Synthesis and [3+2] Cycloaddition Reaction of 3-[(Trimethylsilylmethylamino)(methylthio)-methylene]heterocyclic Compounds

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3-[(Trimethylsilylmethylamino)(methylthio)]methylene-2-coumaranone (**4a**) and 1-methyloxindole (**4b**), readily prepared by reactions of the corresponding bis(methylthio)methylene heterocyclic compounds (**2a, b**), with (trimethylsilylmethyl)amine (**3**), were found to be synthetic equivalents of heterocyclic alkylidene-azomethine ylides. Reactions of **4a**, **b** with reactive heterodipolarophiles such as aldehydes and ketones and reactive alkenes in the presence of cesium fluoride gave the 1,3-dipolar cycloadducts, 3-(2-oxazolidinylidene)-oxindole and -coumaran-2-one derivatives (**8a-j, 9a-h**), as well as pyrrolylidenecoumaran-2-one and oxindole derivatives (**12-15, 17, 18**), *via* the 1,3-elimination of (methylthio)trimethylsilane.

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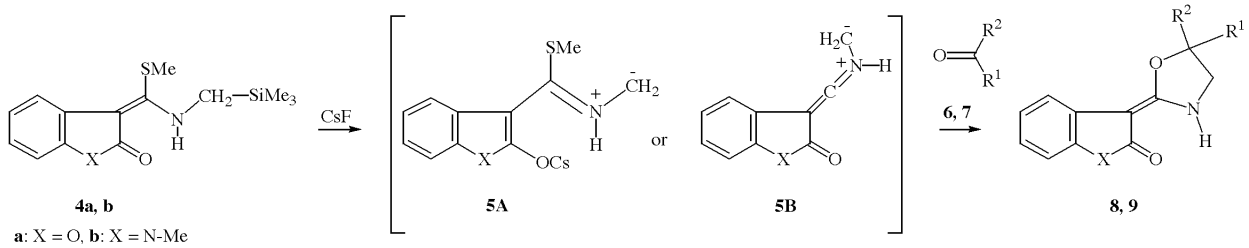
We previously reported the generation of alkylideneazomethine ylides by 1,3-elimination reaction of *N*-(trimethylsilyl)methyl-substituted ketene *N*,*S*-acetals, promoted by fluoride ion and [3+2] cycloaddition [1] of the ylide to various dipolarophiles to provide *N*-containing α-alkylidene heterocycles[2]. These ketene *N*,*S*-acetals, previously precursors of azomethine ylides are obtained by reactions of (trimethylsilylmethyl)amine with the corresponding ketene dithioacetals [3]. This paper reports the preparation of 3-(trimethylsilylmethylamino)(methylthio)methylene-2-coumaranone (**4a**) and -1-methyloxindole (**4b**) as synthetic equivalents of heterocyclic alkylidene azomethine ylides and their reaction with hetero dipolarophiles.

Bis(methylthio)methylene heterocyclic compounds (**2a, b**)[4], readily available from reaction of 2-coumaranone and oxindole, respectively, with carbon disulfide in the presence of sodium hydroxide followed by methylation with methyl iodide or dimethyl sulfate, were treated with (trimethylsilylmethyl)amine (**3**) in methanol under reflux for 30 minutes to afford the corresponding *N*,*S*-acetal derivatives, **4a**, **b** in high yields. The structures of **4a** and **b** were revealed to have the *E*-geometry based on their ir and ^{1}H-nmr spectra (See Experimental Section).

It was previously shown that the synthesis of 2-alkylidene-1,3-oxazolidines from the *N*-(trimethylsilyl)methyl-alkylideneazomethine ylide precursors and carbonyl compounds could be effectively conducted by a stoichiometric amount of cesium fluoride [2,5]. At the start of this study, the reaction of **4a** with 2,6-dichlorobenzaldehyde (**6d**) was attempted in the presence of cesium fluoride in acetonitrile at room temperature for 45 hours as a model reaction with 3 equivalents of aldehyde, the reaction proceeded smoothly to afford the corresponding 2-coumaranone (**8d**) in 60% yield on entry 4. When 2.0 equivalents of aldehyde per one equivalent of **4a** were used and the reaction time was increased to 70 hours the yield of this reaction was improved to 73% (entry 7). Compound **4a** reacted smoothly with other

Scheme 1

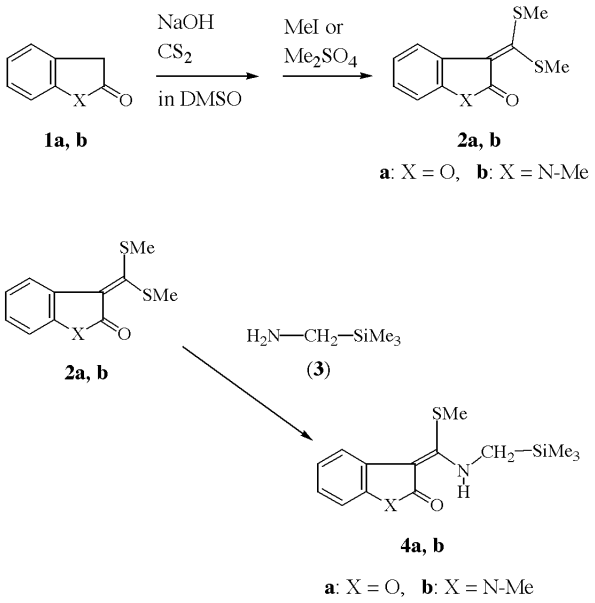


4a, b
a: X = O, **b**: X = N-Me

5A **5B**

8, 9

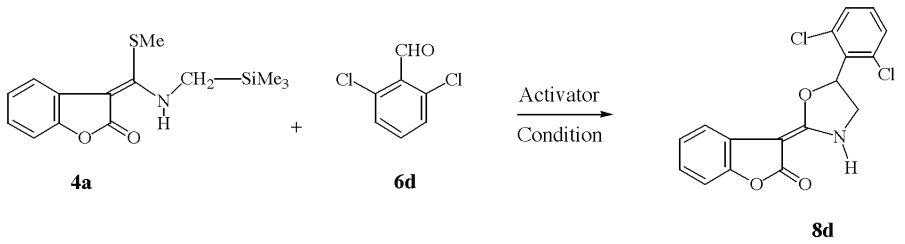
Scheme 2



aldehydes (**6**) in the presence of cesium fluoride to give the corresponding 2-oxazolidinylidene substituted [3+2]cycloaddition products (**8a-i**) in 17-73% yields (Table 2). The reaction of **4** with ketone (**7a**) was conducted under the same conditions to give the corresponding 5,5'-disubstituted 2-oxazolidinylidene derivatives (**8j**) in 11% yield (entry 10). Substituted aromatic aldehydes including those bearing electron-donating (entry 16) and electron-withdrawing groups (entry 6), α, β-unsaturated aldehyde (entry 9) and aromatic ketone (entry 19) also reacted with **4** to give the corresponding oxazolidinylidenes (**8**) in modest yields. Tris(dimethylamino)sulfur(trimethylsilyl)difluoride (TASF) and tetrabutylammonium fluoride (TBAF) could also serve as a sources of fluoride ions in this reaction (Table 1 and 2) [5]. Acids such as trimethylsilyl trifluoromethanesulfonate, iodotrimethylsilane, and trifluoroacetic acid did not give oxazolidinylidenes **8** even in modest yields. Compound **4b** also reacted smoothly with various substituted aldehydes (**6**) and ketone (**7b**) to give the corresponding 2-oxazolidinylidene-1-methyloxindole (**9a-h**) in yields as shown in Table 2.

