# A Competition between 1,3-Dipolar Cycloaddition and Substitution of Trifluoroacetonitrile Oxide

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Trifluoroacetonitrile oxide reacted with conjugated olefins such as styrenes, indenes, and acyclic conjugated dienes to give not only the cycloadduct but also its linear isomeric oxime. Methyl or phenyl group attached to the unsaturated carbon of the dipolarophiles was found to favor the formation of oxime. Such a concomitant reaction was interpreted in terms of a competition between a concerted cycloaddition and a two-step substitution through an electrophilic attack of nitrile oxide. Similar competitions were also investigated with cyclic conjugated dienes, where the competitive ratio of the products was found to depend on the ring size.

In the reactions of dipolar compounds with olefins or acetylenes, the substitution giving 1,3-addition product has been investigated in connection with the mechanism of 1,3-dipolar cycloaddition.[1,2] The reaction of benzonitrile oxide with phenylacetylene is particularly well documented,[3] and the concomitant formation of diphenylisoxazole and acetylenic oxime was interpreted by the independent two pathways, that is, a concerted cycloaddition and a substitution through an electrophilic attack of nitrile oxide on the triple bond of phenylacetylene.[1,4] As far as literatures show, however, such a substitution is limited only to rather unreactive dipolarophiles such as arylacetylenes and furan.

Previously we have reported the regio- and stereoselectivities in the conventional 1,3-dipolar cycloaddition of trifluoroacetonitrile oxide (**1**) with various olefins and acetylenes.[5] In the present paper,

$$CF_3C{\equiv}N{\rightarrow}O$$
**1**

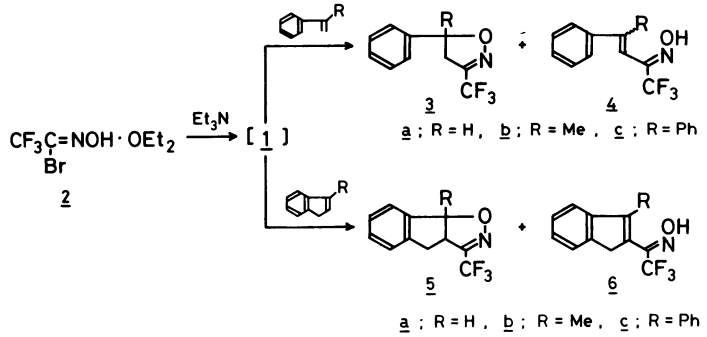
we wish to demonstrate a competition between the 1,3-dipolar cycloaddition and the electrophilic substitution in the reaction of the oxide **1** with rather reactive conjugated olefins.[6]

The oxide **1**, generated from trifluoroacetohydroximoyl bromide etherate (**2**) and triethylamine,[5] reacted with styrene to give 5-phenyl-3-trifluoromethyl-2-isoxazoline (**3a**) along with a trace amount of the 1,3-addition product, 1,1,1-trifluoro-4-phenyl-3-buten-2-one oxime (**4a**). In contrast, the reaction with α-methylstyrene and α-phenylstyrene gave the corresponding oximes **4b** and **4c** in preference to the cycloadducts **3b** and **3c**, respectively (Scheme 1 and Table 1). The structures of **3a—c** and **4a—c** were determined on the basis of the elemental analyses and spectral data. Isomeric composition of **4a—c** and their steric configuration were investigated by means of $^1$H NMR together with GLC. Thus **4a** or **4c** was deduced to be only one isomer and **4b** to consist of two geometric isomers out of four possible ones, respectively. Since **4b** could be hardly separated into

Table 1. Total yields of isoxazolines (**3** or **5**) and oximes (**4** or **6**) and their ratios in the reactions of trifluoroacetonitrile oxide with styrenes and indenes

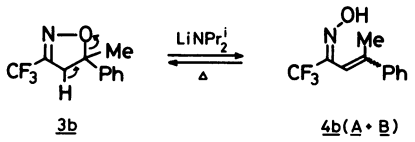
| Product | Total yield, %[a] | Ratio(**3**/**4** or **5**/**6**)[b] |
|---|---|---|
| **3a**, **4a** | 84 | 99.5/0.5[c] |
| **3b**, **4b** | 73 | 33/67 |
| **3c**, **4c** | 42 | 37/63 |
| **5a**, **6a** | 53 | 79/21 |
| **5b**, **6b** | 67 | 37/63 |
| **5c**, **6c** | 35 | 0/100 |

Numbers of products refer to those in Scheme 1.
a) Isolated yield. b) Determined by $^1$H NMR analysis of the reaction mixture unless otherwise noted. c) The ratio of the isolated products.




