Cycloadditions of 3,4-Dihydro-2*H*-pyrrole *N*-Oxide with Thioketones and a Selenoketone

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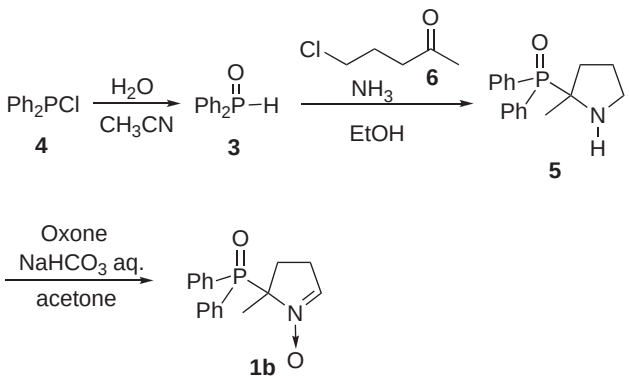
Cycloadditions of 2-diphenylphosphinoyl-2-methyl-3,4-dihydro-2*H*-pyrrole *N*-oxide (DPhPMPO), 3,4-dihydro-2*H*-pyrrole *N*-oxide having a diphenylphosphinoyl group at the C2 position with thioketones afforded the corresponding 1,4,2-oxathiazolidines. Dissociation constants of these 5-membered ring products were determined. The cycloadducts were stabilized by the diphenylphosphinoyl group. The reaction of DPhPMPO with di-*tert*-butyl selenoketone gave the corresponding selenoamide under microwave irradiation. The formation of the selenoamide indicated that the cycloaddition of DPhPMPO with the selenoketone analogue also proceeded through the formation of the corresponding 5-membered ring product.

The pathways of 1,3-dipolar cycloadditions of nitrones to carbon–carbon multiple bonds, such as alkenes, or alkynes to form isoxazolidines or 2,3-dihydroisoxazoles are involved in many synthetic strategies.[1] Studies on the chemical properties of *N*-oxide as a 1,3-dipole are of substantial interest in this regard. It is also well known that compounds having heteroatom–carbon multiple bonds react with electron-rich 1,3-dipoles.[2] Black and Watson have described 1,3-cycloaddition reactions of nitrones including 2,2-dimethyl-3,4-dihydro-2*H*-pyrrole *N*-oxide (DMPO) (**1a**) with thioketones, such as adamantane-2-thione (**2a**) and 2,2,4,4-tetramethyl-3-thioxocyclobutanone (**2b**), to afford 1,4,2-oxathiazolidine derivatives.[3] Huisgen, Sustmann, et al. have reported kinetic studies on these cycloadditions and evaluated the high reactivity of the C=S double bond toward nitrones by using MO calculations.[4] Mloston, Heimgartner, and co-worker have reported the cycloaddition of azole *N*-oxide with several thiocarbonyl compounds.[5] However, to our knowledge, there are no other reports on the 1,3-dipolar cycloaddition reactions of thioketones with nitrones due to the instability and inaccessibility of nitrones. Furthermore, to our knowledge, cycloaddition of 3,4-dihydro-2*H*-pyrrole *N*-oxide with a C=Se bond has not been reported. The difference in reactivity between thioketones and selenoketones toward nitrones is also of interest. We have recently investigated the synthesis of 3,4-dihydro-2*H*-pyrrole *N*-oxide containing a phosphinoyl group as an electron-withdrawing group at the 2-position.[6] In this paper, we report that the cycloaddition reactions of 3,4-dihydro-2*H*-pyrrole *N*-oxide, 2-diphenylphosphinoyl-2-methyl-3,4-dihydro-2*H*-pyrrole *N*-oxide (DPhPMPO) (**1b**), with several dipolarophiles, such as thioketone and selenoketone, behave in a variety of ways.

