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Synthesis of Pyrrole Derivatives from 5,6-Dihydro-4*H*-1,2-oxazines via Reductive Deoxygenation by Use of $Fe_3(CO)_{12}$

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α-Bromooximes such as α-bromoacetophenone oxime and ethyl 3-bromo-2-(hydroxyimino)propanoate react with enamines to give 5,6-dihydro-4*H*-1,2-oxazines in good yields. Dihydro-1,2-oxazine derivatives are also obtained by the reaction of α-bromooximes with vinyl ethers and silyl enol ethers in the presence of Na_2CO_3. Dihydro-1,2-oxazines can be converted into pyrrole derivatives via reductive deoxygenation by treating with $Fe_3(CO)_{12}$ in moderate to excellent yields. Iron carbonyl complexes other than $Fe_3(CO)_{12}$ are also effective for the pyrrole-forming reaction. The efficiency of the complexes for this reaction decreases in the order: $Fe_3(CO)_{12} \gg Et_3NH[HFe_3(CO)_{11}] > Fe_2(CO)_9 \gg Fe(CO)_5$. Both of the dihydro-1,2-oxazine- and pyrrole-forming reactions can be carried out in a single flask, giving pyrrole derivatives in good yields.

Iron carbonyls are useful reagents in organic synthesis. They can be used for deoxygenation of oximes, N-oxides, nitro and nitroso compounds.[1] One attractive application of this reaction in organic synthesis may be the preparation of nitrogen-containing heterocyclic compounds. In a previous communication, we reported a new method for the synthesis of pyrrole derivatives from 5,6-dihydro-6-morpholino-4*H*-1,2-oxazines, which were prepared from α-bromooximes and *N*-vinylmorpholines, by use of iron carbonyls.[2] The reaction proceeded via the reductive deoxygenation of dihydro-1,2-oxazines with elimination of morpholine. In this reaction, however, the structure of synthesized pyrroles is strongly restricted by the preparative accessibility of dihydro-1,2-oxazines. In fact, monosubstituted pyrroles are not readily accessible by this procedure.

Recently, we found that dihydro-1,2-oxazines prepared from α-halooximes and vinyl ethers or silyl enol ethers can also be converted into pyrrole derivatives by use of iron carbonyls. This magnified the synthetic applicability of this methodology and enabled the synthesis of pyrrole derivatives having a wide variety of substitution patterns. In this paper, we describe the detailed accounts of these reactions.

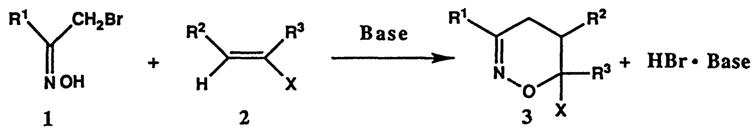
Results and Discussion

Preparation of 5,6-Dihydro-4*H*-1,2-oxazines. The reaction of α-bromooximes **1a**, **b** with *N*-vinylmorpholines **2a—f** in toluene at room temperature gave 5,6-dihydro-6-morpholino-4*H*-1,2-oxazines **3a—f** and **3l** in good yields. The reaction of **1a**, **b** with vinyl ethers **2g—i** and silyl enol ethers **2j**, **k** in CH_2Cl_2 in the presence of Na_2CO_3 afforded 5,6-dihydo-4*H*-1,2-oxazines **3g—q** in good yields, which have oxygen-containing functional groups at 6-position.

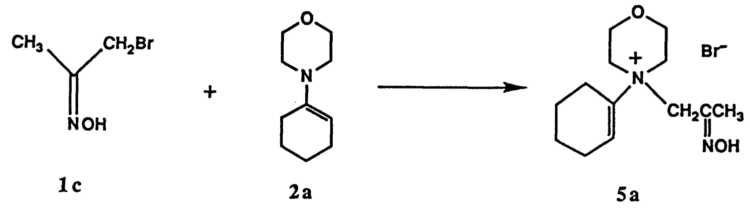
Although each of these methods has its own limitation in applicability due to the availability and the reactivity of the starting materials (see later), a combined use of these methods enables the preparation of dihydro-1,2-oxazines having a wide variety of substitution patterns. The results are summarized in Table 1. The structures of the dihydro-1,2-oxazines were established from their IR, NMR, and mass spectral data and also from their elemental analyses.

