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C-Aminoimidoylation and C-Thiocarbamoylation of Esters, Sulfones, and Ketones

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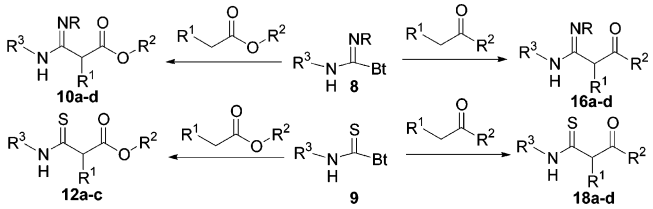
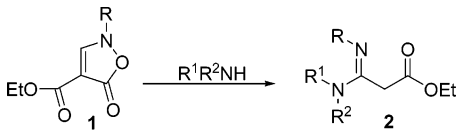


Esters, sulfones, and ketones were C-aminoimidoylated and C-thiocarbamoylated by benzotriazole-1-carboxamidines **8a**−**g** and 1-(alkyl-or-arylthiocarbamoyl)benzotriazoles **9a**−**i**, respectively. The present work represents the first systematic approach to these compound classes, the few previously known examples of which were obtained by diverse approaches.

Introduction

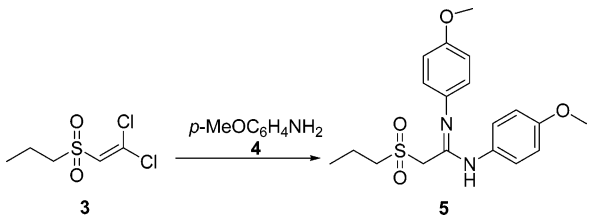
C-Aminoimidoylation and C-thiocarbamoylation are both relatively unexplored synthetically in contrast to the wide attention given to C-acylation[1a−c] and C-imidoylation.[2a−c] This reflects the wide availability of both acylating and imidoylating reagents and the lack of reagents for C-aminoimidoylation and C-thiocarbamoylation. Literature examples of compounds that could conceptually have been made by C-aminoimidoylation and C-thiocarbamoylation have generally been accessed by multistep synthesis.[3a−d]

Substructure searches disclosed no literature examples of the C-aminoimidoylation of esters; known examples of such known products **2** were prepared by nucleophilic attack of amines on isoxazolones **1** leading to ring opening and loss of CO_2.[4]



R, R^1= Ar, Alk
R^2= H, Alk

Likewise, no example of C-aminoimidoylation by C−C bond formation at a sulfone was identified; one possible product of such a reaction **5** was prepared by the reaction of an alkyl β,β-dichlorovinyl sulfone **3** with 4-methoxyaniline **4**.[5]



N,*N*′-Disubstituted ketene aminals **6** are used in many syntheses, especially in the construction of heterocyclic compounds.[3a] Structurally, ketene aminals are C-aminoimid-

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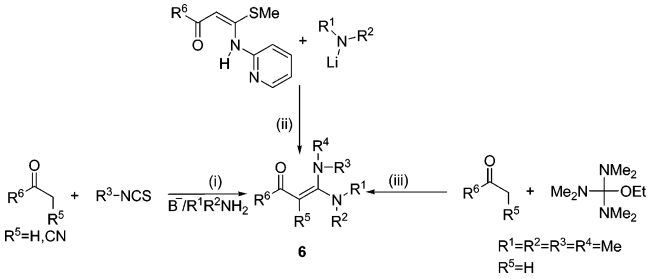
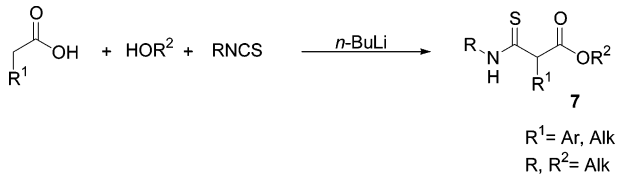
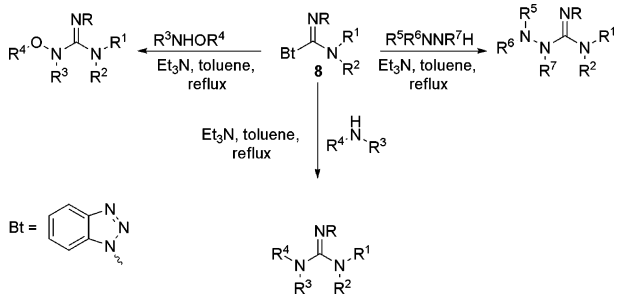
SCHEME 1. Literature Methods for the Preparation of Ketene Aminals 6



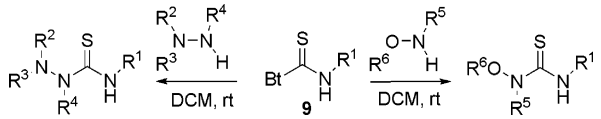
SCHEME 2. Preparation of C-Thiocarbamoylation Product 7



SCHEME 3. *N*-Aminoimidoylation with Benzotriazole-1-carboxamidines 8



SCHEME 4. Reactions of 1-(Alkyl/arylthiocarbamoyl)-benzotriazoles 9



oylated ketones that have been prepared (Scheme 1) starting from (i) activated methylene compounds and isothiocyanates,[3a] (ii) oxoketene *N*,*S*-acetals and lithiated secondary amines or aniline,[3b] or (iii) tris(dimethylamino)ethoxymethane and simple ketones.[3c,d] Methods i−iii (Scheme 1) each consist of multisteps with average overall yields of *ca*. 30%. Methods (i) and (ii) are related to C-aminoimidoylation but no such reaction of a ketone was located in a search of the literature.

