Kinetics and mechanism of the aminolysis of aryl phenyldithioacetates in acetonitrile

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The aminolysis reactions of Z-aryl phenyldithioacetates ($C_6H_5CH_2C(=S)SC_6H_4Z$) with benzylamines ($XC_6H_4CH_2NH_2$) are investigated in acetonitrile at $-25.0\ ^\circ C$. The reactions are predicted to proceed by a stepwise mechanism with rate-limiting expulsion of the thiophenolate anion from the zwitterionic tetrahedral intermediate, $T^\pm$, based on (i) large magnitudes of selectivity parameters, β_X (ρ_X) and β_Z (ρ_Z), (ii) positive and large cross-interaction constants ρ_{XZ} (=2.05), and (iii) adherence to the reactivity–selectivity principle. The significant normal kinetic isotope effects ($k_H/k_D = 1.14$–1.81) involving deuterated amines and low activation enthalpies ($\Delta H^\ddagger \approx 3$ kcal mol^{-1}) together with large negative activation entropies ($\Delta S^\ddagger = -37$ to -53 e.u.) are consistent with concurrent proton transfer of amine hydrogen with the leaving group departure in the transition state.

Introduction

The mechanisms of the aminolysis of aryl esters and carbonates have been well established.[1] These reactions are known to proceed stepwise through a zwitterionic tetrahedral intermediate, $T^\pm$. The existence of the intermediate has been deduced from curved Brønsted-type plots. A biphasic dependence of the rate on the amine basicity showing a change of slope from a large ($\beta_{nuc} \geq 0.8$) to a small ($\beta_{nuc} \approx 0.1$–0.3) value at pK_a°, where the amine and leaving group have the same expulsion rates from $T^\pm$, has been attributed to a change in the rate-limiting step from breakdown to formation of a tetrahedral intermediate as the basicity of the amine increases. Other criteria for this mechanistic change are the sign reversal of the cross-interaction constant,[2] ρ_{XZ} in eqns. (1a) and (1b), where X and Z denote

$$\log (k_{XZ}/k_{HH}) = \rho_X\sigma_X + \rho_Z\sigma_Z + \rho_{XZ}\sigma_X\sigma_Z \quad (1a)$$

$$\rho_{XZ} = \partial\rho_X/\partial\sigma_Z = \partial\rho_Z/\partial\sigma_X \quad (1b)$$

substituents in the nucleophile (amine) and leaving group respectively, from positive ($\rho_{XZ} > 0$) to negative[3] at the pK_a° as the amine basicity is increased, and from adherence to the failure of the reactivity–selectivity principle (RSP).[2,3]

The aminolysis of dithio esters and carbonates, **I**, has been
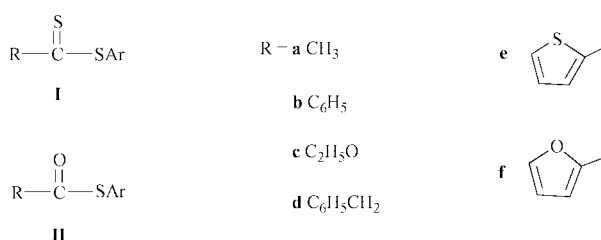
studied in aqueous[4] and acetonitrile solutions.[5] An important advantage of using an acetonitrile medium is that there are no complications arising from a kinetically important proton transfer from $T^\pm$ to the amine[6] (k_{H^+} in Scheme 1). In water, the rate of proton transfer, k_{H^+}, may be faster than that of expul-

sion of arenethiolate, k_b, from $T^\pm$ so that the rate law becomes complex.[6] This kinetic complexity encountered in the aminolysis of dithiocarboxylates (and also thiono) compounds in water is known to originate from the weak π bond energy of CS (compared to CO) which causes the difficulty in reforming the CS double bond when $T^\pm$ breaks down expelling either the amine or ArS$^-$.[6]