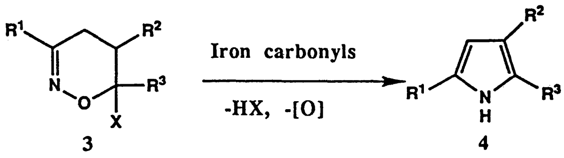
Some examples of dihydro-1,2-oxazine-forming reactions from α-halooximes and enamines[3] or vinyl ethers[4] have been reported. However, in the course of our study, we noted that the yields of dihydro-1,2-oxazines can be improved by taking the following precautions: 1) In the reactions with *N*-vinylmorpholines, at least two molar equivalents of *N*-vinylmorpholines to one molar equivalent of α-halooximes have to be used. This is due to the fact that one molar equivalent of *N*-vinylmorpholines is consumed for trapping eliminated HBr. The addition of other bases such as Et_3N rather reduces the yields of dihydro-1,2-oxazines. 2) In the reactions with vinyl ethers and silyl enol ethers, the addition of Na_2CO_3 causes a dramatic increase in the yields of dihydro-1,2-oxazines. We also found that α-bromooximes bearing alkyl groups at the C=NOH carbon, such as 1-bromo-2-propanone oxime (**1c**) and 1-bromo-2-butanone oxime (**1d**), did not afford the corresponding dihydro-1,2-oxazines. Indeed, the reaction of **1c** with 1-morpholinocyclohexene (**2a**) gave *N*-(2-hydroxyiminopropyl)-*N*-(l-cyclohexenyl)morpholinium bromide (**5a**) as a major product.

Synthesis of Pyrrole Derivatives. Treatment of dihydro-1,2-oxazines **3a—o** with $Fe_3(CO)_{12}$ in 1,2-dichloroethane at 80 °C gave pyrrole derivatives **4a—l** generally in good yields. This reaction proceeded via a reductive deoxygenation, accompanied by elimination of morpholine, phenol, butanol, or trimethylsilanol which was rapidly converted to hexamethyldisiloxane. The results are summarized in Table 2. The structures of pyrroles were identified from their spec-



R^1 = Ph, EtOCO; R^2, R^3 = H, alkyl, phenyl
X = Morpholino, BuO, PhO, Me_3SiO





R^1 = Ph, EtOCO; R^2, R^3 = H, alkyl, phenyl
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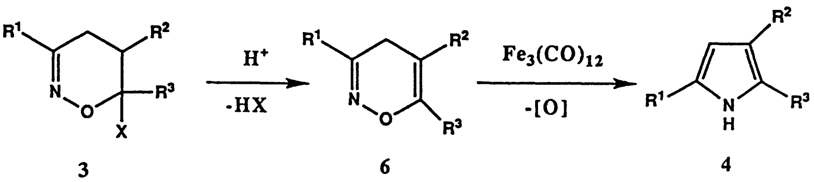

tral data and elemental analyses.

By utilizing these reactions, pyrrole derivatives having a variety of substitution patterns can be synthesized. This methodology is particularly useful for the synthesis of condensed bicyclic pyrroles such as **4a**—**c** and **4j** that are not readily accessible by other methods.

In some cases, the yields of pyrroles were poor. In these cases, however, the yields were appreciably improved by adding trifluoroacetic acid into the reaction systems. This acid may assist elimination of

Table 1. Preparation of 5,6-Dihydro-4*H*-1,2-oxazines

Oxime		Alkene				Solvent	Base	Reaction temp/°C	Reaction time/h	Yield of oxazine/%	
	R^1		R^2	R^3	X						
1a	Ph	2a	$-(CH_2)_4-$		C_4H_4NO[a]	Toluene	—	Rt	3	3a	91
1a	Ph	2b	$-(CH_2)_3-$		C_4H_4NO[a]	Toluene	—	Rt	3	3b	82
1a	Ph	2c	$-(CH_2)_5-$		C_4H_4NO[a]	Toluene	—	Rt	3	3c	90
1a	Ph	2d	Et	H	C_4H_4NO[a]	Toluene	—	Rt	3	3d	80
1a	Ph	2e	Me	Et	C_4H_4NO[a]	Toluene	—	Rt	3	3e	82
1a	Ph	2f	Me	Ph	C_4H_4NO[a]	Toluene	—	Rt	3	3f	78
1a	Ph	2g	H	H	PhO	CH_2Cl_2	Na_2CO_3	Rt	20	3g	99
1a	Ph	2h	H	H	BuO	CH_2Cl_2	Na_2CO_3	Rt	15	3h	99
1a	Ph	2i	Me	H	PhO	CH_2Cl_2	Na_2CO_3	40	4	3i	46
1a	Ph	2j	$-(CH_2)_4-$		Me_3SiO	MeCN	Na_2CO_3	Rt	20	3j	49
1a	Ph	2k	H	Ph	Me_3SiO	MeCN	Na_2CO_3	Rt	20	3k	71
1b	EtOCO	2a	$-(CH_2)_4-$		C_4H_4NO[a]	Toluene	—	Rt	3	3l	86
1b	EtOCO	2g	H	H	PhO	$ClCH_2CH_2Cl$	Na_2CO_3	80	22	3m	84
1b	EtOCO	2h	H	H	BuO	$ClCH_2CH_2Cl$	Na_2CO_3	80	3	3n	91
1b	EtOCO	2i	Me	H	PhO	$ClCH_2CH_2Cl$	Na_2CO_3	80	3	3o	63
1b	EtOCO	2j	$-(CH_2)_4-$		Me_3SiO	CH_2Cl_2	Na_2CO_3	Rt	20	3p	97
1b	EtOCO	2k	H	Ph	Me_3SiO	CH_2Cl_2	Na_2CO_3	Rt	20	3q	74

