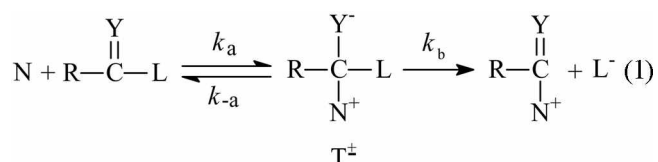# Kinetics and Mechanism of the Aminolysis of Aryl Dithiocyclopentanecarboxylates in Acetonitrile

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The two common mechanisms for the aminolysis of carbonyl. **I**, and thiocarbonyl. **II**, esters and carbonates are (i) concerted through a tetrahedral transition state (TS) and (ii) stepwise through a tetrahedral intermediate.[1] The latter reaction pathway can be described by eq. (1), where R and L are nonleaving and leaving groups. and N represents an amine and Y is either O (**I**) or S (**II**). A nonlinear Brönsted

$$N + R-\underset{\underset{T^{\pm}}{\overset{\|}{C}}-L}{\overset{\overset{Y}{\|}}{}} \underset{k_{-a}}{\overset{k_a}{\rightleftharpoons}} R-\underset{\underset{N^+}{\overset{|}{|}}}{\overset{\overset{Y^-}{|}}{C}}-L \xrightarrow{k_b} R-\underset{\underset{N^+}{\overset{|}{|}}}{\overset{\overset{Y}{\|}}{C}} + L^- \quad (1)$$

plot results from a change in the rate-determining step, from that of k_b at low amine basicity (with $\beta_{nuc} \geq 0.8$) to that of k_a at high amine basicity (with $\beta_{nuc} \leq 0.3$). Applying the steady-state condition to $T^{\pm}$ in eq. (1), the equation $k_N = k_a k_b /(k_{-a} + k_b) \cong (k_a/k_{-a}) \times k_b = K \cdot k_b$ is obtained. and this accounts for the change in the rate-determining step at $pK_a°$ where $k_{-a} = k_b$ applies. The aminolysis mechanisms naturally depend on Y, R, L, N in eq. (1) and solvent. Fixing L (= SC_6H_4Z) and solvent (acetonitrile), we recently found interesting mechanistic changeover due to changes in Y (O or S)[2]. N (benzylamines or anilines)[2-3] and R (CH_3, $C_6H_5CH_2$. C_6H_5 or C_2H_5O).[2-5] For example. change of Y from O to S resulted in lowering of $pK_a°$ for R = CH_3 and C_6H_5 so that the rate-limiting step of the aminolysis for carbonyl esters. **I**. with benzylamines[2a,b] changed from expulsion of thiolate anion. ArS⁻. from $T^{\pm}$ (with $\beta_{nuc} = \beta_X = 1.36$ and 1.86, and $\rho_{XZ} > 0$) to formation of $T^{\pm}$ (with $\beta_X = 0.55$ and 0.63 and $\rho_{XZ} > 0$) for thiocarbonyl esters,[2c,d] **II**. The aminolysis of all the carbonyl (**I**) series except for R = C_2H_5O (concerted. with $\rho_{XZ} < 0$) proceeds through the stepwise path with rate-limiting expulsion of the leaving group (with $\beta_X = 1.36-2.11$ and $\rho_{XZ} > 0$).

Other criteria for this mechanistic change are the sign reversal of the cross-interaction constant.[6] ρ_{XZ} in eqs. (2) where X and Z denote substituents in the nucleophile (amine) and leaving group respectively. from positive

$$\log (k_{XZ}/k_{HH}) = \rho_X \sigma_X + \rho_Z \sigma_Z + \rho_{XZ} \sigma_X \sigma_Z \quad (2a)$$

$$\rho_{XZ} = \partial \rho_X / \partial \sigma_Z = \partial \rho_Z / \partial \sigma_X \quad (2b)$$

($\rho_{XZ} > 0$) to negative at $pK_a°$ as the amine basicity is

increased. and from adherence to failure of the reactivity-selectivity principle (RSP).[6]

The aminolysis of dithio esters and carbonates. **II**. has been studied in aqueous and acetonitrile solutions.[5] An important advantage of using acetonitrile medium is that there are no complications arising from a kinetically important proton transfer from $T^{\pm}$ to the amine.