As an extension of our work on the aminolysis of dithio esters in acetonitrile, we now examine the reactions of benzylamines (BAs) with aryl phenyldithioacetates, **Id**. 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 eqns. (1a) and (1b). We found that the change of R from CH_3[5a] to CH_3CH_2[5e] in **I** results in large increases in β_X ($0.55\rightarrow2.19$) and ρ_{XZ} ($0.61\rightarrow3.51$), and it would be of interest to know what effect R = $C_6H_5CH_2$ will have on the size of β_X and ρ_{XZ}. Since in the tetrahedral intermediate only the inductive effect of R should be operative, we chose the benzyl group in the present work in order to examine the effect of a change in R from inductive electron donors (CH_3 and CH_3CH_2) to an acceptor.

Results and discussion

The rate law obtained in the present reaction is given by eqns. (2) and (3), where ArS$^-$ is the thiolate anion, k_{obs} is the

$$d[ArS^-]/dt = k_{obs}[S] \quad (2)$$

$$k_{obs} = k_N[N] \quad (3)$$

pseudo-first-order rate constant, and k_N is the rate constant for aminolysis of the substrate, (S), with amines (N), respectively.

The values of k_N were obtained as the slopes of plots of k_{obs} *vs.* [N] [eqn. (3)]. The k_N values for the aminolysis with benzylamines are summarized in Table 1 together with the Hammett (ρ_X and ρ_Z) and Brønsted coefficients (β_X and β_Z). The magnitudes of Hammett and Brønsted coefficients in Table 1 are large. The β_X (=β_{nuc}) values of 1.68–2.49 for the reactions of benzylamines are quite large compared to those for the

DOI: 10.1039/b002842h

Table 1 The second order rate constants, k_N ($M^{-1} s^{-1}$) for the reactions of Z-aryl phenyldithioacetates with X-benzylamines in acetonitrile at $-25.0\,°C$

X	Z p-Me	H	p-Cl	p-Br	$\rho_Z{}^a$	$\beta_Z{}^b$
p-OMe		32.3	162	241	3.13 ± 0.27	−1.23 ± 0.05
	8.97[c]			184[c]		
	6.85[d]			139[d]		
p-Me	8.27	26.1	137	179	3.23 ± 0.17	−1.31 ± 0.09
H	3.36	11.6	66.1	101	3.51 ± 0.26	−1.38 ± 0.11
p-Cl	0.645	3.11	24.1	30.1	4.06 ± 0.11	−1.68 ± 0.17
	0.493			23.0		
	0.374			17.3		
m-Cl	0.286	1.55	13.6	17.2	4.33 ± 0.12	−1.79 ± 0.18
p-CF₃	0.0830	0.592	5.06	8.97	4.76 ± 0.34	−1.89 ± 0.28
	0.0639[c]			6.87[c]		
	0.0482[d]			5.21[d]		
$\rho_X{}^e$	−2.70 ± 0.10	−2.21 ± 0.08	−1.87 ± 0.09	−1.83 ± 0.06	$\rho_{XZ}{}^f$ = 2.05 ± 0.33	
$\beta_X{}^g$	2.49 ± 0.11	2.03 ± 0.10	1.73 ± 0.07	1.68 ± 0.10		

[a] The σ values were taken from ref. 9. Correlation coefficients were better than 0.997 in all cases. [b] The pK_a values were taken from ref. 18. Z = p-Br was excluded from the Brønsted plot due to an unreliable pK_a value. Correlation coefficients were better than 0.995 in all cases. [c] At $-35\,°C$. [d] At $-45\,°C$. [e] The source of σ is the same as in footnote a. Correlation coefficients were better than 0.997 in all cases. [f] Correlation coefficient was 0.997. [g] The pK_a values were taken from ref. 19. Correlation coefficients were better than 0.995 in all cases. pK_a = 9.67 and 8.76 were used for X = p-CH₃O and p-CF₃. (See ref. 10a and 17).
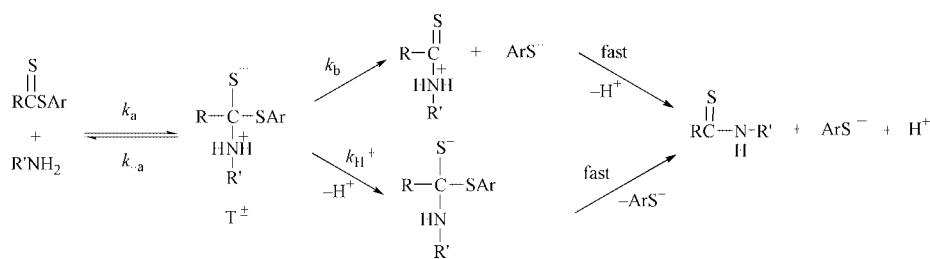
Scheme 1