Scheme 1.

the components, its absolute configuration was ambiguous and the components are shown here as **A** and **B**. It should be noted that both the cycloadducts **3** and the oximes **4** are primary products *via* the independent pathways because they were too stable to interconvert under the reaction conditions unless the more drastic conditions were applied. The isoxazolines **3a** and **3b** were converted in high yields into the oximes **4a** and **4b**(**A** and **B**), respectively, through ring-opening by the treatment with lithium diisopropylamide[7] and, conversely, **4b** cyclized on heating at 150 °C to give **3b**. Such an interconversion



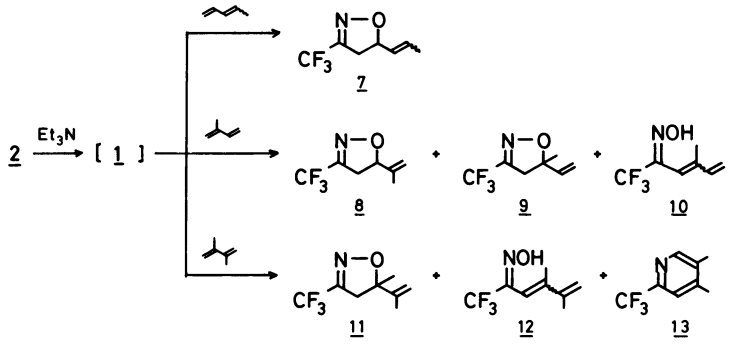

3b 4b(A + B)

might suggest the *E* configuration in respect to C–N double bond of **4**, and **4b-A** and **4b-B** could be the geometrical isomers in respect to C–C double bond. In the case with α-methylstyrene, the effect of the bases was then studied using pyridine and sodium methoxide in place of triethylamine, resulting in no appreciable changes in the ratios of **3b**/**4b** and **4b-A**/**4b-B**, as shown in Table 2.

The concomitant formation of the cycloadducts and the 1,3-addition products was also observed in the reactions of **1** with indenes (Scheme 1). Yields and ratios of these isomers are summarized in Table 1. The reaction of **2** with indene in the presence of triethylamine gave 3a,8a-dihydro-3-trifluoromethyl-4*H*-indeno[2,1-*d*]isoxazole (**5a**) and 2-[2,2,2-trifluoro-1-(hydroxyimino)ethyl]indene (**6a**) in the ratio of 79/21, where their regioisomers were not detected at all. The structure of **5a** was established by the comparable chemical shifts of two methine protons in $^1$H NMR to those of the 3-phenyl analogue reported in the literature.[8] Singlet olefinic proton of **6a** in $^1$H NMR supports that the trifluoro(hydroxyimino)ethyl group is attached to 2-position. In analogy with styrenes, methyl and phenyl groups on 3-position of indene ring favor the formation of the oximes. 3-Methylindene gave a mixture of **5b** and **6b** in the ratio of 37/63 and, with 3-phenylindene, the exclusive formation of the oxime **6c** was observed without any detectable amount of the cycloadduct **5c**.

Similarly with acyclic conjugated dienes, the formation of the oximes competed (Scheme 2). In the reaction with 1,3-pentadiene, only the cycloaddition occurred on the monosubstituted double bond to give exclusively **7** in 63% yield. On the other hand, with 2-methyl-1,3-butadiene, the cycloaddition took place on either double bond to afford **8** and **9**, accompanied by the oxime **10** (87% total yield, **8**/**9**/**10**; 48/40/12). The alternative oxime bearing trifluoro(hydroxyimino)ethyl group at 4-position was not detected. Similarly, the reaction with 2,3-dimethyl-1,3-butadiene gave the cycloadduct **11** and the oxime **12** in the ratio of 69/31. The oxime **12** was so unstable as to be cyclodehydrated intramolecularly during the course of isolation by column chromatography (silica gel) to give 4,5-dimethyl-2-trifluoromethylpyridine (**13**). The detailed study on the conversion to the pyridine is now under progress.