Again, no direct C-thiocarbamoylation of an ester could be found. Potential ester C-thiocabamoylation products **7** were prepared from an isothiocyanate, a carboxylic acid and an alcohol in the presence of *n*-BuLi (Scheme 2).[3b−d]

Recently, we synthesized (i) 1,2,3-trisubstituted guanidines,[6] *N*-hydroxy-, and *N*-amino-guanidines[7] using novel benzotriazole-1-carboxamidine *N*-aminoimidoylating reagents (Scheme

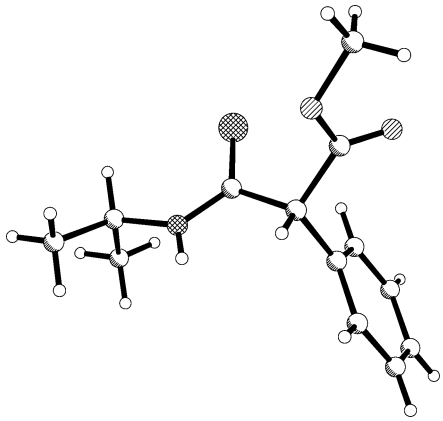
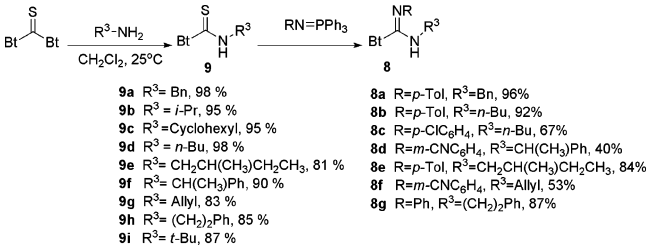


FIGURE 1. X-ray structure of methyl 3-(isopropylamino)-2-phenyl-3-thioxopropanoate **(12a)**.

SCHEME 5. Preparation of Reagents 8 and 9



3), and (ii) di- and trisubstituted thioureas,[8] *N*-hydroxythioureas, and thiosemicarbazides[9] using novel 1-(alkyl/arylthiocarbamoyl)benzotriazole thiocarbamoylating reagents (Scheme 4). In the present paper, we demonstrate that esters, sulfones, and ketones can be C-aminoimidoylated by benzotriazole-1-carboxamidines **8a**−**g** and C-thiocarbamoylated by 1-(alkyl/arylthiocarbamoyl)benzotriazoles **9a**−**i.** Our simple procedure comprises deprotonation of esters, sulfones, and ketones in the presence of a strong base, followed by nucleophilic substitution of the benzotriazolyl group in benzotriazole-1-carboxamidines **8a**−**g** or 1-(alkyl/arylthiocarbamoyl)benzotriazoles **9a**−**i.**

Results and Discussion

Preparation of Benzotriazole-1-carboxamidines 8a−g and 1-(Alkyl/aryl-thiocarbamoyl) Benzotriazoles 9a−i. Bis(benzotriazolyl)methanethione[10] and amines afforded 1-(alkyl-or-arylthiocarbamoyl)benzotriazoles **9a**−**i**[8], converted in turn by triphenylphosphine ylides into the benzotriazole-1-carboxamidines **8a**−**g** (Scheme 5).[6]

C-Aminoimidoylation and C-Thiocarbamoylation of Esters. Reactions of 2.0 equiv of ester enolates (from ester **11** with 2.5 equiv potassium tert-butoxide) with 1.0 equiv of benzotriazole-1-carboxamidines **8a**−**g** or 1-(alkyl-or-arylthiocarbamoyl)benzotriazoles **9a**−**i** afforded **10a**−**d** and **12a**−**c**, respectively; after limited optimization, yields of 20−63% were obtained (Scheme 6, Table 1). Elemental analysis, X-ray data, and NMR spectral data support the structural assignments. Different tautomeric structures are possible for the ester

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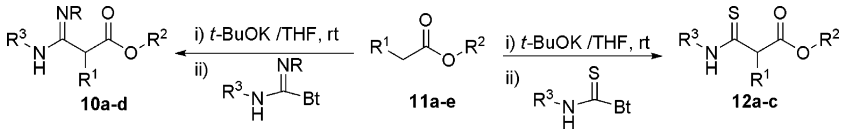
(10) Larsen, C.; Steliou, K.; Harpp, D. N. *J. Org. Chem.* **1978**, *43*, 337.