aminolysis of phenyl dithioacetates (**Ia**) with anilines and *N,N*–dimethylanilines (DMA) in acetonitrile [5a] (β_X = 0.80–0.85), and of phenyl dithiobenzoates (**Ib**) with anilines in acetonitrile (β_X = 0.80–1.07). [5c] These two series of reactions have been predicted to proceed by rate-limiting breakdown of a zwitterionic tetrahedral intermediate, $T^\pm$ in Scheme 1. The magnitudes of ρ_Z and β_Z values ($\beta_Z = -1.23$ to -1.89) are also much larger than for the corresponding reactions of **Ia** with anilines and DMAs [5a] ($\beta_Z = -0.71$ to -0.84) and **Ib** with anilines [5c] ($\beta_Z = -0.49$ to -0.78). A striking difference in the magnitudes of these β_X and β_Z values between the present reactions, **Id**, and **Ia, b**, is that **Ia, b**, exhibit much smaller magnitudes of β_X and β_Z values for the reaction with benzylamines; [5a,c] β_X = 0.46–0.63 and $\beta_Z = -0.45$ to -0.55 for **Ia** and β_X = 0.51–0.73 and $\beta_Z = -0.18$ to -0.29 for **Ib**. This means that for **Ia** (R = CH₃) and **Ib** (R = C₆H₅) the mechanism of the aminolysis changes from rate-limiting breakdown of $T^\pm$ with weakly basic amines (anilines and DMAs) to rate-limiting formation of $T^\pm$ (or concerted processes) with strongly basic amines (benzylamines). In contrast, however, for the present reaction series, **Id** (R = C₆H₅CH₂), the rate determining step, the breakdown of $T^\pm$, is maintained even for the strongly basic amines ($pK_a \leq 9.67$ (for X = p-MeO)). This suggests that for the aminolysis of aryl phenyldithioacetates (**Id**) the break point ($pK_a{}°$) at which the mechanistic change occurs, is higher than pK_a = 9.67 (X = p-MeO), whereas for the aminolysis of **Ia** and **Ib** the $pK_a{}°$ lies below pK_a = 9.14 (X = p-Cl). In these comparisons, the leaving groups are fixed to Z = p-Me, H, p-Cl or p-Br in **I**, and reactions are conducted in acetonitrile in all cases. It is well known that the $pK_a{}°$ depends on the nucleofugality of the leaving group and solvent. [1c,3a,4a] For the aminolysis of aryl thiophene-2-carbodithioates, [7] **Ie**, and furan-2-carbodithioates, [7] **If**, with benzylamines in acetonitrile the β_X values were also large (β_X = 0.86–1.11 for **Ie**, and 1.21–

1.50 for **If**) so that the $pK_a{}°$ values are predicted to be higher than pK_a = 9.14 (for X = p-Cl).