a) C_4H_4NO: morpholino.

Table 2. Synthesis of Pyrrole Derivatives

	Oxazine				Reaction conditions			Yield of pyrrole derivative/%	
	R^1	R^2	R^3	X	Solvent	Temp/°C	Time/h		
3a	Ph	$-(CH_2)_4-$		C_4H_4NO[a]	$ClCH_2CH_2Cl$	80	3	**4a**	99
3a	Ph	$-(CH_2)_4-$		C_4H_4NO[a]	THF	60	20	**4a**	98
3a	Ph	$-(CH_2)_4-$		C_4H_4NO[a]	Toluene	100	3	**4a**	84
3b	Ph	$-(CH_2)_3-$		C_4H_4NO[a]	$ClCH_2CH_2Cl$	80	3	**4b**	28
3b	Ph	$-(CH_2)_3-$		C_4H_4NO[a]	$ClCH_2CH_2Cl$[b]	80	3	**4b**	53
3c	Ph	$-(CH_2)_5-$		C_4H_4NO[a]	$ClCH_2CH_2Cl$	80	3	**4c**	92
3d	Ph	Et	H	C_4H_4NO[a]	$ClCH_2CH_2Cl$	80	3	**4d**	85
3e	Ph	Me	Et	C_4H_4NO[a]	$ClCH_2CH_2Cl$	80	3	**4e**	70
3f	Ph	Me	Ph	C_4H_4NO[a]	$ClCH_2CH_2Cl$	80	3	**4f**	58
3g	Ph	H	H	PhO	$ClCH_2CH_2Cl$	80	20	**4g**	98
3h	Ph	H	H	BuO	$ClCH_2CH_2Cl$	80	20	**4g**	91
3i	Ph	Me	H	PhO	$ClCH_2CH_2Cl$	80	20	**4h**	94
3j	Ph	$-(CH_2)_4-$		Me_3SiO	$ClCH_2CH_2Cl$	80	20	**4a**	38
3k	Ph	H	Ph	Me_3SiO	Toluene	100	20	**4i**	70
3l	EtOCO	$-(CH_2)_4-$		C_4H_4NO[a]	$ClCH_2CH_2Cl$	80	3	**4j**	16
3l	EtOCO	$-(CH_2)_4-$		C_4H_4NO[a]	$ClCH_2CH_2Cl$[b]	80	3	**4j**	55
3m	EtOCO	H	H	PhO	Toluene[b]	110	3	**4k**	60
3n	EtOCO	H	H	BuO	$ClCH_2CH_2Cl$[b]	80	20	**4k**	55
3o	EtOCO	Me	H	PhO	$ClCH_2CH_2Cl$[b]	80	20	**4l**	18
3p	EtOCO	$-(CH_2)_4-$		Me_3SiO	Toluene	110	3	**4j**	26
3q	EtOCO	H	Ph	Me_3SiO	$ClCH_2CH_2Cl$[b]	80	3	**4m**	46

a) C_4H_4NO: morpholino. b) The reaction was conducted in the presence of three molar equivalents of trifluoroacetic acid.

Table 3. Efficiency of Iron Carbonyls and Other Metal Reagents in the Formation of **4a** from **3a**

Reagent	Added amount/mmol[a]	Reaction conditions			Yield of **4a**/%
		Solvent	Temp/°C	Time/h	
$Fe_3(CO)_{12}$	1.5	$ClCH_2CH_2Cl$	80	3	99
$Et_3NH[HFe_3(CO)_{11}]$	1.5	$ClCH_2CH_2Cl$	80	3	57
$Fe_2(CO)_9$	2.25	$ClCH_2CH_2Cl$	80	3	49
$Fe(CO)_5$	4.5	$ClCH_2CH_2Cl$	80	3	Trace
Zn(dust)[b]	4.5	THF	60	20	19
Zn-AcOH[b]	4.5	THF	60	20	18
Al(Hg)[b]	4.5	THF	60	20	Trace

a) One mmol of **3a** was used. b) Metal reagents were activated by the literature procedures: Ref. 8a for Zn(dust), Ref. 8b for Zn-AcOH, Ref. 8c for Al(Hg).