In order to ascertain the stereospecificity of the reaction, we studied the cycloaddition of **4a**, **b** with *cis* and *trans*-disubstituted dipolarphiles. Generally, the azomethine

Table 1
1,3-Dipolar Cycloaddition Reaction of 3-(Trimethylsilylmethylamino)(methylthio)-2-coumaranone (4) with 2,6-Dichlorobenzaldehyde (**6d**)

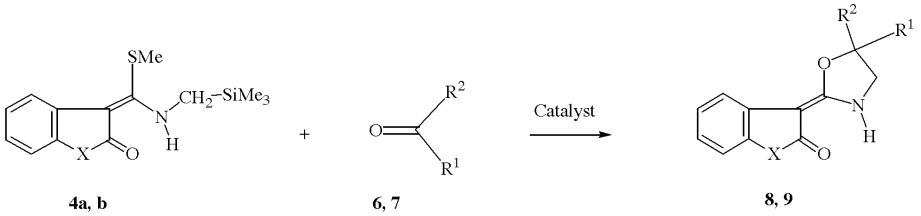


Entry	N,S-Acetal	Aldehyde (mmol)	Activator	Conditions	Yield(%) [a]
1	0.5	1.0	TASF (1.0 equiv.)	THF, rt, 24 hr	72
2	0.5	1.0	TBAF (1.0 equiv.)	THF, rt, 24 hr	60
3	0.5	1.0	TBAF (0.1 equiv.)	THF, rt, 24 hr	69
4	0.5	1.5	CsF (1.2 equiv.)	CH_3CN, rt, 45 hr	60
5	0.5	1.0	CsF (1.2 equiv.)	CH_3CN, rt, 10 hr	67
6	0.5	1.0	CsF (1.2 equiv.)	CH_3CN, rt, 45 hr	69
7	0.5	1.0	CsF (1.2 equiv.)	CH_3CN, rt, 70 hr	73

[a] Isolated yield TASF = Tris(dimethylamino)sulfur (trimethylsilyl)difluoride $[(CH_3)_2N]_3S[(CH_3)_3SiF_2]$: Tetrabutylammonium Fluoride $[CH_3(CH_2)_3]_4NF$.

Table 2

1,3-Dipolar Cycloaddition Reaction of N,S-acetal Derivatives with Carbonyl Compounds [a]



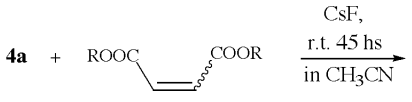
4a, b **6, 7** **8, 9**

Entry	N,S-Acetal X	Carbonyl compound R^1	Carbonyl compound R^2	Catalyst	product	Yield (%)	mp (°C)
1	O	H	C_6H_5 (**6a**)	CsF	**8a** [12]	25	177
2	O	H	4-MeC_6H_4 (**6b**)	CsF	**b**	41	173
3	O	H	4-$C_6H_5C_6H_4$ (**6c**)	CsF	**c**	47	226
4	O	H	2,6-$Cl_2C_6H_3$ (**6d**)	CsF	**d**	73	277
5	O	H	4-ClC_6H_4 (**6e**)	CsF	**e**	60	214
6	O	H	4-$NO_2C_6H_4$ (**6g**)	CsF	**f**	17	202
7	O	H	1-naphthyl (**6h**)	CsF	**g**	46	250
8	O	H	$CH_3(CH_2)_3$ (**6i**)	CsF	**h**	22	119
9	O	H	(E) C_6H_5CH=CH (**6j**)	CsF	**i**	24	173
10	O	C_6H_5	C_6H_5 (**7a**)	CsF	**j**	11	249
11	NMe	H	4-Me-C_6H_5 (**6b**)	CsF	**9a**	75	174
12	NMe	H	4-$C_6H_5C_6H_4$ (**6c**)	CsF	**b**	65	284
13	NMe	H	2,6-$Cl_2C_6H_3$ (**6d**)	CsF	**c**	69	298
14	NMe	H	2,6-$Cl_2C_6H_3$ (**6d**)	TBAF	**c**	45	298
15	NMe	H	4-ClC_6H_4 (**6e**)	CsF	**d**	59	207
16	NMe	H	4-MeOC_6H_4 (**6f**)	CsF	**e**	50	213
17	NMe	H	1-naphthyl (**6g**)	CsF	**f**	53	237
18	NMe	H	$CH_3(CH_2)_3$ (**6h**)	CsF	**g**	16	163
19	NMe	C_6H_5	C_6H_5-CO (**7b**)	CsF	**h**	33	254

[a] All reactions were carried out in a system of **4** (0.5 mmol), carbonyl compound (**6** or **7**) (1.0 mmol), and CsF (0.6 mmol) in MeCN.
[b] Yield after isolation by silica gel column chromatography.

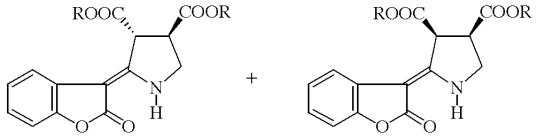
ylides examined so far in the literature have been shown to undergo stereospecific cycloaddition. Interestingly, treatment of **4a** with either dimethyl fumarate (**10a**) or dimethyl maleate (**11a**) at room temperature for 20 hours in the presence of cesium fluoride afforded a 5:3 or 7:5 mixture of *trans* and *cis* cycloadducts, 3-(3,4-dimethoxycarbonylpyrrolidinylidene)-2-indolinone) (**12a**, **13a**), indicating little stereocontrol. The yields of these products were 28 and 37%, respectively. Similarly, reaction of **4a** with diethyl fumarate (**10b**) and diethyl maleate (**11b**) gave the corresponding 1,3-dipolar cycloadducts (**12b**, **13b**) in 55 and 51% yields, respectively (Scheme 3). The ratios of the *trans* to *cis* products were 3:2 and 1:1.

Scheme 3



10a, b, 11a, b

10a: dimethyl fumarate
b: diethyl fumarate
11a: dimethyl maleate
b: diethyl maleate



12a, 12b **13a, 13b**

Yield 28% (from dimethyl fumarate **10a**)*
12a:**13a** = 5:3

Yield 37% (from dimethyl maleate **11a**)*
12a:**13a** = 7:5

Yield 55% (from diethyl fumarate **10b**)*
12b:**13b** = 3:2

Yield 51% (from dimethyl maleate **11b**)*
12b:**13b** = 1:1

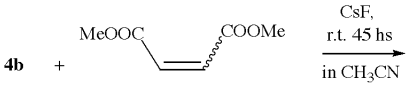
(* Determined by ^{1}H-NMR)

Indole derivative (**4b**) also smoothly reacted with **10a** and **11a** under the same reaction conditions to give a mixture of *cis* and *trans* cycloaddition products **14** and **15** in 59 and 54% yields, respectively. The ratio of these products are shown in Scheme 4. Although the mechanism of these cycloadditions has not been clarified, the results may be rationalized by assuming faster *Z-E* isomerization of the maleate to the fumarate than cycloaddition under the present conditions [6].

The cycloaddition behavior of an unsymmetrically substituted dipolarophile was studied to determine the regioselectivity of the reaction. When methyl or ethyl acrylate (**16a** or **b**) was used as a dipolarophile, a mixture of the cycloadduct **17a, 18a** or **17b, 18b** was obtained in a ratio of about 1:1. The structures of **17** and **18** were established by ^{1}H-nmr, ir, and ms analyses.