In summary, for R = CH₃ and C₆H₅, the $pK_a{}°$ values are lower than those for R = C₆H₅CH₂, 2-thienyl and 2-furyl. In the extreme case of R = C₂H₅O in **II** (**IIc**), the aminolyses are found to proceed concertedly in aqueous solution. [8] These results seem to reflect the strength of "push" provided by the acyl group, R in **I** (and **II**), since the stronger the push provided by the acyl group, the greater is the nucleofugality of the leaving group. [1c] A stronger leaving group leads to a lower $pK_a{}°$. [1c,3a] The acyl groups R = **d**, **e** and **f** are relatively weak resonance donors (the Swain–Lupton resonance parameter [9] $R = -0.05, -0.08$ and -0.08 respectively) in comparison with R = **a**, **b**, and **c** ($R = -0.18, -0.13$ and -0.50 respectively). For R = **c**, the resonance donating effect is so large that the tetrahedral intermediate, $T^\pm$, is strongly destabilized by the strong push provided by C₂H₅O towards the leaving group. [8]

In line with the large magnitudes of ρ_X (β_X) and ρ_Z (β_Z) values, the cross-interaction constant ρ_{XZ} is positive and large (ρ_{XZ} = 2.05). For the aminolysis of **Ia, b, e** and **f**, the ρ_{XZ} values were 0.50–0.75. [5a,7] The much larger magnitudes of β_X, β_Z and ρ_{XZ} in the present work strongly support the stepwise mechanism with rate-limiting expulsion of the leaving group for the aminolysis of aryl phenyldithioacetates in acetonitrile.

The unusually large magnitude of β_X, and the high $pK_a{}°$ value for the reactions with benzylamine, can be accounted for as follows. (1) The expulsion rates of amines from tetrahedral intermediates, $T^\pm$, have been shown to decrease in the order benzylamines > alicyclic secondary amines > anilines > pyridines. [10] This is because breakdown to products of the corresponding tetrahedral intermediate is the rate-determining step for both reaction series, $k_N = (k_a/k_{-a})k_b = Kk_b$ in Scheme 1. The complex k_N value leads to eqn. (4), where β_b is nearly zero and

Table 2 Kinetic isotope effects for the reactions of Z-aryl phenyl-dithioacetates with deuterated X-benzylamines in acetonitrile at $-25.0\,^\circ$C

X	Z	$k_H/M^{-1}\,s^{-1}$	$k_D/M^{-1}\,s^{-1}$	k_H/k_D
p-OMe	p-Me	11.7 ± 0.1	9.14 ± 0.05	1.28 ± 0.01[a]
p-OMe	H	32.3 ± 0.5	25.6 ± 0.3	1.26 ± 0.02
p-OMe	p-Cl	162 ± 3	136 ± 2	1.19 ± 0.02
p-OMe	p-Br	241 ± 4	211 ± 3	1.14 ± 0.02
p-Cl	p-Me	0.645 ± 0.008	0.356 ± 0.005	1.81 ± 0.03
p-Cl	H	3.11 ± 0.04	1.86 ± 0.03	1.67 ± 0.03
p-Cl	p-Cl	24.1 ± 0.3	16.4 ± 0.2	1.47 ± 0.02
p-Cl	p-Br	30.1 ± 0.4	24.1 ± 0.2	1.25 ± 0.02

[a] Standard deviation.

Table 3 Activation parameters[a] for the reactions of Z-aryl phenyl-dithioacetates with X-benzylamines in acetonitrile

X	Z	$\Delta H^{\ddagger}/$ kcal mol^{-1}	$-\Delta S^{\ddagger}/$ cal mol^{-1} K^{-1}
p-OMe	p-Me	2.5	43
p-OMe	p-Br	2.6	37
p-Cl	p-Me	2.6	49
p-Cl	p-Br	2.6	41
p-CF$_3$	p-Me	2.6	53
p-CF$_3$	p-Br	2.6	43

[a] Calculated by the Eyring equation. The maximum errors calculated (by the method of Wiberg, ref. 20) are ± 0.9 kcal mol^{-1} and ± 3 e.u. for $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$, respectively.

$$\beta_X\ (=\beta_{nuc}) = \mathrm{d}\log k_N/\mathrm{d}pK_a(X) = \mathrm{d}\log k_a/\mathrm{d}pK_a(X) - \mathrm{d}\log k_{-a}/\mathrm{d}pK_a(X) + \mathrm{d}\log k_b/\mathrm{d}pK_a(X) = \beta_a - \beta_{-a} + \beta_b \quad (4)$$