As an extension of our work on the aminolysis of dithio esters in acetonitrile. we now examine the reactions of anilines (ANs) with aryl dithiocyclopentanecarboxylates at 10.0 °C. eq. (3). We are interested in the effects of the acyl group. R. and the amines on the mechanism, especially on the sign and magnitude of the cross-interaction constant, ρ_{XZ} in eqs. (2).

$$2 XC_6H_4NH_2 + \underset{}{\overset{}{\bigcirc}}\!\!-\!\!\overset{\overset{S}{\|}}{C}-SC_6H_4Z \xrightarrow[10.0°C]{MeCN} \quad (3)$$

$$\underset{}{\overset{}{\bigcirc}}\!\!-\!\!\overset{\overset{S}{\|}}{C}NHC_6H_4X + XC_6H_4NH_3^+ + ZC_6H_4S^-$$
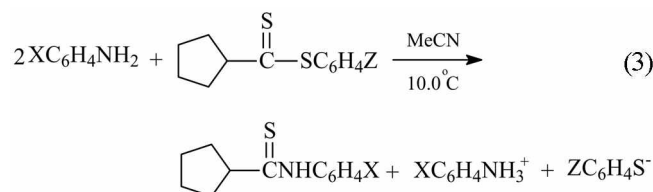
Results and Discussion

The reactions studied in this work followed the rate law described by eqs. (4) and (5). where S and N represent the substrate and nucleophile. aniline. and k_N is the rate constant for aminolysis of the substrate. The values of k_N were

$$\text{Rate} = k_{obs} [S] \quad (4)$$

$$k_{obs} = k_N [N] \quad (5)$$

obtained as the slopes of plots of k_{obs} against [N]. and are summarized in Tables 1 for aryl dithiocyclopentanecarboxylates. In Table 1. the selectivity parameters. ρ_X. β_X. ρ_Z. β_Z and ρ_{XZ}. are also shown. In the determination of Brönsted coefficients. structurally similar amines are known to change in parallel with the pK_a (H_2O) values[5a,7] so that the β_X (β_{nuc}) values are considered reliable. Although the absolute β_Z values may not be reliable. the comparison of β_Z values for different series of substrates is justified since we have determined the β_Z values in the same reaction medium. acetonitrile. Relatively large magnitudes of ρ_X and ρ_Z values for the aminolysis seems to support a stepwise mechanism

Table 1. The Second Order Rate Constants, $k_N \times 10^3$ dm^3 mol^{-1} s^{-1} for the Reactions of Z-Aryl Dithiocyclopentanecarboxylates with X-Anilines in Acetonitrile at 10.0 °C

| X | Z | | | | $\rho_Z{}^a$ | $\beta_Z{}^b$ |
	p-Me	H	*p*-Cl	*p*-Br		
p-OMe	11.4^c	22.1	155	260	3.42 ± 0.07	−1.41 ± 0.01
	7.78			182		
	5.36^d			125		
p-Me	4.42	14.7	108	129	3.03 ± 0.06	−1.50 ± 0.03
H	2.24	7.59	63.5	77.9	3.82 ± 0.07	−1.57 ± 0.02
p-Cl	0.708	2.94	30.1	40.8	4.31 ± 0.08	−1.76 ± 0.04
m-Cl	0.778	2.29	24.0	49.7	4.40 ± 0.09	−1.78 ± 0.04
	0.537			34.8		
	0.365			24.0		
$\rho_X{}^e$	−2.19 ± 0.06	−1.87 ± 0.05	−1.53 ± 0.04	−1.37 ± 0.03	$\rho_{XZ}{}^f$ =	1.87 ± 0.07
$\beta_X{}^g$	0.76 ± 0.04	0.65 ± 0.02	0.53 ± 0.02	0.47 ± 0.02		

