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Synthesis and Urea Derivatization of (*Z*)-2-Aryl-1-(ethoxycarbonyl)vinyl Isocyanates

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Ethyl (*Z*)-3-aryl-2-methylthiocarboxamido acrylic esters **3a–f**, prepared from aldehydes **1a–f** and ethyl *N*-[(dimethylthio)methylene]glycine ester (**2**),[1] gave (*Z*)-2-aryl-1-(ethoxycarbonyl)vinyl isocyanates **4a–f** upon silylation and thermolysis (Scheme 1). This represents the first application of the Kricheldorf method[2] to the synthesis of vinyl isocyanates from vinyl thiocarbamates. The Curtius rearrangement has also afforded these types of compounds (e.g., α-alkyl(aryl)thiovinyl isocyanates, which are synthetic equivalents of acyl isocyanates,[3] and β-carbamoylvinyl isocyanates, which have been detected as transient intermediates in the synthesis of 1,3-oxazin-6-ones[4] (not 1,3-oxazin-2-ones, as has been previously reported[5])). Phosgenation of ketimines[6] and pyrolisis of *N*-phenylimidazoline-4,5-diones hydrochlorides[7] are other alternative methods. In the latter procedure, 4-quinazolones are formed from *N*-phenyl-α-alkylimino isocyanates (azastyryl isocyanates).[7] We also expect that (*Z*)-2-aryl-1-(ethoxycarbonyl)vinyl isocyanates **4a–f** will provide new starting materials for the synthesis of various heterocyclic compounds *via* electrocyclization and cycloaddition reactions.[2c,3,8] We wish to report the synthesis of and some experimental data on the stability of (*Z*)-2-aryl-1-(ethoxycarbonyl)vinyl isocyanates.

When *N*-silylated carbamic methylthio esters **3a–f** were heated in refluxing toluene, they decomposed to isocyanates **4a–f** and silicon compound **5** (Scheme 1). Since compounds **4a–f** and **5** did not undergo either back-reaction[9] or, to an appreciable extent, isocyanate side reactions such as dimerization, trimerization, or polymerization,[10] isocyanates **4a–f** were obtained in quantitative yields. The structures of **4a–f** were established on the basis of spectral data and chemical evidence. Their IR spectra displayed characteristic absorption bands for NCO and CO groups at 2220–2240 and 1700–1715 cm^{-1}, respectively.[11] The ^{1}H NMR spectra showed singlets at 7.04–7.13 ppm for the vinyl protons, although these protons appeared at lower frequency than the olefinic hydrogen signals for precursors **3a–f**.[1] The ^{13}C NMR spectra were in agreement with the structural assignments: α- and β-carbon atoms (calculated δ values: 130 ppm)[12] were assigned on the basis of the different intensity associated with the number of hydrogen atoms directly linked to the carbons.

Heating **4a–f** in refluxing hexane–dry ethyl acetate (1:1 v/v) for 15 minutes gave bis(vinyl)ureas **6a–f**, which neatly precipitated in quantitative yield from the solvent mixture after it was cooled. Evidence for this transformation was again obtained from spectral data. The IR spectra of the products displayed bands at 3280 and 1650 cm^{-1} corresponding to the NH and CO bonds, respectively, of the urea group. At the same time, the absence of the isocyanate bands at 2220–2240 cm^{-1} was observed in the isolated products. The same criteria used to establish the signal assignments for the NMR spectra of compounds **4a–f** were applied to the bis(vinyl)urea derivatives. Since calculated δ values from *trans*-cinnamic acid data combined with the appropriate group contributions for all reported compounds **3a–f**, **4a–f**, and **6a–f** show full agreement with the observed values, the structural and configurational assignments seem likely.

On the other hand, all the vinyl isocyanates remained unchanged when heated in refluxing hexane or toluene for 2 h. Extended reaction time caused trimerization of the isocyanates (ca. 50%). This behavior is in contrast to that observed for vinyl isocyanates **4a–f** in refluxing hexane–ethyl acetate solutions. The unexpected isolation of urea derivatives **6a–f** in hexane–ethyl acetate is believed to proceed via enamine and/or imine formation induced by ethyl acetate (Scheme 2).

