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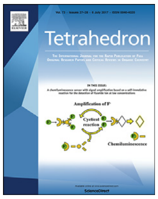

The reactions of 1,1-diarylallenes with *N*-acyliminium cations generated from hydroxylactams

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ABSTRACT

The first example of the reactions of 1,1-diarylallenes with *N*-acyliminium cations is described. 2-Aryl-3-(3-aryl-1*H*-inden-2-yl)isoindolin-1-ones and 6-methylene-5,5-diaryl-6,6a-dihydroisoindolo[2,1-*a*]quinolin-11(5*H*)-ones were prepared by $BF_3 \cdot OEt_2$-mediated reactions of 1,1-diarylallenes with the *N*-acyliminium cations generated from 2-aryl-3-hydroxyisoindolin-1-ones. 2-Aryl-3-(3-aryl-1*H*-inden-2-yl)isoindolin-1-ones underwent an intramolecular cyclization on treatment with methanesulfonic acid with the formation of compounds exhibiting the indeno[2,1-*c*]isoindolo[2,1-*a*]quinoline skeleton.

1. Introduction

Allenes are the simplest class of cumulenes, which possess unique chemical properties.[1,2] The following main reaction modes have been observed in the chemistry of allenes: [2 + 2],[3] [3 + 2],[4] [3 + 3],[5] [4 + 2][6] and [4 + 3][7] cycloadditions to double bonds of allenes, free radical additions,[8] metal-catalyzed additions to allenes[9] and intramolecular cyclizations.[10] However, reactions of allenes with *N*-acyliminium cations have not been studied so far. *N*-Acyliminium cations are known as important intermediates in organic synthesis for the construction of carbon-carbon bonds.[11] Numerous examples of intramolecular cyclizations based on *N*-acyliminium cation can be found in the synthesis of alkaloid derivatives.[12] Recently, we reported the first examples of Lewis acid initiated reactions of *N*-acyliminium cations with vinylidenecyclopropanes[13] and cyclopropenes.[14]

In continuation of our earlier work, we have studied the reactions of 1,1-disubstituted allenes with *N*-acyliminium cations. In the present work, we show for the first time that 1,1-diarylallenes react with *N*-acyliminium cations generated from 2-aryl-3-hydroxyisoindolin-1-ones in the presence of $BF_3 \cdot OEt_2$ to give the corresponding 2-aryl-3-(3-aryl-1*H*-inden-2-yl)isoindolin-1-ones and 5,5-diaryl-6-methylene-6,6a-dihydroisoindolo[2,1-*a*]quinolin-11(5*H*)-ones.

2. Results and discussion

We initiated our investigation by using 1,1-diphenylpropa-1,2-diene (**1a**) and 3-hydroxy-2-phenylisoindolin-1-one (**2b**) as the model substrates. Of the Lewis acids and solvents screened, the combination of $BF_3 \cdot Et_2O$ and anhydrous dichloromethane are the most suitable conditions for the generation of the *N*-acyliminium cation from hydroxylactam **2b** and produced the best result in this reaction. The reaction was carried out at room temperature under an argon atmosphere. After stirring for 2 h and extractive work-up, the formation of a single product was observed with complete disappearance of starting materials by TLC analysis. The desired compound **3ab** was isolated from the reaction mixture by recrystallization from methanol in 72% yield. (Table 1, entry 2).

The structure of adduct **3ab** was determined by ^1H NMR and ^{13}C

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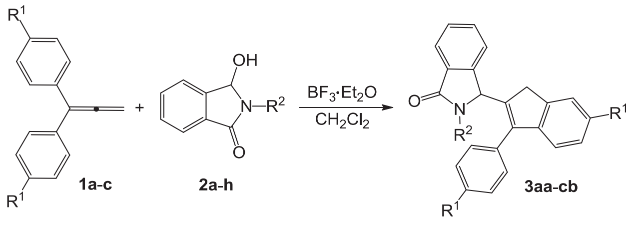
Table 1
Reactions of allenes **1a**–**c** with hydroxylactams **2a**–**h**.[a]