Results and Discussion

Synthesis of DPhPMPO (1b). Nitrone **1b** was synthesized by the following three-step reactions described in Scheme 1. Diphenylphosphine oxide (**3**) was prepared from commercially available chlorodiphenylphosphine (**4**) in 97% yield. 2-(Diphenylphosphinoyl)-2-methyl-1-pyrrolidine (**5**) was obtained by the cyclization of 5-chloro-2-pentanone (**6**) and ammonia with **3** (63% yield). Oxidation of **5** was carried out by using Oxone™ in acetone to give the desired nitrone **1b** in 47% yield without purification by column chromatography. Purifications of the overall synthesis were carried out by recrystallization from water containing acetonitrile. The obtained crystals could be stored at room temperature.



Scheme 1.

The structure of **1b** was confirmed by ^{1}H, ^{13}C, ^{31}P NMR, elemental analysis, and X-ray crystallographic analysis. The X-ray data are reported in Table 1. A single crystal had one stereoisomer, and the crystal lattice had two water molecules. No interaction was observed between the two oxygen atoms on *N*-oxide and the phosphinoyl moiety. The P–C(1) bond is moderately longer than the other P–C bonds. It appered that the position of the diphenylphosphinoyl group caused steric hindrance at the nitrone face in the crystalline state (Fig. 1).

Thermal Reaction of DPhPMPO (1b) with Thioketones. We reacted DPhPMPO with adamantane-2-thione (**2a**). The reaction proceeded quickly in $CHCl_3$ at room temperature to

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give the corresponding oxathiazolidine **7a** in 90% yield. Although the relative configuration was not elucidated, the adduct was obtained as a single diastereomer. The reaction of **1b** with thioxocyclobutanone **2b** gave cycloadduct **7b** as colorless crystals in 60% yield (Scheme 2). These structures were identified by ^{1}H, ^{13}C NMR and elemental analysis. These results were similar to those obtained for the reaction of **1a**. On the other hand, no reaction occurred between **1b** and bornane-6-thione (**2c**) or 1,1,3,3-tetramethylindane-2-thione (**2d**) at room temperature. It has been reported that the steric encumbrance of these thioketones **2a**–**2d** increases in the sequence of **2a** < **2b** < **2c** < **2d**.[7] The poor reactivity of **2c** and **2d** was caused by steric hindrance of thiocarbonyl compounds.

Table 1. Selected Bond Lengths (Å) and Angles (°) of **1b**

P(1)–O(1)	1.481(4)	O(2)–N(1)	1.298(6)	C(2)–C(3)	1.507(9)
P(1)–C(6)	1.800(6)	N(1)–C(4)	1.298(6)	C(3)–C(4)	1.480(10)
P(1)–C(12)	1.802(6)	N(1)–C(1)	1.513(7)		
P(1)–C(1)	1.850(6)	C(1)–C(2)	1.521(8)		
N(1)–C(1)–P(1)	112.7(4)	C(4)–N(1)–C(1)	111.0(5)		
C(2)–C(1)–P(1)	109.7(4)	C(3)–C(2)–C(1)	106.2(6)		
C(5)–C(1)–P(1)	109.4(4)				

