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Trapping the Oxyallyl Cation Intermediate Derived from the Nazarov Cyclization of Allenyl Vinyl Ketones with Nitrogen Heterocycles

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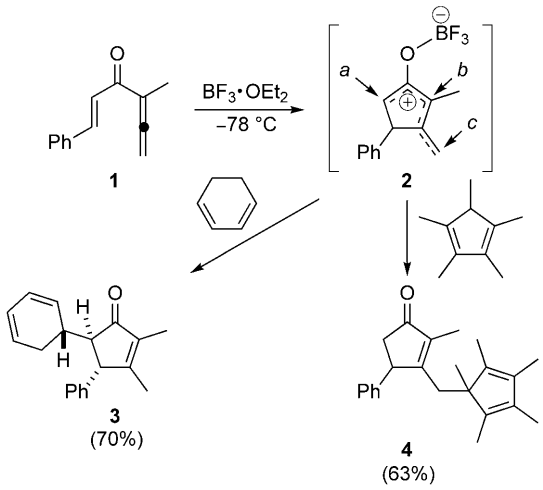
Abstract: The cationic intermediate of the Lewis acid-initiated Nazarov cyclization of an allenyl vinyl ketone (AVK) was trapped by pyrroles and indoles. The yields ranged from modest to high (up to 93%), and in both cases, only two of the three possible products were produced. Cyclopent-2-enones substituted at the 5-position were predominantly produced, however with increasing alkyl substitution or placement of an electron-withdrawing group on the nitrogen, an alternative regioisomer could also be formed. The results of this study suggest that a position α to the oxygen of the oxyallyl cation is the electronically preferred trapping site, whilst an exocyclic position is preferred for more sterically encumbered reacting partners.

Keywords: allenes; cyclization; heterocycles; interrupted reaction; Nazarov reaction

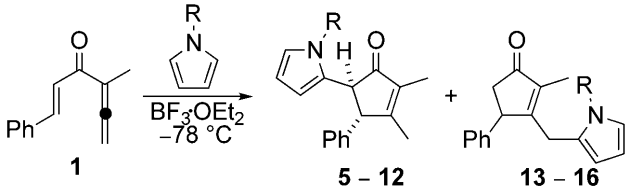
Nazarov reactions are a particularly useful method for the preparation of substituted cyclopentenones.[1,2] The Nazarov reactions of allenyl vinyl ketones (AVKs) have received more attention recently due to their heightened reactivity and the propensity of these reactions to be "interrupted" by the attack of nucleophiles.[3–7] We described Nazarov cyclizations of AVKs such as **1** in the presence of trifluoroacetic acid and Lewis acids. The cyclic, oxyallyl cation intermediate **2** was intercepted by the attack of oxygen,[5] halogen,[6] and carbon nucleophiles.[7] When reactions of **1** were conducted in the presence of acyclic dienes and some electron-rich alkenes, products of [4+3] and [3+2]cyclization onto the oxyallyl cation **2** were obtained. The two additional carbon-carbon bonds had formed at positions *a* and *b* of **2**. On the other hand, Nazarov reactions of **1** in the presence of cyclic dienes yielded products in which only one additional carbon-carbon bond had formed, at either position *a* or at position *c* of **2**. For instance, addition of 1,3-cyclohexadiene gave a cyclopent-2-enone (**3**) from interception at position *a*, and reaction with furan led to a similar product.[7–9] In contrast, addition of 1,2,3,4,5-pentamethylcyclopentadiene gave mainly **4**, *via* interception at position *c* of **2** (Scheme 1).[7]

Our attempts to intercept the oxyallyl cation **2** with enamines gave no identifiable Nazarov-derived products. These stronger nucleophiles reacted prematurely with **1** by Michael addition to the central carbon of the allene.[7] However, Basak and Tius[10] observed the interception of a Nazarov-derived oxyallyl cation from a highly substituted AVK by indole and some simple indole derivatives. Yields ranged from 30 to 72%. Thus, we set out to determine if Nazarov reactions of less substituted AVKs such as **1** might be interrupted with nitrogen-containing nucleophiles if the nucleophiles were nitrogen heterocycles.



