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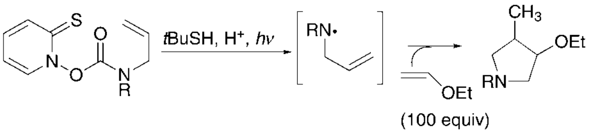
Iodoaziridine Derivatives as Novel Azahomoallyl Radical Precursors for [3+2] Cycloaddition Reactions with Alkenes

Osamu Kitagawa, Yoichiro Yamada, Hiroki Fujiwara, and Takeo Taguchi*

The [3+2] cycloaddition of a homoallyl radical with an alkene is a powerful method for the one-step synthesis of a cyclopentanoid skeleton.[1] If such a cycloaddition could be achieved with an azahomoallyl (allylaminyl) radical, it would provide a new and useful methodology for the preparation of pyrrolidine derivatives from simple substrates. As far as we know, only one example of the generation of an azahomoallyl radical and its reaction with an alkene has been reported, by Newcomb et al. [Eq. (1)].[2] This method using *N*-allyl *N*-hydroxypyridine-2-thione carbamates as an azahomoallyl



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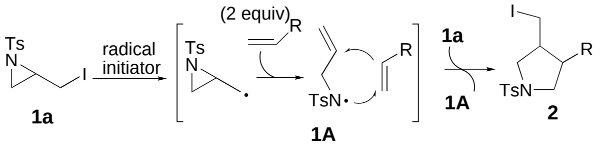
radical precursor requires 100 equiv of alkene to give reasonable yields of products (52–59%). Moreover, a Brønsted acid for the formation of the reactive allylaminium radical[3] and a thiol as a hydrogen donor for the resulting pyrrolidinylmethyl radical are required in these reactions. In addition, due to the limited number of examples, the scope and limitations of this reaction are unclear. Application to alkenes other than enol ethers and reactions with other azahomoallyl radicals such as cycloalkenyl- and prenylaminyl radicals were not investigated. In the addition of a nitrogen-centered radical to an alkene, intramolecular cyclization with a 4-pentenylaminyl radicals has been extensively demonstrated,[1f, 4] while the intermolecular version has so far been uncommon.[5] This may be due to the lower reactivity of nitrogen-centered radicals relative to carbon-centered radicals[1f, 4b, 6] and the lack of a suitable radical precursor. Here we report on radical, iodine-transfer [3+2] cycloaddition with various alkenes and *N*-tosyliodoaziridine derivatives **1** as novel azahomoallyl radical precursors [Eq. (2)].

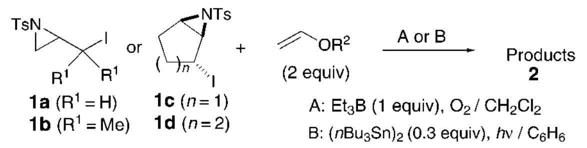


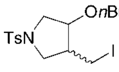
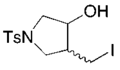
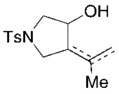
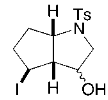
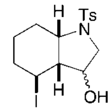
(2)

We expected that: 1) In the presence of a suitable radical initiator, *N*-tosyliodomethylaziridine (**1a**) might efficiently produce *N*-tosylallylamidyl radical **1A** by regioselective cleavage of the C–N bond of an aziridinylmethyl radical;[7] 2) the reaction of **1A** with an alkene would possibly give an iodoalkylated pyrrolidine derivative **2** by a radical iodine-transfer mechanism; 3) *N*-Tosylamidyl radical **1A** may be more reactive toward alkenes than an aminyl radical because of its more electronegative character;[8] and 4) the mild reaction conditions for the generation of **1A** and its addition to alkenes would make a wide range of alkenes employable.[3] Furthermore, **1a** and various other iodoaziridine derivatives **1b–d** can be easily prepared by iodoaziridination of *N*-allyltosylamide derivatives.[9] Thus, the generation of various azahomoallyl radicals such as allyl-, prenyl-, and cycloalkenylamidyl radicals may be also possible.