HX (X=Morpholino, BuO, or PhO) groups from **3**.

Iron carbonyl complexes other than $Fe_3(CO)_{12}$ were also effective for the formation of pyrroles. The efficiencies of various iron complexes for the synthesis of **4a** from **3a** are given in Table 3, together with those of other metallic reducing agents. The efficiencies of iron carbonyl complexes decreased in the order: $Fe_3(CO)_{12} \gg Et_3NH[HFe_3(CO)_{11}] > Fe_2(CO)_9 \gg Fe(CO)_5$. This order of the reactivity seems reflect the order of reducing ability of the iron carbonyl complexes; we found that the reactivity of the reductive coupling of aromatic aldehydes by iron carbonyl complexes decrease in the same order.[5] It has been reported that Zn/acetic acid promotes deoxygenation from 3,6-dihydro-2*H*-1,2-oxazines.[6,7] However, the results of Table 3 indicate that $Fe_3(CO)_{12}$ is extremely effective for the pyrrole-forming reactions.

Table 4. One-pot Synthesis of Pyrroles from α-Bromooximes and Enamines

Oxime		Enamine			Yield of pyrrole derivaftive/%	
	R^1		R^2	R^3		
1a	Ph	**2a**	$-(CH_2)_4-$		**4a**	72
1a	Ph	**2b**	$-(CH_2)_3-$		**4b**	53
1a	Ph	**2c**	$-(CH_2)_5-$		**4c**	86
1a	Ph	**2l**	$-(CH_2)_6-$		**4n**	78
1a	Ph	**2m**	$-(CH_2)_{10}-$		**4o**	36
1a	Ph	**2g**	H	H	**4g**	60
1b	EtOCO	**2a**	$-(CH_2)_4-$		**4j**	50[a]
1b	EtOCO	**2e**	Me	Et	**4p**	67[a]
1e	*p*-MeC_6H_4	**2a**	$-(CH_2)_4-$		**4q**	61
1f	*p*-BrC_6H_4	**2a**	$-(CH_2)_4-$		**4r**	61

a) In the presence of trifluoroacetic acid.

We also found that the pyrrole-forming reactions starting from α-bromooximes and enamines can be carried out in a single flask without isolation of dihydro-1,2-oxazines. In this one-pot reaction, $Fe_3(CO)_{12}$ was added to a toluene solution containing an α-bromooxime and an enamine, and the resulting mixture was heated at 100 °C. The yields of pyrroles were generally good. The results are given in Table 4.

Detailed mechanism for the formation of pyrroles from dihydro-1,2-oxazines is equivocal at present. However, it is most likely that the reactions occur via a reductive deoxygenation of 4*H*-1,2-oxazines **6** that are produced by an acid-assisted elimination of morpholine or alcoholic groups from **3**. This was supported by the fact that when **3f** (R^1=Ph, R^2=CH_3, R^3=Ph, X=Morpholino) was heated at 50 °C for 30 min in $CDCl_3$ containing CF_3COOH in an NMR tube, a singlet signal appeared at 2.05 ppm. This signal can be assigned to methyl protons attached at 5-position of **6f** (R^1=Ph, R^2=CH_3, R^3=Ph). However, attempts to isolate **6f** in a pure form were unsuccessful.

Experimental

Melting points were uncorrected. IR spectra were taken on a JASCO IRA-16 spectrophotometer. NMR spectra were recorded with a Hitachi R-24A spectrometer in $CDCl_3$ using TMS as an internal standard. Mass spectra were measured with a Hitachi RMU-6E mass spectrometer. 2-Bromo-4′-substituted acetophenone oximes,[9] ethyl 3-bromo-2-hydroxyiminopropanoate,[10] 1-phenoxypropene,[11] 1-trimethylsiloxycyclohexene,[12] and α-trimethylsiloxystyrene[13] were prepared according to the literature methods. Enamines were prepared from the corresponding ketones or aldehydes and morpholine by the standard procedures.

