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Ferrier−Petasis Rearrangement of 4-(Vinyloxy)azetidin-2-ones: An Entry to Carbapenams and Carbacephams

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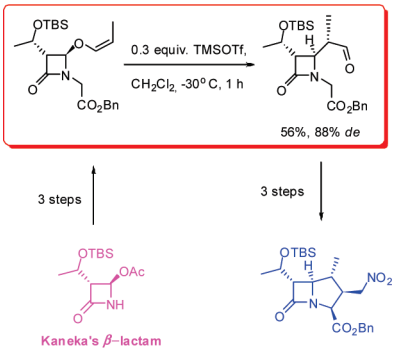

Trimethylsilyl triflate promotes Ferrier−Petasis rearrangement of 4-(vinyloxy)-, 4-(propenyloxy)-, and 4-(isopropenyloxy)azetidin-2-ones to corresponding 4-(carbonylmethyl)azetidin-2-ones. The latter compounds may serve as attractive intermediates in the synthesis of carbapenem antibiotics. To illustrate the potential of this reaction, selected rearrangement products have been transformed into carbapenams.

N-acyliminium ions are important reactive intermediates in organic synthesis that can act as electron-deficient carbocations toward weak, soft nucleophiles, providing useful methodologies for both inter- and intramolecular carbon−carbon and carbon−heteroatom bond formation.[1] In particular, the N-acyliminium cations can be generated in acidic media from lactams bearing a leaving group in a position α to the nitrogen atom.[2] Recently, we have shown that 4-(vinyloxy)-azetidin-2-one (**1**) is an attractive starting material for the synthesis of 5-oxa-[3] and 5-carbacephams.[4] In contrast to the commercially available 4-acetoxyazetidin-2-one,[5] **1** allows for the N-alkylation of the substrate prior to the nucleophilic substitution at the C-4 carbon atom.[3,4] Subsequently, the readily available acyloxyl (formyloxyl, obtained by ozonolysis of the vinyl double bond, for example), in the presence of a Lewis acid, may undergo an intramolecular displacement leading to ring closure.[3,4] We have shown that, in the presence of acid catalysts, the vinyloxyl can also play a role of a leaving group to make possible generation of N-acyliminium cations and consequently to promote reactions similar to those of its 4-acyl congener.[3,4,6] It is worth noting that nucleophilic substitution at C-4 can be done as an intermolecular process.[3,4,7]

Unlike other common Lewis acids, which when added to a mixture of 4-(vinyloxy)- or 4-(acyloxy)azetidinones with nucleophilic reagents promote substitution at the C-4 carbon atom, Me_3SiOTf behaves in a different manner. It promotes a Ferrier−Petasis rearrangement[8] leading to 4-(formylmethyl)-azetidinone (Scheme 1). The mechanism of this reaction involves attack of trimethylsilyl triflate at the vinyloxyl oxygen atom to form a silyl enol ether and an accompanying N-acyliminium cation. Subsequently, as in the case of the Mukaiyama reaction,[9] the enol silyl ether adds to the electrophilic center, C-4 of the azetidinone, to produce the corresponding aldehyde (Scheme 1). The formation of rearrangement

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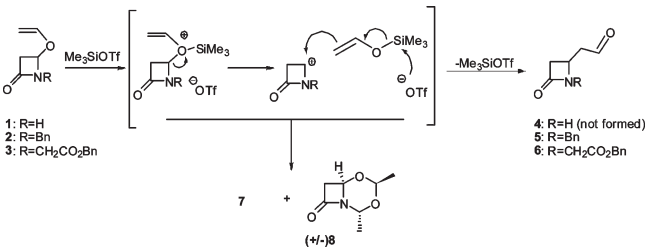
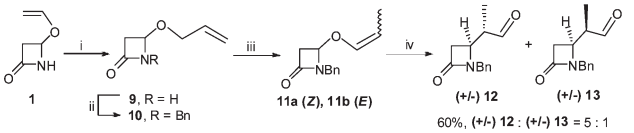
SCHEME 1



SCHEME 2[a]



[a]Legend: (i) 0.6 equiv of $Zn(OAc)_2 \cdot 2H_2O$, 6 equiv of allyl alcohol, PhMe, 80 °C, 24 h, 60%; (ii) 1.0 equiv of Bu_4NBr, 5 equiv of $PhCH_2Br$, 50% NaOH, PhMe, room temperature, 0.5 h, 90%; (iii) 1.0 equiv of [Ni−H], THF, room temperature, 22−67%; (iv) 0.3 equiv of TMSOTf, CH_2Cl_2, −30 °C.