SCHEME 6. Preparation from Esters 11a−e of the C-Aminoimidoylation Products 10a−d and the C-Thiocarbamoylation Products 12a−c



SCHEME 7. Preparation from Sulfone 14 of C-Aminoimidoylation Product 13 and C-Thiocarbamoylation Product 15

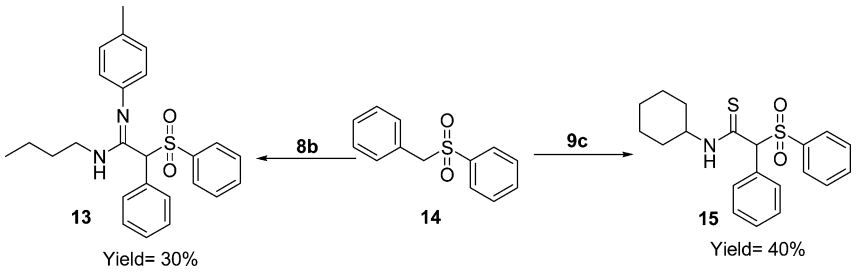


TABLE 1. C-Aminoimidoylation and C-Thiocarbamoylation of Esters 11a−e To Give 10a−d and 12a−c

ester	R^1	R^2	reagent	R^3	R	product	yield, %
11a	H	Me	**8a**	Bn	*p*-Tol	**10a**	63
11b	CO_2Et	Et	**8d**	$CH(CH_3)Ph$	*m*-CNC_6H_4	**10b**	24
11c	CO_2Me	Me	**8e**	$CH_2CH(CH_3)CH_2CH_3$	*p*-Tol	**10c**	51
11d	CN	Et	**8f**	Allyl	*m*-CNC_6H_4	**10d**	20
11e	Ph	Me	**9b**	*i*-Pr	−	**12a**	50
11c	CO_2Me	Me	**9f**	$CH(CH_3)Ph$	−	**12b**	27
11b	CO_2Et	Et	**9h**	$(CH_2)_2Ph$	−	**12c**	49

TABLE 2. C-Aminoimidoylation and C-Thiocarbamoylation of Ketones 17a−d To Give 16a−d and 18a−d

ketone	R^1	R^2	reagent	R^3	R	product	yield, %
17a	H	Ph	**8g**	$(CH_2)_2Ph$	Ph	**16a**	32
17b	H	2-Thienyl	**8b**	*n*-Bu	*p*-Tol	**16b**	27
17c	Me	Me	**8g**	$(CH_2)_2Ph$	Ph	**16c**	27
17a	H	Ph	**8c**	*n*-Bu	*p*-ClC_6H_4	**16d**	31
17a	H	Ph	**9d**	*n*-Bu	−	**18a**	50
17d	Bn	Ph	**9h**	$(CH_2)_2Ph$	−	**18b**	65
17b	H	2-Thienyl	**9d**	*n*-Bu	−	**18c**	51
17c	Me	Me	**9i**	*t*-Bu	−	**18d**	40

products; however, the X-ray data for compound **12a** shows that it exists as the CH rather than OH tautomer in the solid state (Figure 1). More experiments including 2D-NMR were utilized to verify the tautomeric forms of the compounds (as described later in this paper).

C-Aminoimidoylation and C-Thiocarbamoylation of Sulfones. The procedures just described for esters effected the C-aminoimidoylation and C-thiocarbamoylation of sulfone **14** in yields of only around 10%. However, stirring 2.0 equiv of sulfone **14** with 2.5 equiv of potassium *tert*-butoxide in THF at room temperature for 1 h followed by the addition of the corresponding benzotriazole reagent (**8b** or **9c**) afforded compounds **13** and **15** in yields of 30−40% (Scheme 7).

C-Aminoimidoylation and C-Thiocarbamoylation of Ketones. Reaction of enolates from ketones **17a−d** with **8** or **9** gave the C-aminoimidoylation and C-thiocarbamoylation products **16a−d** and **18a−d** (27−65% yields, after limited optimization, Table 2) during 0.5−4.0 h (Scheme 8) as monitored by TLC. For compounds **16a** and **18a−d**, 2D NMR correlation experiments were used to assign the ^1H and ^{13}C chemical shifts (described later in the paper).

Reactions of ketones with **9a** (R^3= Bn) afforded the isomeric oxazolinethiones **19** instead of the expected product (Scheme 9). Structures **19a−c** were verified by NMR and the structure

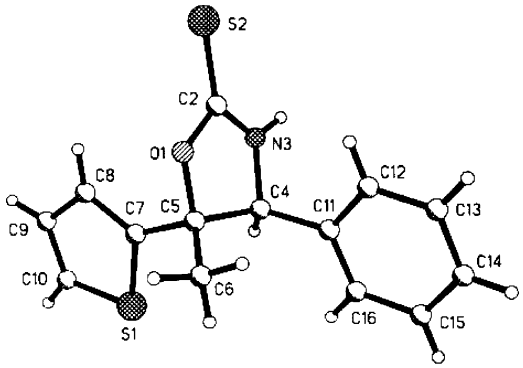


FIGURE 2. X-ray structure of 5-methyl-4-phenyl-5-(2-thienyl)-1,3-oxazolidine-2-thione (**19a**).

of **19a** was corroborated by X-ray crystallography (Figure 2). Literature reports the preparation of 2-thioxo-oxazolidines by cycloaddition of α-metalated alkyl isothiocyanates to carbonyl compounds.[11]

Compound Characterization and Tautomeric Structures. The tautomeric structure of a heterocyclic [or indeed any]

(11) Hoppe, D.; Follmann, R. *Chem. Ber.* **1976**, *109*, 3047.

