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Activation and Substitution of 1-Ferrocenylalkylamines with Allenones: Application to Three-Component Synthesis of 4-(1-Ferrocenylalkyl)pyrazoles

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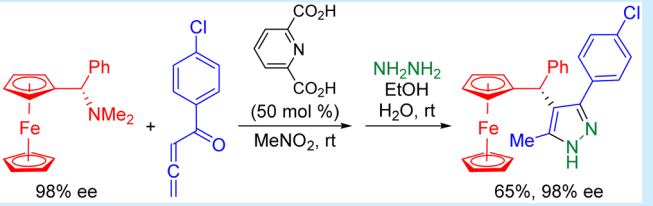
Supporting Information

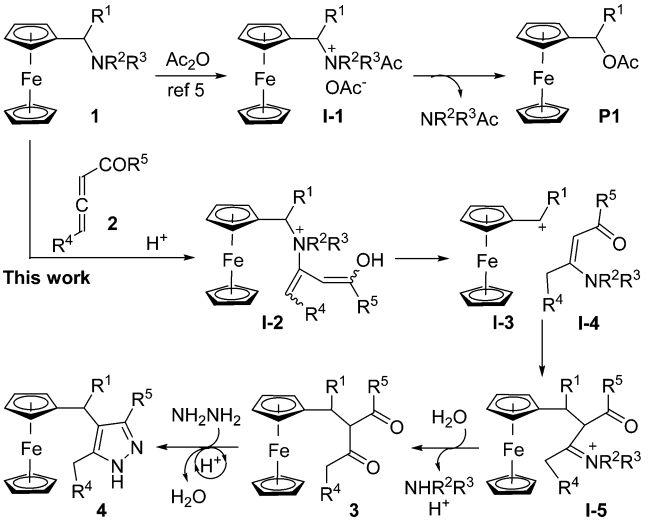
ABSTRACT: A one-pot, two-step three-component synthesis of 4-(1-ferrocenylalkyl)pyrazoles has been developed involving activation and substitution of 1-ferrocenylalkylamines with allenones under mild conditions. A range of 1-ferrocenylalkylamines reacted with allenones in the presence of dipicolinic acid at room temperature without extrusion of air and moisture, and the resulting crude products were treated with hydrazine to afford structurally diverse 4-(1-ferrocenylalkyl)-pyrazoles in moderate to good yields. Moreover, the three-component reaction was successfully extended to an enantioenriched α-ferrocenylbenzylamine with complete retention of configuration.



Conversion of 1-ferrocenylalkylamines to the corresponding ammonium salts followed by nucleophilic substitution is a well-known two-step sequence for the preparation of 1-ferrocenylalkyl-containing compounds,[1] which have found wide applications in catalysis, materials, and medicines.[2] To improve the step economy and facilitate the synthetic manipulation, a few electrophiles[3] and acids[4] have been identified to activate the amino groups of 1-ferrocenylalkylamines in the presence of nucleophiles. Particularly noteworthy is the use of acetic anhydride, the acetyl group of which activates the amino groups of 1-ferrocenylalkylamines and the rest of which, the acetoxy group, participates in nucleophilic substitution to afford esters (Scheme 1).[5] Clearly, such type of single reagent-mediated process exhibits higher step and atom economy relative to other substitution reactions of 1-ferrocenylalkylamines. Herein we report a conceptually new substitution reaction of 1-ferrocenylalkylamines, wherein nucleophiles are generated in situ through activation of electrophiles by the amino groups.

In continuation of our exploration of the synthetic utilities of C−N bond cleavage,[6,7] we designed a new type of direct substitution reaction of 1-ferrocenylalkylamines taking advantage of activation of allenones by the amino groups.[8,9] As depicted in Scheme 1, nucleophilic addition of 1-ferrocenylalkylamine **1** to allenone **2** would generate ammonium salt **I-2**, which would undergo 1,3-rearrangement, involving sequential C−N bond cleavage and C−C bond formation, followed by hydrolysis to afford 2-(1-ferrocenylalkyl)-1,3-diketone **3**. In this process, electrophilic allenone **2** would be activated by the amino group to yield enamine ***I*-4** as a carbon nucleophile. An acid was proposed to accelerate the process by activating allenone **2** and, furthermore, catalyze the transformation of 2-(1-ferrocenylalkyl)-1,3-diketone **3** into 4-(1-ferrocenylalkyl)-pyrazole **4**.[10] Thus, a one-pot, two-step, three-component synthesis was expected to provide unprecedented yet convenient access to 4-(1-ferrocenylalkyl)pyrazoles, particularly chiral ones. It is noteworthy that some 4-(ferrocenylmethyl)-pyrazole/metal complexes exhibit growth inhibitory activity against human cancer cell lines,[11] promising anion-sensing properties,[12] and interesting electrochemical behaviors.[13] These simple 4-(ferrocenylmethyl)pyrazoles were reported to be