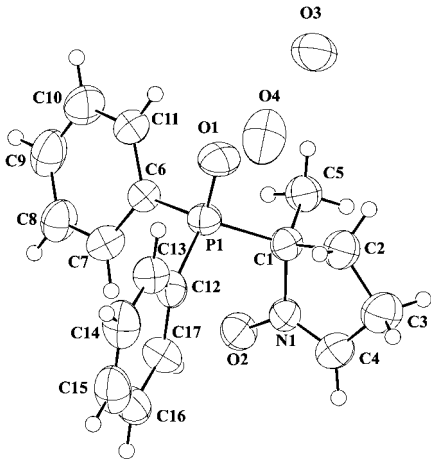


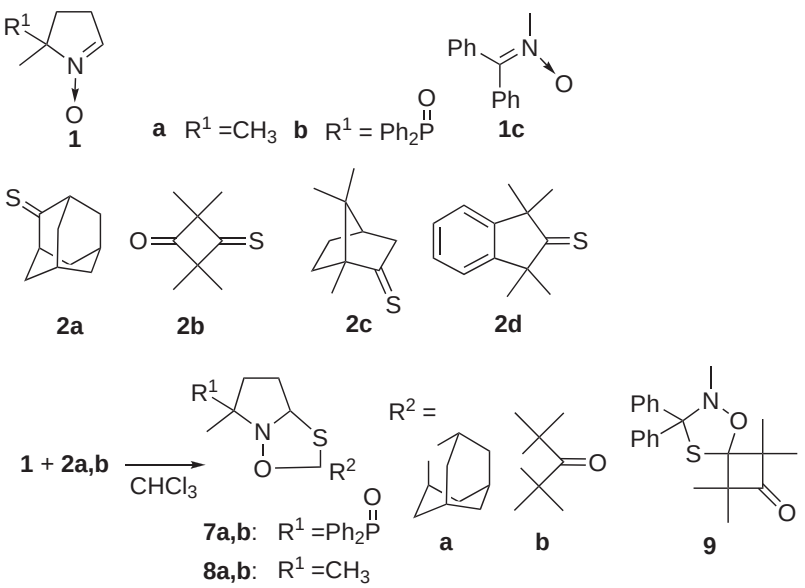
Fig. 1. ORTEP of **1b**.

The reported cycloadducts of nitrones with thioketones dissociate to a large extent in dilute solution. Huisgen et al. have reported that the dissociation constant of the oxathiazolidine **9** generated from linear *N*-(diphenylmethylene)methylamine *N*-oxide (**1c**) with **2b** in $CDCl_3$ was 1.2×10^{-3} mol L^{-1} when the initial concentrations of the nitrone and **2b** were 0.94 and 0.37 mol L^{-1}, respectively.[4] The dissociation constants of adducts **7a** and **7b** at 25 °C in $CDCl_3$ were determined by ^{1}H NMR. The dissociation constants of cycloadducts **8** derived from **1a** and **2** were also determined. These results are summarized in Table 2. Cycloadducts **7a** and **8a** had smaller dissociation constants than those of cycloadducts **7b** and **8b** formed from **2b**. This may be because the steric congestion around *O*,*S*-acetal moiety destabilizes the latter cycloadducts. Although the initial concentrations of **1b** and **2b** for the reaction of **1b** and **2b** were lower than those of the linear nitrone **1c** and **2b** for the corresponding reaction, the dissociation constant of **7b** was three times smaller than that of the adduct of **1c** with **2b**. Compared with these values, our results indicated that the oxathiazolidines **7** generated from **1b** and **2a** or **2b** are more stable than **9** generated from the reaction of the linear nitrone

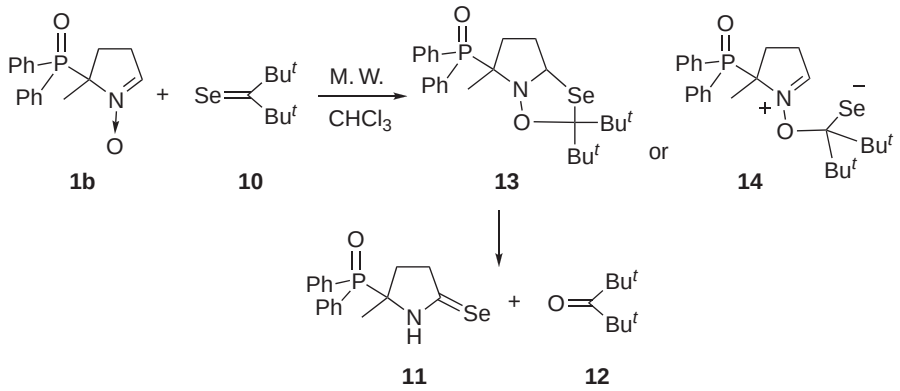
Table 2. Dissociation Constants of 1,3-Cycloadducts **7** and **8**