Scheme 1. Interrupted Nazarov reactions of AVK **1**.

Table 1. Nazarov reactions of AVK **1** with pyrroles.[a]

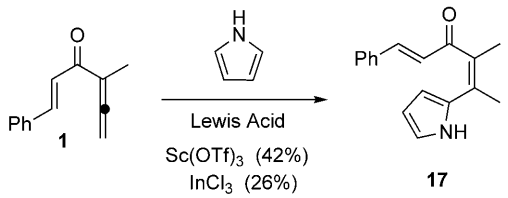


Entry	Pyrrole R	Product(s)	Yield[b]
1	H	**5**	54%
2	Me	**6**	32%
3	Bn	**7**	50%
4	Ph	**8**	67%
5	PMP	**9**	41%
6	TIPS	**10**	31%
7	Moc	**11**+**13** (1:1)[c]	23%
8	Boc	**12**+**14** (1.4:1)[c]	33%
9	Ms	**15**	11% (41%)[d]
10	Ts	**16**	10% (44%)[d]

[a] *Reaction conditions:* AVK **1** (1 equiv.), pyrrole (2 equiv.), $BF_3{\cdot}OEt_2$ (1.1 equiv.), CH_2Cl_2 (0.02 M), −78 °C, 5 min.
[b] Yield after flash chromatography.
[c] Determined by integration of the ^1H NMR spectra of the crude reaction products.
[d] Yields in parentheses were obtained when $InCl_3$ (2 equiv.) was used as the Lewis acid.

AVK **1** was treated with $BF_3{\cdot}OEt_2$ at −78 °C in the presence of an excess of pyrrole, resulting in a product, **5**,[11] that was derived by interception of the oxyallyl cation **2** at position *a* (Table 1, entry 1).[12] The reaction of **1** was subsequently explored in the presence of a range of *N*-substituted pyrrole derivatives (Table 1, entries 2–10). As with pyrrole itself, the predominant Nazarov product with *N*-alkyl-, *N*-aryl-, and *N*-silyl-pyrroles involved carbon-carbon bond formation at position *a* of **2** (entries 2–6). The modest yields of Nazarov products in these cases were mostly a result of a competing Michael addition pathway that was similar to the reaction with enamines, generating products such as **17**.[13,14] Utilization of different Lewis acids, such as $Sc(OTf)_3$ or $InCl_3$, led to no Nazarov product. Only the Michael adduct **17** was isolated (Scheme 2).[15]

No Michael product was detected for pyrroles with electron-withdrawing groups on the nitrogen atom

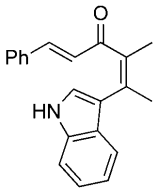


Scheme 2. Michael reactions of AVK **1** with pyrrole.

(Table 1, entries 7–10), and much, or all, of the Nazarov product arose by interception of **2** at position *c*. With *N*-mesyl- and *N*-tosylpyrrole, the low yields with $BF_3{\cdot}OEt_2$ were improved four-fold by using $InCl_3$ as the Lewis acid (entries 9 and 10), and Michael addition products were not detected with these pyrroles.

Interrupted Nazarov reactions mediated by $BF_3{\cdot}OEt_2$ took place in higher yield with indoles than with pyrroles (Table 2). Michael products made up less than 10% of the product mixtures, and cyclopent-2-enones could be produced in good to excellent yield. The regioselectivity for the trapping, i.e., positions *a versus c* of the oxyallyl cation **2**, was modest. Notably, methyl substitution at C-2 of the indole (entries 4 and 5) led to a greater proportion of the Nazarov product that had been trapped at position *c*. The results suggested that position *a* is the electronically preferred site for trapping, whereas position *c* becomes preferred for more sterically encumbered substrates. Although trapping with a more electron-rich derivative, 5-methoxyindole (entry 2), did not affect the yield or selectivity of the reaction, *N*-tosylindole (entry 6), a more electron-poor analogue, failed to generate any trapped product under the same reaction conditions.