General Procedure for Preparation of Dihydro-1,2-oxazines. From α-Bromooximes and Enamines. A toluene solution (20 cm³) of an α-bromooxime (5 mmol) was added to a solution of an enamine (10 mmol) in toluene (50 cm³). The mixture was stirred at room temperature for 3 h, and diluted with water (20 cm³). The organic layer was separated and dried ($MgSO_4$). Evaporation of the solvent gave a dihydro-1,2-oxazine as a white solid. Recrystallization from EtOH gave colorless crystals.

3a: Mp 157—159 °C; Found: C, 71.91; H, 8.23; N, 9.39%. Calcd for $C_{18}H_{24}N_2O_2$: C, 71.97; H, 8.05; N, 9.33%. ^1H NMR ($CDCl_3$) δ=1.30—2.41 (m, 11H), 2.70 (t, *J*=4.0 Hz, 4H), 3.57 (t, *J*=4.0 Hz, 4H), 7.1 7—7.70 (m, 5H).

3b: Mp 89—91 °C; Found: C, 71.06; H, 7.78; N, 9.98%. Calcd for $C_{17}H_{22}N_2O_2$: C, 71.30; H, 7.74; N, 9.78%. ^1H NMR ($CDCl_3$) δ=1.50—2.63 (m, 9H), 2.60—2.82 (m, 4H), 3.59 (t, *J*=4.0 Hz, 4H), 7.20—7.70 (m, 5H).

3c: Mp 111—112.5 °C; Found: C, 72.30; H, 8.29; N, 9.14%. Calcd for $C_{19}H_{26}N_2O_2$: C, 72.58; H, 8.34; N, 8.91%. ^1H NMR ($CDCl_3$) δ=1.30—2.10 (m, 11H), 2.20—2.48 (m, 2H), 2.50—2.80 (m, 4H), 3.55 (t, *J*=4.0 Hz, 4H), 7.12—7.68 (m, 5H).

3d: Mp 126.5—128 °C; Found: C, 69.96; H, 8.16; N, 10.22%. Calcd for $C_{16}H_{22}N_2O_2$: C, 70.04; H, 8.08; N, 10.21%. ^1H NMR ($CDCl_3$) δ=0.95 (t, *J*=7.0 Hz, 3H), 1.28—2.40 (m, 6H), 2.50—2.81 (m, 4H), 3.55 (t, *J*=4.0 Hz, 4H), 7.12—7.68 (m, 5H).

3e: Mp 106—108 °C; Found: C, 70.93; H, 8.54; N, 9.93%. Calcd for $C_{17}H_{24}N_2O_2$: C, 70.80; H, 8.39; N, 9.71%. ^1H NMR ($CDCl_3$) δ=1.00 (t, *J*=7.0 Hz, 3H), 1.05 (d, *J*=7.0 Hz, 3H), 1.57—2.70 (m, 5H), 2.68 (t, *J*=4.0 Hz, 4H), 3.53 (t, *J*=4.0 Hz, 4H), 7.10—7.70 (m, 5H).

3f: Mp 118.5—120 °C; Found: C, 74.86; H, 7.11; N, 8.58%. Calcd for $C_{21}H_{24}N_2O_2$: C, 74.97; H, 7.19; N, 8.33%. ^1H NMR ($CDCl_3$) δ=1.05 (d, *J*=6.8 Hz, 3H), 2.30—3.35 (m, 7H), 3.57 (t, *J*=4.1 Hz, 4H), 7.08—7.70 (m, 10H).

From α-Bromooximes and Vinyl Ethers or Silyl Enol Ethers. A solution containing an α-bromooxime (5.0 mmol), a vinyl ether (15 mmol), and Na_2CO_3 (3.0 g) in CH_2Cl_2 (40 cm³) was stirred at room temperature for 20 h, filtered through Celite, and then the solvent was removed. Column chromatography of the residue on silica gel with petroleum ether-benzene (1 : 1) gave a dihydro-1,2-oxazine as a viscous oil or a white solid. The oily products were distilled by a Kugel Rohr, and the solid products were recrystallized from EtOH.

3g: Mp 117—118 °C; Found: C, 75.67; H, 5.91; N, 5.40%. Calcd for $C_{16}H_{15}NO_2$: C, 75.87; H, 5.97; N, 5.53%. IR (KBr) 3100, 2900, 1590, 1230 cm⁻¹; ^1H NMR ($CDCl_3$) δ=2.55 (m, 2H), 2.85 (m, 2H), 5.95 (m, 1 H), 7.20—7.90 (m, 10H).

