upon standing and was recrystallized from methanol to afford the γ-lactone **35**: mp 120–123 °C; ^{1}H NMR δ 0.98 (t, 3 H), 1.4–2.5 (m, 6 H), 3.80 (s, 3 H), 3.87 (s, 3 H), 4.27 (bs, 1 H), 5.27 (s, 1 H), 5.30 (s, 1 H); IR (CCl_4) 3550, 3000, 1775, 1745, 1725 cm^{-1}.

Dimethyl 1,2-Epoxy-2-ethyl-6-methylcyclohex-5-ene-1,5-dicarboxylate (3). The epoxy triester **34** (52.3 g, 0.168 mol) was dissolved in a solution of sodium methoxide prepared by dissolving 11.81 g (0.52 mol) of sodium metal in 500 mL of anhydrous methanol. The solution was then heated to reflux, after 40 h the reaction mixture was cooled and poured into 1 L of ether and 500 mL of brine, and the phases were separated. The organic phase was first washed with two 300-mL portions of 5% aqueous NaOH to remove traces of methyl 4-hydroxy-2-methylbenzoate and **25a**, both derived from lactone **33** via **28**. Then the organic phase was washed sequentially with 300 mL of water and 500 mL of brine and dried. Evaporation of the ether left 25.1 g of crude **3** which contained about 15% of **39** and several minor components by ^{1}H NMR. These were separated by chromatography on silica gel eluted with 9/1, isooctane/ethyl acetate to afford 2.6 g, 7% yield, of isophthalate **39** as a colorless oil which was kugelrohr distilled: bp 115–125 °C (0.3 mmHg); ^{1}H NMR δ 1.20 (t, 3 H), 2.48 (s, 3 H), 2.59 (q, 2 H), 3.86 (s, 3 H), 3.90 (s, 3 H), 7.11 (d, 1 H), 7.83 (d, 1 H); IR (neat) 3000, 1730, 1610 cm^{-1}; UV (methanol) λ_{max} nm (ε) 234 (12000), 277 (850). Anal. Calcd for $C_{13}H_{16}O_4$: C, 66.1; H, 6.8. Found: C, 66.1; H, 6.7.

Continued chromatography afforded 14.8 g, 35% yield, of the epoxy diester **3** as a clear oil which was kugelrohr distilled: bp 135–150 °C (0.75 mmHg); ^{1}H NMR (200 MHz) δ 1.00 (t, 3 H, J = 7.5 Hz), 1.3–1.4 (m, 2 H), 1.4–1.7 (m, 2 H), 2.06 (s, 3 H), 2.2–2.5 (m, 2 H), 3.70 (s, 3 H), 3.78 (s, 3 H); IR (neat) 2950, 1760, 1725 cm^{-1}; UV (methanol) λ_{max} 232 nm (ε 7100). Anal. Calcd for $C_{13}H_{18}O_5$: C, 61.4; H, 7.1. Found: C, 61.4; H, 7.1.

Pyridylseleno Group in Organic Synthesis. Preparation and Oxidation of α-(2-Pyridylseleno) Carbonyl Compounds Leading to α,β-Unsaturated Ketones and Aldehydes

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α-(2-Pyridylseleno) carbonyl compounds (A) were prepared by the reaction of ketones or aldehydes with 2-pyridylselenenyl bromide under various conditions (acidic, basic, or after conversion to silyl enol ethers) in good to excellent yields. Oxidation of A thus prepared affords α,β-unsaturated carbonyl compounds in excellent yields even in the cases where satisfactory results were not obtained by the oxidation of the corresponding α-phenylseleno carbonyl compounds. These results indicate that the 2-pyridylseleno group is a better leaving group than the phenylseleno group in selenoxide elimination leading to enones.

Among the useful chemistry of organoselenium compounds, preparation of α,β-unsaturated carbonyl compounds by the oxidation of α-phenylseleno carbonyl compounds belongs to one of the most important and widely used reactions.[1-3] However, several examples have been reported where satisfactory results were not obtained by this methodology. We have previously reported that a 2-pyridylseleno group is a better leaving group than phenylseleno in selenoxide elimination to give terminal olefins.[4] Here, we report that oxidation of α-(2-pyridylseleno)carbonyl compounds affords enones in excellent yields, even in cases where satisfactory results were not obtained by the oxidation of the corresponding α-phenylseleno carbonyl compounds. We have also found that α-(2-pyridylseleno) carbonyl compounds can be prepared by the reaction of ketones or aldehydes with 2-pyridylselenenyl bromide under various conditions (acidic, basic, or after conversion to silyl enol ethers) in good to excellent yields. These two reactions may well provide an improved method for dehydrogenation of ketones and aldehydes.[5]

Results and Discussion

2-Pyridylselenenyl bromide and chloride were prepared by the reaction of 2,2′-dipyridyl diselenide with bromine and sulfuryl chloride, respectively, and were used without isolation in the following reactions. If necessary they can be isolated as completely odorless powders and stored almost indefinitely. Alkyl 2-pyridyl selenides and 2,2′-dipyridyl diselenide are also odorless compounds in contrast to the corresponding phenylseleno derivatives.