When the reaction with indole was assessed with $Sc(OTf)_3$, the Michael adduct **24** was obtained in 38% yield, but no Nazarov product was observed. Use of



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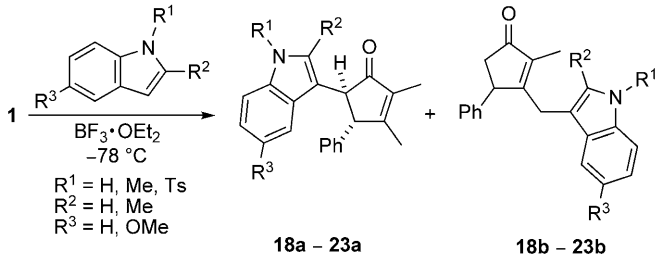
$InCl_3$ led to both the Michael adduct **24** (19%) and the Nazarov products **18a,b** (20%, 1:1 ratio). However, when $InCl_3$ was employed with the previously ineffective *N*-tosylindole (entry 6), Nazarov products **23a,b** were obtained (1:1 ratio).

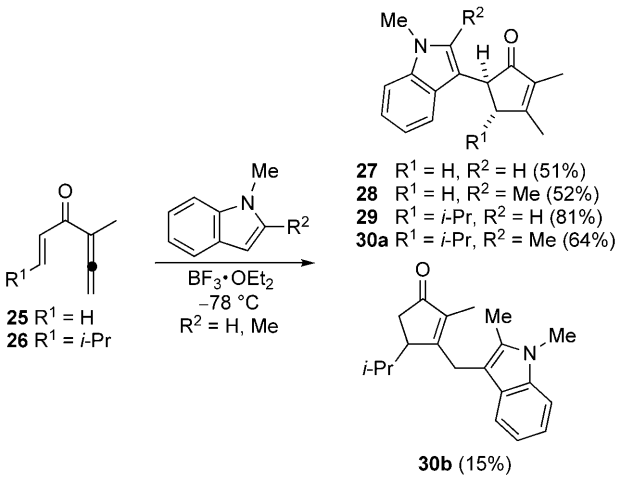
Replacement of the phenyl group of AVK **1** with a hydrogen, as in AVK **25**, or an isopropyl group, as in AVK **26**, might be expected to be significant in terms of the reactivity of the AVKs and the regioselectivity of the Nazarov reactions with substituted indoles (Scheme 3). The less substituted AVK **25** reacted rapidly, just like AVK **1**, with 1-methyl- and 1,2-dimethylindoles but the regioselectivity was much improved. Only the products of trapping at the position corresponding to *a* (**27** and **28**) were obtained. The reactions of AVK **26** were also rapid and much more regioselective than those of AVK **1**, with **29** being the only significant Nazarov product with 1-methylindole,

Table 2. Nazarov reactions of AVK **1** with indoles.[a]



Entry	Products	Ratio of products **a/b**[b]	Combined yield[c]
1	**18a**, **b** (R^1, R^2, R^3 = H)	2.3–3.7:1	88–93%
2	**19a**, **b** (R^1, R^2 = H, R^3 = OMe)	2.5–3.9:1	71–92%
3	**20a**, **b** (R^1 = Me, R^2, R^3 = H)	3.2–3.6:1	88–90%
4	**21a**, **b** (R^1, R^3 = H, R^2 = Me)	1.1–1.6:1	58–60%
5	**22a**, **b** (R^1, R^2 = Me, R^3 = H)	1.4–2.2:1	87–90%
6	**23a**, **b** (R^1 = Ts, R^2, R^3 = H)	1:1	0% (49%)[d]

[a] *Reaction conditions:* AVK **1** (1 equiv.), indole (2 equiv.), $BF_3{\cdot}OEt_2$ (1.1 equiv.), CH_2Cl_2 (0.02 M), −78 °C, 5 min.
[b] Range from three trials, determined by integration of the ^1H NMR spectra of crude products.
[c] Yield after flash chromatography, range from two trials.
[d] Yield in parentheses was obtained when $InCl_3$ (2 equiv.) was used as the Lewis acid.



