HETEROCYCLES, Vol. 79, 2009, pp. 659 - 667. © The Japan Institute of Heterocyclic Chemistry
Received, 26th September, 2008, Accepted, 10th November, 2008, Published online, 13th November, 2008.
DOI: 10.3987/COM-08-S(D)33

SYNTHESIS AND THERMAL STABILITY OF 3-SUBSTITUTED 3-BENZOSTIBEPINES

Shuji Yasuike,[1,2] Masaaki Ikoma,[1] Naoki Kakusawa,[1] Takashi Tsuchiya,[1] and Jyoji Kurita[*1]

[1]Faculty of Pharmaceutical Sciences, Hokuriku University, Kanagawa-machi, Kanazawa 920-1181, Japan. E-mail: j-kurita@hokuriku-u.ac.jp

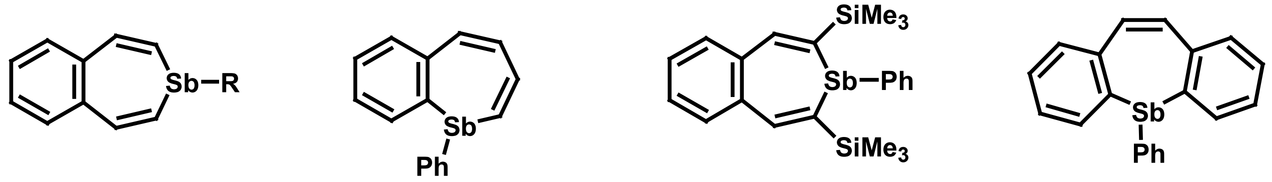
[2]Organization for Frontier Research in Preventive Pharmaceutical Sciences, Hokuriku University, Kanagawa-machi, Kanazawa 920-1181, Japan

Abstract – Fully unsaturated 3-benzostibepines having various aryl groups on antimony have been prepared by a ring closure reaction of an appropriate antimony dihalide ($ArSbBr_2$) with (*Z*,*Z*)-1,2-bis(2-lithiovinyl)benzene generated by treatment of (*Z*,*Z*)-1,2-bis(2-bromovinyl)benzene with *t*-BuLi. All the stibepines obtained here are thermolabile in solution toward heteroatom extrusion. The half-lives of the stibepines estimated from ^1H NMR spectral analysis revealed that the thermal stabilities of the stibepines bearing a heteroatom moiety (N, O) in the vicinity of the antimony are far less stable than others.

INTRODUCTION

Considerable attention has recently been focused on the chemistry of fully unsaturated seven-membered rings (heteroepines) containing group 15 (P, As, Sb, and Bi) and 16 (S, Se, and Te) elements. In general, simple heteroepines (monocyclic or mono aromatic ring-fused) are know to be thermally unstable owing to ready extrusion of heteroatom moiety *via* electrocyclic reaction.[1] With regard to benzostibepines, several reports for the synthesis have been reported in recent years, in that the 7-membered ring was mainly constructed with tin-antimony metal exchange reaction of stannepines[2,3] and with ring closure reaction of 1,6-dilithium compounds with antimony dihalides.[4,5,6] Furthermore, the thermal stability of these compounds is of remarkable interest and is well documented; e.g. i) 3- (**1**) and 1-benzostibepines (**2**) are thermally unstable and decompose to naphthalene with elimination of heteroatom moiety,[2,4] ii) 3-chloro- and 3-alkyl-3-benzostibepines are thermolabile and can be isolated only at low temperature,[2] iii) 3-benzostibepines (**1**) are less stable than the corresponding 1-benzostibepines (**2**),[4] iv) the

3-benzostibepine (**3**) having bulky trimethylsilyl group on both 2- and 4-positions is much more stable than C-unsubstituted compounds,[6] v) the dibenzostibepine (**4**) is thermally stable and remains unchanged even when it is heated over 60 °C.[5a] However, little is known about the influence of antimony ligand upon their thermal stability. This paper describes a versatile synthesis of various 3-substituted 3-benzostibepine derivatives and their thermal stabilities in detail.