^{a}The σ values were taken from C. Hansch, A. Leo, and R. W. Taft. *Chem. Rev.* **1991**, *91*, 165. Correlation oefficients were better than 0.995 in all cases. ^{b}The pKa values were taken from ed., J. Bukingham, *Dictionary of Organic Chemistry*, Chapman and Hall, New York, 1982, 5th, ed. Z=p-Br was excluded from the Brönsted plot for β_Z due to an unreliable pKa values. Correlation coefficients were better than 0.998 in all cases. ^{c}At 20 °C. ^{d}At 0.0 °C. ^{e}The source of σ is the same as for footnote a. Correlation coefficients were better than 0.995 in all cases. ^{f}Correlation coefficients was 0.996. ^{g}The pKa values were taken from: *Introduction to Organic Chemistry*. A. Streitwiser. Jr and C. h. Heathcock, Third Edition. **1989**, p 693. Macmillan Publishing Co., New York. Correlation coefficients were better than 0.997 in all cases.

Table 2. Rates (k_N/dm^3 mol^{-1} s^{-1}) and Selectivity Parameters (ρ_X, β_X, ρ_Z, β_Z, and ρ_{XZ}) for the Aminolysis of Dithioesters [RC(=S)SC$_6$H$_4$Z] with Anilines (XC$_6$H$_4$NH$_2$) in Acetonitrile

Entry	R	$k_N{}^a$	$\rho_X{}^b$	$\beta_X{}^b$	$\rho_Z{}^c$	$\beta_Z{}^c$	$\rho_{XZ}{}^d$	Ref.
1	CH$_3$	9.46 × 10^{-1}(50.0 °C)	−3.05	0.84	1.90	−0.81	0.58	2d
2	Cyclopentyl	7.59 × 10^{-3}(10.0 °C)	−1.87	0.65	3.82	−1.57	1.87	This work
3	C$_6$H$_5$CH$_2$	2.76 × 10^{-1}(45.0 °C)	−2.64	0.93	2.72	−1.10	1.41	3b
4	C$_6$H$_5$	2.85 × 10^{-3}(55.0 °C)	−2.86	1.03	2.26	−0.76	0.60	3a
5	C$_2$H$_5$O	1.71 × 10^{-2}(30.0 °C)	−1.46	0.54	0.45	−0.19	−0.56	4b

^{a}For X = Y = Z = H. ^{b}for Z = H. ^{c}For X = H. ^{d}For Y = H when Y is varied.

with rate limiting expulsion of the aryl thiolate group. In order to facilitate comparisons of rates and selectivity parameters between different substrates, (for different R groups), we have summarized them in Table 2. First of all, the aninolysis of *O*-ethyl *S*-aryl dithiocarbonates[4b] (R = C$_2$H$_5$O) has been reported to proceed concertedly based on (i) small magnitude of β_X (= 0.5) and β_Z (= −0.2) values relative to those reacting stepwise with large β_X (≥ 0.7) and −β_Z (≤ −0.8)[1.8] and (ii) negative ρ_{XZ} (< 0).[6c] For the rest of Rs (entries 1-4), the same mechanism applies with positive ρ_{XZ}, large magnitude of β_X and β_Z, and adherence to the reactivity-selectivity principle (RSP).[6,9] *i.e.*, rate-limiting expulsion of thiolate anion (ArS$^-$) leaving group from the tetrahedral intermediate, T$^\pm$. Reference to Table 2 reveals that the rate is the fastest (k_N is the greatest) with R = c-C$_5$H$_9$ among the four stepwise reaction series (entries 1-4). Albeit exact comparison is difficult due to the k_N values determined at different temperatures, approximate rate order is R = c-C$_5$H$_9$ (σ^* = −0.15) > CH$_3$ (0.0) > C$_6$H$_4$CH$_2$ (+0.22) > C$_6$H$_5$ (+0.60) which is the order of decreasing electron donating ability of the R group represented by the Taft σ^* scale[10] as shown in the parenthesis. This is quite reasonable in view of the rate-limiting expulsion of ArS$^-$ group from T$^-$, since in the tetrahedral structure only the inductive effect is expected to apply and the greater the electron donation by R, the greater will be the leaving ability of ArS$^-$ group (k_b). If the electronic effect of R were predominant in the bond formation

step (k_a). then the rate sequence should have been in the reverse order since a stronger electron acceptor R will lead to a stronger positive charge on the carbonyl carbon in the substrate.