The [3+2] cycloadditions of **1a–d** with alkenes (2 equiv) were investigated in the presence of several radical initiators. The reaction of **1** with electron-rich alkenes such as enol ethers proceeded smoothly (Table 1). For example, the reaction of iodomethylaziridine **1a** with butyl vinyl ether under conditions A (1 equiv Et_3B, O_2 in CH_2Cl_2) efficiently proceeded even with only 2 equiv of the alkene to give functionalized iodomethylpyrrolidine **2a** in good yield (64%; entry 1).[10] The reaction under conditions B (0.1 equiv $(nBu_3Sn)_2$, *hν*) gave a lower yield (48%; entry 2). Since the present reaction can be performed under nonaqueous and neutral conditions,[3] application to acid-sensitive silyl enol ethers is also possible. Thus, hydroxypyrrolidine **2b** was obtained in good yield (conditions A, 66%; conditions B, 80%) after desilylation of the cycloaddition product with 2% HCl (entries 3 and 4). In the reaction of **1a** with silyl enol ethers, conditions B gave better results than conditions A.

Table 1. Radical [3+2] cycloaddition of various iodoaziridines **1** with enol ethers.



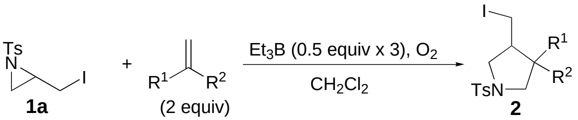
Entry	Aziridine	R²[a]	Conditions	Products **2**	Yield [%][b]	*cis/trans*
1	**1a**	*n*Bu	A	 **2a**	64	1[c]
2	**1a**	*n*Bu	B	**2a**	48	1[c]
3	**1a**	TMS	A	 **2b**	66	1.3[d]
4	**1a**	TMS	B	**2b**	80	1.5[d]
5[e]	**1b**	TMS	A	 **2c**	63[f]	–
6[e]	**1b**	TMS	B	**2c**	37[g]	–
7	**1c**	TMS	A	 **2d**	60	1/1.5[d,h]
8	**1d**	TMS	A	 **2e**	62	1.4[d,h]

[a] TMS = trimethylsilyl. [b] Yield of isolated product. [c] The ratio was determined by ^1H NMR spectroscopy. [d] The ratio was determined on the basis of isolated products. [e] The product (tertiary iodide) was subsequently treated with DBU because of its instability. [f] A mixture of internal double bond product (internal-**2c**) and terminal double bond product (terminal-**2c**) was obtained in a ratio of 4:1. The diastereomer ratio of terminal-**2c** was 5:1, while the configurations were not determined. [g] Internal-**2c**/terminal-**2c** = 4.3. A diastereomer ratio of terminal-**2c** = 5:1 [h] The formation of two stereoisomers was observed. The ratio corresponds to *α*-OH/*β*-OH.

The radical [3+2] cycloaddition reaction with 2 equiv of silyl enol ether can also be applied to the iodoalkylated aziridine derivatives **1b–1d**, which produce prenyl- and cycloalkenylamidyl radicals (entries 5–8). Under conditions A, reaction of **1b** with silyl enol ether also proceeded efficiently to give **2c** in good yield (63%) after treatment of the cycloadduct with 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU; entry 5), while under conditions B, a lower yield was obtained (37%, entry 6). The reactions of bicyclic iodoaziridines **1c** and **1d** gave functionalized bicyclic nitrogen-containing compounds **2d** and **2e** in 60 and 62% yield, respectively (entries 7 and 8).

The present reaction using iodoaziridine **1a** can also be applied to alkyl-substituted alkenes (2 equiv) such as methylenecyclohexane and allylsilane because of the higher reactivity of the *N*-tosylamidyl radical compared to a simple aminyl radical. In these reactions, gradual generation of an *N*-

tosylallylamidyl radical by portionwise addition of Et_3B (3 × 0.5 equiv) increased the yield.[11] Thus, the [3+2] cycloaddition products **2f** and **2g** were obtained in 56 and 51 % yield, respectively [Eq. (3)]. When 1 equiv of Et_3B was added in one portion, considerably lower yields of 28 and 33 %, respectively, were obtained, and *N*-allyltosylamide was formed as a side product. The reaction with the simple 1-alkene 1-hexene gave **2h** in low yield (34 %), even with portionwise addition of Et_3B. These results may indicate that the reactivity of the *N*-tosylamidyl radical towards the alkene decreases with decreasing electron richness of the alkene.



(3)

R^1 R^2 = $(CH_2)_4$ **2f** (56 %)

R^1 = CH_2SiMe_3, R^2 = H **2g** (51 %, *cis / trans* = 2.6)

R^1 = C_4H_9, R^2 = H **2h** (34 %, *cis / trans* = 2.1)

In all reactions shown in Table 1 and Equation (3), formation of regioisomers was not observed. Thus, both cleavage of the C–N bond in the *N*-tosylaziridinylmethyl radical and the attack of the resulting *N*-tosylamidyl radical on the terminal carbon atom of alkene should proceed with complete regioselectivity, while the diastereoselectivities of the reactions are generally low (*cis*/*trans* = 1–2.6).

