Tetrahedron Letters 55 (2014) 2022–2026

Contents lists available at ScienceDirect

Tetrahedron Letters

journal homepage: www.elsevier.com/locate/tetlet

Synthesis of indene derivatives via reactions of vinylidenecyclopropanes with the *N*-acyliminium cations generated from hydroxylactams

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ARTICLE INFO

Article history:
Received 23 November 2013
Revised 21 January 2014
Accepted 12 February 2014
Available online 20 February 2014

Keywords:
Hydroxylactams
Vinylidenecyclopropanes
N-Acyliminium cation
1*H*-Indenes
Lewis acid

ABSTRACT

A novel route for the synthesis of 1*H*-indene derivatives via the reactions of vinylidenecyclopropanes (VCPs) with the *N*-acyliminium cations generated from hydroxylactams is described.

The 1*H*-indene subunit appears in compounds displaying a considerable range of biological activity: cyclooxygenase-2 (COX-2) inhibitors,[1] oxytocin antagonists,[2] estrogen receptor modulators,[3] an 5-HT6 serotonin receptor[4] and in compounds with antiproliferative activity.[5] Indene derivatives are also used as precursors of metallocene complexes for catalytic polymerization processes and as functional materials.[6] Consequently, a number of approaches to the synthesis of the indene ring system have been developed, including new methods such as intramolecular cyclization of tetraaryl substituted 1,3-butadienes,[7] cycloaddition of methylenecyclopropanes with acetals,[8] cycloisomerizations of alkynes,[9] annulation of benzylic alcohols with alkynes,[10] rearrangement of *ortho*-(alkynyl)styrenes,[11] and cycloisomerization of arylvinylcyclopropenes.[12] Tsuji and co-workers have reported a novel synthetic method for the preparation of indenes by the reaction of aliphatic ketones with aryl-substituted alkynes in the presence of $NbCl_3(DME)$[13]

The chemistry of vinylidenecyclopropanes has been explored extensively. Novel intramolecular rearrangements and cycloaddition reactions have been studied.[14,15] However, reactions of vinylidenecyclopropanes with *N*-acyliminium cations have not been previously studied. *N*-Acyliminium ions are known as important reactive species in organic synthesis for the construction of carbon–carbon bonds.[16] Numerous examples of *N*-acyliminium ion based intramolecular cyclizations can be found in the synthesis of alkaloid derivatives.[17] Recently, Wang and Zhang reported the first examples of the Lewis acid catalyzed [4+2] cycloaddition reactions of *N*-acyliminium ions with alkenes.[18] In continuation of our earlier work,[19] we have studied the reactions of non-activated vinylidenecyclopropanes (VCPs) with *N*-acyliminium cations. In the present work we show for the first time that 1-(2-methylpropenylidene)-2,2-diarylcyclopropanes react with the *N*-acyliminium cations generated from hydroxylactams to give the corresponding 5-[2-methyl-1-(3-Ar^1-1*H*-inden-2-yl)prop-1-enyl]-1-Ar^2-1*H*-pyrrol-2(5*H*)-ones and 3-[2-methyl-1-(3-Ar^1-1*H*-inden-2-yl)prop-1-enyl]-2-Ar^2-isoindolin-1-ones in moderate yields. Of the Lewis acids and solvents screened, the combination of $BF_3{\cdot}OEt_2$ and dichloromethane produced the best results in these reactions.

In our initial studies, the reaction of **1a** with VCP **2a** was investigated. Under a nitrogen atmosphere, compound **1a** was reacted with an equimolar amount of **2a** in the presence of $BF_3{\cdot}OEt_2$ (1.0 equiv) in CH_2Cl_2 at ambient temperature for one hour, to give 3-{2-methyl-1-[6-methyl-3-(4-methylphenyl)-1*H*-inden-2-yl]prop-1-en-1-yl}-2-phenylisoindolin-1-one (**3a**) in 41%