The tentative proposed mechanism is based on the assumption of an equilibrium between adduct **7**, which originates from attack of enolized ethyl acetate on isocyanate **4**, and vinylurea **6**. The formation of **6** is driven by its insolubility in the reaction medium. A large number of CH insertion reactions have been carried out on compounds having a RCH_2CO group where R is preferentially, but not necessarily, an electron-withdrawing substituent.[13] Other adducts similar to **7** are believed to react in a stepwise fashion. Thus, unsymmetrical vinylureas such as **8** (Scheme 3) dissociate to enamines **9** in a way that can be formally regarded as a retroene pathway.[8a]

In order to verify the mechanism proposed, two separate control experiments were carried out. Vinyl isocyanate **4b** was refluxed in dry acetone–hexane (1:1, v/v) and in ethyl acetate–hexane (1:1, v/v), and the intermediate ketene was trapped with ethanol. The ethyl acetylacetate and diethyl malonate were unequivocally characterized by GC-MS. The peaks of these adducts were assigned on

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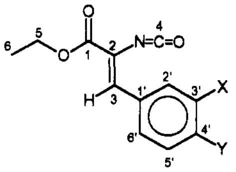
Table 1. Elemental Analyses and Physical and Spectral Data of (*Z*)-2-Aryl-1-(ethoxycarbonyl)vinyl Isocyanates 4a–f



product (formula)	mp, °C	anal.	IR (cm^{-1})^{a}	NMR^{b}
4a X = Y = H ($C_{12}H_{11}NO_3$)	oil	calcd: C, 66.35; H, 5.10; N, 6.45 found: C, 66.09; H, 5.12; N, 6.42	2220, 1700	δ_H 1.41 (t, *J* = 7.2 Hz, 3H), 4.39 (q, *J* = 7.2 Hz, 2H), 7.13 (s, 1H), 7.34–7.85 (m, 5H); δ_c 14.1 (C6), 62.9 (C5), 121.7 (C4), 127.6 (C3), 128.4 (C3′,C5′), 129.7 (C4′), 130.0 (C2′,C6′), 131.4 (C2), 132.7 (C1′), 164.4 (C1)
4b X = H; Y = Me ($C_{13}H_{13}NO_3$)	52–54^{c}	calcd: C, 67.52; H, 5.67; N, 6.06 found: C, 67.29; H, 5.68; N, 6.03	2240, 1710	δ_H 1.40 (t, *J* = 7.2 Hz, 3H), 2.39 (s, 3H), 4.38 (q, *J* = 7.2 Hz, 2H), 7.11 (s, 1H), 7.21–7.77 (AA′XX′ system, 4H); δ_C 14.2 (C6), 21.5 (CH_3-C4′), 62.9 (C5), 120.9 (C4), 127.9 (C3), 129.3 (C3′,C5′), 130.1 (C1′), 130.2 (C2′,C6′), 131.5 (C2), 140.4 (C4′), 164.7 (C1)
4c X = H; Y = Et ($C_{14}H_{15}NO_3$)	oil	calcd: C, 68.56; H, 6.16; N, 5.71 found: C, 68.21; H, 6.18; N, 5.69	2240, 1715	δ_H 1.25 (t, *J* = 7.6 Hz, 3H), 1.40 (t, *J* = 7.2 Hz, 3H), 2.68 (q, *J* = 7.6 Hz, 2H), 4.38 (q, *J* = 7.2 Hz, 2H), 7.11 (s, 1H), 7.23–7.80 (AA′XX′ system, 4H); δ_c 14.1 (C6), 15.2 (CH_3CH_2-C4′), 28.7 (CH_3CH_2-C4′), 62.8 (C5), 120.8 (C4), 127.8 (C3), 128.0 (C3′,C5′), 130.1 (C6′,C2′), 130.2 (C1′), 131.3 (C2), 146.5 (C4′), 164.5 (C1)
4d X = H; Y = Cl ($C_{12}H_{10}ClNO_3$)	oil	calcd: C, 57.27, H, 4.01; N, 5.57 found: C, 57.04; H, 4.03; N, 5.56	2220, 1710	δ_H 1.41 (t, *J* = 7.1 Hz, 3H), 4.39 (q, *J* = 7.1 Hz, 2H), 7.06 (s, 1H), 7.35–7.80 (AA′XX′ system, 4H); δ_C 14.2 (C6), 63.2 (C5), 122.4 (C4), 126.3 (C3), 128.8 (C3′,C5′), 131.0, 131.8 (C2,C1′) 131.4 (C2′,C6′), 135.6 (C4′), 164.3 (C1)
4e X = H; Y = MeO ($C_{13}H_{13}NO_4$)	oil	calcd: C, 63.15; H, 5.30, N, 5.66 found: C, 62.90; H, 5.28; N, 5.68	2240, 1700	δ_H 1.39 (t, *J* = 7.2 Hz, 3H), 3.84 (s, 3H), 4.36 (q, *J* = 7.2 Hz, 2H), 7.08 (s, 1H), 6.91–7.85 (AA′XX′ system, 4H); δ_C 14.6 (C6), 55.6 (CH_3O), 63.2 (C5), 114.3 (C3′,C5′), 119.9 (C4), 126.0 (C1′), 128.0 (C3), 130.8 (C2), 132.4 (C2′,C6′), 161.1 (C4′), 165.1 (C1)
4f X, Y = OCH_2O ($C_{13}H_{11}NO_5$)	72–74^{c}	calcd: C, 59.77; H, 4.24; N, 5.36 found: C, 59.50; H, 4.26; N, 5.24	2220, 1710	δ_H 1.40 (t, *J* = 7.2 Hz, 3H), 4.37 (q, *J* = 7.2 Hz, 2H), 6.03 (s, 2H), 6.84 (d, *J* = 8.1 Hz, 1H), 7.04 (s, 1H), 7.22 (dd, *J* = 8.1 and 1.8 Hz, 1H), 7.61 (d, *J* = 1.8 Hz, 1H); δ_C 14.1 (C6), 62.8 (C5), 101.4 (OCH_2O), 108.3 (C5′), 109.1 (C2′), 119.9 (C4), 126.2 (C6′), 127.1 (C1′), 127.5 (C3), 131.6 (C2), 147.7 (C3′), 148.9 (C4′), 164.5 (C1)

