-benzoylacetone, 99%; methylhydrazine, 98%.

3-Ferrocenylmethylidene-1,3-diphenylpropane-1,3-dione 1a, 3-ferrocenylmethylidenepentane-2,4-dione 1b. These compounds were prepared by condensation of ferrocenecarbaldehyde with dibenzoylmethane, pentane-2,4-dione, respectively, in benzene in the presence of piperidinium acetate [16,17]. The physical and ^{1}H NMR spectroscopic characteristics of compounds 1a,b were in accord with the literature data [18,19].

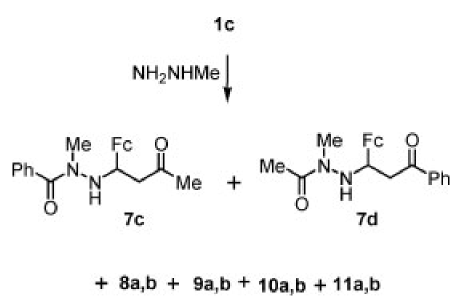
Condensation of ferrocenecarboxaldehyde with 1-benzoylacetone. A mixture of FcCHO (4.3 g, 20 mmol), 1-benzoylacetone (4.86 g, 30 mmol), piperidine (1 mL), pyridine (1 mL), and AcOH (2 mL) in dry benzene (100 mL) was refluxed for 12 h. The reaction mixture was washed with 5% HCl to remove the amines, and the organic layer was concentrated to dryness. Diethyl ether (100 mL) was added to the residue, the precipitate was filtered off, and dried on a filter to give (*Z*)-2-ferrocenylmethylidene-1-phenylbutane-1,3-dione **1c**, yield 5.8 g (81%), violet powder, mp 162–164°C. Subsequent chromatography on Al_2O_3 (hexane/dichloromethane, 4:1) gave 5.44 g (76%) compound **1c**, red crystals, mp 168–169 (lit. [19] 173)°C.

Reactions of 3-ferrocenylmethylidene-1,3-diphenylpropane-1,3-dione 1a or 3-ferrocenylme-thylidenepentane-2,4-dione 1b with *N*-methylhydrazine. A mixture of 1,3-diketone **1a** (2.10 g, 5 mmol) or **1b** (1.48 g, 5 mmol) and *N*-methylhydrazine (1.0 mL) in ethanol (15 mL) was stirred for 18 h at ambient temperature in an inert atmosphere. Yellow crystals of compounds **7a** or **7b** that sedimented were filtered off, washed with ethanol (2 × 5 mL), and dried in air. The yield of compound **7a** was 1.19 g (51%) and **7b** (0.86 g, 50.3%). The filtrates were concentrated *in vacuo* and the residues were chromatographed on alumina (hexane–ether, 3:1) to yield: (1) from **1a—**benzaldehyde *N*-methylhydrazone (**10a**) (0.07 g, 14%, colorless oil [20,21]), *N*′-methylbenzohydrazide **11a** (0.05 g, 12%, yellow oil [22,23]), and pyrazoles **8a** (yellow powder, 0.26 g, 15%) and **9a** (yellow powder, 0.27 g, 16%); (2) from **1b—**compounds **10b** (0.02 g, 10%, colorless oil [20,21]), **11b** (0.022 g, 9%, colorless oil [22,23]), **8b** (0.22 g, 16%), **9b** (0.20 g, 14%).

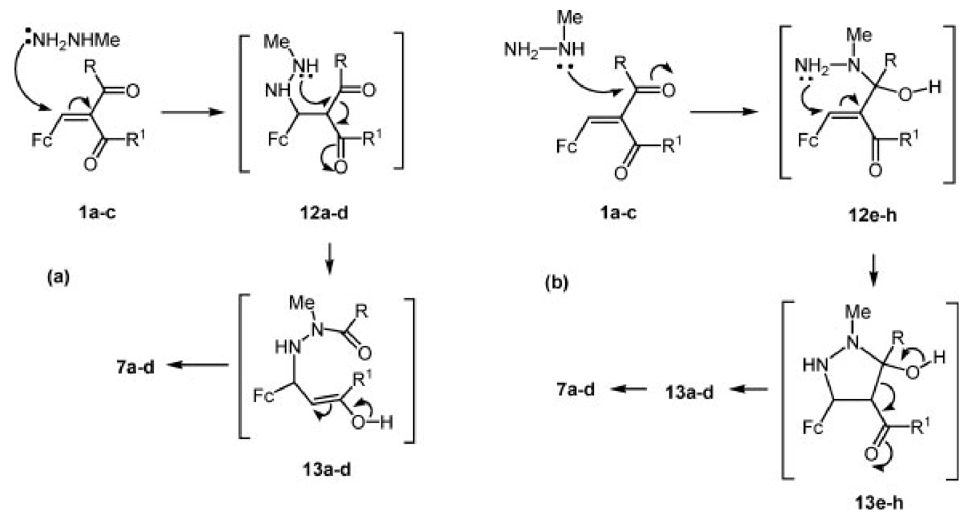
Reaction of *(Z)*-2-ferrocenylmethylidene-1-phenylbutane-1,3-dione 1c with *N*-methylhydrazine. The reaction of compound **1c** (1.79 g, 5 mmol) with *N*-methylhydrazine (1.0 mL) was carried out similarly. Work-up of the reaction mixture as described earlier and column chromatography afforded compounds **10a** + **10b** (0.06 g, 10%, ~1:1), **11a** + **11b** (0.078 g, 13%, ~1:1), **8a** (0.24 g, 14%), **9a** (0.28 g, 16%), and **7c**,**d** (1.17 g, 58%, ~1:1). Compounds **7c,d** were separated by preparative TLC on silica gel (hexane–diethyl ether, 5:1). The yield of compound **7c** was 0.50 g (25%) and that of **7d**, 0.54 g (27%).