Entry	R^1	R^2	Yield, % (product)[b]
1	H (**1a**)	Ph (**2a**)	61 (**3aa**)
2	H (**1a**)	4-MeC_6H_4 (**2b**)	72 (**3ab**)
3	H (**1a**)	4-$MeOC_6H_4$ (**2c**)	69 (**3ac**)
4	H (**1a**)	4-$PhOC_6H_4$ (**2d**)	57 (**3ad**)
5	H (**1a**)	4-ClC_6H_4 (**2e**)	60 (**3ae**)
6	H (**1a**)	4-IC_6H_4 (**2f**)	65 (**3af**)
7	H (**1a**)	4-ClBn (**2g**)	76 (**3ag**)
8	H (**1a**)	2,4-$(MeO)_2C_6H_3$ (**2h**)	–[c]
9	Me (**1b**)	4-MeC_6H_4 (**2b**)	81 (**3bb**)
10	Me (**1b**)	4-$MeOC_6H_4$ (**2c**)	65 (**3bc**)
11	MeO (**1c**)	4-MeC_6H_4 (**2b**)	32 (**3cb**)

[a] Reaction conditions: **1** (0.5 mmol), **2** (0.5 mmol), $BF_3 \cdot Et_2O$ (0.55 mmol), CH_2Cl_2 (8 mL), 2 h, RT.
[b] Isolated yield.
[c] Intractable fluorescent material is formed.

NMR spectroscopy. The ^1H NMR spectrum of the compound **3ab** displayed the signal for *H*-C(3) at δ 6.24 ppm (s), two doublet signals of protons belonging to the CH_2 group of the indene fragment at δ 3.15 and 2.91 ppm with a coupling constant 22.9 Hz, and the signal of the methyl group attached to the aromatic ring at δ 2.31 ppm (s). All the aromatic hydrogens were situated in 6.89–7.59 ppm. Analysis of the ^{13}C NMR spectrum supported by DEPT data revealed the existence of the signals of nine quaternary carbon atoms. The aliphatic carbon atoms CH, CH_2 and CH_3 of the indene **3ab** gave peaks at δ 59.7, 35.7 and 20.9 ppm, respectively. Moreover, the structure of **3ab** was verified by X-ray diffraction analysis. (Fig. 1).

The reactions of allenes **1a**–**c** with hydroxylactams **2a**–**h** were conducted in dichloromethane under similar conditions to those described above (Table 1). The reactions proceeded smoothly at room temperature to give the corresponding indene derivatives **3**. The presence of electron-donating or electron-withdrawing groups on the phenyl ring of the hydroxylactams **2** had a minor effect on the yields of the produced indenes **3**. For example, 1,1-diphenylallene (**1a**) reacted with hydroxylactams **2a**–**h** having electron-donating or electron-withdrawing substituents on the benzene ring to give the corresponding 2-aryl-3-(3-phenyl-1*H*-inden-2-yl)isoindolin-1-ones **3aa**–**ag** in 57–76% yields (Table 1, entries 1–7). Unfortunately, only intractable fluorescent material was formed by using 2-(2,4-dimethoxyphenyl)-3-hydroxyisoindolin-1-one (**2h**) as an *N*-acyliminium ion precursor, possibly due the presence of the electron-rich aromatic ring containing two electron-donating methoxy groups (Table 1, entry 8).