[a] **4a**, **4c–e**: neat; **4b**, **4f**: KBr pellet. [b] $CDCl_3$; ^1H: 300 MHz; ^{13}C: 75 MHz. [b] Recrystallized from hexane.

the basis of retention times observed for standard samples. The mass spectra were successfully compared with the spectra of ethyl acetylacetate and diethyl malonate in the computer data base.

In conclusion, (*Z*)-2-aryl-1-(ethoxycarbonyl)vinyl isocyanates were obtained in quantitative yields from [(methylthio)carbonyl]amino derivatives by means of the Kricheldorf methodology.[2] These isocyanates were shown to be thermally stable in nonenolizable solvents. Furthermore, these isocyanates could be used for the synthesis of symmetrical vinyl ureas in a way that precludes polymerization or hydrolysis side reactions associated with an enamine intermediate.

Experimental Section

Melting points are uncorrected. ^1H NMR and ^{13}C NMR spectra were recorded in $CDCl_3$ or DMSO-d_6. Chemical shifts are quoted as δ values from TMS as an internal reference. GC-MS were recorded with a silica column (internal diameter: 0.22 mm; length: 24 m) and a OV-1 stationary phase. An 80 °C/5 min–150 °C (heating rate: 5 °C/min) temperature program was used to record the chromatographs.

Ethyl acetylacetate and diethyl malonate were purchased from Aldrich. Immediately before use, THF was dried over sodium and distilled from $LiAlH_4$ under argon. Aldehydes **1a–f** (Aldrich) were used without further purification. Ethyl *N*-[(dimethylthio)-methylene]glycine ester was synthesized from ethyl glycinate hydrochloride (Aldrich), carbon disulfide, and methyl iodide.[1] Ethyl 3-aryl-2-[(methylthio)carbonyl]amino acrylic esters **3a–f**, with the exception of **3c**, have been previously reported.[1] Attempts to synthesize the *p*-nitrophenyl analogue were unsuccessful.[14]