1[a)]	**2**[b)]	Adduct	$10^3\ K_{diss}$/mol L^{-1} [c)]
a	**a**	**8a**	6.96 ± 0.39
a	**b**	**8b**	19.5 ± 0.39
b	**a**	**7a**	0.114 ± 0.025
b	**b**	**7b**	0.4107 ± 0.041
c	**b**	**9**	1.2[d)]

a) Initial concentration of [**1**] = 0.049 mol L^{-1}. b) Initial concentration of [**2**] = 0.049 mol L^{-1}. c) Determined by ^{1}H NMR at 25 °C. d) Ref. 4.



Scheme 2.



Scheme 3.

1c with **2b**. The dissociation constant of **8b** was higher than that of **7b**, because adamantane-2-thione (**2a**) is less sterically crowded than thioxocyclobutanone **2b**. These observations suggested that the diphenylphosphinoyl moiety contributes stability to the adduct **7a** and **7b**. The bulky diphenylphosphinoyl moiety did not influence cycloaddition of **1b** with **2a** and **2b**.

The cycloadditions of **1b** with **2c** or **2d** did not proceed at room temperature. When a microwave reaction between **1b** with **2c** was carried out in chloroform, the pale orange solution originating from the thioketone **2c** gradually became colorless. Using TLC analysis, a product ($R_f = 0.65$, EtOAc:MeOH = 9:1) was detected along with **1b** ($R_f = 0.1$) and **2c** ($R_f = 0.95$). From the reaction of **1b** with **2d**, a trace amount of a product ($R_f = 0.45$) was also detected. However, these products were not observed by ^{1}H NMR of the reaction mixture.

Reaction of DPhPMPO with Di-*tert*-butyl Selenoketone. Since selenoketones are also useful 1,3-dipolarophiles, several selenoketones were employed instead of **2**.[8] The reaction of **1b** with di-*tert*-butyl selenoketone (**10**) did not proceed at room temperature. However, under microwave irradiation, the cycloaddition of **1b** with selenoketone **10** afforded the corresponding selenolactam **11** in 92% yield along with the di-*tert*-butyl ketone (**12**) (Scheme 3), suggesting that the initial adduct of the reaction was oxaselenazolidine **13** or betaine **14**. Since the stability of **13** or **14** is lower than that of **7**, rearrangement took place under these conditions.

Conclusion

3,4-Dihydro-2*H*-pyrrole *N*-oxide **1b** reacted like a 1,3-dipole with thiocarbonyl compounds. The dissociation constants indicated that the formation of 5-membered ring products was not decelerated by a bulky group attached to the carbon atom adjacent to the 1,3-dipole. Selenium atom transfer through the oxaselenazolidine intermediate took place with microwave irradiation.

Experimental

General Methods. Solvents were distilled under a nitrogen atmosphere. All chemicals were obtained from a commercial supplier and used without further purification. Adamantane-2-thione (**2a**),[7] 2,2,4,4-tetramethyl-3-thioxocyclobutanone (**2b**),[9] bornane-6-thione (**2c**),[10] 1,1,3,3-tertamethylindane-2-thione (**2d**),[11] and di-*tert*-butyl selenoketone (**10**)[8] were prepared according to literature procedures. Analytical TLC was carried out on precoated plates (Merck, silica gel 60, F254) and flash column chromatography was performed with silica (Merck, 70–230 mesh). NMR spectra (^{1}H at 400 MHz; ^{13}C at 100 MHz; ^{31}P at 161 MHz) were recorded in $CDCl_3$, and the chemical shifts are expressed in ppm relative to the internal standard TMS. ^{31}P NMR spectra were obtained in $CDCl_3$ using 85% H_3PO_4 as an internal standard with broadband ^{1}H decoupling. The melting points are uncorrected.