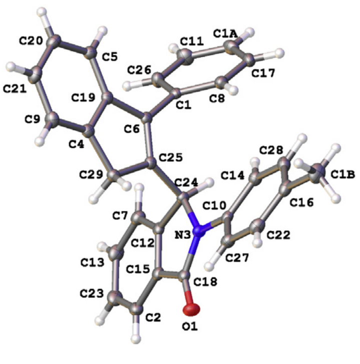
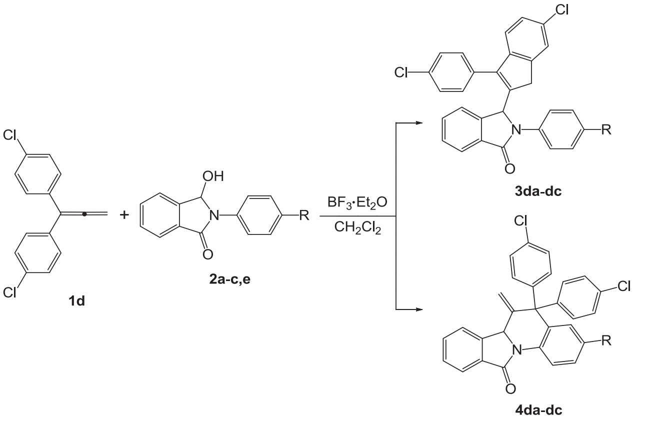


Fig. 1. X-ray structure of **3ab**.

Next, the reactions of allene **1b** with *N*-acyliminium cations generated from hydroxylactams **2b** and **2c** were investigated. The reaction of allene **1b** with **2b** in CH_2Cl_2 (RT, 2 h) in the presence of $BF_3 \cdot Et_2O$ led to the formation of adduct **3bb** in 81% yield (Table 1, entry 9). Similarly, the reaction of **1b** with hydroxylactam **2c** gave indene **3bc** in 65% yield (Table 1, entry 10). As shown in Table 1, compound **3bb** bearing a methyl substituent on the indene fragment was obtained in higher yield (81%) than the unsubstituted derivatives **3aa**–**ag**. The reaction of 1,1-bis(*p*-methoxyphenyl) propadiene (**1c**) with hydroxylactam **2b** produced the indene adduct **3cb** in lower yield (ca. 32%) (Table 1, entry 11). Attempts to obtain positive results in the reactions of allene **1c** and hydroxylactams **2a**, **2c** and **2e** were unsuccessful. In all cases, it was found that the crude reaction mixture contained the starting hydroxylactams **2** along with the complete disappearance of allene **1c**.

For the next step in our study, the reactions of 1,1-bis(*p*-chlorophenyl)propadiene (**1d**) with *N*-acyliminium cations (generated from hydroxylactams **2a**–**c**) were investigated (Table 2). Under an argon atmosphere, compound **1d** was reacted with an equimolar amount of **2b** in the presence of $BF_3 \cdot Et_2O$ (1.1 equiv) in anhydrous dichloromethane at ambient temperature for 2 h. The crude reaction mixture was examined by ^1H NMR spectroscopy. Surprisingly, from the ^1H NMR spectrum it was concluded that the reaction led to the formation of the fused tetracyclic adduct having an exocyclic C=C bond **4db** and indene **3db** in 3:1 ratio, respectively [Table 2, entry 2, the ratio was estimated from the ^1H NMR spectrum by integration of the *H*-C(6a) signal for **4db** and the *H*-C(3) signal for

Table 2
Reactions of allene **1d** with hydroxylactams **2a**–**c**,**e**.[a]



Entry	R	Products	Ratio of 4/3	Overall yield, %[b]
1	H (**2a**)	**3da** + **4da**	1:1[c]	62
2	Me (**2b**)	**3db** + **4db**	3:1[d]	67
3	MeO (**2c**)	**3dc** + **4dc**	1.6:1[e]	45
4	Cl (**2e**)	**3de**	–	48

[a] Reaction conditions: **1d** (0.5 mmol), **2** (0.5 mmol), $BF_3 \cdot Et_2O$ (0.55 mmol), CH_2Cl_2 (8 mL), 2 h, RT.
[b] Isolated yield.
[c] **3da** and **4da** were isolated in pure form by PTLC.
[d] **3db** and **4db** were isolated in pure form by PTLC.
[e] **3dc** and **4dc** were isolated in pure form by PTLC.