Ethyl 3-(4-Ethylphenyl)-2-[[(methylthio)carbonyl]amino] Acrylate (3c). Compound **3c** was prepared by a previously reported procedure.[1] A white solid (2.93 g) was obtained after isolation by flash column chromatography with hexane–ethyl acetate (80:20 v/v) and purification by recrystallization from

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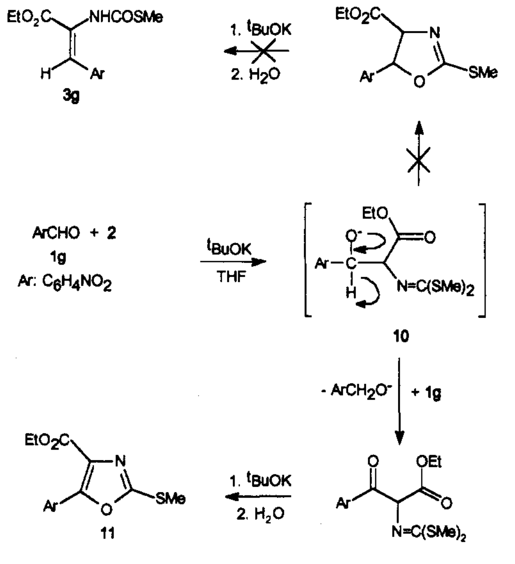
[14] 4-(Ethoxycarbonyl)-2-(methylthio)-5-(*p*-nitrophenyl)oxazole (**11**) (yield 50%) was obtained instead of ethyl (*Z*)-3-(*p*-nitrophenyl)-2-[[(methylthio)carbonyl]amino]acrylate (**3g**). The formation of **11** may be explained by reduction of *p*-nitrobenzaldehyde from intermediate **10** by means of a Cannizzaro reaction (see below), which becomes competitive with the general pathway to give acrylate derivative **3g**. Compound **11** was identified by elemental analysis and comparsion of its spectral data with other related compounds:[15] yellow solid, mp 114 °C (*n*-hexane); IR (KBr) 3100, 1710, 1600, 1570, 1520, 1500, 1220, 1080 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.43 (t, *J* = 7.2 Hz, 3H), 2.77 (s, 3H), 4.45 (q, *J* = 7.2 Hz, 2H), 8.24–8.33 (AA′XX′ system, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.2, 14.6, 61.9, 123.6, 128.6, 130.5, 132.4, 147.9, 153.6, 161.5, 162.2. Anal. Calcd. for $C_{13}H_{12}N_2O_5S$: C, 50.65; H, 3.89; N, 9.09. Found: C, 50.67; H, 3.85; N, 8.98.



Scheme 1

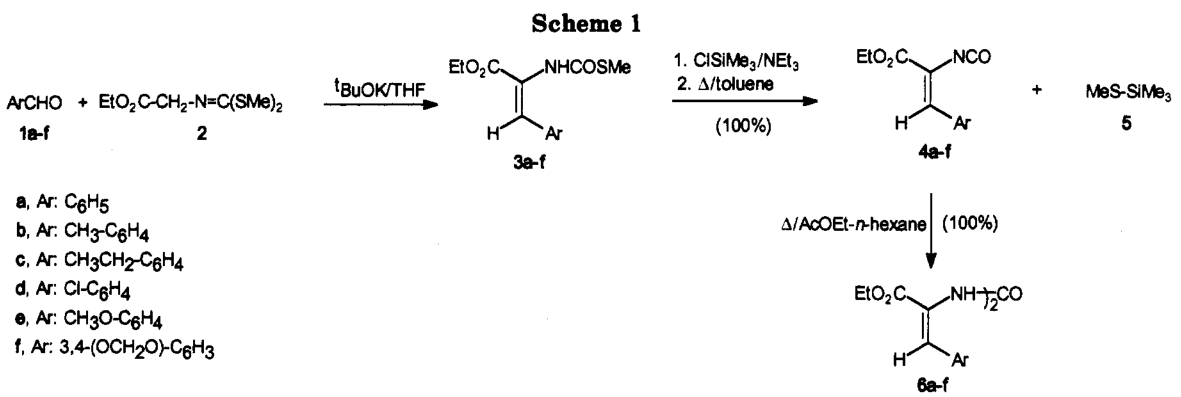
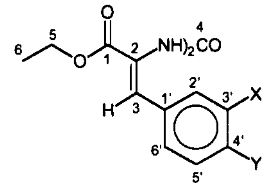