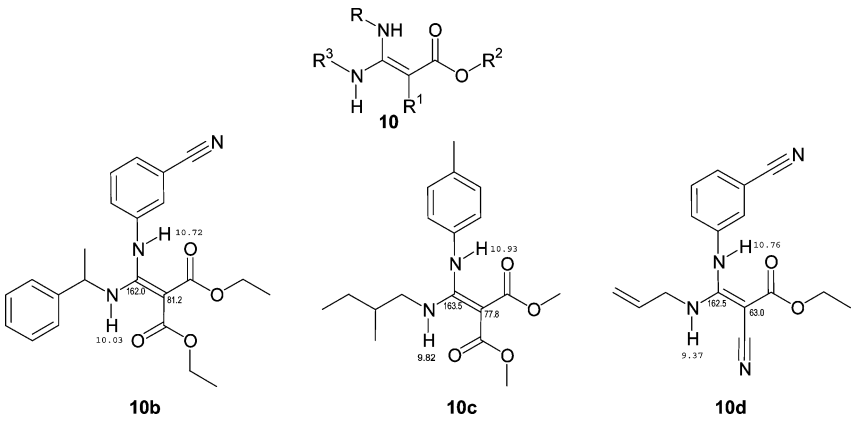


FIGURE 3. Relevant ^{1}H and ^{13}C chemical shifts in compounds **10b**−**d**.

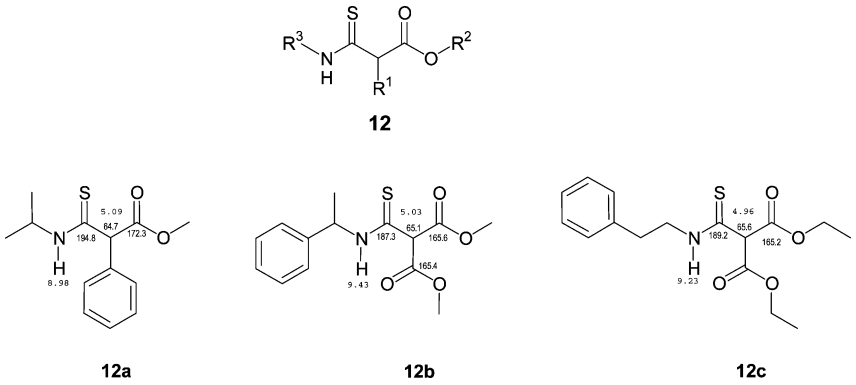
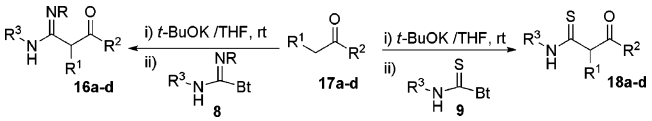
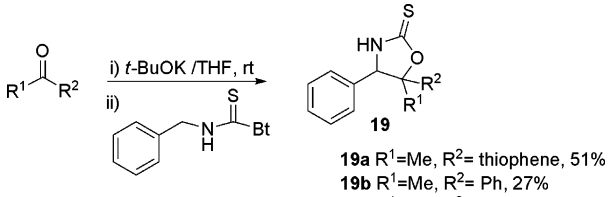


FIGURE 4. Relevant ^{1}H and ^{13}C chemical shifts in compounds **12a**−**c**.

SCHEME 8. Preparation from Ketones 17a−d of the C-Aminoimidoylation Products 16a−d and C-Thiocarbamoylation Products 18a−d



SCHEME 9. Formation of Thioxo-oxazolidines 19



compound can profoundly influence its physical properties [e.g., boiling point, solubility] and chemical properties [e.g., acid/base, electron distribution, reactivity]. It was therefore of interest to investigate the tautomeric structures of the parent compounds, and in particular, to know whether they exist in the enol or keto forms. On examination in chloroform-*d* at 25 °C, no keto tautomers were detected by NMR for any of the compounds **10b**−**d**. Coupling of one of the NH protons with the alpha protons on R^3 allowed assignment of the NH protons, and supported our conclusion that **10b**−**d** all are present in solution as the keto-enamine tautomers, as depicted in Figure 3.

In the chloroform-*d* solutions of **12a**−**c** at 25 °C, the only tautomers detected were the thiocarbonyl forms shown (Figure 4). The *alpha* protons in R^3 couple with the NH proton in all of these compounds. The difference in tautomerism between compounds **10** and compounds **12b**,**c** can be explained by the delocalization of the electrons from the electron-donor R^4N into the electron withdrawing ester groups.

Compounds **13** and **15** exist in chloroform-*d* solutions at 25 °C solely as the imino and thiocarbonyl forms, respectively (Figure 5). The alpha protons in R^3 couple with the NH proton in both compounds. Thus, the tautomeric structure of **13** differs from the compounds of structure **10**: although sulfone and ester groups are both electron-withdrawing, the electron-withdrawing ability of sulfones is mainly exerted via induction, whereas esters have considerable conjugative ability, which may explain the difference in tautomeric character.