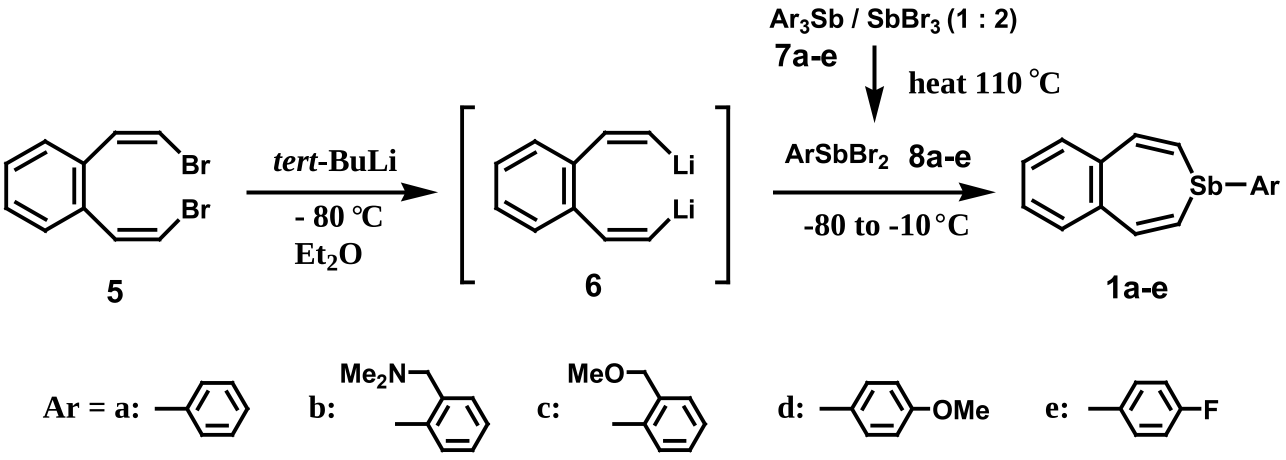


1: R = Cl, Me, *n*Bu, Ph **2** **3** **4**

Scheme 1

RESULTS AND DISCUSSION

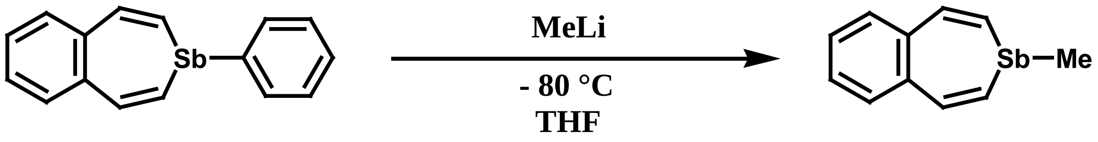
The synthesis of 3-benzostibepines (**1a-e**) from (*Z*,*Z*)-1,2-bis(2-bromovinyl)benzene (**5**) is shown in Scheme 2. The route for the synthesis of 3-aryl-3-benzostibepines (**1a-e**) from **5** is essentially the same as that for the preparation of 3-benzoheteroepines containing group 15 (P, As, Sb, Bi) and 16 (S, Se, Te) heavier elements in our previous paper.[4,6] The key starting bromide (**5**) was prepared stereoselectively in high yield (90%) by a double Wittig reaction of *o*-phthalaldehyde with bromomethyltriphenylphosphonium ylide,[4,7] generated *in situ* by treatment of bromomethyltriphenylphosphonium bromide with potassium *tert*-butoxide in tetrahydrofuran at low temperature (–80 °C). The bromide (**5**) was treated with a large excess of *tert*-butyllithium (7.5 eq) in anhydrous Et_2O at –80 °C under an argon atmosphere, and then with dibromoarylstibanes (**8a-e**) to undergo ring closure giving rise to the expected 3-aryl-3-benzostibepines (**1a-e**) in 10-36% yield, *via* 1,6-dilithium intermediate (**6**). All dibromoarylstibanes (**8a-e**) employed in the present reactions were prepared by treatment of a 1:2 mixture



Scheme 2

of triarylstibanes (**7a-e**) and tribromostibane at 90 °C for 1-3 h, and were used directly without purification.