2,2′-Dipyridyl diselenide is a known compound but reported preparation procedures have been somewhat troublesome.[6] Our improved procedure consists of a one-pot synthesis of 2,2′-dipyridyl diselenide from 2-bromopyridine, selenium powder, and sodium borohydride and isolation by column chromatography. This procedure is suitable for laboratory-scale preparation (see Experimental Section).

Preparation of α-(2-Pyridylseleno) Carbonyl Compounds. α-(2-Pyridylseleno)cyclohexanone (1) was produced by the reaction of cyclohexanone with 2-pyridylselenenyl bromide. The yield of 1, however, was unsatisfactory (11–34%) when the reaction was carried out without the addition of a reagent to facilitate the enolization of cyclohexanone. Acidic conditions were examined first and the addition of 5 equiv of aqueous hydrochloric

(1) For example: Clive, D. L. J. *Tetrahedron* **1978**, *34*, 1049–1132. Reich, H. J. "Oxidation in Organic Chemistry, Part C", Trahanovsky, W., Ed.; Academic Press: New York, 1978; pp 1–130. Reich, H. J. *Acc. Chem. Res.* **1979**, *12*, 22–30.

(2) For aldehyde, see, for example: (a) Sharpless, K. B.; Lauer, R. F.; Teranishi, A. Y. *J. Am. Chem. Soc.* **1973**, *95*, 6137–6139. (b) Ryu, I.; Murai, S.; Niwa, I.; Sonoda, N. *Synthesis* **1977**, 874–876. (c) Nicolaou, K. C.; Magolda, R. L.; Sipio, W. J. *Ibid.* **1979**, 982–984. (d) Williams, D. R.; Nishitani, K. *Tetrahedron Lett.* **1980**, *21*, 4417–4420. (e) Jefson, M.; Meinwald, J. *Ibid.* **1981**, *22*, 3561–3564.

(3) For the use of benzeneseleninic anhydride, see, for example: (a) Barton, D. H. R.; Lester, D. J.; Ley, S. V. *J. Chem. Soc., Perkin Trans. 1* **1980**, 2209–2212. (b) Back, T. G. *J. Org. Chem.* **1981**, *46*, 1442–1446.

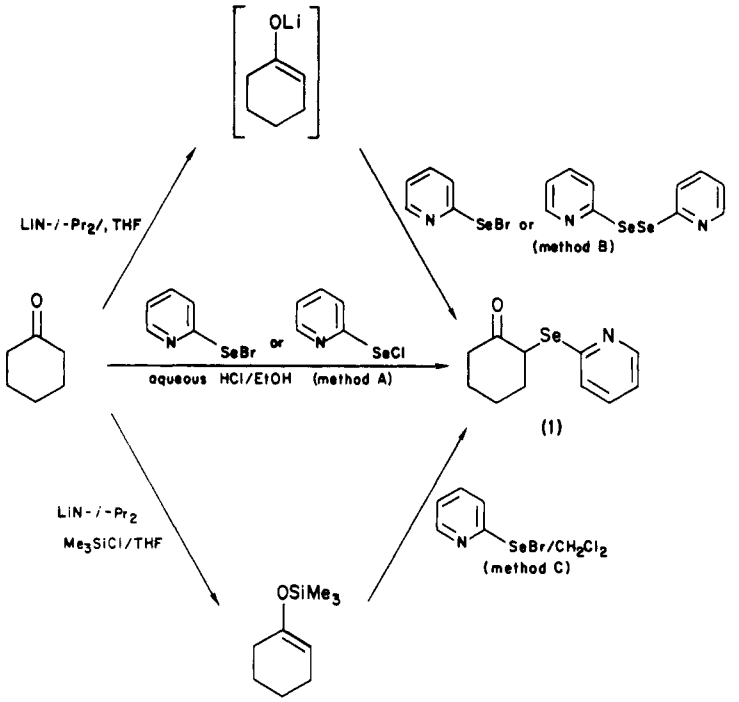
(4) Toshimitsu, A.; Owada, H.; Uemura, S.; Okano, M. *Tetrahedron Lett.* **1980**, *21*, 5037–5038.

(5) Preliminary results of this work: Toshimitsu, A.; Owada, H.; Uemura, S.; Okano, M. *Tetrahedron Lett.* **1982**, *23*, 2105–2108.

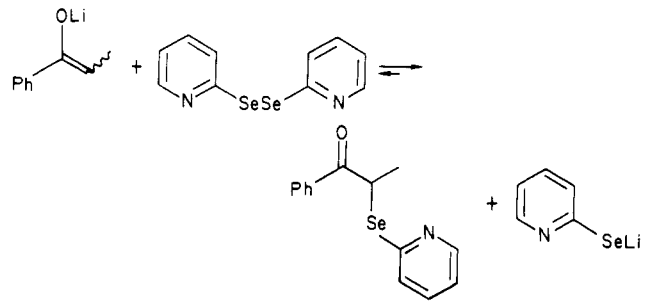
(6) (a) Takaku, H.; Shimada, Y.; Nakajima, Y.; Hata, T. *Nucleic Acid Res.* **1976**, *3*, 1233–1248. (b) Mautner, H.; Chu, S.-H.; Lee, C. M. *J. Org. Chem.* **1962**, *27*, 3671–3673.