Compound **16a** was present in chloroform-*d* solution as a mixture of two compounds in a 7:1 ratio both with the same hydrocarbon skeleton, as revealed by the gHMBC spectra. Exchange peaks in the NOESY spectrum between protons such as 5.43 with 5.35, 7.88 with 7.67, 7.03 with 6.97, 7.13 with 7.26, 2.89 with 3.00, and 3.49 with 3.60 indicated that these species were interconverting. The chemical shift of the carbonyl carbon in **16a** is closer to that expected for an aromatic ketone than for an enol. Furthermore, the chemical shift for the imidamide carbon is closer to that in compounds **10** than that seen in compound **13**. These chemical shifts suggest that both isomers of **16a** are keto-enamine forms. Of the exchange cross-peaks of 11.77, the largest is 4.76, indicating that the two isomers differ in the amine hydrogen facing the carbonyl group

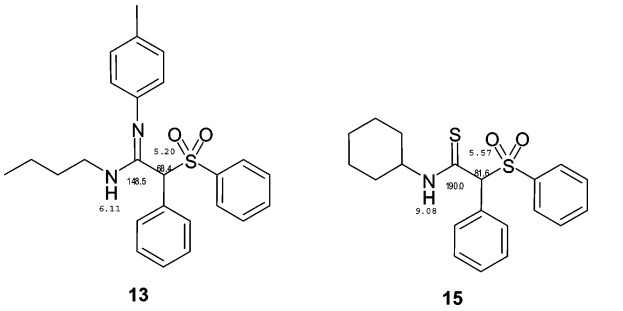


FIGURE 5. Relevant ^{1}H and ^{13}C chemical shifts in compounds **13** and **15**.

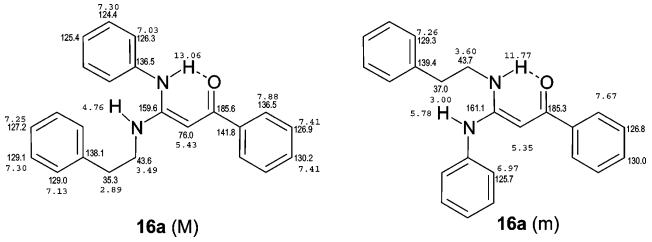


FIGURE 6. ^{1}H and ^{13}C chemical shifts for the Major (M) and minor (m) isomers of compound **16a**.

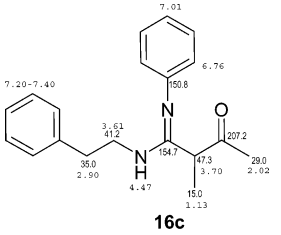


FIGURE 7. Relevant ^{1}H and ^{13}C chemical shifts in compound **16c**.

and involved in the hydrogen bond. In the major isomer of **16a**, NOE's between 5.43 and 3.49, 2.89, and between 4.76 and 7.03 demonstrate that in this isomer the aniline NH is involved in the hydrogen bond and that the alkyl group on the other nitrogen is anti to the aniline nitrogen, as depicted in Figure 6. The chemical shifts of the protons involved in the hydrogen bond agree with this assignment: in compounds **10c** and **10d**, the aniline hydrogen is more deshielded than the alkylamino one. For the minor isomer, the NOE's offered no information on the *syn*/*anti* geometry of the aniline group, because they were mainly transferred NOE's. It is reasonable however to assume the same geometry as in the major isomer. Exchange peaks between 5.43, 5.35, and all the four NH protons indicate that the keto tautomer is present in the equilibrium, although it was not detected in the proton spectra. Another transient species displays a signal at 13.26, in exchange with all of the exchangeable protons in both isomers.

Compounds **16b** and **16d** displayed equilibria similar to that for **16a**. The species with the aniline NH involved in hydrogen bonding is *ca*. 7 times more abundant than the other isomer. Compound **16c** is solely in the imidamide form in chloroform-*d* solution at 25 °C, as indicated by the coupling between the protons at 3.70 and 1.13 (Figure 7). The difference in tautomerism between **16c** and **16a**,**b**,**d**, may be explained by the steric

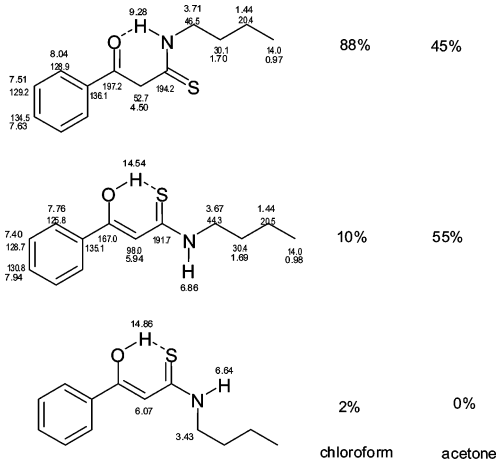


FIGURE 8. ^{1}H and ^{13}C chemical shifts and the tautomers/rotamers for compound **18a**.