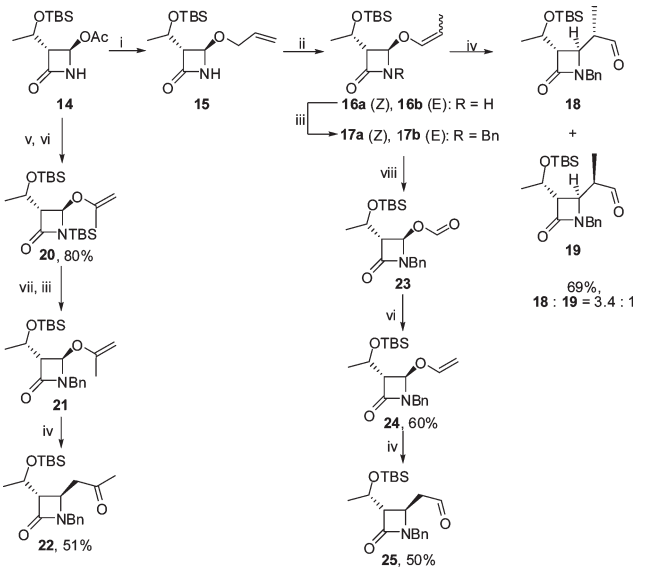
product **4** was not observed for the N-unsubstituted 4-(vinyloxy)-azetidinone (**1**). The mass spectrum of the crude postreaction mixture showed the presence of the unstable dimeric structures **7** (MS: ESI, *m*/*e* 249, $[M + Na]^+$), which was not isolated and characterized, and the dioxacepham **8**, which was isolated in 20% yield. The NMR spectrum proved the structure and relative configuration of **8**.

This Ferrier-Petasis rearrangement which offers an attractive entry to carbapenam and carbacepham antibiotics,[10] prompted us to investigate its scope and limitation. In order to avoid formation of compounds analogous to **7** and **8**, a comparison of the reactivity of different 4-vinyloxy-azetidinones and their methyl substituted congeners (propenyloxy and isopropenyloxy) was carried out with respective *N*-benzyl-azetidinones. As model substrates compounds **2**, **3**, **11**, **17**, **21**, and **24**, derived from 4-vinyloxy-azetidinone (**1**) and commercially available Kaneka's azetidinone **14**[11] were selected.

Compounds **2**, **3**, **11**, **17**, **21**, and **24** were obtained by standard reaction sequences which involved either nucleophilic substitution at C-4 of azetidinones with allyl alcohol followed by a nickel-catalyzed migration of the double bond and subsequent N-benzylation or treatment of the 4-acyloxy group (formyloxyl or acetoxyl) with Tebbe's methylation reagent.[12] The latter reaction can be performed only if the β-lactam nitrogen atom is protected by a silyl or benzyl group. 4-(Propenyloxy)azetidinones can be N-benzylated as easily as their 4-vinyloxy congeners (Schemes 2 and 3). All reactions smoothly proceeded to provide the expected products in good yields.

Special attention was directed at the rearrangement of allyl ethers into the corresponding (*Z*)- and (*E*)-propenyl species, since this reaction could offer an entry to biologically active

SCHEME 3[a]



[a]Legend: (i) 0.6 equiv of $Zn(OAc)_2 \cdot 2H_2O$, 6 equiv of allyl alcohol, PhMe, 80 °C, 12 h, 75%; (ii) 1.0 equiv of [Ni−H], THF, room temperature, 56−68%; (iii) 1.0 equiv. of Bu_4NBr, 5 equiv of $PhCH_2Cl$, 50% NaOH, PhMe, room temperature, 30 min, 90−92%; (iv) 0.3 equiv of TMSOTf, CH_2Cl_2, −30 °C; (v) 1.1 equiv of TBSCl, 1.1 equiv of NEt_3, CH_2Cl_2, room temperature, 12 h, 96%; (vi) 1.0 equiv of Tebbe reagent, PhMe, room temperature, 48 h; (vii) 1.1 equiv of Bu_4NF, THF, 0 °C, 30 min, 95%; (viii) O_3, CH_2Cl_2, −78 °C, than Me_2S, 69%.