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http://dx.doi.org/10.1016/j.tetlet.2014.02.039
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isolated yield (Table 1, entry 1). Although several other products could be seen in the TLC analysis of the reaction mixture, no other potential products were successfully isolated. When the reaction of **1a** with VCP **2a** was carried out at low temperature (−20 °C), the corresponding indene **3a** was produced in 36% yield. Under refluxing conditions, product **3a** was isolated in only 14% yield. The reactions of hydroxylactams **1** with VCPs **2** were carried out in dichloromethane under similar conditions to those described previously (Table 1). The reactions proceeded smoothly to give the corresponding indene derivatives **3** in moderate yields at room temperature. The presence of either electron-donating or electron-withdrawing substituents on the benzene ring of the VCPs **2** had only a slight effect upon the yields of the produced indenes **3**. For example, decreased yields of the indenes **3** were obtained by using VCPs **2** with electron-donating groups (MeO) on the benzene ring (Table 1, entries 2 and 4). The presence of electron-donating or electron-withdrawing groups on the phenyl ring of the hydroxylactams **1** also had a minor effect upon the yields of the produced indenes **3**. 2-[Bis(4-methoxyphenyl)methylene]-5,5-dimethyldihydrofuran-3(2*H*)-one (**4**) was isolated in 7–9% yields as the side product in all the cases of the reactions with bis(4-methoxyphenyl)vinylidenecyclopropane (**2d**). In cases where R^1 was a phenyl group, or R^2 a methyl group (VCPs **2e**–**g**), complicated reaction mixtures were formed under the standard conditions (Table 1, entries 10–12). Dihydrofuranone **4** is the oxidation product of VCP **2d**; its formation might occur either due to aerial oxygen or during chromatographic separation. The exact reaction mechanism for the formation of **4** is still not clear. Using degassed solvent resulted in only a slight decrease of the amount of **4** in the reaction mixture. The reaction of **2d** with $BF_3{\cdot}OEt_2$ in CH_2Cl_2 resulted in the formation of dihydrofuranone **4** in 23% yield. Formation of analogous products **4** was not observed from VCPs **2a**–**c**. The compositions and structures of the products **3** and **4** were established by elemental and spectral analyses. The structures of compounds **3c** and **4** were confirmed by X-ray diffraction analysis (Figs. 1 and 2).[20,21] The single crystal of **3c** clearly showed that the aryl group on the indene segment and the aryl ring of the phthal-

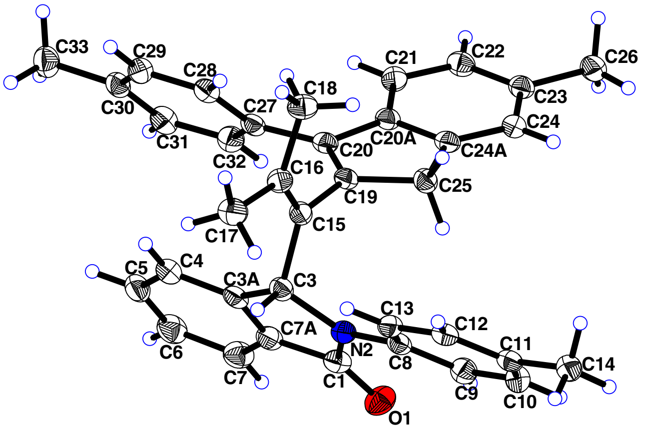


Figure 1. ORTEP representation of **3c**.

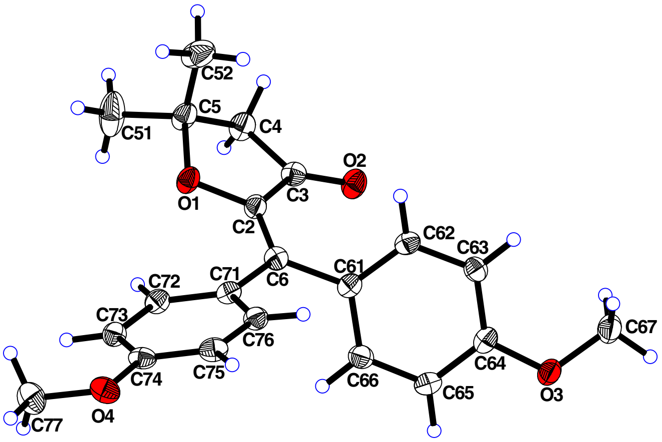
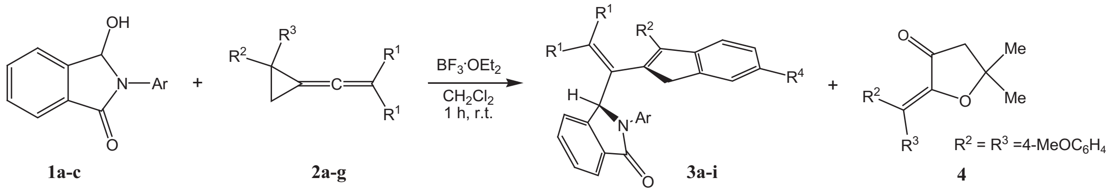


Figure 2. ORTEP representation of **4**.