Synthesis of 2-Diphenylphosphinoyl-2-methyl-3,4-dihydro-2*H*-pyrrole *N*-Oxide (DPhPMPO) (1b). Water (4.5 mL) was added to a solution of chlorodiphenylphosphine (**4**) (4.6 mL, 25 mmol) in acetonitrile (38 mL) and the mixture was refluxed for 6 h. The reaction mixture was then concentrated under reduced pressure. The residue was extracted with CH_2Cl_2 (20 mL × 3) and dried over $MgSO_4$. The solvent was removed in vacuo to give diphenylphosphine oxide (**3**) as a colorless oil (97% yield). ^{1}H NMR ($CDCl_3$) δ 7.98–8.02 (m, 10H), 8.11 (d, 2H, J_{P-H} = 468 Hz). ^{31}P NMR ($CDCl_3$) δ 23.1.

5-Chloro-2-pentanone (**6**) (2.75 mL, 24 mmol) was added to a solution of diphenylphosphine oxide (4.04 g, 20 mmol) in ethanol (16 mL), and the mixture was stirred at 0 °C for 1 h. After stirring at room temperature, the reaction mixture was warmed up to 60 °C, and then gaseous NH_3 was bubbled into the solution for 1 h. After stirring for 3 h, the solvent was removed under reduced pressure. The residue was dissolved in 2 mol L^{-1} HCl (50 mL) and extracted with CH_2Cl_2 (100 mL × 3). The organic layer was dried over $MgSO_4$, and the solvent was removed. The residue was crystallized from ethanol–hexane to give 2-(diphenylphosphinoyl)-2-methyl-1-pyrrolidine (**5**) as colorless crystals (63%). ^{1}H NMR ($CDCl_3$) δ 1.35 (d, 3H, J = 14 Hz), 1.48–1.50 (m, 1H), 1.62–1.65 (m, 1H), 1.76–1.80 (m, 1H), 2.11–2.19 (m, 1H), 2.57–2.59 (m, 1H), 3.07–3.09 (m, 1H), 7.41–7.51 (m, 6H), 8.14–8.20 (m, 4H). ^{13}C NMR ($CDCl_3$) δ 24.8 (J_{P-C} = 9.1 Hz), 25.9 (J_{P-C} = 4.6 Hz), 35.1 (J_{P-C} = 5.1 Hz), 47.8 (J_{P-C} = 6.9 Hz), 62.6 (J_{P-C} = 94.7 Hz), 128.2, 128.3, 128.4, 128.5, 130.8, 131.1, 131.5, 131.6, 131.7, 131.8, 132.1, 132.5, 132.6, 132.7, 132.8, 132.9, 133.1, 133.2. ^{31}P NMR ($CDCl_3$) δ 33.1.

Aqueous $NaHCO_3$ (50 mL, 4.0 g, 48 mmol) and oxone (50 mL, 7.4 g, 12 mmol) were added dropwise to a solution of pyrrolidine **5** in acetone (2.85 g, 10 mmol). After stirring for 1 h at room temperature, the reaction mixture was quenched with 50 mL of 10% sodium thiosulfate and acetone was removed under reduced pressure. The residue was extracted with CH_2Cl_2 (150 mL × 3) and dried over $MgSO_4$. The organic layer was concentrated to give a crude product as a pale yellow oil. Purification was carried out via recrystallization from water–acetonitrile to give 3,4-dihydro-2*H*-pyrrole *N*-oxide **1b** as colorless crystals (47%). mp 137–

138 °C (decomp.). ^{1}H NMR ($CDCl_3$), δ 1.72 (d, 3H, $J = 6.8$ Hz), 1.86–1.97 (m, 1H), 2.12–2.23 (m, 1H), 2.37–2.46 (m, 1H), 3.18–3.28 (m, 1H), 6.66 (dd, 1H, $J = 5.2$, 2.4 Hz), 7.45–7.56 (m, 6H), 8.08–8.12 (m, 2H), 8.39–8.44 (m, 2H). ^{13}C NMR ($CDCl_3$) δ 21.3 ($J_{P-C} = 4.6$ Hz), 25.8, 30.2, 78.7 ($J_{P-C} = 71.0$ Hz), 128.4, 128.6, 128.7, 128.8, 128.9, 129.3, 129.9, 132.1, 132.2, 132.4, 132.6, 133.2, 133.3, 136.3. ^{31}P NMR ($CDCl_3$) δ 34.3. Found: C, 64.49; H, 6.51; N, 4.40%. Calcd for $C_{17}H_{18}NO_2P \cdot H_2O$: C, 64.35; H, 6.35; N, 4.41%.