0022-3263/84/1949-3796$01.50/0

Scheme I



Scheme II



acid (36.5%) in ethanol as solvent (method A) was found to be the condition of choice, affording **1** in 89% isolated yield. The yield of **1** was almost the same when 2-pyridylselenenyl chloride was used under the same conditions, indicating that both 2-pyridylselenenyl bromide and chloride work equally well as selenenylating reagent of carbonyl compounds.[7] Basic conditions were also examined and it was found that the lithium enolate, prepared in situ by the reaction of lithium diisopropylamide with cyclohexanone, reacts with 2-pyridylselenenyl bromide in tetrahydrofuran as the solvent (method B) to afford **1** in 78% isolated yield. The silyl enol ether of cyclohexanone also reacts with 2-pyridylselenenyl bromide in dichloromethane as the solvent (neutral condition; method C) to afford **1** in 84% yield (Scheme I). These three methods were applied to various ketones and aldehydes and the results are summarized in Table I. Generally method C gave the best yields. As shown in the table, α-(2-pyridylseleno) carbonyl compounds were produced in comparable yields to those reported in the introduction of the phenylseleno group into the α-position of carbonyl compounds under analogous conditions.[2a,b,8] In the case of propiophenone (entry 6), both 2-pyridylselenenyl bromide and 2,2′-dipyridyl diselenide react with the enolate to give α-(2-pyridylseleno)propiophenone in almost the same yields. The reverse reaction in Scheme II is not favored in this case. As diphenyl diselenide has been reported not to selenenylate the ketone enolates,[8] this result suggests one of the merits of 2-pyridylseleno group. From 2-methylcyclohexanone, 2-methyl-6-(2-pyridylseleno)cyclohexanone (**2**) was produced almost exclusively (98:2) by the reaction with lithium enolate prepared under kinetically controlled condition (method B; entry 7). On the other hand, 2-methyl-2-(2-pyridylseleno)cyclohexanone (**3**) was the major product (83:17) by the reaction with silyl enol ether prepared under thermodynamically controlled condition[9] (method C, entry 8). The isomer ratios of the products reflected those for the reaction intermediates.

Table I. Dehydrogenation of Ketones and Aldehydes via α-(2-Pyridylseleno) Carbonyl Compounds

entry	carbonyl compound	α-(2-pyridylseleno) carbonyl compound; yield,[a] % A	B	C	enone yield,[b] %
1	cyclopentanone	52	53	77	85
2	cyclohexanone	89	78	84	82
3	cycloheptanone	84	79	97	100[c]
4	cyclooctanone	59	61	88	94[c]
5	cyclododecanone	61	79	100	82[c]
6	propiophenone	73	69[d]	89	97
7	2-methylcyclohexanone		87[e]		90[f]
8	2-methylcyclohexanone			83[g]	79[h]
9	heptanal	53		85	90
10	3-phenylpropanal	64		68	83
11	3-methylbutanal			89	65

[a] Isolated yield by column chromatography. As for method A, B, and C, see text and Experimental Section. [b] Determined by GLC using an internal standard. Oxidizing reagent, O_3; entries 1–8, $NaIO_4$; entries 9–11. [c] Et_2NH (1.5 equiv) was added in the elimination step. [d] 62% when 2,2′-dipyridyl diselenide was used. [e] **2**:**3** = 98:2. [f] The yield of **4** from pure **2**. [g] **2**:**3** = 13:87. [h] The yield of **5** and **6** (68:32) from pure **3**.

(7) It has been reported that phenylselenenyl bromide cannot be substituted for phenylselenenyl chloride in the phenylselenenylation of carbonyl compounds.[2a]

(8) See, for example: Reich, H. J.; Renga, J. M.; Reich, I. L. *J. Am. Chem. Soc.* **1975**, *97*, 5434–5447.

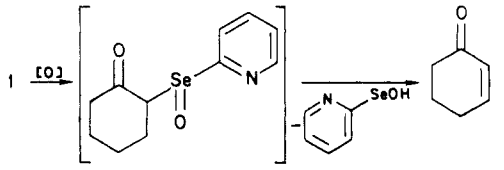
(9) House, H. O.; Czuba, L. J.; Gall, M.; Olmstead, H. D. *J. Org. Chem.* **1969**, *34*, 2324–2336.

Table II. Oxidative Elimination of 1 under Various Conditions[a]

entry	oxidizing reagent	mmol	solvent (mL)	temp, °C	time, h	yield,[b] %
12	ozone[c]	excess	CH_2Cl_2 (10)	−78	0.5	82
13	ozone	excess	CH_2Cl_2 (10)	−78 to 20	2	48
14	$NaIO_4$	2.0	MeOH–H_2O [6:1] (14)	3	1	64
15	*t*-BuOOH	1.5	EtOH (10)	23	1	2
16	*m*-CPBA	1.1	EtOAc (10)	reflux	0.5	45
17	*N*-chlorosuccinimide[d]	1.1	MeOH–CH_2Cl_2 [1:1] (10)	5	1	6
18	*t*-BuOCl[d]	2.2	MeOH–CH_2Cl_2 [1:1] (10)	5	0.3	51
19	H_2O_2	1.5	EtOAc (10)	27	1	58
20	H_2O_2	3.0	EtOAc (10)	3∼21	2	15
21	H_2O_2	1.5	THF (10)	24	1	54

[a] Carried out using 1 (1 mmol). [b] Yields were determined by GLC analysis. [c] After oxidation, the solution of a selenoxide was added to refluxing CCl_4 (30 mL). [d] After the oxidation was carried out, CH_2Cl_2 (10 mL) and 2% aqueous NaOH (15 mL) were added and the resulting mixture was stirred at the same temperature for 0.5 h.

