3-Substituted 2-Acyl-1-sulfonylaziridines from the Reaction of Triphenylbismuthonium 2-Oxoalkylides and *N*-Sulfonylaldimines. Reversal of the *cis*/*trans*-Isomer Ratios Depending on Base and Additive

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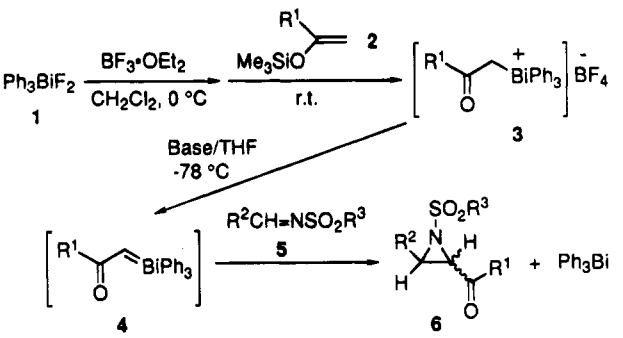
Bismuthonium ylides have been known for many years,[1-3] but their chemistry remains little explored. This is mainly because of the limited number of known approaches to this class of compounds and, especially, the difficult access to their parent onium salts. We have recently developed a convenient route to (2-oxoalkyl)-triphenylbismuthonium compounds **3** which involves the reaction of silyl enolates **2** with triphenylbismuth difluoride **1** in the presence of boron trifluoride diethyl ether (Scheme 1).[4] The ylide **4**, generated *in situ* from salt **3**, readily couples with a variety of aldehydes to give the corresponding acyloxiranes (α,β-epoxyketones) in good yields.[5] This is in accordance with the low affinity for oxygen and the good leaving tendency of the triphenylbismuth moiety. As an extension of this methodology, we now report that reaction of the bismuthonium ylide **4** with *N*-sulfonylaldimines **5** provides a simple route to *cis*- and *trans*-2-acyl-1-sulfonylaziridines **6**, which are convenient precursors to *N*-protected amino- and enaminoketones.[6]

Bismuthonium ylides **4a,b**, generated *in situ* from the 2-oxoalkylbismuthonium tetrafluoroborates **3a,b** and a base in THF at −78 °C, smoothly reacted with *N*-sulfonylaldimines **5a−f** to give a mixture of *cis*/*trans*-2-acyl-1-sulfonylaziridines **6** in moderate to good yields (Scheme 1). Triphenylbismuthine was always recovered quantitatively. Under the same conditions, *N*-benzylideneethylimine did not form an aziridine, probably due to the low electrophilicity of the imino carbon atom. *N*-Sulfonylketimines were also unreactive toward the ylide **4** under these conditions. The aziridines **6** were isolated by column chromatography on silica gel and characterized by NMR, IR, and MS spectroscopy and elemental analysis. The results obtained are summarized in Table 1.

Scheme 1



3a: R^1 = *t*-Bu
3b: R^1 = Ph

5a: R^2 = Ph, R^3 = *p*-Tol
5b: R^2 = *p*-Tol, R^3 = *p*-Tol
5c: R^2 = *p*-ClC_6H_4, R^3 = *p*-Tol
5d: R^2 = (*E*)-PhCH=CH, R^3 = *p*-Tol
5e: R^2 = Ph, R^3 = Ph
5f: R^2 = Ph, R^3 = Me

6aa: R^1 = *t*-Bu, R^2 = Ph, R^3 = *p*-Tol
6ab: R^1 = *t*-Bu, R^2 = *p*-Tol, R^3 = *p*-Tol
6ac: R^1 = *t*-Bu, R^2 = *p*-ClC_6H_4, R^3 = *p*-Tol
6ad: R^1 = *t*-Bu, R^2 = (*E*)-PhCH=CH, R^3 = *p*-Tol
6ba: R^1 = Ph, R^2 = Ph, R^3 = *p*-Tol
6bb: R^1 = Ph, R^2 = *p*-Tol, R^3 = *p*-Tol
6bc: R^1 = Ph, R^2 = *p*-ClC_6H_4, R^3 = *p*-Tol
6be: R^1 = Ph, R^2 = Ph, R^3 = Ph
6bf: R^1 = Ph, R^2 = Ph, R^3 = Me