X-ray Crystallographic Data of DPhPMPO (1b). X-ray crystallographic data were collected using a DIP Image Plate with Cu Kα radiation. The reflections were collected at room temperature (298 K). An orthorhombic lattice was determined from systematic absence of lattice ($hkl, h + k = 2n$). A $P2_12_12_1$ space group was determined from systematic absence ($hol, l = 2n$). A good model was found by direct methods (SIR97) using the $P2_12_12_1$ space group.[12] Crystal data for **1b**: FW 299.31. Orthorhombic, space group $P2_12_12_1$, $a = 11.4480(5)$ Å, $b = 10.3370(4)$ Å, $c = 14.3840(6)$ Å, $V = 1702.17(12)$ Å^3, $Z = 4$, $D_{calcd} = 1.168$ g cm^{-3}, $\mu = 1.457$ mm^{-1}, $R = 0.0778$, $R_w = 0.2131$. Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre: Deposit No. CCDC-629371 for Compound **1b**. Copies of the data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, UK: Fax: +44 1223 336033; or e-mail: deposit@ccdc.cam.ac.uk).

Reaction of 1b with Adamantane-2-thione (2a). Adamantane-2-thione (**2a**) (16.6 mg, 0.1 mmol) was added to a solution of **1b** (30 mg, 0.1 mmol) in $CHCl_3$ (1.0 mL), and the mixture was stirred at room temperature for 15 min. After stirring, the reaction mixture was concentrated under reduced pressure to give a white solid, which was recrystallized from hexane–ether to afford colorless crystals of oxathiazolidine **7a** (41.9 mg, 0.09 mmol). **7a**: mp 128–129 °C. ^{1}H NMR ($CDCl_3$) δ 1.63 (d, 3H, $J_{P-H} = 15.6$ Hz), 1.68–2.19 (m, 18H), 3.96 (dd, 1H, $J = 6.0$, 8.4 Hz), 7.42–7.56 (m, 6H), 7.98–8.02 (t, 2H, $J = 8.4$ Hz), 8.26–8.30 (t, 2H, $J = 8.4$ Hz). ^{13}C NMR ($CDCl_3$) δ 19.2, 25.3, 25.9, 26.4, 30.2, 32.9, 34.0, 34.7, 34.8, 36.2, 37.3, 38.3, 38.7, 69.64 ($J_{P-C} = 94.0$ Hz), 72.3 ($J_{P-C} = 6.3$ Hz), 100.9, 127.2, 127.3, 130.7, 130.8, 131.6, 131.7. ^{31}P NMR ($CDCl_3$) δ 31.7. Found: C, 69.43; H, 6.96; N, 2.93%. Calcd for $C_{27}H_{32}NO_2PS$: C, 69.65; H, 6.93; N, 3.01%.