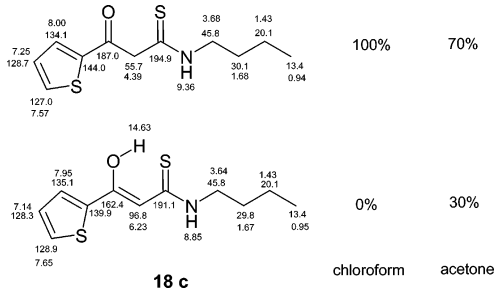


FIGURE 9. ^{1}H and ^{13}C chemical shifts for the tautomers of compound **18c** in acetone-*d6*.

hindrance in the enol of **16c**, where the two methyls, R^1 and R^2 have to be *syn*-periplanar.

Compound **18a** in chloroform-*d* solution at 25 °C displays an equilibrium between three species, in a ratio 44:5:1. The interconversion of these species was demonstrated by exchange peaks in the NOESY spectrum. The major compound is the keto tautomer, whereas the other two are enol tautomers, as demonstrated by the chemical shift of the carbon bearing the oxygen atom. The significant deshielding of the NH proton in the keto form as compared to the enol forms suggests a hydrogen bond in the keto form, as in Figure 8. The spectra were repeated in acetone-*d6*, a hydrogen bond acceptor that would compete with the carbonyl group of **18a** for hydrogen bonding. The chemical shift of the NH proton in the enol moved downfield by 2 ppm, while for the keto form the change was only 0.07 ppm, demonstrating intramolecular hydrogen bonding in the ketone. The two enol species have to be the *Z* and *E* isomers resulting from rotation about the C−N bond in the thioamide. Thioamides are known to prefer the *Z* configuration and this is the configuration in the intramolecular hydrogen-bonded keto species. The similarity of the proton chemical shifts at the NCH_2 in the ketone (3.71 ppm) and in the major enol form (3.67 ppm) indicates that the latter is also in the *Z* configuration. The *E* configuration is present in the enol tautomer and not in the ketone because it strengthens the resonance-assisted hydrogen bonding (RAHB) in the enol. This is demonstrated by the higher chemical shift value of the proton involved in the RAHB in the minor *E* enol form (14.86 ppm) as compared to the *Z* enol (14.54 ppm).

Compound **18c** in chloroform-*d* solution at 25 °C occurs solely as the keto tautomer. The chemical shift of the NH proton is 9.22 ppm, indicating an intramolecular hydrogen bond. In acetone-*d6* solution, both tautomers are present, and the keto:enol ratio is 1:0.44 (Figure 9). For compound **18a** also, the proportion of the enol was larger in acetone (keto:enol = 45:55) than in chloroform (keto:enol = 88:12). As with the case of **18a**, no *E* rotamer of the enol form was detected in acetone solution.

Compounds **18b** and **18d** in chloroform-*d* solution at 25 °C display the keto tautomer only. The enol tautomer is higher in energy when R^1 is not H, due to steric repulsion between R^1 and R^2, which have to be *syn*-periplanar in the enol.

Conclusion

Successful C-aminoimidoylation and C-thiocarbamoylation of esters, sulfones, and ketones were achieved in 40% average yield under mild reaction conditions. This method provides easy access to interesting classes of compounds for further transformations.

Experimental Section

General Procedure for the Preparation of Compounds 10a−d, 12a−c, 13, and 15. To a solution of the desired ester or sulfone (2.0 mmol) in THF (15 mL), was added potassium *t*-butoxide (2.5 mmol). After stirring the mixture for 30 min, 1.0 mmol of the desired reagent **8** or **9** as added to the reaction mixture. The progress of the reaction was monitored by TLC. Upon completion, water (20 mL) was added to quench the reaction followed by extraction with dichloromethane (3 × 30 mL). The combined extracts were dried over magnesium sulfate and the solvent removed under vacuum. The crude mixture was purified by gradient column chromatography over silica gel (EtOAc-hexanes) to give the desired products in moderate yields.

Methyl (Z)-3-(Benzylamino)-3-(4-toluidino)-2-propenoate (10a). Colorless oil (63%); ^{1}H NMR ($CDCl_3$) δ 7.33−7.18 (m, 5H), 7.07 (d, J = 8.2 Hz, 2H), 6.79 (d, J = 8.2 Hz, 2H), 4.28 (br s, 2H), 3.85 (s, 3H), 2.27 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 158.6, 153.4, 145.7, 139.4, 131.7, 130.1, 128.5, 127.1, 126.9, 122.6, 67.6, 53.6, 45.4, 20.7. Anal. Calcd for $C_{18}H_{20}N_2O_2$: C, 72.95; H, 6.80; N, 9.45. Found: C, 73.18; H, 6.46; N, 9.84.