$\beta_a \approx 0.2$–0.3 so that the large β_X is due to the large magnitude of β_{-a}[10a] (≥ -2.0 for the reactions with benzylamines). In the conjugate acid forms (as in the tetrahedral intermediate) of secondary and tertiary amines, the cationic charge is partially delocalized and the sensitivity of the functional N center (positively charged) to the substituent (X) variation should be lower, *i.e.*, β_{-a} should be smaller in magnitude, than that for the primary amines (BAs). Since the expulsion rate of benzylamine from the intermediate, T‡, is high, the ratio k_{-a}/k_b is also high so that the breakpoint, pK_a°, where the nucleofugality of benzylamine and thiophenolate is equal, lies above the pK_a's of the conjugate acids of benzylamines used in this work,[1c,4] and a straight line (not curved) Brønsted plot is obtained. (2) The stepwise reactions exhibit an increase of pK_a° as the leaving ability of the substrate decreases.[1c,3a] Since the ArS$^-$ group is a worse leaving group than the corresponding isobasic ArO$^-$ group,[1c,11] the pK_a° value becomes higher. Moreover, the aminolyses of substrates with leaving groups of low nucleofugality have been shown to give large magnitudes of β_X and β_Z. For example, aminolyses of methyl acetate, trifluoroethyl acetate and acetic acid (pK_a's for the conjugate acids of the leaving groups are 15.54, 12.37 and 15.75, respectively)[12] in aqueous solution at $25.0\,^\circ$C exhibited large β_X (=1.2–1.6) and β_Z (=-1.2 to -1.6) values.[12] (3) The addition of acetonitrile to the aqueous solvent has been shown to increase the fraction of amine expulsion to form the ester.[1c] This is due to the expected stabilization by an aprotic cosolvent of the TS for the breakdown of T‡ to form uncharged products relative to that for the formation of the aryl (or thioaryl) oxide anion and cationic amide. The partitioning ratio, k_{-a}/k_b, has been reported to increase by *ca.* 2.2 times in 7.2% acetonitrile solution.[1c] The increase in k_{-a}/k_b results in a higher pK_a°.[1c,4] Since the present reaction series are carried out in acetonitrile, the high pK_a° (>9.7) observed may be partly ascribed to the solvent effect. (4) The low temperature used in the aminolysis with benzylamines ($-25.0\,^\circ$C) should also contribute to the larger magnitude of selectivity parameters, β_X and β_Z, since the magnitude of all selectivity parameters decreases with an increase in temperature.[13] (5) On the other hand, the change of O$^-$ to S$^-$ is known to stabilize T‡ and decrease the partitioning ratio, k_{-a}/k_b, so that the pK_a° should be lowered.[4b,6a,b] The S$^-$ in T‡ is less able than O$^-$ to form a double bond and expel a leaving group which disfavors amine expulsion from T‡. This aspect should therefore favor a low pK_a°, not a high pK_a° as observed in the present work. In view of our results where large β_X values and high pK_a°'s are observed, this effect due to the change of O$^-$ to S$^-$, seems to be smaller than other opposing effects ((1)–(4) listed above).

The kinetic isotope effects involving deuterated amine nucleophile (XC$_6$H$_4$CH$_2$ND$_2$), k_H/k_D, have been determined[2b] in acetonitrile as shown in Table 2. We note that the k_H/k_D values are significantly greater than unity so they constitute primary

kinetic isotope effects. The amine proton shift is implicated by values of k_H/k_D greater than unity.[2b,3b] 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 2. In the proposed TS structure, the leaving group
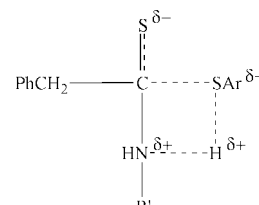
Scheme 2

departure is assisted by partial protonation and therefore the difficulty in forming the C=S bond may be partially alleviated. This could explain the relatively insignificant effect of substitution of S$^-$ for O$^-$ discussed above (item (5)). Since the positive ρ_{XZ} should require a greater degree of bond breaking ($\delta\rho_Z > 0$) and a greater degree of bond formation ($\delta|\rho_X| > 0 \longrightarrow \delta\rho_X < 0$) with a weaker nucleophile ($\delta\sigma_X > 0$) and nucleofuge ($\delta\sigma_Z < 0$) respectively, in accordance with eqn. (1b),[2] 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 2).[2b,3b] 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 break down rapidly to give a tautomer of the ultimate thioamide product.[14]