Scheme 3. Reactions of AVK's **25** and **26** with substituted indoles.

and **30a** and **30b** being produced in a ratio of 4.3:1 with 1,2-dimethylindole.

In summary, allenyl vinyl ketones reacted with pyrroles and indoles to give heterocycle-functionalized cyclopent-2-enones in the presence of $BF_3{\cdot}OEt_2$. Michael reactions of the AVK were competitive with the desired interrupted Nazarov reactions in the presence of the pyrroles, but the regioselectivity of trapping was very good when an alkyl, an aryl, or a silyl substituent was on the nitrogen. Regioselectivity was also good, giving a different type of product, with an electron-withdrawing sulfonyl group on the nitrogen of the pyrrole. Interception of the Nazarov process with indoles in the presence of $BF_3{\cdot}OEt_2$ took place much more efficiently than with pyrroles without the formation of any detectable Michael product. The regioselectivity of the trapping process with indoles showed a strong dependence upon the substitution pattern present in both reacting partners, and regioselectivity became worse with increasing substitution near the reacting carbons. This suggested that position *a* is the electronically preferred trapping site, whereas position *c* is the sterically preferred trapping site. Finally, electron-deficient derivatives, in which the nitrogen atom bore an acyl or sulfonyl substituent, provided products trapped at position *c* in an increased amount, or exclusively. The results of this study contribute to a more complete understanding of the interrupted Nazarov cyclization of allenyl vinyl ketones, and should allow further generalizations to be made in terms of reactivity and regioselectivity, with respect to related substrate classes.

Experimental Section

General Procedure for the Interrupted Nazarov Cyclization of an Allenyl Vinyl Ketone (AVK)

A solution of the AVK (1 equiv.) and the pyrrole (2 equiv.) or the indole (2 equiv.) in CH_2Cl_2 (0.02 M) was cooled to −78 °C, and $BF_3{\cdot}OEt_2$ (1.1 equiv.) or $InCl_3$ (2.0 equiv.) or $Sc(OTf)_2$ (2.0 equiv.) was added. The mixture was stirred for 5 min at −78 °C before it was poured into a separatory funnel containing saturated aqueous $NaHCO_3$. The CH_2Cl_2 layer was removed, and additional CH_2Cl_2 (×2) was used to re-extract the aqueous layer. The combined organic layers

were dried over Na_2SO_4 and then concentrated under reduced pressure. Flash chromatography (230–400 mesh silica gel) of the residue provided the product. The eluting solvents were: for the pyrroles, 10% EtOAc in hexanes with 2.5% triethylamine and then 25% EtOAc in hexanes with 2.5% triethylamine; for the indoles, 10%, increasing to 35%, EtOAc in hexanes.[11]

***trans*-2,3-Dimethyl-4-phenyl-5-(1-phenyl-1*H*-pyrrol-2-yl)-cyclopent-2-enone (8):** AVK **1** (0.10 g, 0.56 mmol) and 1-phenylpyrrole (0.16 g, 1.1 mmol) reacted in the presence of $BF_3{\cdot}OEt_2$ (0.080 mL, 0.62 mmol) to afford **8** as a pale yellow solid; yield: 0.13 g (67%); mp 132–133 °C (CH_2Cl_2/pentane); IR (film): $\nu = 1705$, 1650, 1599 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): $\delta = 7.18$ (6H, m), 7.12 (2H, m), 6.88 (2H, m), 6.74 (1H, dd, $J = 3.2$, 1.7 Hz), 6.24 (1H, t, $J = 3.2$ Hz), 6.00 (1H, dd, $J = 3.2$, 1.7 Hz), 3.77 (1H, br d, $J \approx 3$ Hz), 3.55 (1H, d, $J = 2.9$ Hz), 1.78 (3H, br s), 1.77 (3H, s); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 207.4$, 170.1, 141.1, 139.9, 135.9, 131.4, 129.1 (2C), 129.0 (2C), 127.6 (4C), 127.3, 127.1, 123.0, 108.7, 107.1, 59.7, 53.9, 15.7, 8.8; HR-MS (ESI): $m/z =$ 350.1513, $[C_{23}H_{21}NO + Na]^+$ requires 350.1515.