Methyl 3-(Isopropylamino)-2-phenyl-3-thioxopropanoate (12a). Recrystallized from EtOAc-hexanes to give white microcrystals (20%); mp 105.6−107.4 °C; ^{1}H NMR ($CDCl_3$) δ 8.98 (br s, 1H), 7.38−7.40 (m, 5H), 5.09 (s, 1H), 4.62−4.55 (m, 1H), 3.71 (s, 3H), 1.27 (d, J = 6.6 Hz, 3H), 1.21 (d, J = 6.6 Hz, 3H); ^{13}C NMR δ ($CDCl_3$) 194.8, 172.3, 135.2, 129.2, 128.5, 127.4, 64.7, 52.9, 47.6, 21.0. Anal. Calcd for $C_{13}H_{17}NO_2S$: C, 62.12; H, 6.82; N, 5.57. Found: C, 61.89; H, 6.65; N, 5.48.

Crystal data for 12a: $C_{13}H_{17}NO_2S$, MW 251.34, orthorhombic, space group $P2_12_12_1$, a = 8.1386(3), b = 10.7325(4), c = 15.5997(6) Å, V = 1362.60(9) Å^3, $F(000)$ = 536, Z = 4, T = −180 °C, μ (Mo Kα) = 0.228 mm^{-1}, D_{calcd} = 1.225 g.cm^{-3}, $2\theta_{max}$ 61° (CCD area detector, Mo Kα radiation), GOF = 1.08, w$R(F^2)$ = 0.067 (all 4167 data), R = 0.024 (4105 data with $I > 2\sigma I$).

***N*-Butyl-*N′*-(4-methylphenyl)-2-phenyl-2-(phenylsulfonyl)-ethanimidamide (13).** Recrystallized from EtOAc-hexanes to give white microcrystals (30%); mp 117.6−119.2 °C; ^{1}H NMR δ ($CDCl_3$) 7.66 (t, J = 8.4 Hz, 3H), 7.51 (t, J = 7.1 Hz, 2H), 7.53−7.35 (m, 1H), 7.31−7.30 (m, 7H), 6.92 (d, J = 7.8 Hz, 2H), 6.11 (s, 1H), 6.11 (d, J = 8.1 Hz, 2H), 5.20 (s, 1H), 3.39−3.36 (m, 2H), 1.73−1.67 (m, 2H), 1.52−1.45 (m, 2H), 1.00 (t, J = 7.4 Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 148.5, 146.5, 137.4, 134.2, 131.8, 130.8, 130.1, 129.4, 129.1, 128.9, 128.8, 128.7, 121.8, 68.4, 41.4, 31.0, 20.8, 20.4, 13.9. Anal. Calcd for $C_{25}H_{28}N_2O_2S$: C, 71.40; H, 6.71; N, 6.66. Found: C, 71.55; H, 6.96; N, 6.52.

***N*-Cyclohexyl-2-phenyl-2-(phenylsulfonyl)ethanethioamide (15).** Recrystallized from EtOAc-hexanes to give white microcrystals (40%); mp 148.9−149.7 °C; ^{1}H NMR ($CDCl_3$) δ 9.08 (br s, 1H), 7.76−7.73 (m, 2H), 7.67−7.62 (m, 1H), 7.52−7.47 (m, 2H), 7.41−7.30 (m, 5H), 5.57 (s, 1H), 4.38−4.35 (m, 1H), 2.06 (br s, 2H), 1.78−1.65 (m, 2H), 1.58 (br s, 3H), 1.50−1.34 (m, 3H); ^{13}C NMR ($CDCl_3$) δ 190.0, 137.2, 134.5, 129.7, 129.3, 129.2, 129.0, 128.7, 81.7, 54.8, 31.1, 30.8, 25.4, 24.4. Anal. Calcd for $C_{20}H_{23}NO_2S_2$: C, 64.31; H, 6.21; N, 3.75. Found: C, 63.96; H, 6.25; N, 3.62.

General Procedure for the Preparation of Compounds 16a−d and 18a−d. To a solution of the desired ketone (2.0 mmol) in THF (20 mL) was added 2.5 mmol of potassium *t*-butoxide, followed by 1.0 mmol of the appropriate reagent **8** or **9** (Scheme 8). The mixture was stirred at room temperature until full conversion of starting materials (0.5−4.0 h). The crude was then evaporated under reduced pressure, washed with water (3 × 30 mL), and finally extracted with diethyl ether (3 × 30 mL). Evaporation of the organic fraction followed by flash column chromatography on silica gel afforded **16a−d** or **18a−d** in moderate yields.