We have recently reported that the reaction of organoantimony (III) compounds with Grignard or organolithium reagents resulted in nucleophilic displacement of the substituents on the antimony to give various new antimony (III) compounds.[8] Especially, the displacement of the phenyl substituent on group 15 atoms in 1-phenyl-1-benzoheteroles (As, Sb, Bi) to methyl group occurred easily by treatment with methyllithium.[8a] Taking these results into consideration, we next examined the behavior of 3-benzostibepine toward organolithium reagent. The reaction of 3-phenyl-3-benzostibepine (**1a**) with 1.2 equivalent of methyllithium in tetrahydrofuran at –80 °C underwent the expected substitution on the antimony to give 3-methyl-3-benzostibepine (**1f**) in low yield (12%), which is the first example of nucleophilic displacement of the substituent on antimony of heteroepine (Scheme 3).



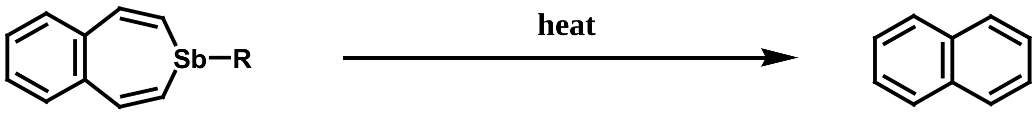
1a **1f**

Scheme 3

Table 1. Selected ^{1}H NMR spectral data for 3-benzoheteroepines (**1**) δ ($CDCl_3$, 400 MHz)

Compd.	1- and 5-H	2- and 4-H	$J_{1,2}$ ($J_{4,5}$) / Hz	-$ArCH_2XR$	XR
1a	7.57	6.52	12.1	---	---
1b	7.56	6.64	12.5	3.49	2.18 (NMe_2)
1c	7.56	6.57	12.5	4.56	3.37 (OMe)
1d	7.54	6.48	12.5	---	---
1e	7.56	6.46	12.1	---	---
1f	7.46	6.50	12.1	---	---

Although 3-methyl- (**1f**)[2] and 3-phenylstibepines (**1a**)[4] are known, the other heteroepines (**1b-e**) obtained here are new compounds. The structures of **1a-f** were mainly established by their HRMS and ^{1}H NMR spectra. The ^{1}H NMR spectroscopic data of the seven-membered ring in **1** are given in Table 1. The values of the chemical shift and coupling constant of $J_{1,2\ (4,5)}$ of the protons are not so affected by the difference of the substituent on antimony. On the other hand, the methyl protons on the hetero atoms for **1b** ($N-CH_3$, δ 2.18) and **1c** ($O-CH_3$, δ 3.37) appeared at a relatively higher field. These results would be interpreted by the shielding effect of the C=C bonds on the seven-membered ring, in that an intramolecular coordination would form between antimony and the hetero atoms (N and O) referred below.



