

Kinetics and Mechanism of the Reactions of Anilines with Ethyl *S*-Aryl Thiocarbonates

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Received October 13, 1998

The reactions of anilines with ethyl *S*-(2,4-dinitrophenyl) thiocarbonate (DNPTC) and ethyl *S*-(2,4,6-trinitrophenyl) thiocarbonate (TNPTC) are subjected to a kinetic study in aqueous solution at 25.0 °C and ionic strength 0.2 (KCl). The reactions are studied by following spectrophotometrically (400 nm) the release of the corresponding substituted benzenethiolate anion. Under aniline excess, pseudo-first-order rate coefficients (k_{obsd}) are found. Plots of k_{obsd} vs $[\text{N}]$ (N is the free substituted aniline) are linear and pH independent, with slope k_{N} . The Brønsted-type plots ($\log k_{\text{N}}$ vs $\text{p}K_{\text{a}}$ of anilinium ions) are linear, with slopes $\beta = 0.9$ for DNPTC, in agreement with a stepwise mechanism where the breakdown of a tetrahedral addition intermediate (T^{\pm}) is rate determining, and $\beta = 0.54$ for TNPTC, consistent with a concerted mechanism. Consideration of the results for aminolysis from the present work and those from previous studies leads to the following conclusions. (i) The tetrahedral intermediate possessing a 2,4-dinitrobenzenethio group is more stable than that including the 2,4,6-trinitrobenzenethio group. (ii) The tetrahedral intermediate possessing the 2,4,6-trinitrobenzenethio group has no existence beyond the limit of a vibration period (concerted mechanism). (iii) Tetrahedral intermediates possessing anilino groups are less stable than those derived from pyridines but are more stable than the tetrahedral intermediates derived from secondary alicyclic amines. (iv) Anilines are more reactive toward the carbonyl group of methyl 2,4-dinitrophenyl carbonate than toward the carbonyl of DNPTC.

Introduction

There is abundant literature on the kinetics and mechanism of the aminolysis of carbonyl and thiocarbonyl compounds such as acetate¹ and benzoate² esters, diaryl³ and alkyl aryl carbonates,⁴ aryl thiobenzoates,⁵ aryl thioacetates,⁶ aryl *O*-ethyl thiocarbonates,⁷ diaryl

and aryl ethyl thionocarbonates,⁸ aryl *O*-ethyl dithiocarbonates, and aryl dithioacetates.⁹ Although much attention has been focused on the effects of the leaving group on the kinetics and mechanism, much less is known about the effects of the amine nature on the mechanisms of the above reactions.

In some of these works, it has been concluded that secondary alicyclic amines are better nucleofuges from a zwitterionic tetrahedral intermediate (T^{\pm}) than isobasic pyridines; this has been deduced from the $\text{p}K_{\text{a}}$ values at the center of the break ($\text{p}K_{\text{a}}^0$) of nonlinear Brønsted plots.^{6b} It has also been found that pyridines are expelled more slowly than isobasic quinuclidines from the zwitterionic tetrahedral intermediate formed in the aminolysis of phenyl 4-nitrophenyl carbonate.³

In the reactions of ethyl *S*-(2,4-dinitrophenyl) thiocarbonate (DNPTC) and ethyl *S*-(2,4,6-trinitrophenyl) thiocarbonate (TNPTC) with secondary alicyclic amines, it has been found that the mechanism is concerted,^{7a,b} whereas in the pyridinolysis of the above substrates, the mechanism is stepwise, i.e., a tetrahedral intermediate is formed on the reaction path.^{7d} This fact indicates that substitution of a pyridine by a secondary alicyclic amine implies a substantial destabilization of T^{\pm} ; this is of such

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magnitude as to prevent the existence of the intermediate with a secondary amino moiety.