In conclusion, we have developed the radical iodine-transfer [3+2] cycloaddition of various alkenes with iodoaziridine derivatives as novel precursors of azahomoallyl radicals. The present reaction should provide a new and efficient methodology for the synthesis of functionalized pyrrolidine derivatives.

Experimental Section

cis/*trans*-**2b**: Et_3B (0.5 mL, 1 M in hexane) was added to a solution of iodoaziridine **1a** (169 mg, 0.5 mmol) and trimethylsilyl vinyl ether (0.15 mL, 1 mmol) in CH_2Cl_2 (4 mL) under Ar. Dry air (20 mL) was subsequently introduced with a syringe. After stirring for 10 h at room temperature, 5 % HCl (4 mL) and MeOH (15 mL) were added, and the mixture was then stirred for 2 h at room temperature. After removal of MeOH by evaporation, the residue was extracted with Et_2O. The Et_2O extracts were washed with brine, dried over $MgSO_4$, and evaporated to dryness. Purification of the residue by column chromatography (hexane/AcOEt 1/1) gave a mixture of *cis*-**2b** and *trans*-**2b**. Further purification of the mixture by MPLC (hexane/AcOEt 2/1) gave *cis*-**2b** (71 mg, 37 %, less polar) and *trans*-**2b** (56 mg, 29 %, more polar). The configurations of *cis*-**2b** and *trans*-**2b** were determined by NOE experiments.

cis-**2b**: white solid, m.p. 130–131 °C; IR (KBr): $\tilde{\nu} = 3492, 1322, 1152\ cm^{-1}$; ^1H NMR (300 MHz, $CDCl_3$, 25 °C, TMS) $\delta = 7.72$ (d, $J = 8.0$ Hz, 2 H), 7.34 (d, $J = 8.0$ Hz, 2 H), 4.31 (q, $J = 3.8$ Hz, 1 H), 3.60 (dd, $J = 7.9, 9.6$ Hz, 1 H), 3.51 (dd, $J = 3.8, 11.6$ Hz, 1 H), 3.43 (dd, $J = 1.0, 11.6$ Hz, 1 H), 3.17 (dd, $J = 9.0, 9.8$ Hz, 1 H), 3.10 (dd, $J = 6.8, 9.8$ Hz, 1 H), 3.01 (dd, $J = 9.6, 10.6$ Hz, 1 H), 2.44 (s, 3 H), 2.42 (m, 1 H), 1.59 (d, $J = 4.9$ Hz, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C, TMS) $\delta = 143.8, 133.6, 129.8, 127.4, 71.2, 56.4, 50.9, 47.3, 21.5, 0.4$; MS: *m*/*z*: 381 [$M^+$]; HRMS calcd for $C_{12}H_{16}INO_3S$ [M^+]: 380.9896; found 380.9869.

trans-**2b**: white solid, m.p. 136–137 °C; IR (KBr): $\tilde{\nu} = 3501, 1338, 1160\ cm^{-1}$; ^1H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 7.71$ (d, $J = 8.3$ Hz, 2 H), 7.34 (d, $J = 8.3$ Hz, 2 H), 4.05 (m, 1 H), 3.56 (dd, $J = 5.9, 10.5$ Hz, 1 H), 3.51 (dd, $J = 7.5, 10.5$ Hz, 1 H), 3.05–3.15 (m, 3 H), 2.97 (dd, $J = 7.8, 10.5$ Hz, 1 H), 2.44 (s, 3 H), 2.28 (m, 1 H), 2.17 (br s, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 144.0, 132.8, 129.9, 127.5, 74.6, 54.3, 52.2, 48.7, 21.6, 4.9$; MS: *m*/*z*: 381 [$M^+$]; HRMS calcd for $C_{12}H_{16}INO_3S$ [M^+]: 380.9896, found: 380.9877.

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[10] This indicates that together with the addition of *N*-tosylamidyl radical to an enol ether, iodine transfer to the resulting pyrrolidinylmethyl radical from iodoaziridine **1a** should also proceed efficiently, that is, the formation of aziridinylmethyl radical may be the thermodynamically favorable process.

[11] **Caution:** When Et_3B was added to the reaction mixture at a high concentration of O_2, an explosion occurred once. Hence, further addition of Et_3B must be performed under Ar or N_2 atmosphere.