1a-f

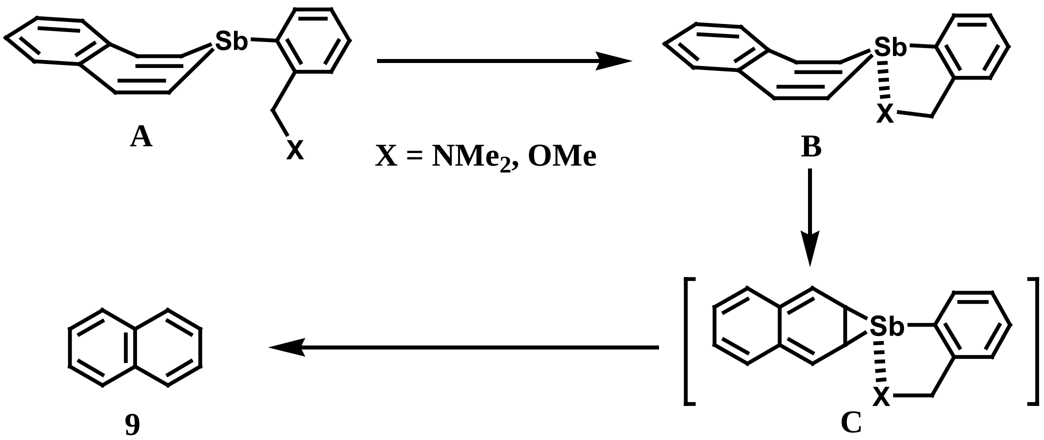
Scheme 4

9

Table 2. Half-lives and activation energies of **1**

Compound	$t_{1/2}$ min at 40 ˚C (d_8-toluene)	Ea / Kcal mol^{-1}
1a	149	25.8
1b	29	26.6
1c	100	24.4
1d	131	22.8
1e	157	28.2
1f	72	24.6

All the 3-benzostibepines (**1**) obtained here were thermolabile in solution toward elimination of the antimony moiety (R-Sb) and gradually decompose to naphthalene even during isolation by column chromatography (Scheme 4). Thus, thermolysis (50 ºC, 2.5 h, in d_8-toluene) of **1a** gave naphthalene almost quantitatively along with black precipitates with metallic glint, biphenyl, and triphenylstibane (^{1}H NMR and TLC analyses). The half-lives ($t_{1/2}$) and activation energies (Ea) of **1a-f** calculated from ^{1}H NMR spectral data are listed in Table 2. In 3-aryl-3-benzostibepines (**1a-e**), the stabilities estimated by their half-lives decrease in the order **1e** > **1a** > **1d** > **1c** > **1b** at 40 °C. The stibepines (**1b, c**) having heteroatom (N, O) substituent at 2-position on the aryl group are far less stable than others, and 3-[2-(*N,N*-dimethylaminomethyl)phenyl]-3-benzostibepine (**1b**) is the most unstable in this series of 3-benzostibepines. A little difference of the thermal stability was observed between the stibepines bearing 4-methoxyphenyl (**1d**) and 4-fluorophenyl groups (**1e**), and **1e** having electron-withdrawing group (-F) is slightly more stable than unsubstituted **1a** and **1d** having electron-donating group (-OCH_3). These results indicate that the electronic nature of the aryl group on the antimony affects the stability of the stibepines. The widely accepted mechanism of heteroatom extrusion involves isomerization of the heteroepine to the corresponding hetero-norcaradiene isomer, followed by irreversible loss of heteroatom moiety.[1, 4, 5] The same route would be applicable in the present extrusive decomposition of the stibepines (**1a-f**). It is also known that the stability of 1*H*-azepine is enhanced by electron-withdrawing substituents on nitrogen, whereas electron-donating substituents suppress the stability.[9] The difference of the stability in **1e** [3-(4-fluorophenyl): half life, 157 min] > **1a** (3-phenyl: 149 min) > **1d** [3-(4-methoxyphenyl): 131 min] would be understood by this interpretation. Also apparent was that the stibepines (**1b, c**) having heteroatom (N, O) moiety at the phenyl group on antimony were apparently far less stable than the other 3-aryl-3-stibepines (**1a**, **1d**, and **1e**). This fact implies that an intramolecular interaction between antimony and hetero atoms (N and O) promotes electrocyclic isomerization of A to C via B and the formation of naphthalene (**9**) as shown in Scheme 5. A similar non-bonding interaction between antimony and hetero atoms such as nitrogen, oxygen, and sulfur has been observed in many antimony compounds, and has been characterized by NMR and X-ray analyses.[10] As noted above, the methyl groups on the heteroatom moiety for **1b** and **1c** were observed at a higher field, indicating the presence of intramolecular coordination between the antimony and hetero atoms in solution.