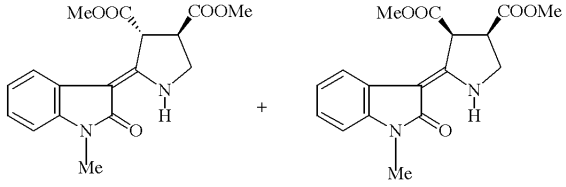
Initially, exposure of compound **4a, b** to cesium fluoride promotes a metal-assisted ionization of the carbonyl group of coumarin or oxindole and a concomitant desilylation to form the stabilized 1,3-dipole (**5**). The 1,3-dipolar cycloaddition of **5** with

Scheme 4



10a, 11a

10a: dimethyl fumarate
11a: dimethyl maleate



14 **15**

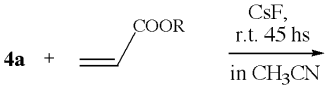
Yield 59% (from dimethyl fumarate **10a**)*
14:**15** = 6:1

Yield 37% (from dimethyl maleate **11a**)*
14:**15** = 5:1

(* Determined by ^{1}H-NMR)

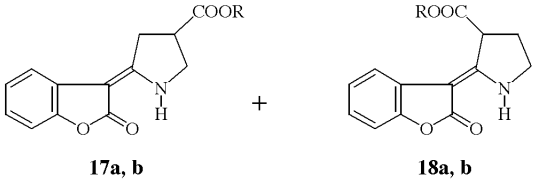
dipolarophiles occurs, followed by elimination of the methylthio group and hydrolysis of cesium salts (**5A**) to yield the corresponding final products. The reaction pathway as shown in Scheme 6, involving the

Scheme 5



16a, b

16a: methyl acrylate
b: diethyl maleate



17a, b **18a, b**

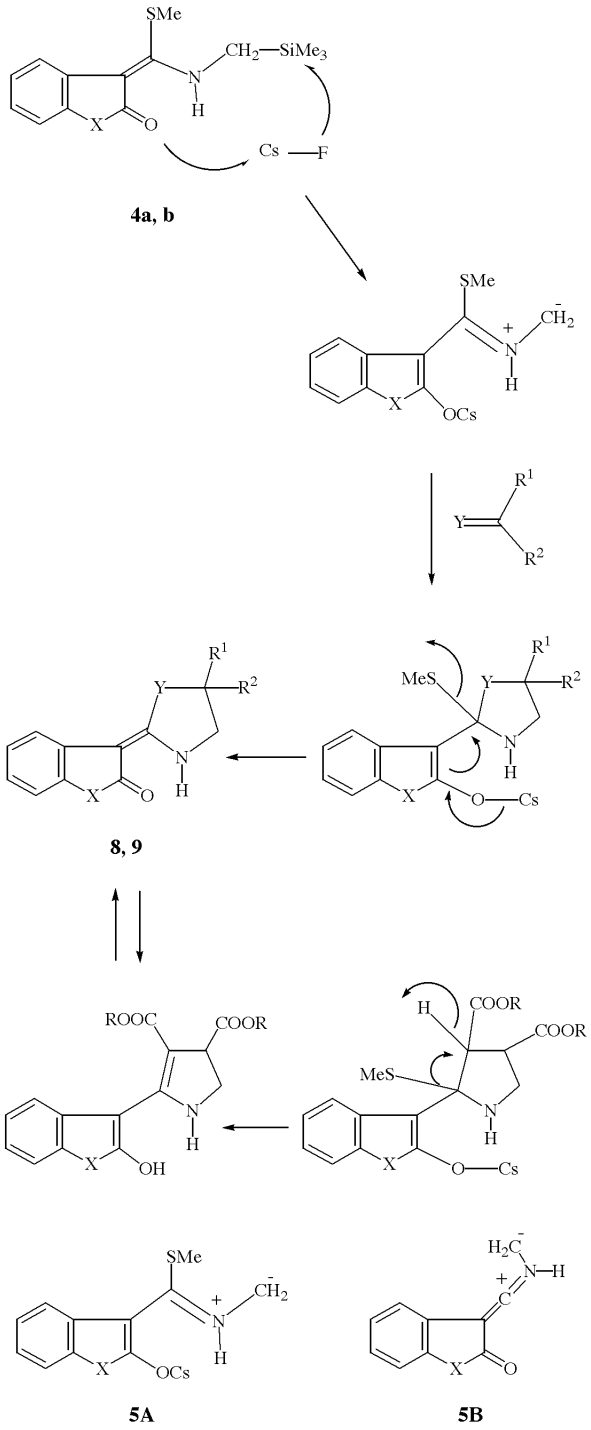
Yield 38%(**17a** +**18a**)(from methyl acrylate **16a**)
17a:**18a** = 1:1

Yield 5%(**17b** + **18b**) (from ethyl maleate**16b**)*
17b:**18b** = 1:1

(* Determined by ^{1}H-NMR)

Scheme 6

Plausible Reaction Pathway



intermediates (**5A** or **5B**), is proposed. The tautomerism shown in Scheme 6 is one of the main causes for the lack of stereospecificity.

It is evident from the present results that *N*-(silylmethyl)-substituted *N,S*-acetals **4a, b** are stable (*i.e.*, storable) and easy-to-handle synthetic equivalents of heterocyclic alkylidene azomethine ylides **5**.

EXPERIMENTAL

All melting points were determined in a capillary tube and are uncorrected. Infrared (IR) spectra were recorded in potassium bromide pellets on JASCO 810 spectrometer and SHIMADZU IR-460 and ultraviolet (UV) absorption spectra were determined in 95% ethanol on a Hitachi 323 spectrometer. Nuclear magnetic resonance (NMR) spectra were obtained on JEOL-PS-100 (100 MHz), JEOL-FX-90Q (90 MHz), JEOL-PMX-60SI (60 MHz) , and JEOL-GX-400 (400MHz) spectrometers with tetramethylsilane as an internal standard. Mass (MS) spectra were recorded on JEOL-01SG and JEOL DX-303 mass spectrometers. Elemental analyses were performed at the Microanalytical Laboratory of the Center for Instrumental Analysis in Nagasaki University.

3-Bis(methylthio)methylene-2-coumaranone (**2a**).

A 300 ml three-neck round-bottom flask was fitted with a mechanical stirrer and two dropping funnels. The flask was charged with a solution of 13.4 g (0.1 mole) of 2-coumaranone in 50 ml of dimethyl sulfoxide and this solution was maintained at 10-15°. One half of a 20% sodium hydroxide solution (sodium hydroxide, 8.0 g, 0.2 mole) was added to the above solution with stirring and cooling at 10-15°. The mixture was stirred for 10 minutes. Then 3.81 g (0.05 mole) of carbon disulfide was added slowly to the mixture with stirring at 10-15° over a period of 20 minutes. Stirring was continued for an additional 20-minutes at the same temperature. The second half of the solution of sodium hydroxide was added to the reaction mixture and stirring was continued for 10 minutes. Then 3.81 g (0.05 mole) of carbon disulfide was again slowly added to the above reaction mixture and stirring was continued for 1 hour at the same temperature. To the reaction product in solution of dimethyl sulfoxide, 56.4 g (0.4 mole) of iodomethane was slowly added dropwise while the reaction mixture was stirred vigorously at 10-20°. After stirring for 1 hour at room temperature, the reaction mixture was poured into 500 ml of ice-water and then allowed to stand for 1 hour. The resulting precipitate was collected by filtration and washed several times with water. After air drying, the product was recrystallized from methanol to give 19.8 g (83.2 mmoles, 83%) of yellow needles, mp 59-60°; ir (potassium bromide): ν max 1742 (C =O) cm^{-1}; ^1H nmr (deuteriochloroform): δ 2.59 (s, 3H, SMe), 2.65 (s, 3H, SMe), 7.10 (dd, 1H, J=1.0, 7.9 Hz, aromatic-H), 7.16 (m, 1H, aromatic-H), 7.27 (m, 1H, aromatic-H), 8.04 (dd, 1H, J=1.0, 7.7 Hz, aromatic-H); ms: m/z 239(M^++1, 11), 238 (M^+, 69), 228(22), 192(14), 191(100), 120(20), 91(83).