An important aspect we note in Tables 2 is that the magnitude of ρ_{XZ} is unusually large (ρ_{XZ} = 1.87) for R = c-C$_5$H$_9$ (entry 2). The size of ρ_{XZ} is considered to represent the intensity of interaction in the TS[6] between the two substituents in the nucleophile (X) and leaving group (Z). and hence the larger the ρ_{XZ}, the stronger is the interaction. *i.e.*, the closer is the two fragments, the nucleophile and leaving group, in the TS.

The kinetic isotope effects involving deuterated amine nucleophile (XC$_6$H$_4$ND$_2$). k_H/k_D, have been determined[6b] in acetonitrile as shown in Table 3. We note that the k_H/k_D values are significantly greater than unity so that constitute primary kinetic isotope effects. The amine proton shift is implicated by these greater than unity k_H/k_D values.[6b] Thus we propose that deprotonation of an amine hydrogen takes place concurrently with the expulsion of the thiophenolate anion, k_b, as shown in Scheme 1. In the proposed TS structure. the leaving group departure is assisted by partial protonation and therefore the difficulty in forming C=S bond may be partially alleviated. This could explain the relatively insignificant effect of substitution of S$^-$ for O$^-$ discussed. Since the positive ρ_{XZ} should require a greater degree of leaving group departure ($\delta\rho_Z$ > 0) and a greater degree of

Table 3. The Secondary Kinetic Isotope Effects for the Reactions of Z-Aryl Dithiocyclopentanecarboxylates with Deuterated X-Anilines in Acetonitrile at 10.0 °C

X	Z	$k_H \times 10^3 (M^{-1}s^{-1})$	$k_D \times 10^3 (M^{-1}s^{-1})$	k_H/k_D
p-OMe	p-Me	7.78(±0.05)	4.52(±0.04)	1.72 ± 0.02^a
p-OMe	H	22.1(±0.30)	13.8(±0.12)	1.60 ± 0.02
p-OMe	p-Cl	155(±4.00)	106(±2.55)	1.45 ± 0.04
P-OMe	p-Br	182(±4.80)	142(±3.25)	1.28 ± 0.03
p-Cl	p-Me	0.708(±0.01)	0.418(±0.008)	1.69 ± 0.02
p-Cl	H	2.94(±0.04)	1.89(±0.03)	1.53 ± 0.03
p-Cl	p-Cl	30.1(±0.60)	21.8(±0.55)	1.38 ± 0.03
p-Cl	p-Br	40.8(±0.75)	32.6(±0.65)	1.25 ± 0.02

^{a}Standard deviations.
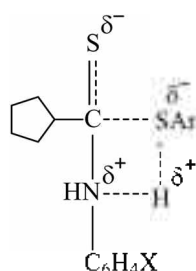
Scheme 1

bond formation ($\delta\rho_X > 0 \rightarrow \delta\rho_X < 0$) with a weaker nucleophile ($\delta\sigma_X > 0$) and nucleofuge ($\delta\sigma_Z < 0$) respectively in accordance with aryl phenyldithioacetate,[6] larger k_H/k_D values *i.e.*, greater degree of proton transfer with X = p-Cl than with X = p-OMe, and with Z = p-Me than with Z = p-Br (or Z = p-Cl), are consistent with the expected trends in both cases (Table 3).[6b] Alternatively, proton transfer can occur from the NH^+ to an anionic (thiocarbonyl) sulfur atom, which could still be rate-limiting since the neutral intermediate should breakdown rapidly to give a tautomer of the ultimate thioamide product.[9]