The oximes are thought to be formed *via* the addition of **1** toward the double bond giving the zwitterionic intermediate **14** followed by the intra-

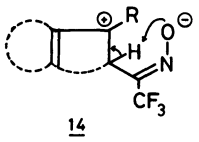



Scheme 2.

Table 2. Effect of base on yields and ratios of the products **3b** and **4b** in the reaction of trifluoroacetonitrile oxide with α-methylstyrene

| Base | Yield(**3b**+**4b**), %[a] | Ratio(**3b**/**4b**)[b] | Ratio(**4b-A**/**4b-B**)[b] |
|---|---|---|---|
| Triethylamine | 73 | 33/67 | 56/44 |
| Pyridine | 39 | 38/62 | 58/42 |
| Sodium Methoxide | 45 | 37/63 | 56/44 |

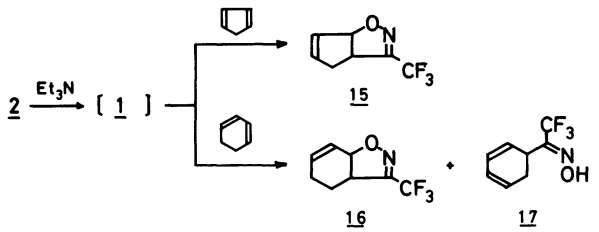
The reactions were carried out in toluene at room temperature for 3 h.
a) Isolated yield. b) Determined by $^1$H NMR analysis of the reaction mixture.



14

molecular proton shift.[9] Caramella *et al.* proposed a competing pathway stabilized by secondary orbital interactions to form oximes by the reactions of benzonitrile oxide with furan or arylacetylenes.[4] Thus the approach of the reagents with alignment, leading to a zwitterionic intermediate, is well stabilized by secondary orbital interactions between the phenyl group of benzonitrile oxide and the furan ring or the aryl group of arylacetylene. However, in the present case of trifluoroacetonitrile oxide **1**, such a stabilizing interaction is unlikely because trifluoromethyl group has no secondary interaction as reported in the Diels-Alder reactions of (trifluoromethyl)ethenes.[10] Therefore, the intermediate **14** might be formed *via* the electrophilic attack of **1** on the double bond owing to the strong electron-withdrawing effect of trifluoromethyl group.[11] The tendency of methyl or phenyl group of dipolarophiles favoring the formation of the oximes may be interpreted by both the steric hindrance which retards the concerted cycloaddition and the electronic effect which stabilizes the intermediate **14**.

A similar competition was further investigated with cyclic conjugated dienes (Scheme 3). While the reaction with cyclopentadiene gave exclusively the cycloadduct **15** in 53% yield, that with 1,3-cyclohexadiene afforded not only the cycloadduct **16** but also the 1,3-addition product **17**, in which trifluoro(hydroxyimino)ethyl group is substituted on the saturated carbon (66% total yield, **16**/**17**; 39/61). The structure of **17** was determined by its $^1$H NMR and UV spectra. The methine proton ($\delta$=4.07) coupled with the adjacent methylene protons and the absorption at 256 nm ($\varepsilon$=3393) due to conjugated diene strongly support that the trifluoro(hydroxyimino)ethyl group is attached to the saturated carbon. The concerted cycloaddition of nitrile oxide to the double bond in a six-membered ring is known to be slower than that to the one in a five-membered ring[12] and this unreactivity seems to cause the formation of the oxime **17**.



Scheme 3.

## Experimental

All melting and boiling points are uncorrected. The IR spectra were recorded on a JASCO IRA-1 spectrometer. The $^1$H and $^{13}$C NMR spectra were measured with JEOL JNM-PMX 60 and -FX 60 spectrometers, respectively, using tetramethylsilane as an internal standard, the chemical shifts being given in $\delta$ppm downfield. The MS spectra were obtained on a Finnigan 4023 GC-MS DS spectrometer. The UV spectra were observed with a Hitachi 340 spectrometer. The bromide **2** was prepared by the method reported in our previous paper.[5]