Anal. Calcd. for $C_{11}H_{10}O_2S_2$: C, 55.44; H, 4.23; S, 26.90. Found: C, 55.43; H, 4.24; S, 26.78.

3-Bis(methylthio)methylene-1-methyloxindole (**2b**).

A 300 ml three-neck round-bottom flask was fitted with a mechanical stirrer and two dropping funnels. The flask was charged with a solution of 13.3 g (0.1 mole) of oxindole in 50 ml of dimethyl sulfoxide and this solution was maintained at 10-15°.

One third of a 20% sodium hydroxide solution (sodium hydroxide, 12 g, 0.3 mole) was added to the above solution with stirring and cooling at 10-15°. The mixture was stirred for 10 minutes. Then 3.81 g (0.05 mole) of carbon disulfide was added slowly to the mixture with stirring at 10-15° over a period of 20 minutes. Stirring was continued for an additional - 20 minutes at the same temperature. Another one third of the solution of sodium hydroxide was added to the reaction mixture and stirring was continued for 10 minutes. Then 3.81 g (0.05 mole) of carbon disulfide was again slowly added to the above reaction mixture and stirring was continued for 1 hour at the same temperature. To the reaction product in solution of dimethyl sulfoxide, 25.2 g (0.2 mole) of dimethyl sulfate was slowly added dropwise while the reaction mixture was stirred vigorously at 10-20°. The mixture was stirred for 1 hour. The remaining one third of the solution of sodium hydroxide was added to the reaction mixture and stirring was continued for 10 minutes. Then 12.6 g (0.1 mole) of dimethyl sulfate was again slowly added to the above reaction mixture. After stirring for 2 hours at room temperature, the reaction mixture was poured into 500 ml of ice-water and then allowed to stand for 1 hour. The resulting precipitate was collected by filtration and washed several times with water. After air drying, the product was recrystallized from methanol to give 17.1 g (68.1 mmoles, 68%) of yellow needles, mp 88-89°, lit [4], mp 85-88°; ^{1}H nmr (deuteriochloroform): δ 2.50 (s, 3H, SMe), 2.63 (s, 3H, SMe), 3.28 (s, 3H, NMe), 6.83 (d, 1H, J=7.7 Hz, aromatic-H), 7.06 (m, 1H, aromatic-H), 7.24 (m, 1H, aromatic-H), 8.17 (d, 1H, J=7.8 Hz, aromatic-H); ms: m/z 251 (M^+, 100), 234 (20), 204(25), 203(27), 190(35), 189(41).

3-(Trimethylsilylmethylthio)(methylthio)methylene-2-coumaranone (**4a**).

To a solution of 1.01 g (4.0 mmole) of **2a** in 16 ml of methanol was added 0.44 g (4.20 mmole) of trimethylsilylmethylamine (**3**). The reaction was exothermic with evolution of methylmercaptan. This reaction mixture was refluxed for 1 hour. After evaporation of the solvent, the residue was cromatographed on a column of silica gel using a 9:1 mixture of hexane and ethyl acetate as eluent to give **4a** (1.15 g, 3.96 mmole) as yellow crystals in 99% yield. An analytical sample was recrystallized from ethanol to give yellow needles; mp 77-78°; ir (potassium bromide): ν max 3200 (NH), 2850, 1690 (C =O), 1595 cm^{-1}; uv (ethanol): λ max nm (log ε) 435(3.87), 250(3.96); ^{1}H nmr (deuteriochloroform): δ 0.17 (s, 9H, $SiMe_3$), 2.46 (s, 3H, SMe), 3.25 (d, J =5.9 Hz, 2H, N-CH_2-), 7.05-7.24 (m, 3H, aromatic-H), 7.71-7.82 (m, 1H, aromatic-H), 9.49 (bs, 1H, NH); ms: m/z 293 (M^+, 100), 246 (49), 73 (73).

Anal. Calcd. for $C_{14}H_{19}O_2NSSi$ (293.447): C, 57.32; H, 6.53; N, 4.78. Found: C, 57.08; H, 6.50; N, 4.67.

3-(Trimethylsilylmethylthio)(methylthio)methylene-2-oxindole (**4b**).

This compound (1.21 g, 3.92 mmole) was synthesized in 98% yield from **1b** (1.01g, 4.0 mmole) and **3** (0.44 g, 4.2 mmole) in a manner similar to that described for the preparation of **4a**; ir (potassium bromide): ν max 3190 (NH), 1620 (C =O) cm^{-1}; uv (ethanol): λ max nm (log ε) 372(4.27), 285(4.25), 280(4.24), 213(4.46); ^{1}H nmr (deuteriochloroform): δ 0.18 (s, 9H, $SiMe_3$), 2.46 (s, 3H, SMe), 3.22 (d, J =5.9 Hz, 2H, N-CH_2-), 3.35 (s, 3H, NMe), 6.71-7.12 (m, 3H, aromatic-H), 7.25-8.04 (m, 1H, aromatic-H), 10.42 (bs, 1H, NH); ms: m/z 306 (M^+, 100), 258 (87), 59 (21); hrms Calcd. for $C_{15}H_{22}ON_2SSi$: 306.1222. Found: 306.1220..

Anal. Calcd. for $C_{15}H_{22}ON_2SSi$: C, 58.78; H,7.24; N, 9.14. Found: C, 58.74; H, 7.21; N, 9.11.

1,3-Dipolar Cycloaddition Reaction of 3 or 4 with Hetero-dipolarophile.

General Method A.

A 50-ml, two necked flask was fitted with a magnetic stirring bar and gas inlet tube. The flask was charged with 0.091 g (0.6 mmole) of CsF and was heated at 100-140 °C with a hot plate stirrer for 1 hour. The apparatus was cooled under purging with nitrogen. A solution of an aldehyde (1.5 mmoles) in 1 ml of dry acetonitrile was then added. A solution of 0.5 mmole of **4a** or **4 b**, in 2 ml of acetonitrile was introduced *via* a syringe with stirring. When all reagents had been added, the reaction mixture was stirred for 45 hours at room temperature. The solvent was removed under reduced pressure on a rotary evaporator to yield a residue. The residue was added to the top of a column containing 20 g of 60-200 mesh silica gel the column was eluted with a mixture of hexane and ethyl acetate. The solvent was removed from those fractions containing the product under reduced pressure on a rotary evaporator to afford the corresponding product as shown in Table 2. An analytical sample of each product was recrystallized from an appropriate solvent.

Method B.