This interpretation based on the proposed TS structure is also supported by the activation parameters in Table 4. The relatively low activation enthalpies, $\Delta H^{\neq}$, and relatively large negative activation entropies, $\Delta S^{\neq}$, are in line with the concurrent proton transfer and leaving group expulsion in the TS. Since the leaving group expulsion and C=S bond formation are partly assisted by the proton transfer, the reaction (or the TS formation) can be a low energy ($\Delta H^{\neq}$ = ~ 5 kcal·mol^{-1}) but highly structured (large negative $\Delta S^{\neq}$ =

Table 4. Activation Parameters^a for the Reactions of Z-Aryl Dithiocyclopentanecarboxylates with X-Anilines in Acetonitrile

X	Z	$\Delta H^{\neq}$/kcal mol^{-1}	$-\Delta S^{\neq}$/cal mol^{-1} K^{-1}
p-OMe	p-Me	5.5	49
p-OMe	p-Br	5.1	44
p-Cl	p-Me	5.4	54
p-Cl	p-Br	5.1	47

^{a}Calculated by the Eyring equation. The maximum errors calculated (by the method of K. B. Wiberg, Physical Organic Chemistry, Wiley, New York, 1964, p 378.) are = 0.5 kcal mol^{-1} and = 2 e.u. for $\Delta H^{\neq}$ and $\Delta S^{\neq}$, respectively.

$-44 \sim -50$ e.u) process. The $\Delta H^{\neq}$ values are rather low but similar values are also reported for the uncatalyzed aminolysis reactions of $CF_3CO_2C_6H_4NO_2$ ($\Delta H^{\neq}$ = 2.6 kcal mol^{-1}, $\Delta S^{\neq}$ = -46 e.u.)[11] and 2,4-dinitrophenyl benzoates ($\Delta H^{\neq}$ = 2.3 kcal mol^{-1}, $\Delta S^{\neq}$ = -44 e.u.).[12] The insensitivity of $\Delta H^{\neq}$ values to the substituents in the amine and leaving group could result from the complex $k_N(k_a/k_{-a}\cdot k_b)$ values since the effects of substituents on k_a, k_{-a} and k_b may compensate each other.

In summary, the aminolysis of Z-aryl dithiocyclopentanecarboxylates with X-anilines proceeds by a stepwise mechanism with rate-limiting expulsion of the leaving group, ArS^-, from a tetrahedral intermediate, $T^{\pm}$. This prediction is based on faster rates for dithio (**II**) than for thiol (**I**) esters, the large selectivity parameters, β_X, β_Z and ρ_{XZ}, and adherence to the reactivity-selectivity principle (RSP). The kinetic isotope effects involving deuterated aniline nucleophiles ($XC_6H_4ND_2$), k_H/k_D = 1.3-1.7, and low $\Delta H^{\neq}$ and large negative $\Delta S^{\neq}$ values suggest that proton transfer occurs concurrently with the leaving group departure in a four-center type transition state.

Experimental Section

Materials. Merck GR acetonitrile was used after three distillations. The benzylamine nucleophiles, Aldrich GR, were used without further purification. Thiophenols and cyclopentanecarbonyl chloride were Tokyo Kasei GR grade.

Preparartions of Thiophenyl Cyclopentanecarboxylates. Thiophenol derivatives and cyclopentanecarbonyl chloride were dissolved in anhydrous ether and added pyridine carefully keeping temperature to 0-5 °C. Ice was then added to the reaction mixture and ether layer was separated, dried on $MgSO_4$ and distilled under reduced pressure to remove solvent. IR (Nicolet 5BX FT-IR) and ^1H and ^{13}C NMR (JEOL 400 MHz) data are as follows:

p-**Thiotolyl cyclopentanecarboxylate:** Liquid, IR (KBr), 2959 (C-H. aromatic), 2932 (C-H. CH_3), 1703 (C=O), 1609 (C=C. aromatic), 817 (C-S); ^1H NMR (400 MHz, CDCl$_3$), 1.40-2.13 (8H, m, CH_2), 2.38 (3H, s, CH_3), 2.40-2.46 (1H, m, CH), 7.24 (2H, d, J = 8.30 MHz, meta H), 7.31 (2H, d, J = 8.30 MHz, ortho H); ^{13}C NMR (100.4 MHz, CDCl$_3$), 201.3 (C=O), 139.3, 134.4, 129.9, 124.6, 52.8, 30.6, 25.9, 21.1.; Mass, *m/z* 220(M$^+$). Anal. Calcd. for $C_{13}H_{16}OS$: C, 70.8; H, 7.32. Found: C, 70.6; H, 7.34.