Reaction of 1b with 2,2,4,4-Tetramethyl-3-thioxocyclobutanone (2b). Thione **2b** (15.6 mg, 0.1 mmol) was added to a solution of **1b** (30 mg, 0.1 mmol) in $CHCl_3$ (1.0 mL), and the mixture was stirred at room temperature for 15 min. After stirring, the reaction mixture was concentrated under reduced pressure to give a white solid, which was recrystallized from hexane–ether to afford colorless crystals of oxathiazolidine **7b** (27.4 mg, 0.06 mmol). **7b**: mp 102–104 °C. ^{1}H NMR ($CDCl_3$) δ 1.1 (s, 3H), 1.29 (s, 3H), 1.31 (s, 3H), 1.38–1.46 (m, 1H), 1.41 (s, 3H), 1.61 (d, 3H, $J_{P-H} = 15$ Hz), 1.94–1.99 (m, 1H), 2.23–2.36 (m, 1H), 2.54–2.64 (m, 1H), 4.71 (brd, 1H, $J = 4.8$ Hz), 7.36–7.55 (m, 6H), 8.08 (t, 2H, $J = 8.4$ Hz), 8.21 (t, 2H, $J = 8.4$ Hz). ^{13}C NMR ($CDCl_3$) δ 18.6, 20.6, 21.0 ($J_{P-C} = 4.4$ Hz), 22.6, 24.5, 27.0, 33.9 ($J_{P-C} = 4.9$), 63.4, 68.1, 71.7, 72.7, 75.4 ($J_{P-C} = 11$ Hz), 103.6, 128.3, 128.4, 128.5, 132.0, 132.1, 132.8, 132.9, 133.0, 219.4. ^{31}P NMR ($CDCl_3$) δ 30.0. Found: C, 65.77; H, 6.65; N, 2.90%. Calcd for $C_{25}H_{30}NO_3PS$: C, 65.91; H, 6.64; N, 3.07%.

Dissociation Constants of Oxathiazolidine 7. DPhPMPO **1b** (0.246 mmol), thioketone (0.246 mmol), and tetrachloroethane (0.246 mmol) in $CDCl_3$ (5.0 mL) reached equilibrium with oxathiazolidine **7** in 24 h. The integral was compared with TCE (s, 5.96). **7b**: 0.224 mmol by the signal at δ 4.71 (brd, C-2). **1b**: 0.022 mmol by δ 6.60 (d, N=C*H*–), $K_{diss} = 0.41 \pm 0.041 \times 10^{-3}$ mol L^{-1} at 25 °C.

General Procedure of Microwave Irradiation Reaction. The appropriate thioketone **2** or selenoketone **10** was added to a solution of **1b** in $CHCl_3$, and the mixture was stirred for 1 min. It was then irradiated with a microwave by Electrolux EMC-M20Y (TOSHIBA). The reaction was monitored by TLC. After the irradiation, the reaction mixture was dissolved in $CDCl_3$ (0.5 mL) for NMR analysis.

Reaction of 1b with Di-*tert*-butyl Selenoketone 10. Di-*tert*-butyl selenoketone (**10**) (41.0 mg, 0.2 mmol) was added to a solution of **1b** (38.9 mg, 0.13 mmol) in $CHCl_3$ (2 mL) and irradiated with a microwave for 5 min. The reaction mixture was concentrated under reduced pressure to give a white solid, which was recrystallized from benzene to afford colorless crystals of selenoamide **11** (44.0 mg, 0.12 mmol). **11**: mp 209–211 °C. ^{1}H NMR ($CDCl_3$) δ 1.60 (d, 3H, $J = 15.6$ Hz), 1.99–2.13 (m, 2H), 2.59–2.64 (m, 1H), 2.65–2.86 (m, 1H), 7.50–7.67 (m, 6H), 7.83–7.87 (m, 2H), 7.97–8.02 (m, 2H), 8.84 (brs, 1H). ^{13}C NMR ($CDCl_3$) δ 23.0 ($J_{P-C} = 7.4$ Hz), 33.4 ($J_{P-C} = 3.4$ Hz), 48.0, 71.4 ($J_{P-C} = 75.8$ Hz), 127.5, 128.5, 128.6, 129.2, 129.3, 129.4, 129.5, 132.1, 132.3, 132.4, 133.0, 133.1, 207.7 ($J_{P-C} = 3.5$ Hz). ^{31}P NMR ($CDCl_3$) δ 31.2. Found: C, 56.37; H, 5.04; N, 3.87%. Calcd for $C_{17}H_{18}NOPSe$: C, 56.36; H, 5.01; N, 3.87%.

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