4-substituted carbapenems.[12] We found that the ratio of *Z* and *E* isomers depended on the type of catalyst (see the Supporting Information). Among the catalysts tested, $NiCl_2(PPh_3)_2$ was found to be the most attractive, since within just 2 h it provided exclusively the *Z* isomer in good yield. We have found that both (*Z*)- and (*E*)-propenyl ethers **11**, **17**, and **30** furnished a similar ratio of the corresponding α-substituted propyl aldehydes **12**/**13**, **18**/**19**, and **31**/**32**. This observation may suggest that under the reaction conditions (TMSOTf), from both diastereomeric aldehydes **12**/**13**, **18**/**19**, and **31**/**32** the same corresponding TMS-enol ether is formed and consequently the ratio of isomeric products does not depend on an *E*,*Z*) configuration of the propenyl ethers **11**, **17**, and **30**.

Since the *Z* isomers **11a** and **16a** offered the most effective rearrangement of allyl ethers into propenyl ones, they were used for the next steps.

Since Me_3SiOTf is the only currently known Lewis acid that promotes the rearrangement, we were unable to test whether the reaction can be carried out as an enantioselective process. In the case of azetidinones **16**, **17**, **21**, and **24** derived from Kaneka's compound **14**, the absolute configuration at C-4 of the azetidinone is well-defined since the nucleophile approaches the four-membered ring exclusively anti to the existing substituent at C-3.[13]

In order to demonstrate the usefulness of the reported Ferrier−Petasis rearrangement in the synthesis of carbapenams, we carried out a reaction sequence following the protocol of Hanessian at al.[14] (Schemes 4 and 5). Compound **6** was selected as the starting material. An analogous reaction sequence was applied to the isomeric compounds **31** and **32**, readily available from **16** by the N-alkylation−rearrangement sequence. In the latter case, we intended to examine

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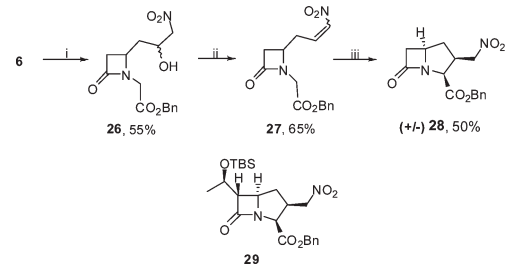
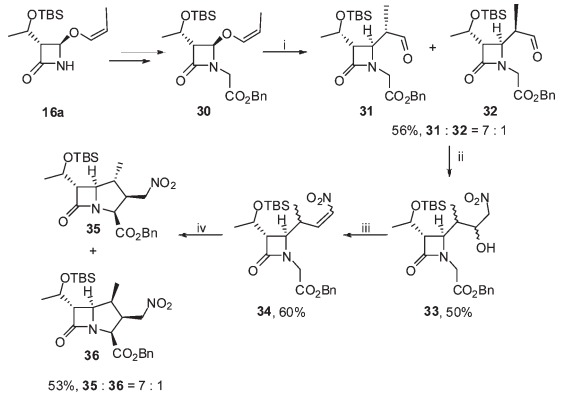
SCHEME 4[a]



[a]Legend: (i) 2.0 equiv of DBU, CH_3NO_2, −20 °C, 1 h; (ii) 1.1 equiv of MsCl, 2.2 equiv of Et_3N, CH_2Cl_2, room temperature, 3 h; (iii) 1.1 equiv of LiHMDS, THF, −78 °C, 1 h.

SCHEME 5[a]



[a]Legend: (i) 0.3 equiv of TMSOTf, CH_2Cl_2, −30 °C, 1 h; (ii) 2.0 equiv of DBU, CH_3NO_2, −20 °C, 1 h; (iii) 1.1 equiv of MsCl, 2.2 equiv of Et_3N, CH_2Cl_2, room temperature, 3 h; (iv) 1.1 equiv of LiHMDS, THF, −78 °C, 1 h.

whether Hanessian's reaction sequence,[14] when applied to the 4-propenyloxy compounds, would furnish the 4-methylcarbacephams. Moreover, the transformation of **16** into **35** and **36** should verify the configuration of both Ferrier−Petasis rearrangement products **31** and **32** if the α-substituted propanal fragment does not undergo epimerization under the reaction conditions.