There are several noteworthy features of this reaction. When potassium *tert*-butoxide (KO-*t*-Bu) or potassium hexamethyldisilazide (KHMDS) was employed as the base, a high *trans* selectivity was observed (entries 1−17). Substituent groups on either the sulfonyl group or the aromatic ring did not significantly influence the *trans* selectivity. Additives such as hexamethylphosphoramide (HMPA) and tetramethylethylenediamine (TMEDA) showed little effect on the *cis*/*trans* selectivity. Performing the reaction in toluene resulted in a decreased yield of **6** with no effect on the stereoselectivity (entry 17). In contrast, the stereoselectivity was somewhat decreased (entries 18 and 19) or entirely lost (entries 23 and 24) when sodium hexamethyldisilazide (NaHMDS) was used as the base. Interestingly enough, the addition of a small amount of HMPA or TMEDA to the NaHMDS-based reaction system was found to reverse the stereoselectivity of the major product from *trans* to *cis* (entries 20−22 and 25). Mutual *cis*/*trans*-isomerization of the products was not observed under the given reaction conditions. The reason for such a remarkable effect of the alkaline metal cations and some additives on the *cis*/*trans* selectivity of the aziridine formation is not clear at present. Since a similar effect was not observed in the epoxidation of aldehydes with ylide **4**,[5] the sulfonamide moiety of imine **5** may be a key factor in controlling the diastereofacial selection. The difference in coordinating ability of sodium and potassium ions toward the additives might be an additional factor. Lithium diisopropylamide and lithium hexamethyldisilazide were also used as bases, but the yields of aziridine **6** were not satisfactory (18%−44%).

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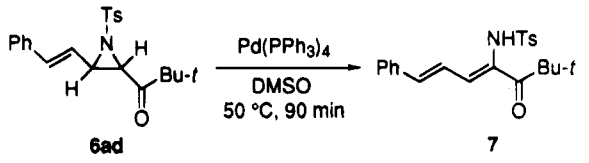
Table 1. 2-Acyl-1-sulfonylaziridines 6 Obtained[a]

entry no.	salt 3	imine 5	base[b]	additive	aziridine 6	yield[c] (%)	isomer ratio *cis/trans*
1	a	a	KO-*t*-Bu		aa	91	5/95
2	a	b	KO-*t*-Bu		ab	80	0/100
3	a	b	KHMDS		ab	74	0/100
4	a	c	KO-*t*-Bu		ac	86	0/100
5	a	c	KHMDS		ac	67	0/100
6	a	c	KHMDS	HMPA (1.2 equiv)	ac	*d*	0/100
7	a	c	KHMDS	TMEDA (1 equiv)	ac	74	0/100
8	a	d	KO-*t*-Bu		ad	58	13/87
9	b	a	KO-*t*-Bu		ba	66	18/82
10	b	b	KO-*t*-Bu		bb	44	0/100
11	b	b	KHMDS		bb	55	0/100
12	b	c	KO-*t*-Bu		bc	67	19/81
13	b	c	KO-*t*-Bu	HMPA (6 equiv)	bc	*d*	21/79
14	b	c	KHMDS		bc	43[e,f]	11/89
15	b	e	KO-*t*-Bu		be	67	9/91
16	b	f	KO-*t*-Bu		bf	61	12/88
17	b	c	KO-*t*-Bu		bc	47[f]	11/89
18	a	b	NaHMDS		ab	88	7/93
19	a	c	NaHMDS		ac	87	19/81
20	a	c	NaHMDS	HMPA (1.2 equiv)	ac	84	72/28
21	a	c	NaHMDS	HMPA (6 equiv)	ac	84	62/38
22	a	c	NaHMDS	TMEDA (1 equiv)	ac	87	86/14
23	b	b	NaHMDS		bb	69	46/54
24	b	c	NaHMDS		bc	44[f]	47/53
25	b	c	NaHMDS	HMPA (1.2 equiv)	bc	40	100/0

[a] Reaction was carried out in THF at −78 °C using salt **3**, base, and imine **5** in an equimolar ratio, unless otherwise noted. [b] KHMDS; potassium hexamethyldisilazide. NaHMDS; sodium hexamethyldisilazide. [c] Yield of the isolated product based on salt **3**. [d] Aziridines were not isolated. Their isomer ratios were estimated from ^{1}H NMR integration of the reaction mixtures. [e] Toluene was the solvent used. [f] HPLC yield based on salt **3**.