3-Oxo-*N*-phenethyl-*N′*,3-diphenylpropanimidamide (Mixture of Tautomers) (16a). Recrystallized from EtOAc-hexanes to give white microcrystals (32%); mp 156.2−157.7 °C. In $CDCl_3$ solution **16a** exists as **16a** (M), 87% and **16a** (m), 13%. ^{1}H NMR ($CDCl_3$) δ 13.06 (s, 0.87H, M) 11.77 (s, 0.13H, m), 7.88 (d, J = 7.1 Hz, 1.74H, M), 7.67 (d, J = 7.1 Hz, 0.26H, m), 7.40−7.41 (m, 2.61H, M), 7.34−7.24 (m, 6.00H, M + m), 7.25 (t, J = 7.6 Hz, 0.87H, M), 7.13 (d, J = 7.6 Hz, 1.74H, M), 7.03 (d, J = 6.6 Hz, 1.74H, M), 6.97 (d, J = 6.6 Hz, 0.26H, m), 5.78 (s, 0.13H, m), 5.43 (s, 0.87H, M), 5.35 (s, 0.13H, m), 4.76 (br s, 0.87H, M), 3.60 (q, J = 5.6 Hz, 0.26H, m), 3.49 (q, J = 5.6 Hz, 1.74H, M), 3.00 (t, J = 6.9 Hz, 0.26H, m), 2.89 (t, J = 6.9 Hz, 1.74H, M); ^{13}C NMR ($CDCl_3$) δ 185.6, 185.3, 161.1, 159.6, 141.8, 139.4, 138.1, 136.5, 136.5, 130.2, 130.0, 129.3, 129.1, 129.0, 127.2, 126.9, 126.8, 126.3, 125.7, 125.4, 124.4, 76.0, 43.7, 43.6, 37.0, 35.3. Anal. Calcd for $C_{23}H_{24}N_2O_2$: C, 76.64; H, 6.71; N, 7.77. Found: C, 76.61; H, 6.32; N, 7.64.

***N*-Butyl-3-oxo-3-phenylpropanethioamide (Mixture of Tautomers) (18a).** Brown oil (50%). In $CDCl_3$ solution **18a** exists as a major isomer, **18a** (M), 88% and two minor isomers, **18a** (m), 10% and **18a** (m′), 2%. ^{1}H NMR ($CDCl_3$) δ 14.86 (br s, 0.02H, m′), 14.54 (br s, 0.10H, m), 9.28 (br s, 0.88H, M), 8.04 (d, J = 7.3 Hz, 1.76H, M), 7.94 (d, J = 7.3 Hz, 0.04H, m), 7.76 (d, J = 7.3 Hz, 0.20H, m), 7.63 (d, J = 7.5 Hz, 0.88H, M), 7.51 (t, J = 7.5 Hz, 1.76H, M), 7.46−7.38 (m, 0.35H, m + m′), 6.07 (s, 0.02H, m′), 5.94 (s, 0.10H, m), 4.50 (s, 1.76H, M), 3.73−3.65 (m, 1.96H, M + m), 1.73−1.63 (m, 1.96H, M + m), 1.48−1.40 (m, 1.96H, M + m), 0.97 (t, J = 7.3 Hz, 2.94H, M + m); ^{13}C NMR ($CDCl_3$) δ 197.2, 194.2, 191.7, 167.0, 136.1, 135.1, 134.5, 130.8, 129.2, 128.9, 128.7, 125.8, 98.0, 52.7, 46.5, 44.3, 30.4, 30.1, 20.5, 20.4, 14.0. Anal. Calcd for $C_{13}H_{17}NOS$: C, 66.35; H, 7.28; N, 5.95. Found: C, 66.62; H, 7.41; N, 5.52.

General Procedure for the Preparation of Compounds 19a−c. To a solution of the desired ketone (2.0 mmol) in THF (20 mL) was added potassium *t*-butoxide (2.5 mmol). After stirring the mixture for 30 min, 1.0 mmol of *N*-benzyl-1H-benzo[d][1,2,3]-triazole-1-carbothioamide **9** was added to the reaction mixture. The mixture was stirred at room temperature for 4.0 h. The reaction was then stopped and the solvent evaporated under vacuum. The crude product was washed with water and then extracted with diethyl ether. Evaporation of the organic fraction followed by flash column chromatography on basic alumina afforded **19a−c** in moderate yields.

5-Methyl-4-phenyl-5-(2-thienyl)-1,3-oxazolidine-2-thione (19a). Recrystallized from EtOAc-hexanes to give white microcrystals (51%); mp 157.3−158.8 °C; ^{1}H NMR ($CDCl_3$) δ 7.39−7.37 (m, 1H), 7.27−7.26 (m, 2H), 7.15−7.14 (m, 1H), 7.06−7.03 (m, 2H), 5.23 (s, 1H), 1.43 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 188.7, 145.9, 134.3,

129.4, 129.1, 127.2, 126.8, 126.1, 124.7, 91.7, 70.8, 23.8. Anal. Calcd. for $C_{14}H_{13}NOS_2$: C, 61.06; H, 4.76; N, 5.09. Found: C, 61.40; H, 4.78; N, 5.09.

Crystal Data for 19a. $C_{14}H_{13}NOS_2$, MW 275.37, monoclinic, space group *P*2/n, $a = 14.3023(4)$, $b = 5.7750(2)$, $c = 17.5354(5)$ Å, $\beta = 112.690(1)°$, $V = 1336.26(7)$ Å^3, $F(000) = 576$, $Z = 4$, $T = -180$ °C, μ (Mo Kα) = 0.385 mm^{-1}, $D_{calcd} = 1.369$ g.cm^{-3}, $2\theta_{max}$ 55° (CCD area detector, Mo Kα radiation), GOF = 1.05, w$R(F^2) = 0.076$ (all 3065 data), $R = 0.028$ (2981 data with $I > 2\sigma I$).

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Supporting Information Available: Characterization data for compounds (**10b**−**d**), (**12b**−**c**), (**16b**−**d**), (**18b**−**d**), and (**19b**−**c**) and full details of the X-ray structure determinations as CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

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