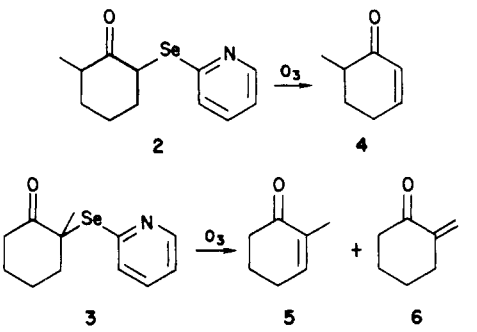
Scheme III



Although method B was not applicable to aldehydes, α-(2-pyridylseleno) aldehydes were produced in good to excellent yields by the use of method A and/or C. The results are also shown in Table I.

Oxidative Elimination of α-(2-Pyridylseleno) Carbonyl Compounds. By the oxidation of 1, 2-pyridylselenenic acid was eliminated to afford 2-cyclohexenone (Scheme III). Oxidizing reagents were examined first and the results are summarized in Table II. As shown in the table, usual oxidizing reagents such as sodium metaperiodate, *m*-chloroperbenzoic acid, *tert*-butyl hypochlorite, and aqueous hydrogen peroxide afforded 2-cyclohexenone only in moderate yields. Ozonization of 1 at −78 °C in dichloromethane followed by warm up to the ambient temperature (entry 13) did not improve the yield. 2-Cyclohexenone was produced in 82% yield by the addition of the cooled solution of the selenoxide, prepared by ozonization of 1 at −78 °C in dichloromethane, to refluxing carbon tetrachloride[8] (entry 12). This method was applied to various α-(2-pyridylseleno) ketones and the results are shown in Table I. As shown in entries 1–8, α,β-unsaturated ketones were produced in excellent yields. In the cases of α-(2-pyridylseleno)cycloheptanone, -octanone, and -dodecanone (entries 3–5), the yields of enones were unsatisfactory when the selenoxide eliminations were carried out under standard conditions described above. The addition of diethylamine in the elimination step improved the yield to excellent or quantitative. It should be noted here that oxidative elimination of α-(2-pyridylseleno) ketones afforded enones in better yields (by 10–45%) than that of α-phenylseleno ketones, which met with some difficulties in the formation of nonsubstituted cyclic enones.[8] By the oxidation of **2** (entry 7), 6-methyl-2-cyclohexenone (**4**) was produced selectively. While a mixture of 2-methyl-2-cyclohexenone (**5**) and α-methylenecyclohexanone (**6**) was formed by the oxidation of **3** (entry 8), endo isomer **5** being the major product (68:32) (Scheme IV). α-(2-Pyridylseleno) aldehydes were oxidized by 2 equiv of sodium metaperiodate in methanol–water (6:1) as the solvent to afford α,β-unsaturated aldehydes in good to excellent yields (entries 9–11). Under these reaction conditions, oxidation of the aldehyde group was not observed. It has been reported that 2-hepten-1-al was not obtained by the oxidation of 2-(phenylseleno)heptan-1-al.[2d] In sharp contrast to this, 2-hepten-1-al (trans) was produced in 90% yield by our procedure (entry 9). Our procedure is also feasible for the formation of β,β-disubstituted α,β-unsaturated aldehyde (entry 11). These results indicate that the 2-pyridylseleno group is a better leaving group than the phenylseleno group in selenoxide elmination leading to enones.

Scheme IV



Experimental Section

IR spectra were recorded with a Hitachi EPI-S2 spectrometer. ^1H and ^{13}C NMR spectra were obtained with Varian EM-360 and JEOLCO JNM-PFT-100 instruments on solutions in $CDCl_3$ with Me_4Si as an internal standard. GLC analyses were carried out with a Schimadzu 4CMPF apparatus by using EGSS-X (15%)–Chromosorb W (1 m) and Silicon DC QF-1 (5%)–Chromosorb W (1 m) columns (N_2 as carrier gas). Melting points were determined with a Schimadzu MM-2 micro melting point determination apparatus and were uncorrected.

Silyl enol ether of ketones under kinetically controlled conditions were prepared by the reported method[9] with tetrahydrofuran (THF) as the solvent. The silyl enol ether of 2-methylcyclohexanone under thermodynamically controlled condition was synthesized by the reported method.[9] The silyl enol ethers of aldehydes were prepared by heating the aldehyde with trimethylchlorosilane in benzene in the presence of triethylamine, hydroquinone, and zinc chloride.[10] These silyl enol ethers were purified by distillation.