Table 1
Reactions of hydroxylactams **1a–c** with vinylidenecyclopropanes **2a–d**



Entry	Ar	R^1	R^2	R^3	R^4	Yield of **3**[a] (%)
1	Ph (**1a**)	Me	4-MeC_6H_4	4-MeC_6H_4 (**2b**)	Me	41 (**3a**)
2	Ph (**1a**)	Me	4-$MeOC_6H_4$	4-$MeOC_6H_4$ (**2d**)	MeO	32 (**3b**)[b]
3	4-MeC_6H_4 (**1b**)	Me	4-MeC_6H_4	4-MeC_6H_4 (**2b**)	Me	39 (**3c**)
4	4-MeC_6H_4 (**1b**)	Me	4-$MeOC_6H_4$	4-$MeOC_6H_4$ (**2d**)	MeO	29 (**3d**)[c]
5	4-MeC_6H_4 (**1b**)	Me	Ph	Ph (**2a**)	H	40 (**3e**)
6	4-ClC_6H_4 (**1c**)	Me	4-ClC_6H_4	4-ClC_6H_4 (**2c**)	Cl	66 (**3f**)
7	4-ClC_6H_4 (**1c**)	Me	Ph	Ph (**2a**)	H	43 (**3g**)
8	Ph (**1a**)	Me	4-ClC_6H_4	4-ClC_6H_4 (**2c**)	Cl	58 (**3h**)
9	4-MeC_6H_4 (**1b**)	Me	4-ClC_6H_4	4-ClC_6H_4 (**2c**)	Cl	44 (**3i**)
10	Ph (**1a**)	Me	Me	Ph (**2e**)	H	—[d]
11	Ph (**1a**)	Ph	Me	Ph (**2f**)	H	—[d]
12	Ph (**1a**)	Ph	Ph	Ph (**2g**)	H	—[d]

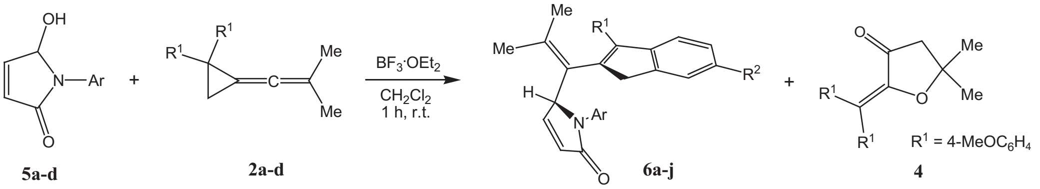
[a] Isolated yield.

[b] 7% of **4** was also formed.

[c] 9% of **4** was also formed.

[d] A complicated reaction mixture was observed.

Table 2
Reactions of hydroxylactams **5a–d** with vinylidenecyclopropanes **2a–d**



5a-d + **2a-d** → **6a-j** + **4**

Entry	Ar	R^1	R^2	Yield of **6**[a] (%)
1	Ph (**5a**)	4-MeC_6H_4 (**2b**)	Me	43 (**6a**)
2	4-MeC_6H_4 (**5b**)	4-MeC_6H_4 (**2b**)	Me	45 (**6b**)
3	4-$MeOC_6H_4$ (**5d**)	4-MeC_6H_4 (**2b**)	Me	42 (**6c**)
4	Ph (**5a**)	Ph (**2a**)	H	40 (**6d**)
5	4-MeC_6H_4 (**5b**)	Ph (**2a**)	H	28 (**6e**)
6	4-ClC_6H_4 (**5c**)	Ph (**2a**)	H	37 (**6f**)
7	4-$MeOC_6H_4$ (**5d**)	Ph (**2a**)	H	31 (**6g**)
8	4-MeC_6H_4 (**5b**)	4-ClC_6H_4 (**2c**)	Cl	55 (**6h**)
9	4-ClC_6H_4 (**5c**)	4-ClC_6H_4 (**2c**)	Cl	57 (**6i**)
10	4-MeC_6H_4 (**5b**)	4-$MeOC_6H_4$ (**2d**)	MeO	(**6j**+**4**)[b]
11	4-ClC_6H_4 (**5c**)	4-$MeOC_6H_4$ (**2d**)	MeO	—[c]

[a] Isolated yield.
[b] A chromatographically inseparable mixture of **6j** and **4** was obtained.
[c] Only a trace amount of the indene was observed; dihydrofuranone **4** was isolated in 12% yield.