***trans*-5-(1,2-Dimethyl-1*H*-indol-3-yl)-2,3-dimethyl-4-phenylcyclopent-2-enone (22a) and 3-[(1,2-dimethyl-1*H*-indol-3-yl)methyl]-2-methyl-4-phenylcyclopent-2-enone (22b):** AVK **1** (0.10 g, 0.56 mmol) and 1,2-dimethylindole (0.16 g, 1.1 mmol) reacted in the presence of $BF_3{\cdot}OEt_2$ (0.080 mL, 0.62 mmol). Flash chromatography of the product mixture provided **22a** (yield: 0.11 g, 62%) and **22b** (yield: 0.052 g, 28%).

22a: pale yellow solid, mp 164–166 °C (CH_2Cl_2/pentane); IR (film): $\nu = 1702$, 1648, 1602 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): $\delta = 7.31$ (2H, m), 7.25 (2H, m), 7.12 (1H, m), 7.06 (2H, m), 6.97 (2H, m), 3.90 (1H, br d, $J \approx 3$ Hz), 3.65 (1H, d, $J = 3.2$ Hz), 3.61 (3H, s), 2.03 (3H, s), 1.97 (3H, br s), 1.94 (3H, s); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 209.3$, 169.9, 142.1, 137.4, 137.2, 135.0, 129.1 (2C), 127.7 (2C), 127.1, 126.1, 120.9, 119.1, 118.2, 109.0, 108.0, 58.6, 54.9, 29.8, 15.7, 10.5, 8.9; HR-MS (ESI): $m/z = 352.1667$, $[C_{23}H_{23}NO + Na]^+$ requires 352.1672.

22b: pale yellow solid, mp 199–201 °C (CH_2Cl_2/pentane); IR (film): $\nu = 1698$, 1641, 1602 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): $\delta = 7.25$ (4H, m), 7.16 (1H, m), 7.12 (1H, m), 7.01 (1H, m), 6.86 (2H, m), 3.92 (1H, d, $J = 16$ Hz), 3.62 (1H, m), 3.61 (3H, s), 3.37 (1H, d, $J = 16$ Hz), 2.74 (1H, dd, $J =$ 19, 7.4 Hz), 2.24 (1H, dd, $J = 19$, 2.2 Hz), 2.04 (3H, s), 1.85 (3H, s); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 209.9$, 174.5, 142.7, 137.1, 136.8, 134.4, 128.9 (2C), 127.8, 127.6 (2C), 127.0, 121.0, 119.2, 118.0, 108.8, 105.9, 46.2, 45.1, 29.8, 25.0, 10.0, 8.9; HR-MS (ESI): $m/z = 352.1676$, $[C_{23}H_{23}NO + Na]^+$ requires 352.1672.

***trans*-2,3-Dimethyl-4-phenyl-5-(1-tosyl-1*H*-indol-3-yl)cyclopent-2-enone (23a) and 2-methyl-4-phenyl-3-[(1-tosyl-1*H*-indol-3-yl)methyl]cyclopent-2-enone (23b):** AVK **1** (0.10 g, 0.56 mmol) and 1-(toluenesulfonyl)indole (0.30 g, 1.1 mmol) reacted in the presence of $InCl_3$ (0.24 g, 1.1 mmol). Flash chromatography of the product mixture provided **23a** (yield: 0.064 g, 25%) and **23b** (yield: 0.061 g, 24%).