Scheme 1. Plausible Mechanism for the Synthesis of 4-(1-Ferrocenylalkyl)pyrazoles



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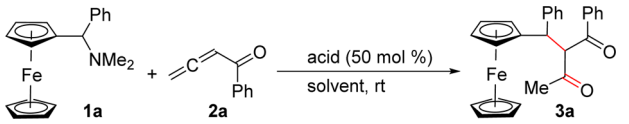
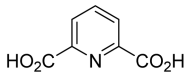
prepared in two steps by substitution of ferrocenylmethanol with 1,3-diketones followed by condensation with hydrazine.

To test the above hypothesis, we examined a number of readily accessible Lewis acids and Brønsted acids (50 mol %) to catalyze the reaction between α-ferrocenylbenzylamine **1a** and allenone **2a** in nitromethane at room temperature without extrusion of air and moisture (Table 1, entries 1−14). The

Table 1. Optimization of the Reaction Conditions[a]



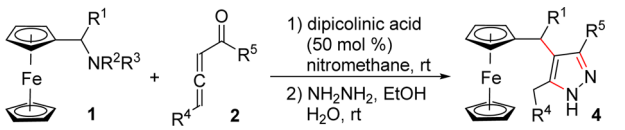
entry	acid	solvent	yield (%)[b]
1	none	nitromethane	trace
2	$AlCl_3$	nitromethane	trace
3	$FeCl_3$	nitromethane	trace
4	$CuBr_2$	nitromethane	26
5	$ZnCl_2$	nitromethane	trace
6	HCl	nitromethane	0
7	H_2SO_4	nitromethane	0
8	H_3PO_4	nitromethane	27
9	TsOH	nitromethane	0
10	$PhCO_2H$	nitromethane	54
11	HOAc	nitromethane	34
12	$HO_2CCH_2CH_2CO_2H$	nitromethane	66
13	$HO_2CCH_2CH(OH)CO_2H$	nitromethane	63
			
14	dipicolinic acid	nitromethane	70
15	dipicolinic acid	acetonitrile	40
16	dipicolinic acid	*N*,*N*-dimethylformamide	9
17	dipicolinic acid	dimethyl sulfoxide	48
18	dipicolinic acid	dioxane	55
19	dipicolinic acid	tetrahydrofuran	47
20	dipicolinic acid	1,2-dichloroethane	35
21	dipicolinic acid	chloroform	37
22	dipicolinic acid	toluene	42
23[c]	dipicolinic acid	nitromethane	50
24[d]	dipicolinic acid	nitromethane	30
25[e]	dipicolinic acid	nitromethane	42

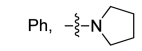
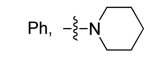
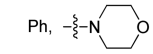
[a]Reaction conditions: **1a** (0.10 mmol), **2a** (0.12 mmol), acid (0.050 mmol), solvent (2.0 mL), rt, 12 h. [b]Isolated yield. [c]The reaction was run at 50 °C. [d]10 mol % dipicolinic acid was used. [e]100 mol % dipicolinic acid was used.

reaction efficiency was dramatically affected by the acid catalysts, and gratifyingly, the use of dipicolinic acid afforded the desired 2-(α-ferrocenylbenzyl)-1,3-diketone **3a** in the highest yield: 70% (Table 1, entry 14).[14] Replacing nitromethane with a few other solvents led to lower yields (Table 1, entries 15−22). Moreover, the yield decreased dramatically when elevating the temperature to 50 °C or decreasing the catalyst loading to 10 mol % (Table 1, entries 23 and 24). The requirement of a high catalyst loading (50 mol %) was rationalized by the partial consumption of dipicolinic acid with two amines, α-ferrocenylbenzylamine **1a**, and dimethylamine (the sole byproduct of the reaction). Nevertheless, the yield also decreased when increasing the catalyst loading because more α-ferrocenylbenzylamine **1a** was consumed by the acid catalyst (Table 1, entry 25).