This interpretation based on the proposed TS structure is also supported by the activation parameters given in Table 3. The relatively low activation enthalpies, $\Delta H^{\ddagger}$, and relatively large negative activation entropies, $\Delta S^{\ddagger}$, 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 ($\Delta H^{\ddagger} \approx 3$ kcal mol^{-1}) but highly structured (large negative $\Delta S^{\ddagger} = -37$ to -53 e.u.) process. The $\Delta H^{\ddagger}$ values are rather low but similar values are also reported for the uncatalyzed aminolysis reactions of CF$_3$CO$_2$C$_6$H$_4$NO$_2$ ($\Delta H^{\ddagger} = 2.6$ kcal mol^{-1}, $\Delta S^{\ddagger} = -46$ e.u.)[15] and 2,4-dinitrophenyl benzoates ($\Delta H^{\ddagger} = 2.3$ kcal mol^{-1}, $\Delta S^{\ddagger} = -44$ e.u.).[16] The insensitivity of $\Delta H^{\ddagger}$ values to the substituents in the amine and leaving group could result from the complex $k_N(k_a/k_{-a}k_b)$ values since the effects of substituents on k_a, k_{-a} and k_b may compensate each other.

Lastly, the data in Tables 1 and 2 reveal that greater reactivities are invariably accompanied by smaller selectivities, *i.e.*, the reactivity–selectivity principle holds.[3,10a]

In summary, the aminolysis of aryl phenyldithioacetates with benzylamines in acetonitrile exhibits (i) large magnitudes of β_X (and ρ_X) and β_Z (and ρ_Z), (ii) positive and large ρ_{XZ} values,

(iii) significant primary kinetic isotope effects ($k_H/k_D > 1.0$) involving deuterated amines, (iv) low $\Delta H^{\ddagger}$ and large negative $\Delta S^{\ddagger}$ values and (v) adherence to the RSP. These results are consistent with proton transfer concurrent with leaving group departure from tetrahedral intermediate, $T^{\ddagger}$, in the rate-determining step.

Experimental

Materials

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

Preparations of *S*-phenyl phenylthioacetates

Thiophenol derivatives and phenylacetyl chloride were dissolved in anhydrous ether and KOH was added carefully keeping the temperature to 0–5 °C. Ice was then added to the reaction mixture and the ether layer was separated, dried on MgSO$_4$ and distilled under reduced pressure to remove solvent. The melting point, IR (Nicolet 5BX FT-IR), ^{1}H and ^{13}C NMR (JEOL 400 MHz), data are as follows.

S-*p*-Methylphenyl phenylthioacetate. Mp 62–64 °C; IR(KBr)/cm^{-1} 1703 (C=O), 1501 (C–C, aromatic), 1495 (C=C, aromatic), 1434 (C–H, CH$_2$), 1329 (C–H, CH$_3$), 675 (C–H, aromatic); ^{1}H NMR (400 MHz, CDCl$_3$) 2.35 (3H, d, $J = 2.66$ Hz, CH$_3$), 3.90 (2H, s, CH$_2$), 7.18–7.37 (9H, m, aromatic ring); ^{13}C NMR (100.4 MHz, CDCl$_3$) 195.8 (C=O), 139.7, 134.4, 133.4, 130.0, 129.2, 128.5, 127.5, 127.0, 124.0, 123.7, 50.0, 21.3.