23a: colorless solid, mp 76–78 °C (CH_2Cl_2/pentane); IR (film): $\nu = 1708$, 1650, 1605 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): $\delta = 7.94$ (1H, m), 7.74 (2H, d, $J = 8.5$ Hz), 7.33 (4H, m), 7.27 (1H, m), 7.22 (2H, d, $J = 8.5$ Hz), 7.08 (3H, m), 7.03 (1H, m), 3.80 (1H, br d, $J \approx 3$ Hz), 3.67 (1H, d, $J =$ 3.0 Hz), 2.34 (3H, s), 1.92 (3H, br s), 1.89 (3H, s); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 207.1$, 170.4, 145.1, 141.2, 136.9, 135.6, 135.3, 130.1 (3C), 129.3 (2C), 127.8 (2C), 127.6, 127.1 (2C), 125.0, 123.8, 120.2, 120.1, 113.9, 58.1, 53.7, 21.8, 15.8, 8.8; HR-MS (ESI): $m/z = 478.1424$, $[C_{28}H_{25}NO_3S + Na]^+$ requires 478.1447.

23b: colorless solid, mp 61–63 °C (CH_2Cl_2/pentane); IR (film): $\nu = 1704$, 1650, 1601 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): $\delta = 8.01$ (1H, m), 7.75 (2H, d, $J = 8.4$ Hz), 7.31 (4H, m), 7.25 (2H, d, $J = 8.4$ Hz), 7.19 (2H, m), 7.08 (1H, s), 6.93 (2H, m), 3.79 (1H, d, $J = 16$ Hz), 3.67 (1H, m), 3.28 (1H, d, $J = 16$ Hz), 2.82 (1H, dd, $J = 19$, 7.2 Hz), 2.36 (s, 3H), 2.34 (1H, dd, $J = 19$, 2.1 Hz), 1.92 (3H, s); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 209.3$, 171.1, 145.3, 141.8, 138.1, 135.5, 135.4, 130.5, 130.1 (2C), 129.2 (2C), 127.7 (2C), 127.5, 127.0 (2C), 125.2, 124.4, 123.5, 119.3, 117.9, 114.1, 46.7, 44.8, 25.2, 21.8, 8.9; HR-MS (ESI): $m/z = 478.1431$, $[C_{28}H_{25}NO_3S + Na]^+$ requires 478.1447.

2,3-Dimethyl-5-(1-methyl-1*H*-indol-3-yl)cyclopent-2-enone (27): AVK **25** (0.075 g, 0.69 mmol) and 1-methylindole (0.17 mL, 1.4 mmol) reacted in the presence of $BF_3{\cdot}OEt_2$ (0.090 mL, 0.76 mmol) to afford **27** as a colorless oil; yield: 0.084 g (51%); IR (film): $\nu = 1697$, 1654 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): $\delta = 7.37$ (1H, m), 7.28 (1H, m), 7.20 (1H, m), 7.05 (1H, m), 6.95 (1H, s), 3.84 (1H, dd, $J = 7.3$, 2.7 Hz), 3.72 (3H, s), 3.12 (1H, dd, $J = 18$, 7.3 Hz), 3.12 (1H, br dd, $J = 18$, ~3 Hz), 2.11 (3H, s), 1.81 (3H, s); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 209.8$, 168.6, 137.5, 135.7, 127.2, 126.8, 121.9, 119.2, 119.1, 112.9, 109.6, 43.1, 41.2, 32.8, 17.3, 8.4; HR-MS (ESI): $m/z = 262.1190$, $[C_{16}H_{17}NO + Na]^+$ requires 262.1202.

Acknowledgements

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[11] Under the same reaction conditions but in the presence of thiophene, no identifiable Nazarov product was obtained.

[12] The *trans* stereochemistry was confirmed by NOE measurements and the magnitudes of coupling constants.

[13] The ratio of Nazarov product **5** to Michael adduct **17**, for example, was 3:1 by integration of the ^{1}H NMR spectrum of the crude reaction mixture.

[14] Interception of the Nazarov reaction was also attempted with 2-ethyl-, 3,4-diethyl-, and 3-ethyl-2,4-dimethylpyrrole, but these compounds failed to be incorporated into any cyclopent-2-enone product. It appeared by ^{1}H NMR spectroscopy of the crude product mixtures that **1** was reacting mainly by Michael reactions with the pyrroles.

[15] Observation of NOE's established the *Z*-geometry of **17**.