*Reactions of 2 with Styrenes.* To a mixture of **2** (2.64 g, 9.9 mmol) and $\alpha$-methylstyrene (2.34 g, 19.8 mmol) in 20 cm$^3$ of toluene was added dropwise a solution of triethylamine (2.7 cm$^3$) in 10 cm$^3$ of toluene. The mixture was stirred at room temperature for 3 h. Then hexane was added and the salt, triethylamine hydrobromide, was collected on a filter. The filtrate was washed with water and brine and dried over magnesium sulfate. Removal of the solvent left an oily residue which was a mixture of **3b** and **4b(A+B)**. The residue was distilled (boiling range, 118—119 °C/9 mmHg (1 mmHg=133.322 Pa) to give 1.65 g (73% total yield) of a mixture of **3b** and **4b(A+B)**. The isoxazoline **3b** and **4b(A+B)** were separated by column chromatography (silica gel, hexane and chloroform) followed by preparative GLC: **3b**, $^1$H NMR ($CCl_4$) $\delta$=1.73 (s, 3H), 3.23 (q, 2H), 7.3 (s, 5H), IR (neat) 1625 (C=N), 1180 and 1131 cm$^{-1}$ ($CF_3$).

Found: C, 57.75; H, 4.31; N, 5.92%. Calcd for $C_{11}H_{10}F_3NO$: C, 57.64; H, 4.40; N, 6.11%.

**4b-A**, $^1$H NMR ($CDCl_3$) $\delta$=2.29 (d, 3H), 5.87 (q, 1H), 7.2—7.6 (m, 5H), 8.6 (br.s, 1H); **4b-B**, $^1$H NMR ($CDCl_3$) $\delta$=2.13 (s, 3H), 6.10 (s, 1H), 7.4—7.7 (m, 5H), 8.6 (br.s, 1H).

Found: C, 57.71; H, 4.42; N, 6.05% (for a mixture of **4b(A+B)**). Calcd for $C_{11}H_{10}F_3NO$: C, 57.64; H, 4.40; N, 6.11%.

Similarly, the reactions with styrene and $\alpha$-phenylstyrene were performed to give the corresponding **3** and **4**. Yields and ratios of these products are summarized in Table 1 and physical and spectral data are as follows: **3a**, bp 85—87 °C/3.5 mmHg (lit,[5] 85—87 °C/3.5 mmHg); **4a**, mp 142—143 °C (hexane-chloroform), $^1$H NMR ($CDCl_3$) $\delta$=7.1—7.6 (m, 7H), 9.2 (br.s, 1H), IR (KBr) 3320 (OH), 1622 (C=N, C=C), 1105 cm$^{-1}$ ($CF_3$), MS (CI, *m/z*) 216 $(M+H)^+$, 244 $(M+Et)^+$, $^{13}$C NMR ($CDCl_3$), $\delta$=93.8, 112.1, 130.3, 148.6 ($CF_3$), 110.9 (d, HC=), 127.3, 128.6, 129.3, 135.7 (Ph), 137.3 (d, HC=), 141.5, 143.5, 145.5, 147.6 (C-$CF_3$).

Found: C, 55.89; H, 3.64; N, 6.45%. Calcd for $C_{10}H_8F_3NO$: C, 55.82; H, 3.75; N, 6.51%.

**3c**, $^1$H NMR ($CDCl_3$) $\delta$=3.76 (q, 2H), 7.2—7.8 (m, 10H), IR (neat) 1632 (C=N), 1190 and 1130 cm$^{-1}$ ($CF_3$).

Found: C, 66.47; H, 4.15; N, 4.39%. Calcd for $C_{16}H_{12}F_3NO$: C, 65.98; H, 4.15; N, 4.81%.

**4c**, mp 113—114 °C (hexane-chloroform), $^1$H NMR ($CDCl_3$) $\delta$=6.18 (s, 1H), 7.0—7.4 (m, 10H), 8.6 (br.s, 1H), IR (KBr) 3370 (OH), 1609 (C=N), 1163 and 1093 cm$^{-1}$ ($CF_3$).

Found: C, 66.12; H, 4.20; N, 4.80%. Calcd for $C_{16}H_{12}F_3NO$: C, 65.98; H, 4.15; N, 4.81%.