S-Phenyl phenylthioacetate. Liquid, IR(KBr)/cm^{-1} 1717 (C=O), 1515 (C–C, aromatic), 1475 (C=C, aromatic), 1468 (C–H, CH$_2$), 702 (C–H, aromatic); ^{1}H NMR (400 MHz, CDCl$_3$) 4.15 (2H, s, CH$_2$), 7.24–7.35 (10H, m, aromatic ring); ^{13}C NMR (100.4 MHz, CDCl$_3$) 202.5 (C=O), 139.5, 134.3, 132.1, 131.4, 130.4, 130.2, 129.0, 128.2, 127.9, 127.0, 125.9, 123.1, 51.2.

S-*p*-Chlorophenyl phenylthioacetates. Mp 58–61 °C, IR(KBr)/cm^{-1} 1710 (C=O), 1524 (C–C, aromatic), 1475 (C=C, aromatic), 1459 (C–H, CH$_2$), 702 (C–H, aromatic); ^{1}H NMR (400 MHz, CDCl$_3$) 4.16 (2H, s, CH$_2$), 7.26–7.37 (9H, m, aromatic ring); ^{13}C NMR (100.4 MHz, CDCl$_3$) 200.3 (C=O), 139.3, 133.9, 133.1, 129.3, 128.5, 128.5, 128.2, 127.1, 126.9, 124.2, 50.5.

S-*p*-Bromophenyl phenylthioacetate. Mp 57–59 °C, IR(KBr)/cm^{-1} 1703 (C=O), 1501 (C–C, aromatic), 1468 (C=C, aromatic), 1454 (C–H, CH$_2$), 674 (C–H, aromatic); ^{1}H NMR (400 MHz, CDCl$_3$) 4.12 (2H, s, CH$_2$), 7.26–7.37 (9H, m, aromatic ring); ^{13}C NMR (100.4 MHz, CDCl$_3$) 197.6 (C=O), 139.4, 134.2, 132.9, 130.3, 129.8, 129.5, 129.1, 128.5, 128.1, 126.9, 126.6, 123.8, 50.4.

Preparation of phenyl phenyldithioacetates

The phenyl phenylthioacetates prepared as above were dissolved in dry toluene and refluxed with Lawesson's reagent (Aldrich GR grade) which is used to convert carbonyl to thiocarbonyl. After extraction of the reaction mixture with dichloromethane, the solvent was dried and removed by distillation under reduced pressure. Separation by column chromatography gave the products, for which the following analytical data were obtained.

p-Methylphenyl phenyldithioacetate. Mp 64–66 °C, IR(KBr)/cm^{-1} 1510 (C–C, aromatic), 1498 (C=C, aromatic), 1454 (C–H, CH$_2$), 1332 (C–H, CH$_3$), 1219 (C=S), 1125 (C–S), 702 (C–H, aromatic); ^{1}H NMR (400 MHz, CDCl$_3$) 2.39 (3H, d, $J = 2.66$

Hz, CH$_3$), 4.51 (2H, s, CH$_2$), 7.18–7.37 (9H, m, aromatic ring); ^{13}C NMR (100.4 MHz, CDCl$_3$), 135.4, 134.6, 133.2, 132.5, 131.9, 131.6, 130.3, 129.9, 129.1, 128.5, 127.2, 123.4, 100.5 (C=S), 57.4 (CH$_2$), 26.8 (CH$_3$). Mass, m/z 258 (M$^+$). Anal. Calcd for C$_{15}$H$_{14}$S$_2$: C, 69.7; H, 5.50. Found: C, 69.5; H, 5.48%.