Trimethylchlorosilane and a solution of *n*-butyllithium in hexane (1.5 M) were commercial products and were used without purification. All other organic materials were commercial products and were purified before use by distillation. All inorganic materials were commercial products and were used without purification.

2,2′-Dipyridyl Diselenide. [**Caution**: This reaction should be carried out in a well-ventilated hood (H_2 containing H_2Se evolves).] To a suspension of selenium powder (6.0 g, 76 mmol) in ethanol (100 mL) was added a suspension of sodium borohydride (3.5 g, 92 mmol) in ethanol (50 mL) in small portions during 40 min under ice bath cooling. The resulting pale brown solution was allowed to stand for 30 min. 2-Bromopyridine (12 g, 76 mmol) was added and the resulting mixture was heated under

(10) Ishida, A.; Mukaiyama, T. *Bull. Chem. Soc. Jpn.* **1977**, *50*, 1161–1168.

reflux for 96 h, during which period a white voluminous precipitate formed. After being cooled down to room temperature, oxygen gas was bubbled into the suspension for 30 min. The precipitate thus formed was filtered and washed with ethanol (20 mL × 3). Ethanol was removed from the filtrate (+ washings) under reduced pressure. Water (100 mL) was added to the residue and organic products were extracted with CH_2Cl_2 (50 mL × 3). The organic layer was washed with water and dried over $MgSO_4$. Evaporation of the solvent left a red residue which was subjected to column chromatography (silica gel) to give 2,2′-dipyridyl diselenide [9.9 g, 31.5 mmol, 83%; hexane–ethyl acetate (5:1–2:1) as eluent] as yellow needles; mp 48.0–49.0 °C [from petroleum ether (30–70 °C)] (lit.[6a] mp 48 °C); IR (KBr disk) 3060, 1565, 1552, 1444, 1408, 1105, 1076, 1041, 983, 749, 695 cm^{-1}; ^1H NMR δ 6.95 (ddd, 2 H, J = 1.4, 4.5, 7.0 Hz), 7.41 (ddd, 2 H, J = 1.8, 7.0, 8.0 Hz), 7.69 (ddd, 2 H, J = 1.0, 1.4, 8.0 Hz), 8.34 (ddd, 2 H, J = 1.0, 1.8, 4.5 Hz); ^{13}C NMR δ 120.6 (d), 122.8 (d), 136.7 (d), 148.8 (d), 153.6 (s).

2-Pyridylselenenyl Bromide. To a solution of 2,2′-dipyridyl diselenide (0.16 g, 0.5 mmol) in CH_2Cl_2 (3 mL) was added a solution of bromine (0.080 g, 0.5 mmol) in the same solvent (2 mL), and the resulting mixture was stirred at ambient temperature for 0.5 h. The yellow precipitate thus formed was collected by filtration and washed with small amounts of ether to give pure 2-pyridylselenenyl bromide: 0.21 g (0.87 mmol, 87%); mp 115–116 °C dec; IR (KBr disk) 3080, 1577, 1552, 1442, 1409, 1267, 1177, 1002, 769, 756, 692, 630 cm^{-1}. Anal. Calcd for C_5H_4NBrSe: C, 25.34; H, 1.70; N, 5.91. Found: C, 25.18; H, 1.44; N, 5.81.

2-Pyridylselenenyl Chloride. To a solution of 2,2′-dipyridyl diselenide (0.63 g, 2.0 mmol) in ethyl acetate (10 mL) was added a solution of sulfuryl chloride (0.27 g, 2.0 mmol) in the same solvent (2 mL), and the resulting mixture was stirred at ambient temperature for 1 h. The yellow precipitate thus formed was collected by filtration and washed with small portions of ethyl acetate to afford pure 2-pyridylselenenyl chloride: 0.72 g (3.7 mmol, 93%); mp 118–119 °C dec; IR (KBr disk) 3100, 1604, 1588, 1522, 1441, 1372, 755 cm^{-1}. Anal. Calcd for C_5H_4NClSe: C, 31.20; H, 2.09; N, 7.28. Found: C, 30.89; H, 2.20; N, 7.19.

2-(2-Pyridylseleno)cyclooctanone. Method A. General Procedure. To a solution of 2,2′-dipyridyl diselenide (0.63 g, 2.0 mmol) in ethanol (28 mL) was added a solution of bromine (0.32 g, 2.0 mmol) in ethanol (4 mL) at ambient temperature to give a yellow suspension. After 0.5 h, cyclooctanone (0.51 g, 4.0 mmol) in ethanol (4 mL) and aqueous (36.5%) HCl (2.1 g, 20 mmol) in ethanol (4 mL) were added successively, and the resulting mixture was heated under reflux for 0.5 h. After being cooled down to room temperature, saturated aqueous $NaHCO_3$ (40 mL) was added and the products were extracted with $CHCl_3$ (20 mL × 3). The organic layer was dried over $MgSO_4$ and then the solvent was removed under reduced pressure. A yellow residue was subjected to column chromatography (silica gel) to give 2-(2-pyridylseleno)cyclooctanone [0.66 g, 2.4 mmol, 60%; hexane–ethyl acetate (2:1) as eluent] as a pale yellow oil: IR (film) 3050, 2930, 2860, 1690, 1575, 1560, 1450, 1415, 1110, 760, 703 cm^{-1}; ^1H NMR δ 1.0–2.4 (m, 10 H), 2.4–3.0 (m, 2 H), 4.45 (dd, 1 H, J = 8, 6 Hz), 6.8–7.1 (m, 1 H), 7.1–7.5 (m, 2 H), 8.2–8.5 (m, 1 H). Anal. Calcd for $C_{13}H_{17}NOSe$: C, 55.32; H, 6.07; N, 4.96. Found: C, 55.43; H, 6.22; N, 5.09.