*Conversion of 3 into 4.* A 1.55 mol dm$^{-3}$ solution of butyllithium (3.3 cm$^3$) in hexane was added dropwise to a solution of 1.00 g (4.7 mmol) of **3a** and 0.52 g (5.1 mmol) of

diisopropylamine in 10 $cm^3$ of tetrahydrofuran cooled in a dry ice–acetone bath. The mixture was allowed to warm to room temperature over a period of 3 h. After stirring at room temperature for an additional 2.5 h, saturated aq ammonium chloride was added to the mixture. The solvent was removed and the resulting aqueous layer was extracted twice with diethyl ether. The ethereal extracts were washed with brine and dried over magnesium sulfate. Removal of the solvent left a residue which was submitted to column chromatography (silica gel, chloroform) to give 0.93 g (93% yield) of **4a**. Thus obtained **4a** was further purified by recrystallization from hexane–chloroform, mp 142—143 °C, $^1H$ NMR and IR spectra are consistent with those obtained above.

The similar treatment of 1.14 g (5.0 mmol) of **3b** with lithium diisopropylamide gave 0.48 g (42%) of a mixture of **4b-A** and **4b-B** in the ratio of 57/43 ($^1H$ NMR analysis).

*Conversion of 4b into 3b.* A mixture of 1.15 g (5.0 mmol) of **4b** (**4b-A**/**4b-B**; 56/44) and 10 $cm^3$ of chloroform in a sealed tube was stirred at 150 °C for 65 h. The similar procedure to the above afforded 0.68 g (59%) of **3b** and recovered 0.40 g (35%) of a mixture of **4b-A** and **4b-B** in the ratio of 13/87.

*Reactions of 2 with Indenes.* To a mixture of **2** (2.58 g, 9.7 mmol) and indene (3.41 g, 29.4 mmol) in 20 $cm^3$ of toluene was added dropwise a solution of triethylamine (2.8 $cm^3$) in 10 $cm^3$ of toluene. After being stirred at room temperature for 3 h, hexane was added and the deposited salt was filtered out. The filtrate was washed with water and brine, dried over magnesium sulfate, and evaporated to leave an oily mixture of **5a** and **6a** (79/21 by $^1H$ NMR analysis). The oil was distilled (boiling range, 118—119 °C/6 mmHg) to give 1.17 g (53% total yield) of a mixture of **5a** and **6a**. Each isomer was separated by column chromatography (silica gel, hexane and chloroform) and further purification was carried out by recrystallization: **5a**, mp 46—46.5 °C (hexane), $^1H$ NMR ($CDCl_3$) $\delta$=3.37 (d, 2H), 4.25 (dtq, 1H), 6.28 (d, 1H), 7.2—7.6 (m, 4H), IR (KBr) 1605 (C=N), 1160 and 1120 $cm^{-1}$ ($CF_3$).

Found: C, 58.11; H, 3.54; N, 6.12%. Calcd for $C_{11}H_8F_3NO$: C, 58.16; H, 3.55; N, 6.17%.

**6a**, mp 170—171 °C (hexane), $^1H$ NMR ($CDCl_3$–DMSO-$d_6$) $\delta$=3.94 (s, 2H), 7.2—7.5 (m, 4H), 7.64 (s, 1H), 12.6(s, 1H), IR (KBr) 3200 (OH), 1155 and 1122 $cm^{-1}$ ($CF_3$), MS (CI, *m/z*) 228 $(M+H)^+$, 210 $(M-OH)^+$, 141 $(M-CF_3OH)^+$.

Found: C, 58.17; H, 3.54; N, 6.15%. Calcd for $C_{11}H_8F_3NO$: C, 58.16; H, 3.55; N, 6.17%.

In a similar manner, **5b** and **6b-c** were obtained from the reactions with 3-methyl- and 3-phenylindenes, respectively, and their spectral data are as follows: **5b**, colorless oil, $^1H$ NMR ($CCl_4$) $\delta$=1.77 (s, 3H), 3.27 (d, 2H), 3.77(tm, 1H), 7.1—7.5 (m, 4H), IR (neat) 1613 (C=N), 1191 and 1131 $cm^{-1}$ ($CF_3$).

Found: C, 59.49; H, 3.98; N, 5.61%. Calcd for $C_{12}H_{10}F_3NO$: C, 59.75; H, 4.18; N, 5.81%.