Scheme 5

In conclusion, the general synthesis of 3-substituented 3-benzostibepines was attained by the ring closure reaction between antimony dihalides (**8a-e**) and 1,6-dilithium intermediate (**6**) generated from easily available (*Z,Z*)-1,2-bis(2-bromovinyl)benzene (**5**). The benzostibepines prepared here were thermolabile in solution and decomposed to naphthalene accompanied by extrusion of antimony moiety with ease. In particular, the stibepines bearing heteroatom substituents in the vicinity of antimony were far less stable than others. Further studies including trapping of antimony moiety formed during the present heteroatom extrusion with diene are now in progress.

EXPERIMENTAL

Melting points were measured on a Yanagimoto micro melting point hot stage apparatus and are uncorrected. Mass spectra (MS) and high-resolution mass spectra (HRMS) were recorded on a JEOL JMP-DX300 instrument. NMR spectra were determined with a JEOL JNM-GSX-400 (400 MHz) spectrometer in $CDCl_3$ using tetramethylsilane as an internal standard unless otherwise stated, and spectral assignments were confirmed by spin-decoupling experiments. Column chromatography was performed on silica gel (BW-127ZH, Fuji Silysia) or activated alumina (Aluminium oxide 90, Merck).

Tris[2-(*N,N*-dimethylaminomethyl)phenyl]stibane (**7b**),[10c] tris(4-methoxyphenyl)stibane (**7d**)[11] and tris(4-fluorophenyl)stibane (**7e**)[12] were prepared according to the reported procedure. Microanalyses were performed in the Microanalytical Laboratory of this Faculty by Ms. C. Kuroda and Ms. M. Kashihara.

Synthesis of tris[2-(methoxymethyl)phenyl]stibane (7c)

To a solution of 2-(methoxymethyl)bromobenzene (20.1 g, 0.1 mol) in Et_2O (100 mL) was added *n*-butyllithium (1.56 M in hexane, 71 mL, 0.11 mol) at -20 °C under an argon atmosphere, and the solution was stirred for 1.6 h. To this was added a solution of antimony trichloride (7.62 g, 33.4 mmol) in Et_2O (70 mL) over 40 min at -15 °C, and the mixture was stirred for 1 h at the same temperature. The mixture was quenched with water (150 mL) and diluted with Et_2O (300 mL). The organic layer was separated and the aqueous layer was extracted with Et_2O (50 mL x 2). The combined organic layer was washed with brine, dried, and evaporated *in vacuo*. The residue was chromatographed on silica gel with hexane/EtOAc (20:1) to give **7c**. Colorless prisms (11.6 g, 71%), mp 60.5-61 °C (from MeOH-Et_2O); ^1H NMR(400 MHz) δ : 3.14 (9H, s, OMe), 4.58 (6H, s, benzyl-H), 7.11-7.35 (12H, m, Ar-H); MS *m/z* (EI) 484 (M^+). Anal. Calcd for $C_{24}H_{27}O_3Sb$: C, 59.41; H, 5.61. Found: C, 59.36; H, 5.53.

General procedure for the preparation of 3-aryl-3-benzostibepines (1a-e)

A solution of (*Z,Z*)-1,2-bis(2-bromovinyl)benzene (**5**: 576 mg, 2 mmol) in anhydrous Et_2O (20 mL) was added dropwise over a 10 min period to a solution of *tert*-buthyllithium (1.5 M pentane solution, 10 mL, 15 mmol) in anhydrous Et_2O (20 mL) with stirring at –80 °C under an argon atmosphere, then the mixture was stirred for an additional 10 min at the same temperature. Dibromoarylstibanes (**8a-e**: 4 mmol) [prepared from redistribution reaction on heating a 1:2 mixture of triarylstibane (**7a-e**) and tribromostibane ($SbBr_3$) for 1-3 h at 90 °C] were added in small portions over a 10 min period to the above mixture with stirring at –80 °C. The mixture was allowed to warm to –10 °C and stirred for 3 h, and then warmed to rt. Et_2O (100 mL) and water (100 mL) were added to the mixture with stirring. The solution was separated and the aqueous layer was extracted with Et_2O (100 mL x 2). The combined organic layer was washed with brine, dried, and evaporated *in vacuo*. The resulting residue was chromatographed on silica gel or aluminum oxide with pentane/Et_2O to give **1a-e**.