A 50 ml, two-necked flask was fitted with a magnetic stirring bar and gas inlet tube. To a solution of 0.50 mmole of **4a** or **b** and 1.0 mmole of the corresponding aldehyde in 5 ml of absolute THF was added 1.0 mmole of TBAF. The mixture was stirred for 22 hours at room temperature. After removal of the solvent by evaporation, the residue was added to the top of a column combining 20 g of 60-200 mesh silica gel and the column was eluted with a mixture of hexane and ethyl acetate. The solvent was removed from those fractions containing the product under reduced pressure on a rotary evaporator to afford the corresponding product. The results of a typical experiment in the case of synthesis of **8d** are shown in Table 1.

3-(4-Phenyl-1,3-oxazolidin-2-ylidene)-2-coumaranone (**8a**).

An analytical sample was recrystallized from ethanol to give yellow needles, mp 176-177°; ir (potassium bromide): ν max 3260 (NH), 1720 (C =O), 1640 cm^{-1}; uv (ethanol): λ max nm (log ε) 560(3.82), 370(3.87), 225(4.13); ^{1}H nmr (deuteriochloroform): δ 3.74 (dd, J=10.4, 7.7 Hz, 1H, N-CH_α-), 4.28 (dd, J=10.4, 8.8 Hz, 1H, NH-CH_β-), 3.35 (s, 3H, NMe), 6.13 (dd, J=8.8, 7.7 Hz, 1H, O-CH-), 7.42-7.91 (m, 9H, aromatic-H), 9.11 (bs, 1H, NH); ms: m/z 279 (M^+, 3), 119(100), 160(47).

Anal. Calcd. for $C_{17}H_{13}NO_3$: C, 73.11; H, 4.69; N, 5.02. Found: C, 72.98; H, 4.79; N, 5.02.

3-[4-(4-Methyl)phenyl-1,3-oxazolidin-2-ylidene]-2-coumaranone (**8b**).

An analytical sample was recrystallized from ethanol to give colorless needles, mp 172-173°, ir (potassium bromide) ν max 3350(NH), 1715(CO), 1635 cm^{-1}: uv (ethanol): λ max nm(log ε) 309(4.44), 243(3.23); ^{1}H nmr (deuteriochloroform): δ 2.39 (3H, s, Me), 3.82 (dd, J=10.3, 7.7 Hz, 1H, N-CH_α-), 4.24 (dd, J=10.3,

8.8 Hz, NH-CH_β-), 5.91 (dd, J=8.8, 7.7 Hz, 1H, O-CH-), 6.95-7.38 (8H, m, H), 8.08 (1H, bs, NH); ms: m/z 294(M^++1, 11), 293(M^+, 55), 160(24), 133(100).

Anal. Cacd for $C_{18}H_{15}NO_3$: C, 73.70; H, 5.16; N, 4.78. Found: C, 73.61; H, 5.22; N, 4.77.

3-[4-(4-Phenyl)phenyl-1,3-oxazolidin-2-ylidene]-2-coumaranone (**8c**).

An analytical sample was recrystallized from ethanol to give colorless needles, mp 224-226°; ir (potassium bromide): ν max 3260 (NH), 1720 (C =O), 1640 cm^{-1}; uv (ethanol): λ max nm (log ε) 560(3.82), 370(3.87), 225(4.13); ^{1}H nmr (deuteriochloroform): δ 3.80 (dd, J=10.3, 7.7 Hz, 1H, N-CH_α-), 4.31 (dd, J=10.3, 8.8 Hz, 1H, NH-CH_β-), 6.19 (dd, J=8.8, 7.7 Hz, 1H, O-CH-), 6.89-7.80 (m, 9H, aromatic-H), 9.08 (bs, 1H, NH); ms: m/z 355 (M^+, 15), 195(100), 40(100).

Anal. Calcd. for $C_{23}H_{17}NO_3$: C, 77.73; H, 4.82; N, 3.94. Found: C, 77.88; H, 5.00; N, 3.84.

3-[4-(2,6-Dichloro)phenyl]-1,3-oxazolidin-2-ylidene]-2-coumaranone (**8d**).

An analytical sample was recrystallized from ethanol to give colorless needles, mp 274-277°; ir (potassium bromide): ν max 3340 (NH), 1720 (C =O), 1645 cm^{-1}; uv (ethanol): λ max nm (log ε) 355(2.15), 346(1.85), 310(4.38), 244(4.18), 203(4.81); ^{1}H nmr (deuteriochloroform): δ 3.88 (dd, J=10.3, 7.7 Hz, 1H, N-CH_α-), 4.31 (dd, J=10.3, 8.8 Hz, 1H, NH-CH_β-), 6.65-7.68 (m, 8H, O-CH-, aromatic-H), 9.31 (bs, 1H, NH); ms: m/z 347 (M^+, 10), 160(18), 40(100).

Anal. Calcd. for $C_{17}H_{11}Cl_2NO_3$: C, 58.64; H, 3.19; N, 4.02. Found: C, 58.72; H, 3.43; N, 4.07.

3-[4-(4-Chlorophenyl)-1,3-oxazolidin-2-ylidene]-2-coumaranone (**8e**).

An analytical sample was recrystallized from ethanol to give colorless needles, mp 212-214°; ir (potassium bromide): ν max 3375 (NH), 1720 (C =O), 1650 cm^{-1}; uv (ethanol): λ max nm (log ε) 310(4.39), 244(4.19); ^{1}H nmr (deuteriochloroform): δ 3.72 (dd, J=10.3, 7.7 Hz, 1H, N-CH_α-), 4.28 (dd, J=10.3, 8.8 Hz, 1H, NH-CH_β-), 6.14 (dd, J=8.8, 7.7 Hz, 1H, O-CH-), 6.96-7.50 (m, 9H, aromatic-H), 9.05 (bs, 1H, NH); ms: m/z 313 (M^+, 45), 160(61), 153(100).

Anal. Calcd. for $C_{17}H_{12}NClO_3$: C, 65.08; H, 3.86; N, 4.46. Found: C, 65.07; H, 4.05; N, 4.48.

3-[4-(4-Nitrophenyl)-1,3-oxazolidin-2-ylidene]-2-coumaranone (**8f**).

An analytical sample was recrystallized from ethanol to give tan needles, mp 192-202°; ir (potassium bromide): ν max 3340 (NH), 1720 (C =O), 1640, 1520 cm^{-1}; uv (ethanol): λ max nm (log ε) 309(4.38), 292(4.28); ^{1}H nmr (deuteriochloroform): δ 3.80 (dd, J=10.3, 7.3 Hz, 1H, N-CH_α-), 4.31 (dd, J=10.3, 9.0 Hz, 1H, NH-CH_β-), 6.31 (dd, J=7.3, 9.0 Hz, 1H, O-CH-), 6.91-8.35 (m, 8H, aromatic-H), 9.16 (bs, 1H, NH); ms: m/z 355 (M^+, 15), 195(90), 40(100).

Anal. Calcd. for $C_{17}H_{12}N_2O_5$: C, 62.95; H, 3.73; N, 8.64. Found: C, 62.43; H, 3.82; N, 8.55.

3-(4-Naphth-1-yl-1,3-oxazolidin-2-ylidene)-2-coumaranone (**8g**).

An analytical sample was recrystallized from ethanol to give yellow needles, mp 248-250°; ir (potassium bromide): ν max 3290 (NH), 1710 (C =O), 1625 cm^{-1}; uv (ethanol, insufficient solubility): λ max nm 309, 292, 244, 222; ^{1}H nmr (deuteriochloroform): δ 3.78 (dd, J=9.9, 7.3 Hz, 1H, N-CH_α-), 4.54 (dd, J=9.9, 9.5 Hz, 1H, NH-CH_β-), 6.80-8.11 (m, 9H, O-CH-, aromatic-H), 9.25 (bs, 1H, NH); ms: m/z 329 (M^+, 16), 169(30), 40(100).