2-(2-Pyridylseleno)cyclododecanone. Method B. General Procedure. All reactions were carried out under argon atmosphere. To a solution of diisopropylamine (0.17 mL, 1.2 mmol) in THF (6 mL) was added a solution of n-butyllithium in hexane (1.5 M, 0.77 mL, 1.15 mmol) at −78 °C, and the resulting solution was stirred at −20 °C for 0.5 h. Cyclododecanone (0.18 g, 1.0 mmol) was added to this solution at −78 °C and then the solution was stirred at −78 to −40 °C for 2 h. The solution of lithium enolate of cyclododecanone thus prepared was added by a syringe to a stirred suspension of 2-pyridylselenenyl bromide (1.0 mmol, prepared in situ) in THF (10 mL) at −65 °C. The temperature of the reaction mixture was allowed to rise to 25 °C during 0.5 h. The reaction was quenched by addition of 10% aqueous NH_4Cl (20 mL), and after the usual workup, 2-(2-pyridylseleno)cyclododecanone was isolated by column chromatography [silica gel, hexane–ethyl acetate (5:1) as eluent]: 0.27 g, 0.79 mmol, 79%; mp 78.0–78.5 °C (from hexane); IR (KBr disk) 3070, 2960, 2880, 1700, 1573, 1555, 1468, 1452, 1112, 759, 727, 700 cm^{-1}; ^1H NMR δ 1.0–3.0 (m, 20 H), 4.91 (dd, 1 H, J = 4, 11 Hz), 6.8–7.2 (m, 1 H), 7.2–7.5 (m, 2 H), 8.3–8.4 (m, 1 H). Anal. Calcd for $C_{17}H_{25}NOSe$: C, 60.35; H, 7.45; N, 4.14. Found: C, 60.13; H, 7.61; N, 4.10.

2-(2-Pyridylseleno)cycloheptanone. Method C. General Procedure. To a suspension of 2-pyridylselenenyl bromide (0.24 g, 1.0 mmol) in CH_2Cl_2 (10 mL) was added a solution of silyl enol ether of cycloheptanone (0.19 g, 1.0 mmol) in CH_2Cl_2 (6 mL) at 25 °C under argon atmosphere. The precipitate of 2-pyridylselenenyl bromide disappeared immediately and the resulting pale yellow solution was stirred at ambient temperature for 0.5 h. After the usual workup, 2-(2-pyridylseleno)cycloheptanone was isolated by preparative TLC [silica gel, hexane–ethyl acetate (2:1) as eluent] as a pale yellow oil: 0.26 g, 0.97 mmol, 97%; IR (film) 3080, 2960, 2890, 1699, 1574, 1559, 1451, 1412, 1112, 756, 699 cm^{-1}; ^1H NMR δ 1.0–2.4 (m, 8 H), 2.4–2.9 (m, 2 H), 4.59 (dd, 1 H, J = 10, 5 Hz), 6.8–7.2 (m, 1 H), 7.2–7.6 (m, 2 H), 8.3–8.6 (m, 1 H). Anal. Calcd for $C_{12}H_{15}NOSe$: C, 53.74; H, 5.64; N, 5.22. Found: C, 53.47; H, 5.56; N, 5.10.

Spectral data of other α-(2-pyridylseleno) carbonyl compounds are as follows. All compounds are pale yellow oils.

2-(2-Pyridylseleno)cyclopentanone: IR (film) 1738 cm^{-1}; ^1H NMR δ 1.8–2.7 (m, 6 H), 4.15 (t, 1 H, J = 7 Hz), 6.8–7.2 (m, 1 H), 7.2–7.6 (m, 2 H), 8.2–8.5 (m, 1 H). Anal. Calcd for $C_{10}H_{11}NOSe$: C, 50.01; H, 4.62; N, 5.83. Found: C, 49.76; H, 4.59; N, 5.74.

2-(2-Pyridylseleno)cyclohexanone (1): IR (film) 1704 cm^{-1}; ^1H NMR δ 1.6–3.1 (m, 8 H), 4.67 (dd, 1 H, J = 8, 6 Hz), 6.8–7.1 (m, 1 H), 7.1–7.6 (m, 2 H), 8.3–8.5 (m, 1 H). Anal. Calcd for $C_{11}H_{13}NOSe$: C, 51.98; H, 5.16; N, 5.51. Found: C, 52.21; H, 5.22; N, 5.38.