After the reaction of α-ferrocenylbenzylamine **1a** with allenone **2a** in nitromethane proceeded at room temperature for 12 h, the nitromethane solvent was removed under reduced pressure and the resulting crude product was treated with hydrazine hydrate in ethanol at room temperature for 12 h. To our delight, the desired 4-(α-ferrocenylbenzyl)pyrazole **4a** was isolated in 75% yield (Table 2, entry 1).[15] The one-pot, two-

Table 2. Three-Component Synthesis of 4-(1-Ferrocenylalkyl)pyrazoles[a]



entry	**1**	R^1, NR^2R^3	**2**	R^4, R^5	**4**	yield (%)[b]
1	**1a**	Ph, NMe_2	**2a**	H, Ph	**4a**	75
2	**1b**	Ph, 	**2a**	H, Ph	**4a**	50
3	**1c**	Ph, 	**2a**	H, Ph	**4a**	72
4	**1d**	Ph, 	**2a**	H, Ph	**4a**	75
5	**1e**	Ph, N(Me)Ph	**2a**	H, Ph	**4a**	0
6	**1f**	Ph, NHMe	**2a**	H, Ph	**4a**	54
7	**1g**	Ph, NH_2	**2a**	H, Ph	**4a**	31
8	**1h**	4-MeC_6H_4, NMe_2	**2a**	H, Ph	**4b**	65
9	**1i**	PMP, NMe_2	**2a**	H, Ph	**4c**	57
10	**1j**	4-ClC_6H_4, NMe_2	**2a**	H, Ph	**4d**	74
11	**1k**	3-MeC_6H_4, NMe_2	**2a**	H, Ph	**4e**	60
12	**1l**	2-MeC_6H_4, NMe_2	**2a**	H, Ph	**4f**	59
13	**1m**	2-naphthyl, NMe_2	**2a**	H, Ph	**4g**	78
14	**1n**	2-thienyl, NMe_2	**2a**	H, Ph	**4h**	32
15	**1o**	Et, NMe_2	**2a**	H, Ph	**4i**	52
16	**1p**	$Me(CH_2)_{10}$, NMe_2	**2a**	H, Ph	**4j**	68
17	**1q**	H, NMe_2	**2a**	H, Ph	**4k**	0
18	**1a**	Ph, NMe_2	**2b**	H, 4-MeC_6H_4	**4l**	58
19	**1a**	Ph, NMe_2	**2c**	H, PMP	**4m**	72
20	**1a**	Ph, NMe_2	**2d**	H, 4-ClC_6H_4	**4n**	68
21	**1a**	Ph, NMe_2	**2e**	H, 3-MeC_6H_4	**4o**	49
22	**1a**	Ph, NMe_2	**2f**	H, 2-MeC_6H_4	**4p**	57
23	**1a**	Ph, NMe_2	**2g**	H, 2-naphthyl	**4q**	62
24	**1a**	Ph, NMe_2	**2h**	H, 2-thienyl	**4r**	51
25	**1a**	Ph, NMe_2	**2i**	H, $PhCH_2CH_2$	**4s**	68
26	**1a**	Ph, NMe_2	**2j**	H, cyclohexyl	**4t**	63
27	**1a**	Ph, NMe_2	**2k**	H, $Me(CH_2)_{10}$	**4u**	84
28	**1a**	Ph, NMe_2	**2l**	Me, Ph	**4v**	54
29	**1a**	Ph, NMe_2	**2m**	Ph, Ph	**4w**	0

[a]Reaction conditions: (1) **1** (0.20 mmol), **2** (0.24 mmol), acid (0.10 mmol), nitromethane (4.0 mL), rt, 12 h; (2) 85% aqueous hydrazine (0.20 mL), ethanol (2.0 mL), rt, 12 h. [b]Isolated yield.

step, three-component synthesis of 4-(α-ferrocenylbenzyl)-pyrazole **4a** was successfully extended to trialkylamines **1b−d** but not to less nucleophilic aromatic amine **1e** (Table 2, entries 2−5). Secondary amine **1f** and primary amine **1g** could also participate in the three-component reaction to afford 4-(α-ferrocenylbenzyl)pyrazole **4a** but in lower yields (Table 2, entries 6 and 7). A range of 1-ferrocenylalkylamines, including α-ferrocenylbenzylamines, reacted with allenone **2a** and