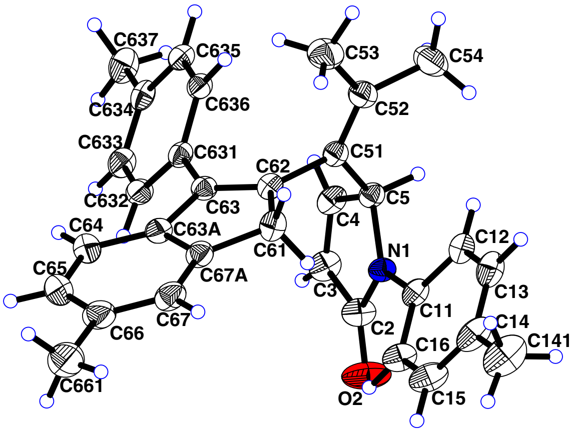


Figure 3. ORTEP representation of **6b**.

imide fragment were face-to-face aligned. As could be seen from the NMR spectra, it was apparent that compounds **3a–i** existed as a mixture of rotamers at ambient temperature on account of slow C3–C1 and C1–C2 bond rotation. In all cases, the presence of rotamers made the NMR spectra complex. At room temperature, the ^{1}H NMR spectra of products **3a–i** revealed two sets of signals for each CH_3 group of the isopropylidene fragment. Similarly, the ^{1}H NMR spectra of compounds **3** have two sets of signals belonging to the methylene group of the indene ring. Rotational isomerism was confirmed by temperature-dependent NMR experiments on compounds **3a**,**f**,**g**: coalescence was observed at 75–80 °C (see Supplementary information, Figs. 43–45).

For the next step in our study, we treated VCPs **2a–d** with hydroxylactams **5a–d** (Table 2). The reactions proceeded smoothly at room temperature producing the corresponding indene derivatives **6** in trace-to-moderate yields (Table 2). It should be noted that the yield did not improve upon stirring the reaction for a longer period of time or at a higher temperature. The formation of a trace amount of indene **6** was observed in the reaction of **5c** with

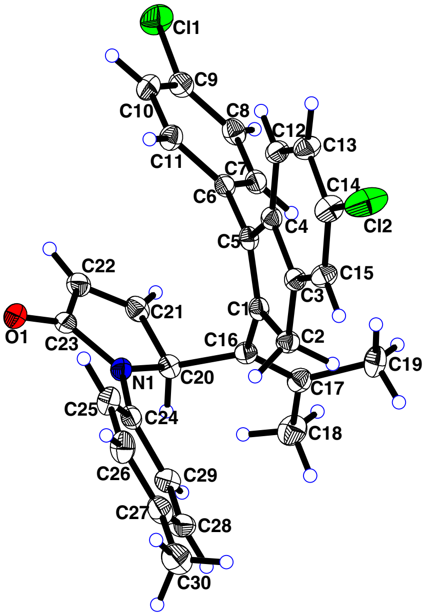
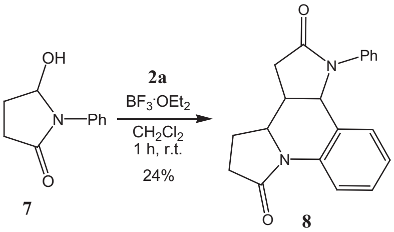
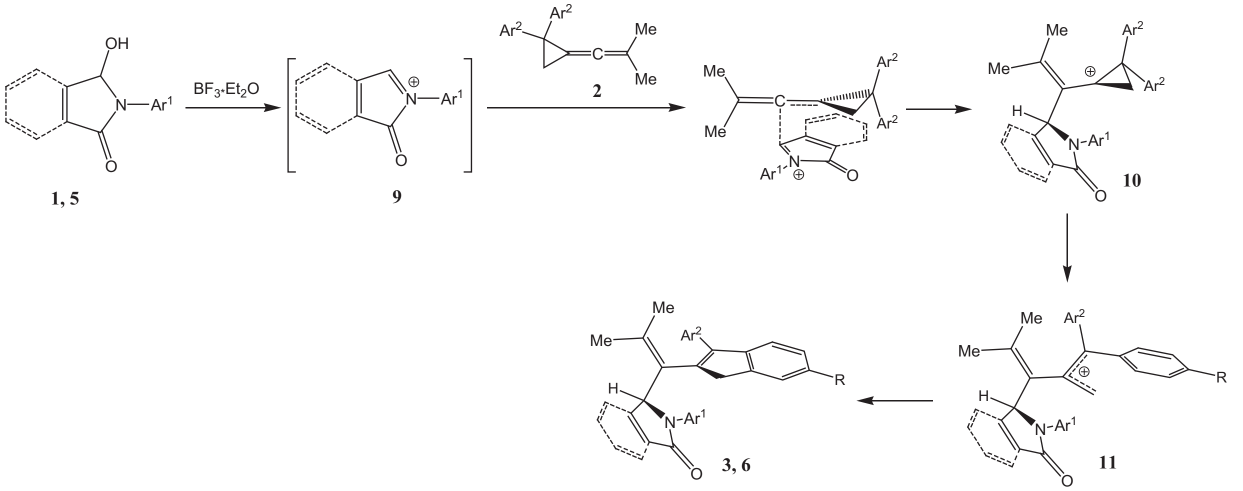