Scheme 2



To our knowledge, the present reaction opens the first direct route to 2-acylaziridines **6** starting from imines and ylides. The mode of reaction stands in marked contrast to that of phosphonium ylides, which undergo the aza-Wittig-type reaction with imines to give olefins and phosphinimine.[7] The weak interaction between the bismuth and imino nitrogen atoms results in an ylide–imine reaction following the aziridination pathway.[8]

2-Acylaziridines (aziridino ketones) are useful as synthetic intermediates, since the ethyleneimine structure is susceptible to regioselective ring opening and ring expansion, giving a wide range of amino compounds and nitrogen-containing heterocycles.[6] As an example that illustrates the synthetic utility of this class of compounds, aziridine **6ad** was converted to 2,2-dimethyl-7-phenyl-4-(tosylamino)hepta-4,6-dien-3-one **7** in good yield (64%) under catalysis by tetrakis(triphenylphosphine)palladium (Scheme 2).

Although limited to activated imines **5**, the present method provides a new and simple entry into 2-acylaziridines. It features control of the *cis*/*trans* stereochemistry of the products by a proper choice of base and additive. This feature is of special interest, since the Darzens-type condensation between α-halo ester enolate anions and aldimines has generally been known to give *cis*-rich aziridino esters.[9] Therefore, the synthesis of 2-acylaziridines described herein constitutes a useful addition to the existing methodologies.

Experimental Section

General. Melting points are uncorrected. ^{1}H NMR spectra were recorded at 200 or 500 MHz in $CDCl_3$ with TMS as an internal standard. EI mass spectra were measured at 70 eV. Elemental analyses were performed at Microanalytical Laboratories of Kyoto University. All reactions were carried out under an Ar atmosphere. THF was distilled from sodium benzophenone ketyl before use. Toluene was distilled from sodium wire and stored over 4A molecular sieves. Bismuthonium salts **3** were prepared as previously reported.[4] *N*-Sulfonylaldimines **5** were prepared according to the literature procedure.[10] Column chromatography was performed on silica gel (Wakogel, 200 mesh).

Caution: Bismuth is generally considered to be one of the less toxic heavy metals, and some bismuth compounds are used as internal medicines and face powders. However, industrial bismuth poisoning might be misdiagnosed as plumbism.

2-Acyl-1-sulfonylaziridines (6): Typical Procedure. To a suspension of (3,3-dimethyl-2-oxobutyl)triphenylbismuthonium tetrafluoroborate **3a** (125 mg, 0.2 mmol) in THF (5 mL) was added KO-*t*-Bu (23 mg, 0.2 mmol) at −78 °C. After the mixture was stirred for 30 min, *N*-tosylbenzylidenimine **5a** (52 mg, 0.2 mmol) was added, and the resulting mixture was allowed to warm to ambient temperature. After 5 h, the mixture was

(7) For example, see: Johnson, A. W. *Ylides and Imines of Phosphorus*; Wiley: Chichester, 1993, and references cited therein. Triphenylphosphonium phenacylide, however, did not react with imine **5a** even after 24 h of refluxing in benzene.

(8) A theoretical study has been made on the reactivity of ylides derived from group 15 elements N, P, As, Sb, and Bi toward aldehyde; it claims that the Corey-type epoxidation is the thermodynamically preferred pathway for the reaction between bismuthonium ylide $H_3Bi{=}CH_2$ and formaldehyde. Naito, T.; Nagase, S.; Yamataka, H. *J. Am. Chem. Soc.* **1994**, *116*, 10080.