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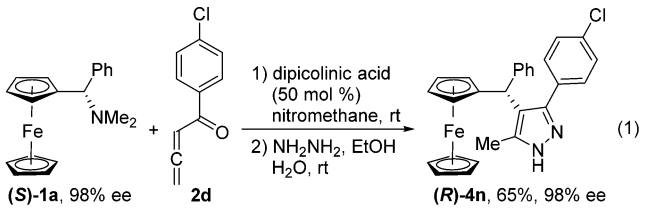
hydrazine to afford structurally diverse 4-(1-ferrocenylalkyl)-pyrazoles in moderate to good yields (Table 2, entries 8−16). The desired reaction failed to occur with ferrocenylmethylamine **1q** due to the inferior reactivity regarding C−N bond cleavage under the standard conditions (Table 2, entry 17). The three-component reaction worked well with a range of terminal allenyl aryl ketones and allenyl alkyl ketones (Table 2, entries 18−27). While γ-methylallenone **2l** participated in the three-component reaction to afford 4-(α-ferrocenylbenzyl)-pyrazole **4v** in 54% yield, a complex mixture was observed for the corresponding reaction with γ-phenylallenone **2m** (Table 2, entries 28 and 29).

The one-pot, two-step, three-component reaction was further extended to enantioenriched α-ferrocenylbenzylamine (*S*)-**1a**, and the desired 4-(α-ferrocenylbenzyl)pyrazole (*R*)-**4n** was obtained in 65% yield with complete retention of configuration (eq 1). The structure and the absolute configuration of product



(1)

(*R*)-**4n** were assigned by single crystal X-ray analysis (CCDC 1546895).[16] The stereochemical outcome can be rationalized by the participation of iron in the formation of a chiral α-ferrocenylbenzyl cation from the enantioenriched α-ferrocenylbenzylamine as depicted in Scheme 1.[17]

In summary, we have developed a one-pot, two-step, three-component synthesis of 4-(1-ferrocenylalkyl)pyrazoles involving activation and substitution of 1-ferrocenylalkylamines with allenones under mild conditions. A range of 1-ferrocenylalkylamines reacted with allenones in the presence of dipicolinic acid at room temperature without extrusion of air and moisture, and the resulting crude products were treated with hydrazine to afford structurally diverse 4-(1-ferrocenylalkyl)pyrazoles in moderate to good yields. Moreover, the three-component reaction was successfully extended to an enantioenriched α-ferrocenylbenzylamine with complete retention of configuration.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.7b02830.

Experimental procedures, characterization data, copies of ^{1}H NMR and ^{13}C NMR spectra and HPLC traces, and crystal data of compound (*R*)-**4n** (PDF)

Crystallographic data for (*R*)-**4n** (CIF)

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Notes

The authors declare no competing financial interest.

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(14) The desired substitution reaction was not observed when replacing α-ferrocenylbenzylamine **1a** with α-ferrocenylbenzyl alcohol or *N*,*N*-dimethyldiphenylmethanamine. On the other hand, the substitution of α-ferrocenylbenzylamine **1a** with $PhCOCH_2COMe$ did not occur under the standard conditions. Therefore, allenone **2a** is unlikely to be converted to $PhCOCH_2COMe$ prior to the C−C bond formation via hydrolysis of enamine intermediate **I-4a** ($R^2 = R^3 = Me$, $R^4 = H$, $R^5 = Ph$) (Scheme 1).

(15) The desired pyrazole was not obtained when replacing hydrazine with a monosubstituted hydrazine, such as phenylhydrazine and *p*-toluenesulfonyl hydrazide.

(16) For details, see the Supporting Information.

(17) For a review, see: (a) Gleiter, R.; Bleiholder, C.; Rominger, F. *Organometallics* **2007**, *26*, 4850. For earlier reports, see: (b) Richards, J. H.; Hill, E. A. *J. Am. Chem. Soc.* **1959**, *81*, 3484. (c) Hill, E. A.; Richards, J. H. *J. Am. Chem. Soc.* **1961**, *83*, 3840. (d) Traylor, T. G.; Ware, J. C. *J. Am. Chem. Soc.* **1967**, *89*, 2304. (e) Gokel, G. W.; Marquarding, D.; Ruch, E.; Ugi, I. K. *J. Org. Chem.* **1972**, *37*, 3052.

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