3-Phenyl-3-benzostibepine (1a)

Colorless needles (163 mg, 25%), mp 76-78 °C (from MeOH). The compound (**1a**) was identical with the authentic sample prepared in our previous paper.[4]

3-[2-(*N*, *N*-Dimethylaminomethyl)phenyl]-3-benzostibepine (1b)

The compound (**1b**) was purified by aluminum oxide using pentane as an eluent. Colorless oil (76 mg, 10%); ^{1}H NMR (400 MHz) δ: 2.18 (6H, s, NMe_2), 3.49 (2H, s, benzyl-H), 6.64 (2H, d, *J* = 12.5 Hz, 2- and 4-H), 7.56 (2H, d, *J* = 12.5 Hz, 1- and 5-H), 7.11-7.81 (8H, m, Ar-H); MS *m/z* (EI) 255 (M^+-$C_{10}H_8$). HRMS Calcd for $C_9H_{12}NSb$: 255.0008. Found: 255.0012.

3-[2-(Methoxymethyl)phenyl]-3-benzostibepine (1c)

The compound (**1c**) was purified by silica gel using pentane-Et_2O (20:1) as an eluent. Colorless oil (74 mg, 11%); ^{1}H NMR (400 MHz) δ: 3.37 (3H, s, OMe), 4.56 (2H, s, benzyl-H), 6.57 (2H, d, *J* = 12.5 Hz, 2- and 4-H), 7.56 (2H, d, *J* = 12.5 Hz, 1- and 5-H), 7.19-7.82 (8H, m, Ar-H); MS *m/z* (EI) 242 (M^+-$C_{10}H_8$). HRMS Calcd for C_8H_9OSb: 241.9690. Found: 241.9697.

3-(4-Methoxyphenyl)-3-benzostibepine (1d)

The compound (**1d**) was purified by silica gel using pentane as an eluent. Yellow prisms (185 mg, 26%), mp 80-85 °C (decomp.) (from MeOH); ^{1}H NMR (400 MHz) δ: 3.83 (3H, s, OMe), 6.48 (2H, d, *J* = 12.1 Hz, 2- and 4-H), 7.54 (2H, d, *J* = 12.1 Hz, 1- and 5-H), 6.90-7.64 (8H, m, Ar-H); MS *m/z* (EI) 228 (M^+-$C_{10}H_8$). Anal. Calcd for $C_{17}H_{15}OSb$: C, 57.19; H, 4.23. Found: C, 57.06; H, 4.14.

3-(4-Fluorophenyl)-3-benzostibepine (1e)

The compound (**1e**) was purified by silica gel using pentane as an eluent. Colorless prisms (144 mg, 21%), mp 63-68 °C (decomp.) (from MeOH); ^{1}H NMR (400 MHz) δ: 6.46 (2H, d, *J* = 12.1 Hz, 2- and 4-H), 7.56 (2H, d, *J* = 12.1 Hz, 1- and 5-H), 7.22-7.69 (8H, m, Ar-H); MS *m/z* (EI) 216 (M^+-$C_{10}H_8$). Anal. Calcd for $C_{16}H_{12}FSb$: C, 55.70; H, 3.51. Found: C, 55.87; H, 3.69.

Synthesis of 3-methyl-3-benzostibepine (1f)

Methyllithium (1.14 M in pentane, 0.2 mL, 0.23 mmol) was added dropwise to a solution of **1a** (62 mg, 0.19 mmol) in THF (2 mL) with stirring at -78 °C and the solution was stirred for an additional 20 min. After addition of pentane (10 mL) and water (10 mL), the reaction mixture was stirred for 10 min at -10 °C. The organic layer was separated, washed with brine, dried, and evaporated *in vacuo*. The residue was chromatographed on silica gel using pentane as an eluent to give **1f**. Pale yellow oil (6 mg, 12%); ^{1}H NMR (400 MHz) δ: 0.96 (3H, s, Me), 6.50 (2H, d, *J* = 12.1 Hz, 2- and 4-H), 7.46 (2H, d, *J* = 12.1 Hz, 1- and 5-H), 7.19-7.48 (4H, m, Ph-H); MS *m/z* (EI) 264 (M^+); HRMS Calcd for $C_{11}H_{11}Sb$ 263.9900. Found 263.9902.