2-(2-Pyridylseleno)propiophenone: IR (film) 1675 cm^{-1}; ^1H NMR δ 1.82 (d, 3 H, J = 7 Hz), 5.71 (q, 1 H, J = 7 Hz), 6.9–7.6 (m, 6 H), 7.9–8.1 (m, 2 H), 8.2–8.6 (m, 1 H). Anal. Calcd for $C_{14}H_{13}NOSe$: C, 57.94; H, 4.52; N, 4.83. Found: C, 57.89; H, 4.46; N, 4.79.

2-Methyl-6-(2-pyridylseleno)cyclohexanone (2) (cis:trans mixture; ~55:45): IR (film) 1703 cm^{-1}; ^1H NMR (100 MHz) δ 1.06 (d, 3 H, J = 7 Hz, trans), 1.08 (d, 3 H, J = 7 Hz, cis), 1.2–3.3 (m, 7 H), 4.49 (t, 1 H, J = 4 Hz, trans), 4.86 (dd, 1 H, J = 12, 6 Hz, cis), 6.9–7.1 (m, 1 H), 7.2–7.6 (m, 2 H), 8.3–8.5 (m, 1 H). Anal. Calcd for $C_{12}H_{15}NOSe$: C, 53.74; H, 5.64; N, 5.22. Found: C, 53.52; H, 5.73; N, 4.97.

2-Methyl-2-(2-pyridylseleno)cyclohexanone (3): IR (film) 1700 cm^{-1}; ^1H NMR (100 MHz) δ 1.58 (s, 3 H), 1.6–2.6 (m, 7 H), 3.42 (ddd, 1 H, J = 14, 13, 6 Hz), 7.0–7.6 (m, 3 H), 8.4–8.6 (m, 1 H). Anal. Found: C, 53.82; H, 5.66; N, 5.34.

2-(2-Pyridylseleno)heptan-1-al: IR (film) 1714 cm^{-1}; ^1H NMR δ 0.7–2.3 (m, 11 H), 4.47 (dt, 1 H, J = 2, 7 Hz), 6.8–7.1 (m, 1 H), 7.1–7.5 (m, 2 H), 8.2–8.4 (m, 1 H), 9.42 (d, 1 H, J = 2 Hz). Anal. Calcd for $C_{12}H_{17}NOSe$: C, 53.34; H, 6.34; N, 5.18. Found: C, 53.13; H, 6.25; N, 4.97.

3-Phenyl-2-(2-pyridylseleno)propan-1-al: IR (film) 1710 cm^{-1}; ^1H NMR δ 3.12 (dd, 1 H, J = 14, 7 Hz), 3.46 (dd, 1 H, J = 14, 7 Hz), 4.84 (dt, 1 H, J = 2, 7 Hz), 6.9–7.5 (m, 8 H), 8.3–8.6 (m, 1 H), 9.63 (d, 1 H, J = 2 Hz). Anal. Calcd for $C_{14}H_{13}NOSe$: C, 57.94; H, 4.52; N, 4.83. Found: C, 57.93; H, 4.67; N, 4.63.

3-Methyl-2-(2-pyridylseleno)butan-1-al: IR (film) 1706 cm^{-1}; ^1H NMR (100 MHz) δ 1.10 (d, 6 H, J = 7 Hz), 2.18 (octet, 1 H, J = 7 Hz), 4.27 (dd, 1 H, J = 7, 3 Hz), 6.9–7.1 (m, 1 H), 7.2–7.6 (m, 2 H), 8.3–8.5 (m, 1 H), 9.47 (d, 1 H, J = 3 Hz). Anal. Calcd for $C_{10}H_{13}NOSe$: C, 49.60; H, 5.41; N, 5.78. Found: C, 49.84; H, 5.36; N, 5.94.

Oxidative Elimination of 2-(2-Pyridylseleno)cyclooctanone. General Procedure for Oxidation by Ozone. A solution of 2-(2-pyridylseleno)cyclooctanone (0.28 g, 1.0 mmol) in CH_2Cl_2 (10 mL) was cooled to −78 °C under argon, and ozone gas was introduced until the solution was purple. After 15 min, nitrogen gas was introduced until the solution became colorless (to remove excess ozone) and cold diethylamine (0.073 g, 1.0 mmol) was added. The cold solution was transfered via a Teflon tube to refluxing CCl_4 (30 mL) containing diethylamine (0.037 g, 0.5 mmol), and the resulting solution was stirred under reflux for 0.5 h. After being cooled down to room temperature, GLC analysis of the solution using benzyl acetate as an internal standard revealed the presence of 2-cyclooctenone; 0.94 mmol, 94%.

Oxidative Elimination of 2-(2-Pyridylseleno)heptan-1-al. General Procedure for Oxidation by Sodium Metaperiodate. To a solution of 2-(2-pyridylseleno)heptan-1-al (0.27 g, 1.0 mmol) in methanol (12 mL) was added a solution of sodium metaperiodate (0.43 g, 2.0 mmol) in water (2 mL) at room temperature. The resulting white turbid mixture was stirred for 1 h. After the addition of saturated aqueous $NaHCO_3$ (30 mL), the products were extracted with $CHCl_3$ (20 mL × 3). GLC analysis of the organic layer using *p*-methylanisole as an internal standard showed the presence of *trans*-2-hepten-1-al; 0.90 mmol, 90%.

Oxidative elimination of 2-(2-pyridylseleno)-3-methylbutanal was carried out in the same way at 40 °C.