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evaporated under reduced pressure and the residue was extracted with benzene. Removal of the solvent gave an oily residue, which was chromatographed on silica gel using hexane–EtOAc (5:1) as the solvent to successively elute triphenylbismuthine (81 mg, 92%) and 2-(2,2-dimethyl-1-oxopropyl)-3-phenyl-1-tosylaziridine **6aa** (65 mg, 91%). The structure assignment of the product was made by the ^1H–^1H coupling constants of the methine protons on the imino ring (*cis*, ca. 7–8 Hz; *trans*, ca. 4 Hz), and the isomer ratio was determined by the integral values of ^1H NMR absorption due to these protons. The analytically pure *trans* isomer was obtained by fractional crystallization from hexane–EtOAc (10:1).

***trans*-2-(2,2-Dimethyl-1-oxopropyl)-3-phenyl-1-tosylaziridine (6aa)**: ^1H NMR (200 MHz) δ 1.27 (s, 9H), 2.37 (s, 3H) 3.98 (d, J = 4.1 Hz, 1H), 4.29 (d, J = 4.1 Hz, 1H), 7.20–7.37 (m, 7H), 7.73 (d, J = 8.4 Hz, 2H); IR (neat) 1717 (C=O), 1335 (SO_2), 1163 (SO_2) cm^{-1}; MS m/z 300 (M^+ − t-Bu). Anal. Calcd for $C_{20}H_{23}NO_3S$: C, 67.20; H, 6.48; N, 3.92. Found: C, 67.05; H, 6.52; N, 3.87.

***trans*-2-(2,2-Dimethyl-1-oxopropyl)-3-(4-methylphenyl)-1-tosylaziridine (6ab)**: mp 146–147 °C; ^1H NMR (200 MHz) δ 1.26 (s, 9H), 2.34 (s, 3H), 2.41 (s, 3H), 4.01 (d, J = 4.2 Hz, 1H), 4.23 (d, J = 4.2 Hz, 1H), 7.10–7.25 (m, 6H), 7.73 (d, J = 8.0 Hz, 2H); IR (KBr) 1711 (C=O), 1333 (SO_2), 1159 (SO_2) cm^{-1}; MS m/z 371 (M^+). Anal. Calcd for $C_{21}H_{25}NO_3S$: C, 67.90; H, 6.78; N, 3.77. Found: C, 67.76; H, 6.76; N, 3.72.

***trans*-3-(4-Chlorophenyl)-2-(2,2-dimethyl-1-oxopropyl)-1-tosylaziridine (6ac)**: mp 162–163 °C; ^1H NMR (200 MHz) δ 1.26 (s, 9H), 2.42 (s, 3H), 3.93 (d, J = 4.1 Hz, 1H), 4.25 (d, J = 4.1 Hz, 1H), 7.15–7.30 (m, 6H), 7.73 (d, J = 8.4 Hz, 2H); IR (KBr) 1713 (C=O), 1335 (SO_2), 1159 (SO_2) cm^{-1}; MS m/z 334 (M^+ − t-Bu). Anal. Calcd for $C_{20}H_{22}ClNO_3S$: C, 61.29; H, 5.66; N, 3.57. Found: C, 61.29; H, 5.62; N, 3.52.

***cis*-3-(4-Chlorophenyl)-2-(2,2-dimethyl-1-oxopropyl)-1-tosylaziridine (6ac)**: mp 103–105 °C; ^1H NMR (200 MHz) δ 0.99 (s, 9H), 2.44 (s, 3H), 4.06 (d, J = 7.6 Hz, 1H), 4.14 (d, J = 7.6 Hz, 1H), 7.22 (s, 4H), 7.34 (d, J = 8.2 Hz, 2H), 7.90 (d, J = 8.2 Hz, 2H); IR (KBr) 1717 (C=O), 1347 (SO_2), 1163 (SO_2) cm^{-1}; MS m/z 236 (M^+ − Ts). Anal. Calcd for $C_{20}H_{22}ClNO_3S$: C, 61.29; H, 5.66; N, 3.57. Found: C, 61.23; H, 5.65; N, 3.40.