Compound **6** was subjected to a nitro aldol reaction with nitromethane followed by a two-step sequence (elimination of water and intramolecular conjugated addition to the double bond) that led to the racemic compound **28** as the sole product (Scheme 4). The relative configuration at the three stereogenic centers in **28** was established with the help of NOE experiments, which showed spin−spin interactions between the H-2, H-3, and H-5 protons. The relative configuration in **28** was found to be the same as that of compound **29** obtained by Hanessian's group.[14]

The same reaction sequence was carried out with the isomerically defined **16a** (Scheme 5). **16a** was alkylated with benzyl bromoacetate to afford **30**, which subsequently was subjected to a Ferrier−Petasis rearrangement to afford an inseparable mixture of **31** and **32** in a ratio of about 7:1. The configuration of both products was established by analyzing the results of the subsequent steps of the synthesis.

A mixture of **31** and **32** was subjected to the same sequence of reactions as for compound **6** to afford a mixture of carbapenams **35** and **36** in a ratio of about 7:1, respectively, which was separated by HPLC into individual pure components. The assignment of the absolute configuration of diastereomers **35** and **36** was established as above by NOE's. The proportion of stereoisomers did not change during transformation steps from **31**/**32** to **35**/**36**; therefore, the absolute configuration of the α-substituted propanal fragment at C-4 of the azetidinone ring in **31** and **32** was assumed to be the same. By analogy, the same structural assignment can be made for the stereoisomeric pairs **12**/**13** and **18**/**19**.

It was demonstrated that the Ferrier−Petasis rearrangement at the C-4 carbon atom of azetidin-2-ones can be performed in good yield, and this reaction offers an attractive entry to carbapenem and carbacephem antibiotics. So far, the enantioselective protocol was not achieved, owing to the specific character of the activating reagent, which enables silylation of the vinyloxyl oxygen atom. In the case of a diastereoselective process, however, the Ferrier−Petasis rearrangement offers an alternative entry to known antibiotics. It is also worth noting that Tebbe's olefination reaction can be used to effectively modify the 4-acyl group to give simple vinyloxy or isopropenyloxy residues.

Experimental Section

Typical Procedure for Rearrangement of Allyl Ethers. To a solution of $NiCl_2(PPh_3)_2$ (0.196 g, 0.3 mmol, 1.0 equiv) in THF (5 mL) at room temperature was added $LiBHEt_3$ in THF (0.3 mL, 1.0 M, 1.0 equiv) under an argon atmosphere. After 15 min allyl ether **10** (65 mg, 0.3 mmol, 1.0 equiv) was added. The reaction mixture was stirred for 2 h until disappearance of the starting material (TLC) and diluted with 5% HCl (5 mL). The aqueous phase was extracted with ether (3 × 10 mL). The organic extracts were combined and dried over Na_2SO_4. The solution was filtered and the filtrate evaporated. The crude product was purified by column chromatography (silica gel, 2:3 hexane−diethyl ether) to give 44 mg (0.20 mmol) of **11a** as a yellow species: yield 67%. IR (film): ν 1764 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ 1.57 (dd, J = 6.9, 1.8 Hz, 3H, CH_3CH=), 2.96 (dd, J = 14.9, 1.2 Hz, 1H, CH_2), 3.12 (dd, J = 14.9, 3.9 Hz, 1H, CH_2), 4.11 (d, J = 15.2 Hz, 1H, CH_2N), 4.57 (dq, J = 6.2, 6.9 Hz, 1H, =CHCH$_3$), 4.66 (d, J = 15.2 Hz, 1H, CH_2N), 5.08 (dd, J = 3.9, 1.2 Hz, 1H, CHO), 5.94 (dq, J = 6.2, 1.8 Hz, 1H, CH=), 7.28 (m, 2H, Ph), 7.34 (m, 3H, Ph). ^{13}C NMR (125 MHz, $CDCl_3$): δ 9.4, 44.5, 80.9, 105.1, 127.8, 128.4, 128.8, 135.4, 140.5, 165.5. HR MS (ESI): m/z calcd for $[M + Na]^+$ $C_{13}H_{15}NO_2Na$ 240.0995, found 240.0993.