Determining the crystal structure. The unit cell parameters and the X-ray diffraction intensities were recorded on a

Scheme 5



Scheme 6

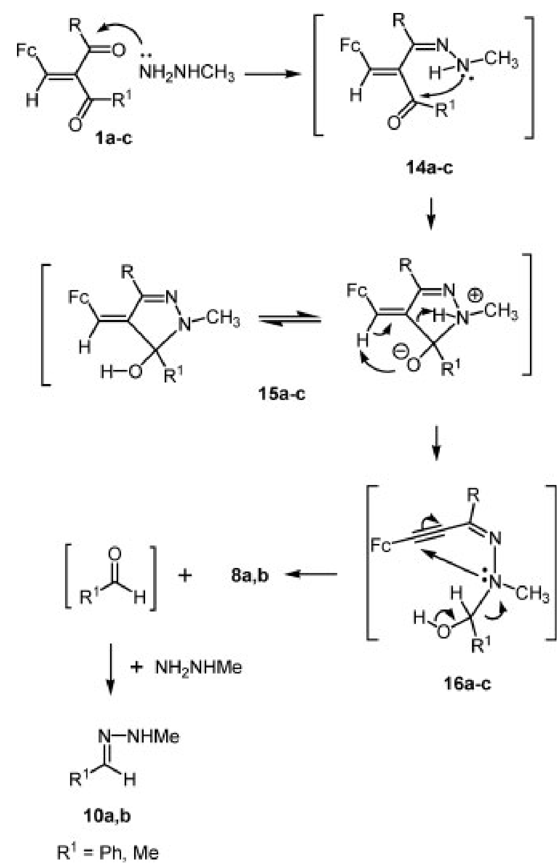


R = R[1] = Ph (**a,e**); R = R[1] = Me (**b,f**); R = Ph, R[1] = Me (**c,g**); R = Me, R[1] = Ph (**d,h**)

Siemens P4 diffractometer. The structures of compounds **1c** and **7a** were solved by direct methods (SHELXS-97 [24]) and refined using full-matrix least squares on F^2.

Crystal data for $C_{21}H_{18}FeO_2$ (**1c**): $M = 358.20$ g mol^{-1}, monoclinic P21/n, $a = 10.044(2)$, $b = 17.091(4)$, $c = 10.6900(17)$ Å, $\alpha = 90$, $\beta = 109.360(14)$, $\gamma = 90°$, $V = 1731.3(6)$ Å^3, $T = 298(2)$ K, $Z = 4$, $\rho = 1.374$ Mg/m^3, λ (Mo–Kα) = 0.71073 Å, $F(000) = 744$, absorption coefficient 0.880 mm^{-1}, index ranges $-1 \leq h \leq 13$, $-1 \leq k \leq 23$, $-14 \leq l \leq 14$, scan range $2.34 \leq \theta \leq 28.99°$, 4200 independent reflections, $R_{int} = 0.1571$, 5533 total reflections, 218 refinable parameters, final R indices [$I > 2\sigma(I)$] $R_1 = 0.0727$, $wR_2 = 0.1340$, R indices (all data) $R_1 = 0.1725$, $wR_2 = 0.1781$, largest difference peak and hole 0.503/−0.399 e Å^{-3}.

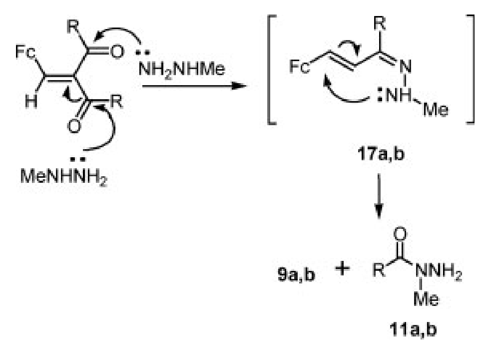
Scheme 7



Crystal data for $C_{27}H_{26}FeN_2O_2$ (**7a**): $M = 466.35$ g mol^{-1}, monoclinic P2(1)/n, $a = 7.8840(8)$, $b = 21.2430(19)$, $c = 13.4820(14)$ Å, $\alpha = 90$, $\beta = 91.506(9)$, $\gamma = 90°$, $V = 2257.2(4)$ Å^3, $T = 293(2)$ K, $Z = 4$, $\rho = 1.372$ Mg/m^3, λ (Mo–Kα) = 0.71073 Å, $F(000) = 976$, absorption coefficient 0.695 mm^{-1}, index ranges $-1 \leq h \leq 10$, $-1 \leq k \leq 27$, $-17 \leq l \leq 17$, scan range $1.79 \leq \theta \leq 27.00°$, 4912 independent reflections, $R_{int} = 0.0415$, 6307 total reflections, 247 refinable parameters, final R indices [$I > 2\sigma(I)$] $R_1 = 0.0473$, $wR_2 = 0.1169$, R indices (all data) $R_1 = 0.0746$, $wR_2 = 0.1321$, largest difference peak and hole 0.280/−0.271 e·Å^{-3}.

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 689870 for compound **1c** and no. 687244 for

Scheme 8



compound **7a**. These data can be obtained free of charge at http://www.ccdc.cam.ac.uk/const/retrieving.html.

Acknowledgments. This work was supported by the grant DGAPA–UNAM (Mexico, grant IN 214209).

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