3h: Oil; Found: C, 72.21 ; H, 8.25; N, 6.13%. Calcd for $C_{14}H_{19}NO_2$: C, 72.07; H, 8.21; N, 6.00%. IR (neat) 3030, 2980, 1600, 1260, 1060 cm⁻¹; ^1H NMR ($CDCl_3$) δ=0.92 (t, *J*=7.0 Hz, 3H), 1.00—2.57 (m, 8H), 3.45—3.80 (m, 2H), 4.80—4.95 (m, 1H), 7.05—7.65 (m, 5H).

3i: Oil; Found: C, 76.33; H, 6.39; N, 5.44%. Calcd for $C_{17}H_{17}NO_2$: C, 76.38; H, 6.41; N, 5.24%. IR (neat) 3030, 2980, 1600, 1260, 1050 cm⁻¹; ^1H NMR ($CDCl_3$) δ=0.58 (d, *J*=6.7 Hz, 3H), 1.50—2.65 (m, 3H), 4.80 (d, *J*=4.8 Hz, 1H), 6.40—7.25 (m, 10H).

3j: Mp 128—131 °C; Found: C, 67.52; H, 8.29; N, 4.88%. Calcd for $C_{17}H_{25}NO_2Si$: C, 67.28; H, 8.30; N, 4.62%. IR (KBr) 3100, 2960, 1280, 1240, 1165, 1118, 885, 860 cm⁻¹; ^1H NMR ($CDCl_3$) δ=0.21 (s, 9H), 1.14—2.40 (m, 11H), 7.07—7.48 (m, 5H).

3k: Mp 143—145 °C; Found: C, 70.30; H, 7.05; N, 4.43%. Calcd for $C_{19}H_{23}NO_2Si$: C, 70.11; H, 7.12; N, 4.30%. IR (KBr) 3100, 2960, 1230, 1160, 1100, 1060, 885, 864 cm⁻¹; ^1H NMR ($CDCl_3$) δ=0.21 (s, 9H), 2.32 (m, 2H), 2.80 (m, 2H), 7.16—7.52 (m, 10H).

3l: Mp 73—75.5 °C; Found: C, 60.81 ; H, 8.22; N, 9.39%. Calcd for $C_{15}H_{24}N_2O_4$: C, 60.79; H, 8.16; N, 9.45%. ^1H NMR ($CDCl_3$) δ=1.34 (t, *J*=6.8 Hz, 3H), 1.10—2.44 (m, 11H), 2.50—2.73 (m, 4H), 3.57 (t, *J*=4.0 Hz, 4H), 4.28 (q, *J*=6.8 Hz, 2H).

3m: Oil; Found: C, 62.55; H, 6.13; N, 5.51%. Calcd for $C_{13}H_{15}NO_4$: C, 62.64; H, 6.07; N, 5.62%. IR (neat) 3100, 2980, 1745, 1600 cm⁻¹; ^1H NMR ($CDCl_3$) δ=1.30 (t, *J*=7.0 Hz, 3H), 1.90—2.30 (m, 2H), 2.40—2.70 (m, 2H), 4.23 (q, *J*=7.0 Hz, 2H), 5.60—5.70 (m, 1H), 6.90—7.40 (m, 5H).

3n: Oil; Found: C, 57.58; H, 8.13; N, 6.25%. Calcd for $C_{11}H_{19}NO_4$: C, 57.62; H, 8.35; N, 6.12%. IR (neat) 2980, 1745, 1600 cm⁻¹; ^1H NMR ($CDCl_3$) δ=0.65—1.05 (m, 10H), 1.20—1.50 (m, 2H), 1.55—2.00 (m, 2H), 2.80—3.55 (m, 2H), 3.82 (q, 2H), 4.60 (m, 1H).

3o: Mp 59—60 °C; Found: C, 63.77; H, 6.58; N, 5.39%. Calcd for $C_{14}H_{17}NO_4$: C, 63.86; H, 6.51; N, 5.32%. IR (KBr) 2900, 1745, 1600 cm⁻¹; ^1H NMR ($CDCl_3$) δ=0.95—1.40 (m, 6H), 1.70—2.80 (m, 3H), 4.15 (q, 2H), 5.40 (m, 1H), 6.85—7.30 (m, 5H).

3p: Mp 87—89 °C; Found: C, 56.29; H, 8.26; N, 4.71%. Calcd for $C_{14}H_{25}NO_4Si$: C, 56.15; H, 8.42; N, 4.68%. IR (KBr) 2980, 1745, 1240, 1100, 865 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.21 (s, 9H), 1.10—2.40 (m, 14H), 4.12 (q, 2H).