Table 2. Elemental Analyses and Physical and Spectral Data of 1,3-Bis[(*Z*)-2-aryl-1-(ethoxycarbonyl)vinyl]ureas 6a–f



product (formula)	mp, °C	anal.	IR (cm^{-1})[a]	NMR[b]
6a X = Y = H ($C_{23}H_{24}N_2O_5$)	190–191	calcd: C, 67.63; H, 5.92; N, 6.86 found: C, 67.43; H, 5.88; N, 6.83	3280, 1720, 1650	δ_H 1.24 (t, *J* = 7.2 Hz, 3H), 4.17 (q, *J* = 7.2 Hz, 2H), 7.07 (s, 1H), 7.35–7.48 (m, 3H), 7.60–7.63 (M, 2H), 8.24 (bs, 1H); δ_C 14.1 (C6), 60.9 (C5), 126.9 (C2), 128.5 (C3′,C5′), 129.1 (C4′), 129.4 (C1′), 129.7 (C2′,C6′), 133.8 (C3), 153.8 (C4), 165.4 (C1)
6b X = H; Y = Me ($C_{25}H_{28}N_2O_5$)	206–207	calcd: C, 68.79; H, 6.47; N, 6.42 found: C, 68.47; H, 6.49; N, 6.40	3270, 1710, 1650	δ_H 1.22 (t, *J* = 6.9 Hz, 3H), 2.33 (s, 3H), 4.15 (q, *J* = 6.9 Hz, 2H), 7.05 (s, 1H), 7.22–7.56 (AA′XX′ system, 4H), 8.11 (bs, 1H); δ_C 14.1(C6), 21.0 (*C*H$_3$-C4′), 60.8 (C5), 126.2 (C2), 129.2 (C3′,C5′), 129.8 (C2′,C6′), 131.0 (C3), 131.1 (C1′), 138.9 (C4′), 153.7 (C4), 165.6 (C1)
6c X = H; Y = Et ($C_{27}H_{32}N_2O_5$)	198–199	calcd: C, 69.81; H, 6.94; N, 6.03 found: C, 69.76; H, 6.98; N, 6.05	3280, 1720, 1650	δ_H 1.15 (t, *J* = 7.5 Hz, 3H), 1.19 (t, *J* = 7.2 Hz, 3H), 2.55 (q, *J* = 7.5 Hz, 2H), 4.14 (q, *J* = 7.2 Hz, 2H), 6.98 (s, 1H), 7.16–7.50 (AA′XX′ system, 4H), 8.02 (bs, 1H); δ_C 14.2 (C6), 15.5 (*C*H$_3$CH$_2$-C4′), 28.0 (CH$_3$*C*H$_2$-C4′), 60.9 (C5), 128.1(C2), 128.3 (C3′,C5′), 130.0 (C2′,C6′), 131.4 (C3), 132.1 (C1′), 145.2 (C4′), 153.8 (C4), 165.7 (C1)
6d X = H; Y = Cl ($C_{23}H_{22}Cl_2N_2O_5$)	190–192	calcd: C, 57.87; H, 4.65; N, 5.87 found: C, 57.74; H, 4.67; N, 5.88	3280, 1720, 1650	δ_H 1.23 (t, *J* = 7.0 Hz, 3H), 4.18 (q, *J* = 7.0 Hz, 2H), 7.08 (s, 1H), 7.45–7.67 (AA′XX′ system, 4H), 8.25 (bs, 1H); δ_C 13.9 (C6), 60.9 (C5), 127.2 (C2), 127.7 (C1′), 128.4 (C3′,C5′), 131.2 (C2′,C6′), 132.7 (C3), 133.3 (C4′), 153.1 (C4), 165.1 (C1)
6e X = H; Y = MeO ($C_{25}H_{28}N_2O_7$)	214–215	calcd: C, 64.09; H, 6.02; N, 5.98 found: C, 63.88; H, 6.03; N, 6.01	3260, 1710, 1650	δ_H 1.23 (t, *J* = 7.1 Hz, 3H), 3.80 (s, 3H), 4.16 (q, *J* = 7.1 Hz, 2H), 7.11 (s, 1H), 6.95–7.70 (AA′XX′ system, 4H), 8.05 (bs, 1H); δ_C 14.0 (C6), 55.1 (CH$_3$O), 60.5 (C5), 113.9 (C3′,C5′), 124.5 (C1′), 126.2 (C2), 129.5 (C3), 131.5 (C2′,C6′), 153.8 (C4), 159.8 (C4′), 165.5 (C1)
6f X, Y = OCH$_2$O ($C_{25}H_{24}N_2O_9$)	233–234	calcd: C, 60.48; H, 4.87; N, 5.64 found: C, 60.20; H, 4.91; N, 5.66	3260, 1720, 1640	δ_H 1.21 (t, *J* = 7.0 Hz, 3H), 4.15 (q, *J* = 7.0 Hz, 2H), 6.06 (s, 2H), 6.95 (d, *J* = 7.8 Hz, 1H), 7.07 (s, 1H), 7.20 (d, *J* = 7.8 Hz, 1H), 7.35 (bs, 1H), 8.04 (bs, 1H); δ_C 13.0 (C6), 60.6 (C5), 101.4 (OCH$_2$O), 108.3 (C5′), 108.8 (C2′), 125.6 (C6′), 127.6 (C2), 129.0 (C1′), 132.8 (C3), 147.4 (C3′), 148.0 (C4′), 154.1 (C4), 165.4 (C1)