All of the enones thus prepared are either commercially available or reported compounds.[11]

(11) Cyclopentenone, cyclohexenone, *trans*-2-hepten-1-al, *trans*-3-phenyl-2-propen-1-al, and 3-methyl-2-buten-1-al are commercially available. References for spectral data and/or preparation procedure of reported compounds are as follows: 2-cycloheptenone, 2-cyclooctenone, *trans*-2-cyclododecenone, 1-phenyl-2-propen-1-one, and 6-methyl-2-cyclohexenone, ref 8; 2-methyl-2-cyclohexenone, Warnhoff, E. W.; Martin, D. G.; Johnson, W. S. "Organic Syntheses"; Wiley: New York, 1963; Collect. Vol. IV, pp 162–166; 2-methylenecyclohexanone, Ksander, G. M.; McMurry, J. E.; Johnson, M. *J. Org. Chem.* **1977**, *42*, 1180–1185.

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Registry No. **1**, 82998-12-7; (*cis*)-**2**, 91491-57-5; (*trans*)-**2**, 91491-58-6; **3**, 91491-59-7; **4**, 6610-21-5; **5**, 1121-18-2; selenium, 7782-49-2; 2-bromopyridine, 109-04-6; 2,2′-dipyridyl diselenide, 59957-75-4; 2-pyridylselenenyl bromide, 91491-61-1; 2-pyridylselenenyl chloride, 82998-10-5; cyclooctanone, 502-49-8; 2-(2-pyridylseleno)cyclooctanone, 82998-14-9; cyclododecanone, 830-13-7; 2-(2-pyridylseleno)cyclododecanone, 91491-56-4; cycloheptanone, 502-42-1; 2-(2-pyridylseleno)cycloheptanone, 82998-13-8; 2-(2-pyridylseleno)cyclopentanone, 82998-11-6; cyclopentanone, 120-92-3; cyclohexanone, 108-94-1; 2-(2-pyridylseleno)propiophenone, 82998-15-0; propiophenone, 93-55-0; 2-methylcyclohexanone, 583-60-8; 2-(2-pyridylseleno)heptan-1-al, 82998-17-2; heptan-1-al, 111-71-7; 3-phenyl-2-(2-pyridylseleno)-propan-1-al, 82998-16-1; 3-phenylpropan-1-al, 104-53-0; 3-methyl-2-(2-pyridylseleno)butan-1-al, 91491-60-0; 3-methylbutan-1-al, 590-86-3; 2-cyclooctenone, 1728-25-2; *trans*-2-hepten-1-al, 18829-55-5; 2-cyclopentenone, 930-30-3; 2-cyclohexenone, 930-68-7; 2-cycloheptenone, 1121-66-0; 2-cyclododecenone, 42858-38-8; 1-phenyl-2-propen-1-one, 768-03-6; *trans*-3-phenyl-2-propen-1-al, 14371-10-9; 3-methyl-2-buten-1-al, 107-86-8.

Conformational Analysis of Tricyclo[7.3.1.$0^{5,13}$]tridecane (Perhydrophenalene) by Molecular Mechanics

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Molecular mechanics were used to calculate the steric energy of the stable conformations of *trans,trans,trans*-, *cis,cis,trans*-, *cis,trans,trans*-, and *cis,cis,cis*-tricyclo[7.3.1.$0^{5,13}$]tridecane (perhydrophenalene). The pseudorotation of the flexible forms is studied with idealized models and compared with the results from the force field calculations.

Fused ring systems are of considerable interest to organic chemists because of their widespread occurrence in saturated products and as models for conformational studies. Conformational analysis of a variety of bicyclic systems has been examined in detail, but related studies upon fused tricarbocyclic systems have hitherto concentrated upon perhydrophenanthrene[1] and perhydroanthracene.[2-4]

The tricyclo[7.3.1.$0^{5,13}$]tridecanes (perhydrophenalenes) have attracted little attention and the available information about the stability of the different forms is scarce. In an early study by Schneider et al.,[5] aluminum halide catalyzed isomerization of perhydrofluorene at 0 °C gives one compound, perhydrophenalene, with all trans ring fusions. Equilibrium constants and compositions of perhydroanthracene and the most stable methylperhydrophenalenes were estimated.[6]

Reaction of the cis,cis isomer of perhydro-13-boraphenalene with potassium cyanide and then trifluoroacetic anhydride, followed by oxidation gives *trans,trans,trans*-perhydrophenalen-13-ol,[7] whereas carbonylation–oxidation yields the all cis isomer.[8]

Starting from spiro[cyclohexanone-2,4′-cyclohex-2′-en]-1′-one, Seshu Sekhara Rao et al.[9] synthesized perhydrophenalene-2,6-dione, which they assumed to be in the all trans configuration.

The steric energy of the four possible isomers of 13-methylperhydrophenalene were calculated by Gund and Gund[10] by using Boyd's program.[11] Assuming a printing error for the cis,cis,trans form,[12] the energy sequence is trans,trans,trans < cis,cis,trans < cis,cis,cis = cis,trans,-trans.

Interest in the conformations of perhydrophenalene arises out of work carried out in this laboratory[13] on syn-

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