***trans*-2-(2,2-Dimethyl-1-oxopropyl)-3(*E*)-(2-phenylethenyl)-1-tosylaziridine (6ad)**: mp 117–119 °C; ^1H NMR (200 MHz) δ 1.17 (s, 9H), 2.41 (s, 3H), 3.60 (dd, J = 4.0, 9.6 Hz, 1H), 4.05 (d, J = 4.0 Hz, 1H), 6.55 (dd, J = 9.6, 15.8 Hz, 1H), 6.83 (d, J = 15.8 Hz, 1H), 7.25–7.45 (m, 7H), 7.83 (d, J = 8.4 Hz, 2H); IR (KBr) 1715 (C=O), 1325 (SO_2), 1159 (SO_2) cm^{-1}; MS m/z 298 (M^+ − t-BuC=O). Anal. Calcd for $C_{22}H_{25}NO_3S$: C, 68.90; H, 6.57; N, 3.65. Found: C, 68.54; H, 6.62; N, 3.58.

***trans*-2-Benzoyl-3-phenyl-1-tosylaziridine (6ba)**: mp 141–142 °C; ^1H NMR (200 MHz) δ 2.40 (s, 3H), 4.29 (d, J = 4.2 Hz, 1H), 4.52 (d, J = 4.2 Hz, 1H), 7.23 (d, J = 8.3 Hz, 2H), 7.34 (s, 5H), 7.49 (t, J = 7.7 Hz, 2H), 7.63 (t, J = 7.6 Hz, 1H), 7.72 (d, J = 8.3 Hz, 2H), 8.06 (d, J = 7.7 Hz, 2H); IR (KBr) 1684 (C=O), 1321 (SO_2), 1159 (SO_2) cm^{-1}; MS m/z 377 (M^+). Anal. Calcd for $C_{22}H_{19}NO_3S$: C, 70.01; H, 5.07; N, 3.71. Found: C, 70.23; H, 5.03; N, 3.64.

***trans*-2-Benzoyl-3-(4-methylphenyl)-1-tosylaziridine (6bb)**: mp 114–115 °C; ^1H NMR (200 MHz) δ 2.35 (s, 3H), 2.40 (s, 3H), 4.32 (d, J = 4.2 Hz, 1H), 4.46 (d, J = 4.2 Hz, 1H), 7.1–7.3 (m, 6H), 7.48 (t, J = 7.6 Hz, 2H), 7.62 (t, J = 7.4 Hz, 1H), 7.72 (d, J = 8.4 Hz, 2H), 8.05 (d, J = 7.1 Hz, 2H); IR (KBr) 1692 (C=O), 1325 (SO_2), 1163 (SO_2) cm^{-1}; MS m/z 391 (M^+). Anal. Calcd for $C_{23}H_{21}NO_3S$: C, 70.56; H, 5.41; N, 3.58. Found: C, 70.43; H, 5.28; N, 3.57.

***trans*-2-Benzoyl-3-(4-chlorophenyl)-1-tosylaziridine (6bc)**: mp 149–150 °C; ^1H NMR (200 MHz) δ 2.41 (s, 3H), 4.24 (d, J = 4.3 Hz, 1H), 4.48 (d, J = 4.3 Hz, 1H), 7.20–7.35 (m, 6H), 7.49 (t, J = 7.7 Hz, 2H), 7.62 (d, J = 7.3 Hz, 1H), 7.71 (d, J = 8.4 Hz, 2H), 8.04 (d, J = 7.0 Hz, 2H); IR (KBr) 1696 (C=O), 1331 (SO_2), 1163 (SO_2) cm^{-1}; MS m/z 256 (M^+ − Ts). Anal. Calcd for $C_{22}H_{18}ClNO_3S$: C, 64.15; H, 4.40; N, 3.40. Found: C, 64.19; H, 4.34; N, 3.21.