[a] KBr pellet. [b] DMSO-d_6; ^{1}H: 300 MHz; ^{13}C: 75 MHz.

hexane–ethyl acetate (yield: 75%): mp 75 °C; IR (KBr) 3200, 1710, 1680 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.24 (t, *J* = 7.6 Hz, 3H), 1.35 (t, *J* = 7.2 Hz, 3H), 2.35 (s, 3H), 2.66 (q, *J* = 7.6 Hz, 2H), 4.30 (q, *J* = 7.2 Hz, 2H), 6.93 (bs, 1H), 7.16–7.54 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 12.4, 14.2, 15.1, 28.7, 61.7, 122.8, 128.2, 130.1, 130.5, 146.3, 165.0, 168.8. Anal. Calcd for $C_{15}H_{19}NO_3S$: C, 61.43; H, 6.48; N, 4.78. Found: C, 61.41; H, 6.43; N, 4.79.

Preparation and Pyrolysis of *N*-Silylated Carbamic Methylthio Esters. General Procedure. Triethylamine (0.906 mmol) was added to acrylate **3** (0.755 mmol) in toluene (4 mL). The solution was heated at reflux, and then TMSCl (0.906 mmol) was added dropwise. The reaction mixture was stirred and heated at reflux for an additional 2 h. After the reaction mixture cooled, the precipitate, triethylammonium chloride, was filtered off. The filtrate was evaporated in vacuo to give isocyanate **4** as the sole product in quantitative yield (TLC silica gel; hexane:ethyl acetate 80:20 v/v). All compounds displayed elemental analyses, IR, and NMR data consistent with the assigned structures (Table 1): (*Z*)-1-(ethoxycarbonyl)-2-phenylvinyl isocyanate (**4a**); (*Z*)-1-(ethoxycarbonyl)-2-*p*-tolylvinyl isocyanate (**4b**); (*Z*)-1-(ethoxycarbonyl)-2-(*p*-ethylphenyl)vinyl isocyanate (**4c**); (*Z*)-2-(*p*-chlorophenyl)-1-(ethoxycarbonyl)vinyl isocyanate (**4d**); (*Z*)-1-(ethoxycarbonyl)-2-(*p*-methoxyphenyl)vinyl isocyanate (**4e**); (*Z*)-1-(ethoxycarbonyl)-2-[(3,4-(methylenedioxy)phenyl]vinyl isocyanate (**4f**).