Typical Procedure for Ferrier−Petasis Rearrangement. To a solution of β-lactam **2** (102 mg, 0.5 mmol, 1.0 equiv) in CH_2Cl_2 (10 mL) was added TMSOTf (27 μL, 0.15 mmol, 0.3 equiv) at −30 °C under an argon atmosphere. The reaction mixture was stirred at 0 °C until disappearance of the starting material (TLC) and diluted with saturated $NaHCO_3$ (10 mL). The aqueous phase was extracted with CH_2Cl_2 (3 × 15 mL). The organic

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extracts were combined and dried over $MgSO_4$. The solution was filtered and the filtrate evaporated. The crude product was purified by column chromatography (silica gel, 95:5 dichloromethane−diethyl ether) to give 49 mg (0.24 mmol) of **5** as a colorless oil: yield 48%. IR (film): ν 1732 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ 2.63 (ddd, J = 18.1, 6.6, 1.0 Hz, 1H, CH_2CO), 2.66 (dd, J = 14.8, 2.2 Hz, 1H, CH_2), 2.73 (ddd, J = 18.1, 6.1, 1.0 Hz, 1H, CH_2CO), 3.21 (dd, J = 14.8, 5.1 Hz, 1H, CH_2), 3.95 (m, 1H, CH), 4.36 (d, J = 15.2 Hz, 2H, CH_2N), 7.25−7.36 (m, 5H, Ar), 9.62 (t, J = 1.0 Hz, 1H, CHO). ^{13}C NMR (125 MHz, $CDCl_3$): δ 43.1, 45.3, 46.1, 47.6, 127.9, 128.4, 128.6, 136.0, 166.5, 198.81. HR MS (ESI): m/z calcd for $[M + MeOH + Na]^+$ $C_{13}H_{17}NO_3Na$ 258.1101, found 258.1094.

Typical Procedure for Reaction with Tebbe's Reagent. To a solution of β-lactam **23** (78 mg, 0.3 mmol, 1.0 equiv) in toluene (5 mL) at room temperature was added Tebbe's reagent in toluene (0.6 mL, 0.5 M, 1.0 equiv) under an argon atmosphere. The reaction mixture was stirred for 48 h until disappearance of starting material (TLC) and diluted with 5% HCl (5 mL). The aqueous phase was extracted with ethyl acetate (3 × 10 mL). The organic extracts were combined and dried over $MgSO_4$. The solution was filtered and the filtrate evaporated. The crude product was purified by column chromatography (silica gel, 4:1 hexane−ethyl acetate) to give 65 mg (0.18 mmol) of **24** as a yellow wax: yield 60%. $[\alpha]_D$ = +8.05° (c = 0.8, $CHCl_3$). IR (film): ν 1771 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ 0.03, 0.06 (2 s, 6H, $(CH_3)_2Si$), 0.83 (s, 9H, $(CH_3)_3CSi$), 1.23 (d, 3H, J = 6.1 Hz, CH_3CH), 3.11 (d, J = 3.6 Hz, 1H, CH), 4.11 (dd, J = 6.3, 1.5 Hz, 1H, CH_2=), 4.21−4.14 (m, 2H, CH-OTBS, CH_2N), 4.39 (d, J = 15.2 Hz, 1H, CH_2N), 4,45 (dd, J = 13.9, 1.5 Hz, 1H, CH_2=); 5.19 (s, 1H, CHO), 6.21 (dd, J = 13.9, 6.3 Hz, 1H, CH=), 7.36−7.24 (m, 5H, Ph). ^{13}C NMR (125 MHz, $CDCl_3$): δ −4.7, −4.6, 17.9, 22.6, 25.7, 44.3, 64.1, 65.0, 82.8, 92.1, 127.7, 128.4, 128.7, 128.8, 135.2, 148.1, 166.3. HR MS (ESI): m/z calcd for $[M + Na]^+$ $C_{20}H_{31}NO_3NaSi$ 384.1965, found 384.1950.

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Supporting Information Available: Text, figures, and tables giving general experimental procedures, characterization data, and ^1H NMR and ^{13}C NMR spectra of all new compounds and additional information on the rearrangement of allyl ethers. This material is available free of charge via the Internet at http://pubs.acs.org.