***cis*-2-Benzoyl-3-(4-chlorophenyl)-1-tosylaziridine (6bc)**: mp 117–118 °C; ^1H NMR (200 MHz) δ 2.45 (s, 3H), 4.30 (d, J = 7.5 Hz, 1H), 4.41 (d, J = 7.5 Hz, 1H), 7.16 (s, 4H), 7.34–7.44 (m, 4H), 7.56 (t, J = 7.5 Hz, 1H), 7.85 (d, J = 7.1 Hz, 2H), 7.96 (d, J = 8.3 Hz, 2H); IR (KBr) 1698 (C=O), 1331 (SO_2), 1161 (SO_2) cm^{-1}; MS m/z 256 (M^+ − Ts). Anal. Calcd for $C_{22}H_{18}ClNO_3S$: C, 64.15; H, 4.40; N, 3.40. Found: C, 64.30; H, 4.43; N, 3.32.

***trans*-1-(Benzenesulfonyl)-2-benzoyl-3-phenylaziridine (6be)**: mp 133–134 °C; ^1H NMR (200 MHz) δ 4.32 (d, J = 4.3 Hz, 1H), 4.54 (d, J = 4.3 Hz, 1H), 7.34 (s, 5H), 7.40–7.70 (m, 6H), 7.85 (d, J = 7.0 Hz, 2H), 8.05 (d, J = 7.1 Hz, 2H); IR (KBr) 1684 (C=O), 1331 (SO_2), 1163 (SO_2) cm^{-1}; MS m/z 222 (M^+ − SO_2Ph). Anal. Calcd for $C_{21}H_{17}NO_3S$: C, 69.40; H, 4.71; N, 3.85. Found: C, 69.04; H, 4.76; N, 3.79.

***trans*-2-Benzoyl-1-mesyl-3-phenylaziridine (6bf)**: mp 99–100 °C; ^1H NMR (200 MHz) δ 3.17 (s, 3H), 4.28 (d, J = 4.3 Hz, 1H), 4.45 (d, J = 4.3 Hz, 1H), 7.40–7.70 (m, 8H), 8.07 (d, J = 7.1 Hz, 2H); IR (KBr) 1686 (C=O), 1327 (SO_2), 1148 (SO_2) cm^{-1}; MS m/z 222 (M^+ − Ms). Anal. Calcd for $C_{16}H_{15}NO_3S$: C, 63.77; H, 5.02; N, 4.65. Found: C, 63.87; H, 4.95; N, 4.60.

No attempts were made to isolate the *cis* isomers of the aziridines **6aa**, **6ab**, **6ad**, **6ba**, **6bb**, **6be**, and **6bf** because of their minor presence in the crude products.

Pd-Catalyzed Ring Opening of Aziridine 6ad to Enaminoketone 7. A mixture of aziridine **6ad** (192 mg, 0.5 mmol), $Pd(PPh_3)_4$ (17 mg, 0.015 mmol), and DMSO (5 mL) was heated at 50 °C. After 90 min, the mixture was cooled to room temperature and diluted with saturated aqueous NH_4Cl (20 mL) and Et_2O (30 mL). The organic phase was separated, washed successively with water (20 mL) and brine (20 mL), and dried with $MgSO_4$. Removal of the solvent left an oily residue, which was chromatographed on silica gel using hexane–EtOAc (5:1) as the solvent to yield 2,2-dimethyl-7-phenyl-4-(tosylamino)-hepta-4,6-dien-3-one **7** (123 mg, 64%) as colorless crystals: mp 143–144 °C (hexane–EtOAc, 10:1); ^1H NMR (500 MHz) δ 1.07 (s, 9H), 2.37 (s, 3H), 6.95 (d, J = 15.9 Hz, 1H), 7.03 (s, 1H), 7.20 (d, J = 11.0 Hz, 1H), 7.23 (d, J = 8.3 Hz, 2H), 7.33 (t, J = 7.3 Hz, 1H), 7.38 (t, J = 7.3 Hz, 2H), 7.54 (d, J = 7.3 Hz, 2H), 7.59 (dd, J = 11.0, 15.9 Hz, 1H), 7.65 (d, J = 8.3 Hz, 2H); IR (KBr) 3210 (NH), 1661 (C=O), 1337 (SO_2), 1171 (SO_2) cm^{-1}; MS m/z 383 (M^+). Anal. Calcd for $C_{22}H_{25}NO_3S$: C, 68.90; H, 6.57; N, 3.65. Found: C, 68.96; H, 6.54; N, 3.55.

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