Urea Derivatization of 4a–f. General Procedure. (*Z*)-β-(Ethoxycarbonyl)styryl isocyanate **4** (0.5 mmol) was dissolved in dry ethyl acetate (5 mL). The solution was heated at reflux for 15 min, and then *n*-hexane (5 mL) was added. After the reaction mixture was cooled to rt, the precipitated product was filtered off and washed with *n*-hexane. A quantitative yield was obtained in all cases. Elemental analysis and spectral data were consistent with the assigned structures (Table 2): 1,3-bis[(*Z*)-1-(ethoxycarbonyl-2-phenylvinyl]urea (**6a**); 1,3-bis[(*Z*)-1-(eth-

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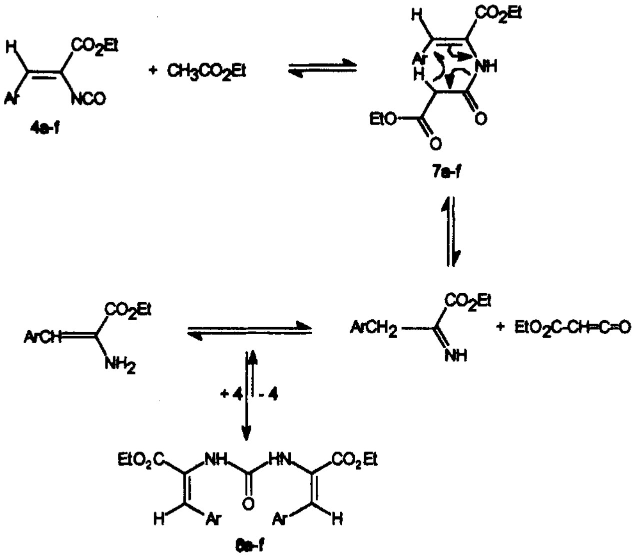
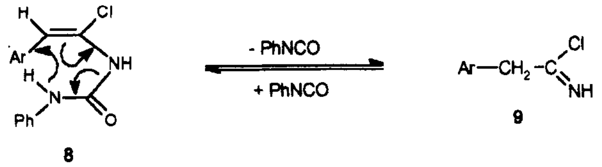
(15) Alvarez-Ibarra, C.; Mendoza, M.; Orellana, G.; Quiroga, M. L. *Synthesis* **1989**, *7*, 560.

Scheme 2



Scheme 3



oxycarbonyl)-2-*p*-tolylvinyl]urea (**6b**); 1,3-bis[(*Z*)-1-(ethoxycarbonyl)-2-(*p*-ethylphenyl)vinyl]urea (**6c**); 1,3-bis[(*Z*)-(2-(*p*-chlorophenyl)-1-(ethoxycarbonyl)vinyl]urea (**6d**); 1,3-bis[(*Z*)-1-(ethoxycarbonyl)-2-(*p*-methoxyphenyl)vinyl]urea (**6e**); 1,3-bis[(*Z*)-1-(ethoxycarbonyl)-2-[(3,4-(methylenedioxy)phenyl]vinyl]-urea (**6f**).

Control Experiments. Two separate control experiments were carried out, one in acetone and one in ethyl acetate. (*Z*)-1-(Ethoxycarbonyl)-2-*p*-tolylvinyl isocyanate (**4b**) (0.21 mmol) was dissolved in a mixture of dry acetone–hexane (1:1, 1 mL) or dry ethyl acetate–hexane (1:1, 1 mL). The solution was heated under argon atmosphere at reflux for 15 min and then cooled to rt. A white solid precipitated. A sample of the supernatant was removed with a syringe and added to a vial containing 0.5 mL of dry ethanol and a drop of perchloric acid. These samples were directly analyzed by GC-MS. The peaks at 4.5 and 8.1 min were unequivocally characterized as ethyl acetylacetate and diethyl malonate, respectively, by comparison of their retention times with standard samples. MS of selected peaks were successfully compared with the spectra of ethyl acetylacetate and diethyl malonate in the computer data base. The precipitated white solid was characterized as 1,3-*bis*[(*Z*)-1-(ethoxycarbonyl)-2-*p*-tolylvinyl]urea (**6b**).

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