**6b**, mp 115—116 °C (hexane), $^1H$ NMR ($CDCl_3$) $\delta$=2.16 (t, 3H), 3.60 (q, 2H), 7.2—7.6 (m, 4H), 8.9 (s, 1H), IR (KBr) 3250 (OH), 1184 and 1124 $cm^{-1}$ ($CF_3$).

Found: C, 60.30; H, 3.89; N, 5.62%. Calcd for $C_{12}H_{10}F_3NO$: C, 59.75; H, 4.18; N, 5.81%.

**6c**, mp 168—169 °C (hexane–chloroform), $^1H$ NMR ($CDCl_3$–DMSO-$d_6$) $\delta$=3.76 (s, 2H), 7.2—7.6 (m, 9H), 11.8 (s, 1H), IR (KBr) 3310 (OH), 1175 and 1123 $cm^{-1}$ ($CF_3$).

Found: C, 67.48; H, 3.92; N, 4.52%. Calcd for $C_{17}H_{12}F_3NO$: C, 67.33; H, 3.99; N, 4.62%.

*Reactions of 2 with Acyclic Conjugated Dienes.* To a solution of **2** (5.21 g, 19.6 mmol) and 2,3-dimethyl-1,3-butadiene (3.21 g, 39.1 mmol) in 40 $cm^3$ of diethyl ether was added dropwise a solution of triethylamine (5.5 $cm^3$) in 20 $cm^3$ of diethyl ether. The reaction mixture was stirred at room temperature for 4 h. Then diethyl ether was added and the salt was filtered out. The filtrate was washed with water and brine and dried over magnesium sulfate. The dried organic layer was evaporated to give a mixture of **11** and **12** in the ratio of 69/31 ($^1H$ NMR analysis). This mixture was distilled (boiling range, 110—112 °C/40 mmHg) and chromatographed on silica gel with hexane and then chloroform to yield **11** (1.44 g, 38% yield), **12** (0.15 g, 4% yield), and **13** (0.46 g, 13% yield). Each product was further purified by preparative GLC: **11**, $^1H$ NMR ($CCl_4$) $\delta$=1.53 (s, 3H), 1.81 (d, 3H), 2.87 (dq, 1H), 3.20 (dq, 1H), 4.93 (q, 1H), 5.10 (s, 1H), IR (neat) 1650 (C=C), 1625 (C=N), 1195 and 1139 $cm^{-1}$ ($CF_3$).

Found: C, 49.68; H, 5.08; N, 7.12%. Calcd for $C_8H_{10}F_3NO$: C, 49.74; H, 5.22; N, 7.25%.

**12**, $^1H$ NMR ($CCl_4$) $\delta$=1.86 (s, 3H), 2.00 (s, 3H), 5.14 (s, 1H), 5.31 (s, 1H), 5.73 (s, 1H), 8.7 (br.s, 1H), IR (neat) 3340 (OH), 1630 and 1605 (C=C, C=N), 1195 and 1140 $cm^{-1}$ ($CF_3$).

Found: C, 49.28; H, 5.16; N, 7.05%. Calcd for $C_8H_{10}F_3NO$: C, 49.74; H, 5.22; N, 7.25%.

**13**, $^1H$ NMR ($CCl_4$) $\delta$=2.37 (s, 6H), 7.40 (s, 1H), 8.40 (s, 1H), IR (neat) 1165 and 1132 $cm^{-1}$ ($CF_3$).

Found: N, 8.00%. Calcd for $C_8H_8F_3N$: N, 8.00%.

In a similar manner to the above, the reactions with 1,3-pentadiene and 2-methyl-1,3-butadiene were carried out to give **7**, **8**, **9**, and **10**, respectively. Spectral data of these products are as follows: **7**, bp 89—90 °C/46 mmHg, $^1H$ NMR ($CCl_4$) $\delta$=1.77 (d, 3H), 2.6—3.5 (m, 2H), 4.9—6.2 (m, 3H), IR (neat) 1680 (C=C), 1624 (C=N), 1183 and 1134 $cm^{-1}$ ($CF_3$).

Found: C, 46.44; H, 4.36; N, 7.81%. Calcd for $C_7H_8F_3NO$: C, 46.93; H, 4.50; N, 7.82%.