Anal. Calcd. for $C_{21}H_{15}NO_3$: C, 76.58; H, 4.59; N, 4.25. Found: C, 76.26; H, 4.76; N, 4.21.

3-(4-Butyl-1,3-oxazolidin-2-ylidene)-2-coumaranone (**8h**).

An analytical sample was recrystallized from ethanol to give colorless needles, mp 118-119°; ir (potassium bromide): ν max 3330 (NH), 1710 (C =O), 1620 cm^{-1}; uv (ethanol): λ max nm (log ε) 307(4.36), 243(4.17), 207(4.39); ^{1}H nmr (deuteriochloroform): δ 0.88-2.11 (m, 7H, butyl-H), 3.50 (dd, J=8.8, 7.9 Hz, 1H, N-CH_α-), 4.02 (dd, J=8.8, 8.4 Hz, 1H, NH-CH_β-), 5.02 (dd, J=8.4, 7.9 Hz, 1H, O-CH-), 6.97-7.36 (m, 4H, aromatic-H), 7.98 (bs, 1H, NH); ms: m/z 245 (M^+, 13), 160(100), 69(13).

Anal. Calcd. for $C_{14}H_{15}NO_3$: C, 68.55; H, 6.16; N, 5.71. Found: C, 68.20; H, 6.27; N, 5.58.

3-(4-Styryl-1,3-oxazolidin-2-ylidene)-2-coumaranone (**8i**).

An analytical sample was recrystallized from ethanol to give yellow needles, mp 171-173°; ir (potassium bromide): ν max 3375 (NH), 1720 (C =O), 1640 cm^{-1}; uv (ethanol): λ max nm (log ε) 310(4.44), 246(4.50), 205(4.67); ^{1}H nmr (deuteriochloroform): δ 3.67 (dd, J=10.1, 7.9 Hz, 1H, N-CH_α-), 4.07 (dd, J=10.1, 8.5 Hz, 1H, NH-CH_β-), 5.72 (dd, J=8.5, 7.9 Hz, 1H, O-CH-), 6.53 (dd, J=15.8, 8.5 Hz, 1H, -CH=), 6.84-7.60 (m, 10H, =CH-Ph, aromatic-H), 9.07 (bs, 1H, NH); ms: m/z 305 (M^+, 39), 160(20), 145(100), 40(78).

Anal. Calcd. for $C_{19}H_{15}NO_3$: C, 74.74; H, 4.95; N, 4.59. Found: C, 74.24; H, 5.05; N, 4.54.

3-(4,4-Diphenyl-1,3-oxazolidin-2-ylidene)-2-coumaranone (**8j**).

An analytical sample was recrystallized from ethanol to give colorless needles, mp 247-249°; ir (potassium bromide): ν max 3330 (NH), 1730 (C =O), 1640 cm^{-1}; uv (ethanol): λ max nm (log ε) 311(4.37), 292(4.16), 244(4.16); ^{1}H nmr (deuteriodimethlsulfoxide): δ 4.50 (s, 2H, N-CH_2-), 46.99-7.63 (m, 14H, aromatic-H), 8.41 (bs, 1H, NH); ms: m/z 355 (M^+, 12), 195(33), 40(100).

Anal. Calcd. for $C_{22}H_{16}NO_3 \cdot 1/3H_2O$: C, 76.44; H, 4.93; N, 3.88. Found: C, 76.64; H, 4.97; N, 3.94.

1-Methyl-3-[4-(4-methylphenyl)-1,3-oxazolidin-2-ylidene]-2-oxindole (**9a**).

An analytical sample was recrystallized from ethanol to give yellow needles, mp 173-174°; ir (potassium bromide): ν max 3200 (NH), 1760 (C =O), 1600 cm^{-1}; uv (ethanol): λ max nm (log ε) 360(1.75), 304(4.42), 265(4.39), 258(4.38); ^{1}H nmr (deuteriochloroform): δ 2.37 (s, 3H, Ph-Me), 3.38 (s, 3H, NMe), 3.75 (dd, J=9.3, 7.9 Hz, 1H, N-CH_α-), 4.20 (dd, J=9.3, 8.4 Hz, 1H, NH-CH_β-), 5.85 (dd, J=8.4, 7.9 Hz, 1H, O-CH-), 6.83-7.49 (m, 8H, aromatic-H), 7.88 (bs, 1H, NH); ms: m/z 306 (M^+, 37), 173(46), 133(100).

Anal. Calcd. for $C_{19}H_{18}N_2O_2$: C, 74.48; H, 5.92; N, 9.14. Found: C, 74.46; H, 5.92; N, 9.14.

1-Methyl-3-[4-(4-phenylphenyl)-1,3-oxazolidin-2-ylidene]-2-oxindole (**9b**).

An analytical sample was recrystallized from ethanol to give colorless needles, mp 283-284°; ir (potassium bromide): ν max 3200 (NH), 1660 (C =O), 1600 cm^{-1}; uv (ethanol): λ max nm (log ε) 304(4.41), 255(4.60), 202(4.82); ^1H nmr (deuteriochloroform): δ 3.40 (s, 3H, NMe), 3.82 (dd, J=9.8, 7.7 Hz, 1H, N-CH_α-), 4.20 (dd, J=9.8, 8.8 Hz, 1H, NH-CH_β-), 5.95 (dd, J=8.8, 7.7 Hz, 1H, O-CH-), 6.85-7.70 (m, 8H, aromatic-H), 8.24 (bs, 1H, NH); ms: m/z 368 (M^+, 32), 195(100), 173(35).

Anal. Calcd. for $C_{24}H_{20}N_2O_2$: C, 78.24; H, 5.47; N, 7.61. Found: C, 78.03; H, 5.58; N, 7.53.

3-[4-(2,6-Dichlorophenyl)-1,3-oxazolidin-2-ylidene]-1-methyl-2-oxindole (**9c**).

An analytical sample was recrystallized from ethanol to give colorless needles, mp 296-298°; ir (potassium bromide): ν max 3300 (NH), 1660 (C =O), 1600 cm^{-1}; uv (ethanol): λ max nm (log ε) 304(4.41), 266(4.40); ^1H nmr (deuteriochloroform): δ 3.38 (s, 3H, NMe), 4.01 (dd, J=10.1, 9.2 Hz, 1H, N-CH_α-), 4.23 (dd, J=10.1, 8.8 Hz, 1H, NH-CH_β-), 6.66 (dd, J=9.2, 8.8 Hz, 1H, O-CH-), 6.81-7.48 (m, 8H, aromatic-H), 8.30 (bs, 1H, NH); ms: m/z 360 (M^+, 26), 187(25), 173(100).

Anal. Calcd. for $C_{18}H_{14}N_2Cl_2O_2$: C, 59.85; H, 3.91; N, 7.76. Found: C, 59.86; H, 4.01; N, 7.71.

[3-(4-Chlorophenyl)-1,3-oxazolidin-2-ylidene]-1-methyl-2-oxindole (**9d**).