Thiophenyl cyclopentanecarboxylate: Liquid, IR (KBr), 2958 (C-H. aromatic), 1705 (C=O), 1473 (C=C, aromatic), 809 (C-S); ^1H NMR (400 MHz, CDCl$_3$), 1.36-1.99 (8H, m, CH_2), 2.35-2.45 (1H, m, CH), 7.26 (2H, d, J = 7.81 MHz, meta H), 7.30 (2H, d, J = 7.81 MHz, ortho H); ^{13}C NMR (100.4 MHz, CDCl$_3$), 200.6 (C=O), 134.3, 129.0, 128.9, 128.1, 52.8, 30.5, 25.8.; Mass, *m/z* 206 (M$^-$). Anal. Calcd. for $C_{12}H_{14}OS$: C, 69.8; H, 6.84. Found: C, 70.1; H. 6.86.

p-**Chlorothiophenyl cyclopentanecarboxylate:** Liquid, IR (KBr), 2957 (C-H. aromatic), 1703 (C=O), 1498 (C=C. aromatic), 806 (C-S); ^1H NMR (400 MHz, CDCl$_3$), 1.53-2.00 (8H, m, CH_2), 2.25-2.34 (1H, m, CH), 7.31 (2H, d, J = 8.78 MHz, meta H), 7.35 (2H, d, J = 8.78 MHz, ortho H); ^{13}C

NMR (100.4 MHz, CDCl₃), 200.3 (C=O), 135.7, 135.5, 129.3, 126.5, 53.0, 30.5, 25.8.; Mass. *m/z* 240 (M⁺). Anal. Calcd. for C₁₂H₁₃ClOS: C, 59.8; H, 5.44. Found: C, 60.1; H, 5.46.

p-**Bromothiophenyl cyclopentanecarboxylate**: Liquid. IR (KBr). 2957 (C-H, aromatic), 1707 (C=O), 1498 (C=C. aromatic), 812 (C-S); ¹H NMR (400 MHz, CDCl₃), 1.38-2.16 (8H, m. CH₂), 2.25-2.34 (1H, m. CH), 7.24 (2H, d. *J* = 8.78 MHz, meta H), 7.50 (2H, d. *J* = 8.78 MHz, ortho H); ¹³C NMR (100.4 MHz, CDCl₃), 200.1 (C=O). 135.9, 132.2, 127.2, 123.7, 53.0, 30.5, 25.8.; Mass. *m/z* 283 (M⁺). Anal. Calcd. for C₁₂H₁₃BrOS: C, 50.5; H, 4.59. Found: C, 50.7; H, 4.57.

Preparartions of phenyl dithiocyclopentanecarboxylates. The thiophenyl cyclopentanecarboxylates prepared as above were dissolved in dry toluene and refluxed with Lawesson's reagent (Aldrich G R. grade). After extraction of the reaction mixture with dichloromethane, dried and removed solvent by distillation under reduced pressure. Separation by column chromatography gave the products. for which the following analytical data were obtained.

p-**Tolyl dithiocyclopentanecarboxylate**: Liquid. IR (KBr), 2975 (C-H. aromatic). 2933 (C-H. CH₃), 1705 (C=S). 1499. 1487 (C=C, aromatic); ¹H NMR (400 MHz. CDCl₃). 1.33-2.03 (8H, m, CH₂). 2.30 (3H. s. CH₃). 2.41 (1H. m. CH). 7.15-7.32 (4H, m, aromatic ring); ¹³C NMR (100.4 MHz. CDCl₃), 200.7 (C=S). 134.4. 133.4, 129.8. 129.5. 52.7, 30.5. 25.8. 21.1. Mass, *m/z* 252 (M⁺). Anal. Calcd. for C₁₃H₁₆OS₂: C, 61.8; H, 6.39. Found: C, 62.0; H. 6.41.