3q: Mp 119—120 °C; Found: C, 59.81; H, 7.23; N, 4.19%. Calcd for $C_{16}H_{23}NO_4Si$: C, 59.78; H, 7.21; N, 4.36%. IR (KBr) 3030, 1745, 1600, 1240, 1100, 880 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.21 (s, 9H), 1.45 (t, J=7.0 Hz, 3H), 1.55—2.70 (m, 4H), 4.32 (q, J=7.0 Hz, 2H), 7.28—7.65 (m, 5H)

General Procedure for the Synthesis of Pyrrole Derivatives. A mixture of a dihydro-1,2-oxazine (1.0 mmol) and $Fe_3(CO)_{12}$ (1.5 mmol) in $ClCH_2CH_2Cl$ (15 ml) was stirred under argon at 80 °C for 3—20 h and filtered. The solvent was removed, and the residue was chromatographed on silica gel with hexane-benzene (1 : 1) to give a pyrrole derivative. Recrystallization from petroleum ether-benzene gave the pure sample as colorless crystals.

4a: Mp 112—113 °C;[13] IR (KBr) 3400 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.65—1.95 (m, 4H), 2.36—2.75 (m, 4H), 6.18 (d, J=2.0 Hz, 1H), 7.03—7.47 (m, 5H), 7.50—8.00 (m, 1H); MS *m/z* 197 (M^+).

4b: Mp 121—122 °C; Found: C, 85.43; H, 7.06; N, 7.55%. Calcd for $C_{13}H_{13}N$: C, 85.20; H, 7.15; N, 7.65%. IR (KBr) 3380 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=2.15—2.83 (m, 6H), 6.18 (d, J=2.0 Hz, 1H), 6.95—7.40 (m, 5H), 7.72—8.11 (m, 1H); MS *m/z* 183 (M^+).

4c: Mp 111—112.5 °C; Found: C, 85.16; H, 8.18; N, 6.90%. Calcd for $C_{15}H_{17}N$: C, 85.26; H, 8.11; N, 6.63%. IR (KBr) 3400 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.45—1.90 (m, 6H), 2.40—2.83 (m, 4H), 6.18 (d, J=2.0 Hz, 1H), 7.03—7.47 (m, 5H), 7.50—8.03 (m, 1H).

4d: Mp 106.5—108 °C; Found: C, 84.30; N, 7.58; N, 8.22%. Calcd for $C_{12}H_{13}N$: C, 84.18; H, 7.65; N, 8.18%. IR (KBr) 3380 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.22 (t, J=7.0 Hz, 3H), 2.55 (q, J=7.0 Hz, 2H), 6.30—6.45 (m, 1H), 6.53—6.67 (m, 1H), 7.12—7.50 (m, 5H), 7.70—7.95 (m, 1H); MS *m/z* 171 (M^+).

4e: Mp 105—107 °C; Found: C,84.18; H, 8.23; N, 7.71%. Calcd for $C_{13}H_{15}N$: C, 84.28; H, 8.16; N, 7.56%. IR (KBr) 3280 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.22 (t, J=7.0 Hz, 3H), 2.03 (s, 3H), 2.58 (q, J=7.0 Hz, 2H), 6.30 (d, J=2.0 Hz, 1H), 7.10—7.50 (m, 5H), 7.70—7.95 (m, 1H).

4f: Mp 102—103 °C; Found: C, 87.39; H, 6.45; N, 6.20%. Calcd for $C_{17}H_{15}N$: C, 87.51 ; H, 6.48; N, 6.00%. IR (KBr) 3400 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=2.28 (s, 3H), 6.38 (d, J=2.0 Hz, 1H), 7.11—7.48 (m, 10H), 7.55—7.93 (m, 1H); MS *m/z* 233 (M^+).

4g: Mp 129—131 °C;[14] IR (KBr) 3400 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=6.06 (m, 1H), 6.30 (m, 1H), 6.53 (m, 1H), 7.00—7.35 (m, 5H), 7.51—7.70 (1H, m).

4h: Mp 152—153 °C;[15] IR (KBr) 3400 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=2.07 (s, 3H) , 6.20 (s, 1H), 6.53 (s, 1H), 7.03—7.32 (m, 5H) , 10.10 (m, 1H).

4i: Mp 107—108.5 °C;[16] IR (KBr) 3460 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=6.35 (s, 2H), 7.12—7.45 (m, 10H), 10.20 (m, 1H).

4j: Mp 107—108.5 °C; Found: C, 68.51; H, 7.88; N, 7.35%. Calcd for $C_{11}H_{15}NO_2$: C, 68.37; H, 7.82; N, 7.25%. IR (KBr) 3260 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.31 (t, J=7.0 Hz, 3H) , 1.56—1.87 (m, 4H), 2.33—2.68 (m, 4H), 4.23 (q, J=7.0 Hz, 2H), 6.56 (d, J=2.0 Hz, 1H), 8.50—9.25 (m, 1H); MS *m/z* 193 (M^+).