An analytical sample was recrystallized from ethanol to give colorless needles, mp 206-207°; ir (potassium bromide): ν max 3300 (NH), 1680, 1670 (C =O), 1610 cm^{-1}; uv (ethanol): λ max nm (log ε) 304(4.41), 266(4.40), 220(4.56); ^1H nmr (deuteriochloroform): δ 3.39 (s, 3H, NMe), 3.74 (dd, J=9.0, 7.8 Hz, 1H, N-CH_α-), 4.25 (dd, J=9.0, 8.9 Hz, 1H, NH-CH_β-), 5.88 (dd, J=8.9, 7.8 Hz, 1H, O-CH-), 6.84-7.48 (m, 8H, aromatic-H), 8.00 (bs, 1H, NH); ms: m/z 326 (M^+, 63), 153(94), 44(100).

Anal. Calcd. for $C_{18}H_{15}N_2ClO_2$: C, 66.16; H, 4.63; N, 8.57. Found: C, 66.19; H, 4.72; N, 8.52.

1-Methyl-3-[4-(4-methoxyphenyl)-1,3-oxazolidin-2-ylidene]-2-oxindole (**9e**).

An analytical sample was recrystallized from ethanol to give colorless needles, mp 212-213°; ir (potassium bromide): ν max 3220 (NH), 1660 (C =O), 1605 cm^{-1}; uv (ethanol): λ max nm (log ε) 304(4.43), 265(4.40), 258(4.39), 223(4.52); ^1H nmr (deuteriochloroform): δ 3.38 (s, 3H, NMe), 3.66-3.86 (m, 2H, N-CH_2-), 3.82 (s, 1H, NMe), 4.19 (dd, J=9.0, 8.9 Hz, 1H, O-CH-), 6.88-7.47 (m, 8H, aromatic-H), 7.90 (bs, 1H, NH); ms: m/z 328 (M^+, 32), 149(100), 44(40).

Anal. Calcd. for $C_{19}H_{18}N_2O_3$: C, 70.79; H, 5.63; N, 8.69. Found: C, 70.44; H, 5.73; N, 8.71.

1-Methyl-3-(naphth-1-yl-1,3-oxazolidin-2-ylidene)-2-oxindole (**9f**).

An analytical sample was recrystallized from ethanol to give colorless needles, mp 235-237°; ir (potassium bromide): ν max 3260 (NH), 1670, 1670 (C =O) cm^{-1}; uv (ethanol): λ max nm (log ε) 304(4.46), 265(4.45), 223(4.56); ^1H nmr (deuteriochloroform): δ 3.43(s, 3H, NMe), 3.47 (dd, J=9.1, 7.5 Hz, 1H, N-CH_α-), 4.49 (dd, J=9.1, 9.0 Hz, 1H, NH-CH_β-), 6.63 (dd, J=8.9, 7.8 Hz, 1H, O-CH-), 6.93-7.48 (m, 8H, aromatic-H), 8.38 (bs, 1H, NH); ms: m/z 342 (M^+, 23), 169(44), 44(100).

Anal. Calcd. for $C_{22}H_{18}N_2O_2$: C, 77.17; H, 5.30; N, 8.18. Found: C, 77.16; H, 5.32; N, 8.12.

3-(*n*-Butyl-1,3-oxazolidin-2-ylidene)-1-methyl-2-oxindole (**9g**).

An analytical sample was recrystallized from ethanol to give tan needles, mp 156-163°; ir (potassium bromide): ν max 3270 (NH), 1660 (C =O), 1610 cm^{-1}; uv (ethanol): λ max nm (log ε) 303(2.23), 256(4.25), 211(4.36); ^1H nmr (deuteriochloroform): δ 0.93-2.03 (m, 7H, butyl-H), 3,07-3.53 (m, 4H, NMe, N-CH_α-), 3.90 (dd, J=9.0, 8.4 Hz, 1H, NH-CH_β-), 5.28 (dd, J=8.4, 8.2 Hz, 1H, O-CH-), 6.79-7.46 (m, 4H, aromatic-H), 8.04 (bs, 1H, NH); ms: m/z 258 (M^+, 14), 173(100), 163(34), 40(100).

Anal. Calcd. for $C_{15}H_{18}N_2O_2$: C, 69.74; H, 7.02; N, 10.84. Found: C, 69.72; H, 7.00; N, 10.76.

1-Methyl-3-(4-benzoyl-4-phenyl-1,3-oxazolidin-2-ylidene)-2-oxindole (**9h**).

An analytical sample was recrystallized from ethanol to give yellow needles, mp 252-254°; ir (potassium bromide): ν max 3290 (NH), 1670 (C =O), 1620 cm^{-1}; uv (ethanol): λ max nm (log ε) 304(4.51), 254(4.51); ^1H nmr (deuteriochloroform): δ 3.39 (s, 3H, NMe), 3.84 (d, J=9.9 Hz, 1H, N-CH_α-), 5.02 (d, J=9.9 Hz, 1H, NH-CH_β-), 6.91-8.08 (m, 14H, aromatic-H), 8.38 (bs, 1H, NH); ms: m/z 396 (M^+, 44), 222(37), 105(33), 44(100).

Anal. Calcd. For $C_{25}H_{20}N_2O_3$: C, 75.74; H, 5.09; N, 7.07. Found: C, 75.20; H, 5.26; N, 6.95.

1,3-Dipolar Cycloaddition Reaction of **4a** with Dimethyl Fumarate (**10a**) or Dimethyl Maleate (**11a**).

A 50 ml, two necked flask was fitted with a magnetic stirring bar and gas inlet tube. The flask was charged with 0.091 g (0.6 mmole) of CsF and was heated at 100-140 °C with hot plate stirrer for 1 hour. The apparatus was cooled under purging with nitrogen. A solution of methyl fumarate (**10a**) (0.144 g, 1.0 mmole) in 1 ml of dry acetonitrile was then added. A solution of **4a** (0.147 g, 0.5 mmole) in 2 ml of acetonitrile was introduced *via* a syringe with stirring. When all reagents had been added, the reaction mixture was stirred for 24 hours at room temperature. The solvent was removed under reduced pressure on a rotary evaporator to yield a residue. The residue was added to the top of a column containing 20 g, 60-200 mesh silica gel chromatography column and the column was eluted with 90% dichloromethane-10% ethyl acetate solvent mixture. The solvent was removed from those fractions containing the product under reduced pressure on a rotary evaporator to afford 0.060 g (0.189 mmole, 28%) of a white product, which was a 5:3 mixture of **12a** and **13a**. A mixture of **12a** and **13a** (0.059 g, 0.186 mmole) was also prepared from **4a** (0.147g, 0.5 mmole) and dimethyl maleate (**11a**) (0.144 g, 1.0 mmole) under the same conditions in 37% yield. This product was a 7:5 mixture of **12a** and **13a**. An analytical sample was recrystallized from isopropanol, mp 167-170 °C; ir (potassium bromide): ν max 3330 (NH), 1740 (C =O), 1600 cm^{-1}; ^1H nmr (deuteriochloroform): δ 3.58-3.96 (m, 3H, N-*CH_2*-*CH*-), 3.67 (s, 3H, OMe), 3.68 (s, 3H, OMe), 4.67 (d, J=1.8 Hz, 3/8H, N-C(=)-*CH*- of **13a**), 4.80 (d, J=2.6 Hz, 5/8H, N-C(=)-CH- of **12a**), 7.06-7.73 (m, 4H, aromatic-H), 8.92 (bs, 5/8H, NH), 9.18 (bs, 3/8NH); ms: m/z 396 (M^+, 44), 222(37), 44(40).

Anal. Calcd. for $C_{16}H_{15}NO_6$: C, 60.57; H, 4.77; N, 4.41. Found: C, 60.66; H, 4.63; N, 4.45.