General procedure for thermal conversion of 3-benzostibepines (1a-f) to naphthalene (9)

A solution of stibepine **1a-f** (6-20 mg, 0.02-0.06 mmol) in d_8-toluene (0.7 mL) was heated at each temperature. The disappearance of **1** and appearance of **9** were monitored by NMR integration. The first order rate constants are shown below; **1a**: $k^{313} = 7.73 \times 10^{-5}$ s^{-1}, $k^{323} = 2.56 \times 10^{-4}$ s^{-1}, $k^{333} = 9.09 \times 10^{-4}$ s^{-1}, **1b**: $k^{297} = 3.85 \times 10^{-5}$ s^{-1}, $k^{303} = 8.75 \times 10^{-5}$ s^{-1}, $k^{313} = 3.97 \times 10^{-4}$ s^{-1}, **1c**: $k^{303} = 3.57 \times 10^{-5}$ s^{-1}, $k^{313} = 1.13 \times 10^{-4}$ s^{-1}, $k^{323} = 4.23 \times 10^{-4}$ s^{-1}, **1d**: $k^{313} = 8.75 \times 10^{-5}$ s^{-1}, $k^{323} = 2.21 \times 10^{-4}$ s^{-1}, $k^{333} = 7.81 \times 10^{-4}$ s^{-1}, **1e**: $k^{313} = 7.40 \times 10^{-5}$ s^{-1}, $k^{323} = 2.04 \times 10^{-4}$ s^{-1}, $k^{333} = 1.09 \times 10^{-3}$ s^{-1}, and **1f**: $k^{303} = 4.51 \times 10^{-5}$ s^{-1}, $k^{313} = 1.60 \times 10^{-4}$ s^{-1}, $k^{323} = 5.35 \times 10^{-4}$ s^{-1}.

ACKNOWLEDGEMENTS

This work was supported by a Grant-in Aid for Scientific Research (C) (to J. K.), and the "Academic Frontier" Project for Private Universities from the Ministry of Education, Culture, Sports, Science and Technology of Japan (to S. Y.). Financial support by the Special Research Fund from Hokuriku University is also gratefully acknowledged.

REFERENCES

1. (a) G. Märkl and W. Burger, *Angew. Chem., Int. Ed. Engl.*, 1984, **23**, 894; (b) *Idem*, *Tetrahedron Lett.*, 1983, **24**, 2545; (c) S. Shiratori, S. Yasuike, J. Kurita, and T. Tsuchiya, *Chem. Pharm. Bull.*, 1994, **42**, 2441; (d) I. Murata and K. Nakatsuji, *Top. Curr. Chem.*, 1981, **97**, 33; (e) K. Yamamoto and S. Yamazaki, "Comprehensive Heterocyclic Chemistry II," Vol. 9, ed. by A. R. Katritzky, C. W. Rees, and E. F. V. Scriven, Pergamon, Oxford, 1996, pp. 67-111; (f) H. Hori, S. Yamazaki, K. Yamamoto, and I. Murata, *Angew. Chem., Int. Ed. Engl.*, 1990, **29**, 424; (g) H. Sashida, H. Kurahashi, and T. Tsuchiya, *J. Chem. Soc., Chem. Commun.*, 1991, 802.
2. A. J. Ashe III, L. Goossen, J. W. Kampf, and H. Konishi, *Angew. Chem., Int. Ed. Engl.*, 1992, **31**, 1642.
3. (a) H. Sashida, *Heterocycles*, 2000, **53**, 49; (b) H. Sashida and A. Kuroda, *J. Chem. Soc., Perkin Trans. 1*, 2000, 1965.
4. S. Yasuike, T. Kiharada, J. Kurita, and T. Tsuchiya, *Chem. Commun.*, 1996, 2183.
5. (a) S. Yasuike, H. Ohta, S. Shiratori, J. Kurita, and T. Tsuchiya, *J. Chem. Soc., Chem. Commun.*, 1993, 1817; (b) S. Yasuike, S. Shiratori, J. Kurita, and T. Tsuchiya, *Chem. Pharm. Bull.*, 1999, **47**, 1108.
6. S. Yasuike, S. Shiratori, T. Tsuchiya, and J. Kurita, *Chem. Pharm. Bull.*, 2003, **51**, 1283.
7. (a) M. Matsumoto and K. Kuroda, *Tetrahedron Lett.*, 1980, **21**, 4021; (b) M. A. Romero and A. G. Fallis, *Tetrahedron Lett.*, 1994, **35**, 4711.