4k: Mp 39—40 °C;[17] IR (KBr) 3270 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.23 (t, J=7.0 Hz, 3H), 4.18 (q, J=7.0 Hz, 2H), 5.5—6.15 (m, 1H), 6.59—6.85 (m, 2H), 10.10—10.75 (m, 1H).

4l: Mp 33—35 °C; Found: C, 62.58; H, 7.14; N, 9.29%. Calcd for $C_8H_{11}NO_2$: C, 62.72; H, 7.24; N, 9.14%. IR (KBr) 3270 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.28 (t, J=7.0 Hz, 3H), 2.14 (s, 3H), 4.22 (q, J=7.0 Hz, 2H), 6.50—6.65 (m, 2H), 9.50—10.2 (m, 1H).

4m: Mp 125—126 °C; Found: C, 72.35; H, 6.01; N, 6.33%. Calcd for $C_{13}H_{13}NO_2$: C, 72.53; H, 6.09; N, 6.51%. IR (KBr) 3280 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.33 (t, J=7.0 Hz, 3H), 4.20 (q, J=7.0 Hz, 2H), 6.20—6.50 (m, 1H), 6.65—6.80 (m, 1H), 7.00—7.40 (m, 5H), 8.60—9.20 (m, 1H).

4n: Mp 140—141 °C; Found: C, 85.33; H, 8.48; N, 6.12%. Calcd for $C_{16}H_{19}N$: C, 85.28; H, 8.50; N, 6.22%. ^{1}H NMR ($CDCl_3$) δ=1.30—2.00 (m, 8H), 2.50—2.92 (m, 4H), 6.35 (d, J=2.0 Hz, 1H), 7.19—7.60 (m, 5H), 7.55—7.93 (m, 1H).

4o: Mp 64—66 °C; Found: C, 85.41; H, 9.88; N, 4.49%. Calcd for $C_{20}H_{27}N$: C, 85.35; H, 9.67; N, 4.98%. ^{1}H NMR ($CDCl_3$) δ=1.10—1.95 (m, 16H), 2.25—2.78 (m, 4H), 6.22 (d, J=2.0 Hz, 1H), 7.00—7.45 (m, 5H), 7.55—7.93 (m, 1H).

4p: Mp 42—45 °C; Found: C, 66.35; H, 8.48; N, 7.58%. Calcd for $C_{10}H_{15}NO_2$: C, 66.27; H, 8.34; N, 7.73%. ^{1}H NMR ($CDCl_3$) δ=1.20 (t, J=7.0 Hz, 3H), 1.30 (t, J=7.0 Hz, 3H), 1.98 (s, 3H), 2.55 (q, J=7.0 Hz, 2H), 4.22 (q, J=7.0 Hz, 2H), 6.57 (d, J=2.0 Hz, 1H), 8.80—9.20 (m, 1H).

4q: Mp 141—142 °C; Found: C, 85.21; H, 8.21; N, 6.77%. Calcd for $C_{15}H_{17}N$: C, 85.26; H, 8.11; N, 6.63%. ^{1}H NMR ($CDCl_3$) δ=1.45—1.95 (m, 4H), 2.29 (s, 3H), 2.33—2.75 (m, 4H), 6.15 (d, J=2.0 Hz, 1H), 6.90—7.35 (m, 4H), 7.50—8.10 (m, 1H).

4r: Mp 175—177 °C; Found: C, 60.88; H, 5.19; N, 5.01%. Calcd for $C_{14}H_{14}BrN$: C, 60.88; H, 5.11; N, 5.07%. ^{1}H NMR ($CDCl_3$) δ=1.55—1.93 (m, 4H), 2.37—2.80 (m, 4H), 6.19 (d, J=2.0 Hz, 1H), 7.03—7.55 (m, 4H), 7.58—8.02 (m, 1H).

Synthesis of Pyrrole Derivatives from α-Brommooximes and Alkenes in a Single Flask. A Typical Procedure. A mixture of α-bromoacetophenone oxime (1.5 mmol) and 1-morpholinocyclohexene (3.0 mmol) in toluene (15 cm^3) was stirred at room temperature for 3 h. After adding $Fe_3(CO)_{12}$ (2.25 mmol), the reaction mixture was heated at 100 °C for 3 h. Work-up of the reaction mixture in a similar manner as above gave 2-phenyl-4,5,6,7-tetrahydroindole **4a** in a 72% yield.

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