1,3-Dipolar Cycloaddition Reaction of **4a** with Diethyl Fumarate (**10b**) or Diethyl Maleate (**11b**).

The reaction of **4a** (0.147 g, 0.5 mmole) with diethyl fumarate (**10b**) (0.172 g, 1.0 mmole) in the presence of CsF (0.091 g, 0.6 mmole) gave a mixture of **12b** and **13b** (a mixture of 3:2 ratio determined by the ^{1}H nmr spectrum) (0.095 g, 0.275 mmole) in 55% yield in a manner similar to that described for the preparation of a mixture of **12a** and **13a**. A mixture of **12b** and **13b** (0.151 g, 0.38 mmole) was also prepared from **4a** (0.147 g, 0.5 mmole) and diethyl maleate (**11b**) (0.172 g, 1.0 mmole) under the same conditions in 51% yield. This product was a 1:1 mixture of **12b** and **13b**. An analytical sample was recrystallized from isopropanol, mp 160-165 °C; ir (potassium bromide): ν max 3280 (NH), 1730 (C =O), 1600 cm^{-1}; ^{1}H nmr (deuteriodimethyl sulfoxide): δ 1.05-1.29 (m, 6H, O-CH_2-*CH_3*), 4.03-4.20 (m, 7H, O-CH_2-, N-*CH_2-CH*), 4.62 (d, J=1.8 Hz, 1/2H, NH-C(=)-CH-, of **13b**), 4.76 (d, J=2.6 Hz, 1/2H, NH-C(=)-CH- of **12b**), 7.03-7.69 (m, 4H, aromatic-H), 8.79 (bs, 1/2H, NH), 9.22 (bs, 1/2H, NH); ms: m/z 345 (M$^+$, 59), 226(62), 44(100).

Anal. Calcd. for $C_{18}H_{15}NO_6$: C, 62.60; H, 5.55; N, 4.60. Found: C, 62.31; H, 5.54; N, 4.04.

1,3-Dipolar Cycloaddition Reaction of **4b** with Dimethyl Fumarate (**10b**) or Dimethyl Maleate (**11b**): 3-(*trans* 3,4-Dimethoxycarbonylpyrrolidin-2-ylidene)-2-coumaranone (**14**) and 3-(*cis* 3,4-Dimethoxycarbonylpyrrolidin-2-ylidene)-2-coumaranone (**15**).

These compounds (0.097 g, 0.285 mmole) were prepared in 59% yield from dimethyl fumarate (**10b**) (0.144g, 1.0 mmole), **4b** (0.153 g, 0.5 mmole), and CsF (0.091 g, 0.6 mmol) in a manner similar to that described for the preparation of a mixture of **12a** and **13a**, as a yellow oil. This product was a 6:1 mixture of **14** and **15**. A mixture of **14** and **15** (0.151 g, 0.38 mmole) was also prepared from **4b** (0.147 g, 0.5 mmole) and dimethyl maleate (**11a**) (0.144 g, 1.0 mmole) under the same conditions in 37% yield. This product was a 5:1 mixture of **14** and **15**; ir (potassium bromide): ν max 3280 (NH), 1735 (C =O), 1660 cm^{-1}; ^{1}H nmr (deuteriochloroform): δ 2.49-4.54 (m, 12H, N-CH_2-CH-, 2xOMe, NMe), 4.67 (d, J=1.8 Hz, 1/7H, N-C(=)-CH of **15**), 4.85 (d, J=4.8 Hz, 6/7H, NH-C(=)-CH- of **14**), 6.79-7.60 (m, 4H, aromatic-H), 9.11 (bs, 1/7H, NH), 9.14(bs, 6/7H, NH); ms: m/z 330 (M$^+$, 59), 239(62), 44(100).

Anal. Calcd. for $C_{17}H_{18}N_2O_6$: C, 61.81; H, 5.49; N, 8.48. Found: C, 61.97; H, 5.54; N, 8.21.

3-(3-Methoxycarbonylpyrrolidin-2-ylidene)-2-coumaranone (**17a**) and 3-(4-Methoxycarbonylpyrrolidin-2-ylidene)-2-coumaranone (**18a**).

These compounds (0.050 g, 0.193 mmole) were prepared in 38% yield from methyl acrylate (**16a**) (0.086 g, 1.0 mmole), **4a** (0.147 g, 0.5 mmole), and CsF (0.091 g, 0.6 mmole) in a manner similar to that described for the preparation of a mixture of **12a** and **13a**, as colorless needles. This product was a 1:1 mixture of **17a** and **18a**. An analytical sample was recrystallized from isopropanol to give colorless needles, mp 172-175 °C; ir (potassium bromide): ν max 3320 (NH), 1730, 1695 (C =O), 1620 cm^{-1}; ^{1}H nmr (deuteriodimethyl sulfoxide): δ 2.05-2.53 (m, 2H, N-CH_2-), 3.44-3.83 (m, 2.5H, NH-C(=)-CH_2-, CH-COOMe of **17a**), 3.68 (s, 3H, OMe), 4.38-4.55 (m, 0.5H, CH-COOMe of **18a**), 7.00-7.68 (m, 4H, aromatic-H), 8.61 (bs, 1/2H, NH), 8.99 (bs, 1/2H, NH); ms: m/z 259 (M$^+$, 100), 200(83), 84(22).

Anal. Calcd. for $C_{14}H_{13}NO_4$: C, 64.86; H, 5.05; N, 5.40. Found: C, 64.61; H, 5.11; N, 5.45.

3-(3-Ethoxycarbonylpyrrolidin-2-ylidene)-2-coumaranone (**17b**) and 3-(4-Ethoxycarbonylpyrrolidin-2-ylidene)-2-coumaranone (**18b**).

These compounds (0.013 g, 0.025 mmole) were prepared in 5% yield from ethyl acrylate (**16b**) (0.100 g, 1.0 mmole), **4a** (0.147 g, 0.5 mmole), and CsF (0.091 g, 0.6 mmole) in a manner similar to that described for the preparation of a mixture of **12a** and **13a**, as pale yellow needles. This product was a 1:1 mixture of **17b** and **18b**. An analytical sample was recrystallized from isopropanol to give colorless needles, mp 155-160 °C; ir (potassium bromide): ν max 3310 (NH), 1725 (C =O), 1620 cm^{-1}; ^{1}H nmr (deuteriodimethyl sulfoxide): δ 1.05-1.30(m, 3H, O-CH_2-*CH_3*), 2.20-2.53(m, 2H, NH-CH_2-), 3.38-4.26(m. 6.5H, O-*CH_2*-CH_3, O-CH_2-, NH-C(=)-*CH_2*-, C*H*-COOEt) of **18b**), 4.38-5.34(m. 0.5H, C*H*-COOEt of **17b**), 7.00-7.73(m, 4H, aromatic-H), 8.98(bs, 1/2H, NH), 9.25(bs, 1/2H, NH); ms: m/z 273 (M$^+$, 34), 44(19), 40(100).

Anal. Calcd. for $C_{15}H_{15}NO_4$: C, 65.92; H, 5.53; N, 5.13. Found: C, 65.64; H, 5.52; N, 5.16.

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[5] Fluoride ions promoted protodesilylation of **4a** in acetonitrile to give the corresponding [(dimethylamino)(methylthio)]methylene-2-coumaranone which was alternatively prepared by the displacement reaction of **2a** with methylamine in methanol in good yield.

[6] It was found that methylthiolate, generated in situ, catalyzed this *Z-E* isomerization and cycloaddition to the fumarate was faster than to the maleate.