8. (a) J. Kurita, M. Ishii, S. Yasuike, and T. Tsuchiya, *Chem. Pharm. Bull.*, 1994, **42**, 1437; (b) N. Kakusawa, T. Ikeda, A. Osada, J. Kurita, and T. Tsuchiya, *Synlett*, 2000, 1503.

9. R. K. Smalley, “Comprehensive Heterocyclic Chemistry ,” Vol. 7, ed. by A. R. Katritzky and C. W. Rees, Pergamon, Oxford, 1984, pp. 491-546.

10. For examples; (a) K. Ohkata, S. Takemoto, M. Ohnishi, and K. –y. Akiba, *Tetrahedron Lett.*, 1989, **30**, 4841; (b) Y. Yamamoto, X. Chen, S. Kojima, K. Ohdoi, M. Kitano, Y. Doi, and K. –y. Akiba, *J. Am. Chem. Soc.*, 1995, **117**, 3922; (c) S. Kamepalli, C. J. Carmalt, R. D. Culp, A. H. Cowley, R. A. Jones, and N. C. Norman, *Inorg. Chem.*, 1996, **35**, 6179; (d) E. Bräu, A. Zickgraf, M. Dräger, E. Mocellin, M. Maeda, M. Takahashi, M. Takeda, and C. Mealli, *Polyhedron*, 1998, **17**, 2655; (e) S. Yasuike, S. Tsukada, J. Kurita, T. Tsuchiya, Y. Tsuda, H. Kiuchi, and S. Hosoi, *Heterocycles*, 2000, **53**, 525; (f) T. Tokunaga, H. Seki, S. Yasuike, M. Ikoma, J. Kurita, and K. Yamaguchi, *Tetrahedron*, 2000, **56**, 8833; (g) S. Okajima, S. Yasuike, N. Kakusawa, A. Osada, K. Yamagichi, H. Seki, and J. Kurita, *J. Organomet. Chem.*, 2002, **656**, 234; (h) K. Hoshino, T. Ogawa, S. Yasuike, H. Seki, J. Kurita, T. Tokunaga, and K. Yamagichi, *J. Phys. Chem. B*, 2004, **108**, 18698; (i) P. Sharma, J. G. Lopez, C. Ortega, N. Rosas, A. Cabrera, C. Alvarez, A. Toscano, and E. Reyes, *Inorg. Chem. Commun.*, 2006, **9**, 82; (j) S. Yasuike, Y. Kishi, S. Kawara, K. Yamagichi, and J. Kurita, *J. Organomet. Chem.*, 2006, **691**, 2213; (k) P. Sharma, D. Pérez, J. Vázquez, A. Toscano, and R. Gutiérrez, *Inorg. Chem. Commun.*, 2007, **10**, 389; (l) L. Dostál, L. Jambor, A. Růžička, R. Jirásko, I. Císařová, and J. Holeček, *J. Fluorine Chem.*, 2008, **129**, 167, and references cited therein.

11. A. F. M. M. Rahman, T. Murafuji, M. Ishibashi, Y. Miyoshi, and Y. Sugihara, *J. Organomet. Chem.*, 2005, **690**, 4280.

12. R. F. Ketelaere, F. T. Delbeke, and G. P. Kelen, *J. Organomet. Chem.*, 1971, **30**, 365.