Figure 4. ORTEP representation of **6h**.



7 **8**

Scheme 1. $BF_3·OEt_2$-mediated reaction of **7** with **2a** at room temperature.



Scheme 2. A possible pathway for the reaction of hydroxylactams **1** and **5** with vinylidenecyclopropanes **2**.

VCP **2d**, which contains electron-donating groups (MeO) on the phenyl rings, and only the dihydrofuranone **4** was isolated in this case (Table 2, entry 11). The reaction of hydroxylactam **5b** with VCP **2d** led to an inseparable mixture of **6j** and **4** (Table 2, entry 10). The reaction products were purified by preparative thin-layer chromatography on silica. The structures of **6b** and **6h** were established unequivocally by X-ray diffraction analysis (Figs. 3 and 4).[22,23] In the reaction of 5-hydroxy-1-phenylpyrrolidin-2-one (**7**) with **2a**, no indene product was observed, but dimer **8** derived from **7** under the reaction conditions was produced as a mixture of isomers (Scheme 1)[18,24]

Based on the above results, a plausible mechanism for the formation of compounds **3** and **6** is proposed in Scheme 2. Activation of the C–O by $BF_3{\cdot}OEt_2$ leads to the formation of *N*-acyliminium cations **9**. Next, regioselective attack of the *N*-acyliminium cations **9** on the central carbon atom of the allene system results in the formation of cyclopropyl cation **10**, which undergoes a cyclopropyl–allyl rearrangement to give cation **11**. This undergoes cyclization to give substituted indenes **3** and **6**. Clearly, the steric factors are favorable to the addition of the *N*-acyliminium cations to the vinylidenecyclopropanes from the less sterically hindered side.

In conclusion, we have developed novel Lewis acid ($BF_3{\cdot}OEt_2$) mediated reactions of vinylidenecyclopropanes (VCPs) with the *N*-acyliminium cations generated from hydroxylactams, which can be utilized for the synthesis of indene derivatives.

Acknowledgments

We gratefully acknowledge the financial support from the Russian Foundation for Basic Research (Project No. 12-03-01008-a). This research made use of resources from the X-ray Diffraction Centre, the Centre for Magnetic Resonance and the Centre for Chemical Analysis and Materials of Saint-Petersburg State University.

Supplementary data

Supplementary data (experimental procedures, characterization data, and copies of NMR spectra) associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.tetlet.2014.02.039. These data include MOL files and InChiKeys of the most important compounds described in this article.

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20. Crystallographic data for the structure **3c** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC 936478. Copies of these data can be obtained on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (email: deposit@ccdc.cam.ac.uk).
21. Crystallographic data for the structure **4** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC 970376. Copies of these data can be obtained on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (email: deposit@ccdc.cam.ac.uk).
22. Crystallographic data for the structure **6b** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC 936477. Copies of these data can be obtained on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (email: deposit@ccdc.cam.ac.uk).
23. Crystallographic data for the structure **6h** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC 963391. Copies of these data can be obtained on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (email: deposit@ccdc.cam.ac.uk).
24. Spectroscopic and analytical characterizations for **8** have been previously reported in Ref. [18a].