Phenyl dithiocyclopentanecarboxylate: Liquid, IR (KBr). 2978 (C-H, aromatic). 1707 (C=S), 1501. 1488 (C=C. aromatic); ¹H NMR (400 MHz, CDCl₃). 1.38-2.02 (8H, m. CH₂). 2.43 (1H, m, CH), 7.29-7.35 (5H. m. aromatic ring); ¹³C NMR (100.4 MHz. CDCl₃). 200.8 (C=S), 134.4, 129.1. 129.0. 128.1, 52.8, 30.5, 25.8. Mass, *m/z* 222 (M⁻). Anal. Calcd. for C₁₂H₁₄S₂: C, 64.8; H, 6.35. Found: C. 64.6; H. 6.37.

p-**Chlorophenyl dithiocyclopentanecarboxylate**: Liquid. IR (KBr). 2982 (C-H. aromatic). 1711 (C=S), 1502. 1491 (C=C, aromatic); ¹H NMR (400 MHz, CDCl₃), 1.34-1.99 (8H. m. CH₂), 2.45 (1H, m. CH), 7.21-7.29 (4H, m, aromatic ring); ¹³C NMR (100.4 MHz, CDCl₃). 200.1 (C=S). 135.6. 135.3. 129.1. 126.5. 52.8. 30.4. 25.8. Mass. *m/z* 256 (M⁺). Anal. Calcd. for C₁₂H₁₃ClS₂: C. 56.1; H, 5.10. Found: C. 56.3; H. 5.12.

p-**Bromophenyl dithiocyclopentanecarboxylate**: Liquid. IR (KBr). 2981 (C-H. aromatic). 1707 (C=S). 1502. 1490 (C=C. aromatic); ¹H NMR (400 MHz, CDCl₃), 1.36-2.05 (8H, m. CH₂), 2.44 (1H, m. CH), 7.07-7.59 (4H, m, aromatic ring); ¹³C NMR (100.4 MHz, CDCl₃). 200.0 (C=S). 135.8. 132.1. 127.2, 123.6. 52.9, 30.5, 25.8. Mass. *m/z* 299 (M⁺). Anal. Calcd. for C₁₂H₁₃BrS₂: C, 47.8; H. 4.35. Found: C. 47.9; H, 4.37.

Kinetic Measurement. Rates were measured conductometrically at 10.0 ± 0.05 °C. The conductivity bridge used in this work was a self-made computer automatic A/D converter conductivity bridge. Pseudo-first-order rate constants, k_{obs} were determined by the Guggenheim method[13] with large excess of aniline. Second-order rate constants. k_N were obtained from the slope of a plot of k_{obs} vs. aniline with more

than five concentrations of more than three runs and were reproducible to within ± 3%.

Product Analysis. Substrate. phenyl dithiocyclopentanecarboxylate (0.05 mole) was reacted with excess aniline (0.5 mole) with stirring for more than 15 half-lives at 10.0 °C in acetonitrile, and the products were isolated by evapolating the solvent under reduced pressure. The product mixture was treated with column chromatography (silica gel, 20% ethylacetate-*n*-hexane). Analysis of the product gave the following results.

Cyclopentyl-C(=S)NHC₆H₄-OCH₃: liquid, IR (KBr). 3448 (N-H), 2943 (C-H. CH₃), 1707 (C=S). 1535 (C=C, aromatic); ¹H NMR (400 MHz. CDCl₃). 1.34-2.05 (8H, m, CH₂). 2.45 (1H. m. CH). 3.71 (3H. s. CH₃). 7.08-7.60 (4H, m. aromatic ring); ¹³C NMR (100.4 MHz, CDCl₃). 200.1 (C=S), 135.9, 132.2. 127.2. 123.7. 56.9, 52.9, 30.5. 25.8. Mass, *m/z* 235 (M⁻). Anal. Calcd. for C₁₃H₁₇NOS: C, 66.3; H, 7.28. Found: C, 66.5; H, 7.26.

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