**8**, $^1H$ NMR ($CCl_4$) $\delta$=1.77 (d, 3H), 2.87 (ddq, 1H), 3.27(ddq, 1H), 4.9—5.3 (m, 3H), IR (neat) 1660 (C=C), 1635 (C=N), 1190 and 1140 $cm^{-1}$ ($CF_3$), MS (CI, *m/z*) 180 $(M+H)^+$, 208 $(M+Et)^+$.

Found: C, 47.46; H, 4.57; N, 7.72% (for a mixture of **8** and **10**). Calcd for $C_7H_8F_3NO$: C, 46.93; H, 4.50; N, 7.82%.

**9**, $^1H$ NMR ($CCl_4$) $\delta$=1.55 (s, 3H), 2.82 (dq, 1H), 3.08 (dq, 1H), 5.17 (dd, 1H), 5.30 (dd, 1H), 5.95 (dd, 1H), IR (neat) 1645 (C=C), 1625 (C=N), 1190 and 1140 $cm^{-1}$ ($CF_3$), MS (CI, *m/z*) 180 $(M+H)^+$, 208 $(M+Et)^+$.

Found: C, 47.12; H, 4.55; N, 7.79%. Calcd for $C_7H_8F_3NO$: C, 46.93; H, 4.50; N, 7.82%.

**10**, $^1H$ NMR ($CDCl_3$) $\delta$=1.83 (s, 3H), 5.28 (d, 1H), 5.45(d, 1H), 5.72 (s, 1H), 6.48 (dd, 1H), 7.1(br.s, 1H), IR (neat) 3300 (OH), 1605 (C=C, C=N), 1190 and 1140 $cm^{-1}$ ($CF_3$), MS (CI, *m/z*) 180 $(M+H)^+$, 208 $(M+Et)^+$.

*Reactions of 2 with Cyclic Conjugated Dienes.* To a solution of **2** (2.36 g, 8.9 mmol) and 1,3-cyclohexadiene (2.08 g, 26.0 mmol) in 20 $cm^3$ of toluene, a solution of triethylamine (2.4 $cm^3$) in 10 $cm^3$ of toluene was added. After the reaction mixture was stirred at room temperature for 3 h, hexane was added and the salt was collected on a

filter. The filtrate was washed with water and brine and dried over magnesium sulfate. Removal of the solvent left an oily mixture of **16** and **17** (39/61 by $^1$H NMR analysis). The oil was distilled (boiling range, 104—105 °C/27 mmHg) to give 1.12 g (66% total yield) of a mixture of **16** and **17**. Each isomer was isolated by preparative GLC; **16**, $^1$H NMR ($CDCl_3$) $\delta$=1.4—2.3 (m, 4H), 3.3—3.7 (m, 1H), 5.03 (dd, 1H), 5.8—6.5 (m, 2H), IR (neat) 1611 (C=N), 1180 and 1130 cm$^{-1}$ ($CF_3$).

Found: C, 50.65; H, 4.21; N, 6.87%. Calcd for $C_8H_8F_3NO$: C, 50.27; H, 4.22; N, 7.33%.

**17**, $^1$H NMR ($CDCl_3$) $\delta$=2.3—2.6 (m, 2H), 4.07 (ddm, 1H), 5.6—6.2 (m, 4H), 9.2 (br.s, 1H), IR (neat) 3300 (OH), 1189 and 1130 cm$^{-1}$ ($CF_3$). UV, $\lambda_{max}^{EtOH}(\varepsilon)$ 256 nm (3393).

Found: C, 50.12; H, 4.25; N, 7.32%. Calcd for $C_8H_8F_3NO$: C, 50.27; H, 4.22; N, 7.33%.

Similarly, **15** was obtained from the reaction with cyclopentadiene. **15**, bp 87—89 °C/31 mmHg, $^1$H NMR ($CCl_4$) $\delta$=2.7—2.8 (m, 2H), 3.8—4.2 (m, 1H), 5.7—6.1 (m, 3H), IR (neat) 1616 (C=N), 1184 and 1131 cm$^{-1}$ ($CF_3$).

Found: C, 47.44; H, 3.17; N, 7.80%. Calcd for $C_7H_6F_3NO$: C, 47.47; H, 3.41; N, 7.91%.

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