Phenyl phenyldithioacetate. Liquid, IR(KBr)/cm^{-1} 1501 (C–C, aromatic), 1474 (C=C, aromatic), 1438 (C–H, aromatic), 1226 (C=S), 1132 (C–S), 716 (C–H, aromatic); ^{1}H NMR (400 MHz, CDCl$_3$) 4.38 (2H, s, CH$_2$), 7.26–7.46 (9H, m, aromatic ring); ^{13}C NMR (100.4 MHz, CDCl$_3$), 133.6, 132.7, 131.7, 130.8, 130.4, 127.8, 126.9, 125.7, 123.6, 122.4, 120.9, 120.5, 109.1 (C=S), 54.4 (CH$_2$). Mass, m/z 244 (M$^+$). Anal. Calcd for C$_{14}$H$_{12}$S$_2$: C, 68.8; H, 4.91. Found: C, 68.9; H, 4.89%.

p-Chlorophenyl phenyldithioacetate. Liquid, IR(KBr)/cm^{-1} 1517 (C=C, aromatic), 1500 (C=C, aromatic), 1477 (C–H, CH$_2$), 1253 (C=S), 1150 (C–S), 712 (C–H, aromatic); ^{1}H NMR (400 MHz, CDCl$_3$) 4.38 (2H, s, CH$_2$), 7.19–7.41 (9H, m, aromatic ring); ^{13}C NMR (100.4 MHz, CDCl$_3$), 139.9, 138.0, 137.6, 136.9, 135.9, 134.7, 134.0, 132.5, 131.2, 130.4, 128.9, 127.2, 104.1 (C=S), 57.6 (CH$_2$). Mass, m/z 278 (M$^+$). Anal. Calcd for C$_{14}$H$_{12}$ClS$_2$: C, 60.3; H, 4.01. Found: C, 60.1; H, 4.02%.

p-Bromophenyl phenyldithioacetate. Liquid, IR(KBr)/cm^{-1} 1540 (C–C, aromatic), 1501 (C=C, aromatic), 1491 (C–H, CH$_2$), 1248 (C=S), 1180 (C–S), 705 (C–H, aromatic); ^{1}H NMR (400 MHz, CDCl$_3$) 4.36 (2H, s, CH$_2$), 7.22–7.42 (9H, m, aromatic ring); ^{13}C NMR (100.4 MHz, CDCl$_3$) 137.1, 136.3, 135.8, 134.2, 132.9, 131.3, 130.7, 129.6, 128.8, 128.5, 126.3, 125.1, 114.3 (C=S), 59.0 (CH$_2$). Mass, m/z 323 (M$^+$). Anal. Calcd for C$_{14}$H$_{11}$BrS$_2$: C, 52.0; H, 3.42. Found: C, 51.8; H, 3.40%.

Kinetic measurements

The reactions were followed conductometrically under pseudo-first-order conditions with an excess amount of amine, [substrate] $\approx 10^{-3}$ M and [N] ≈ 0.01–0.7 M. The rate constants, k_N, were obtained as described previously.[7,17] The rate constants reported were averages of more than two determinations and were reproducible to within ±5%.

Product analysis

Substrate, phenyl phenyldithioacetate (0.005 mol), was reacted with excess benzylamine (0.5 mol) with stirring for more than 15 half-lives at −25.0 °C in acetonitrile, and the products were isolated by evaporating the solvent under reduced pressure. The product mixture was subjected to column chromatography (silica gel, 20% ethyl acetate–*n*-hexane). Analysis of the product gave the following results.

C$_6$H$_5$CH$_2$C(=S)NHCH$_2$C$_6$H$_4$-OMe. Liquid, IR(KBr)/cm^{-1} 1608 (N–H), 1503 (C–C, aromatic), 1464 (C=C, aromatic), 1435 (C–H, CH$_2$), 1281 (C=S), 693 (C–H, aromatic); ^{1}H NMR (400 MHz, CDCl$_3$) 2.92 (1H, s, NH), 4.60 (2H, s, CH$_2$), 7.11–7.48 (9H, m, aromatic ring); ^{13}C NMR (100.4 MHz, CDCl$_3$), 137.7, 135.8, 134.6, 132.3, 121.0, 129.4, 127.7, 126.1, 125.6, 124.3, 121.2, 119.0, 102.3 (C=S), 60.2 (CH$_2$), 33.8 (OCH$_3$). Mass, m/z 271 (M$^+$). Anal. Calcd for C$_{16}$H$_{17}$NOS: C, 70.8; H, 6.31. Found: C, 70.6; H, 6.32%.

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