The comparison of the reactions of 2,4-dinitrophenyl methyl carbonate with pyridines, secondary alicyclic amines, and anilines suggests that anilines render T[±] more stable than do secondary alicyclic amines but less stable than do pyridines.^{4e}

In the present work, we undertake a mechanistic study on the reactions of DNPTC and TNPTC with anilines with the aim to (i) shed more light on the reaction mechanism of thiocarbonates, (ii) examine the influence of the amine nature by comparison of the title reactions with those of the same substrates with pyridines^{7d} and secondary alicyclic amines,^{7a,b} and (iii) examine the influence of the leaving group by comparison of the title reactions among them and by comparison of these reactions of DNPTC with those of methyl 2,4-dinitrophenyl carbonate with anilines.^{4e}

Experimental Section

Materials. The anilines (Aldrich) were purified either by distillation or recrystallization. DNPTC and TNPTC were obtained as previously reported.^{7a,b} *O*-Ethyl phenyl carbamate (EtOCONHPh) was synthesized as follows. To a solution of ethyl chloroformate (1.5 mL, 15 mmol) dissolved in acetonitrile (10 mL) was added slowly a solution of aniline (2.8 mL, 30 mmol) in acetonitrile (10 mL). The mixture was left 30 min at ambient temperature. Chloroform (15 mL) was added to this mixture, and the solution washed with 10% HCl and water. The organic layer was dried with MgSO₄ and filtered under vacuum, and the solvent was evaporated off. The crystallized product melted at 52–53 °C (lit¹⁰ mp 52 °C) and was identified as follows: ¹H NMR (200 MHz, CDCl₃) δ 7.20–7.40 (m, 4H), 7.10 (d, 1H), 6.7 (s, 1H), 4.2 (c, 2H, *J* = 7.1 Hz) 1.3 (t, 3H, *J* = 7.1 Hz); IR (KBr) 1703 (C=O), 1599 (C=C), 1234 (C–N carbamate), 746 and 694 (CH, arom) cm⁻¹.

Determination of p*K*_a. The p*K*_a of the 4-methylaniline was determined spectrophotometrically at 232 nm, 25.0 ± 0.1 °C, and ionic strength 0.2 M (KCl).

Kinetic Measurements. These were carried out by means of a Hewlett-Packard 8453 diode array spectrophotometer in water, at 25.0 ± 0.1 °C, ionic strength 0.2 M (KCl), and phosphate buffer 0.005 M. The reactions were followed at 400 nm (formation of the substituted benzenethiolate anions). All reactions were studied under excess of the aniline over the substrate (20-fold at least). The initial substrate concentration was 5 × 10⁻⁵ M.

Pseudo-first-order rate coefficients (*k*_{obsd}) were found for all reactions; for most of them, *k*_{obsd} was determined by means of the “infinity” method, except for the slowest reactions (DNPTC with 3-aminoacetophenone and with 3-aminobenzonitrile), where the initial rate method was used. The experimental conditions of the reactions and the *k*_{obsd} values are shown in Tables 1 and 2.

Product Studies. For the present reactions, one of the products was identified as the corresponding benzenethiolate; this was achieved by comparison of the UV–vis spectra after completion of the reactions with authentic samples under the same conditions. For the reactions of both substrates with aniline, the other product was identified as *O*-ethyl phenyl carbamate by comparison with an authentic sample by HPLC, column Eurospher C-18 (10 cm, 7 μm), eluant acetonitrile/water 70/30, isocratic mode 0.5 mL/min.

Results and Discussion

The general rate law obtained in the present reactions is given by eqs 1 and 2, where Ar is 2,4-dinitro- or 2,4,6-

Table 1. Experimental Conditions and *k*_{obsd} Values for the Reactions of Anilines with *O*-Ethyl *S*-(2,4-Dinitrophenyl) Thiocarbonate (DNPTC)^a

aniline substituent	pH	10 ³ [aniline] _{tot} ^b (M)	10 ⁵ <i>k</i> _{obsd} (s ⁻¹)	runs
4-methoxy	7.00	2.0–15	2.7–26	6
	7.20	2.0–15	3.0–30	6
	7.50	2.0–15	3.3–26	6
4-methyl	7.00	6.0–30	5.5–20	6
	7.20	6.0–30	5.2–20	6
	7.50	6.0–30	5.5–20	6
none	7.00	5.0–80	1.1–9.1	6
	7.20	5.0–80	1.1–9.3	6
	7.50	5.0–80	1.5–10	6
3-methoxy	7.00	9.0–90	0.88–5.6	6
	7.20	9.0–90	0.83–5.9	6
	7.50	9.0–90	1.0–5.8	6
3-acetyl	7.00	2.0–16	0.22–0.80	5
	7.20	2.0–16	0.20–0.82	5
	7.50	2.0–16	0.23–0.77	5
3-cyano	7.00	8.0–80	0.14–0.47	6
	7.20	8.0–80	0.26–0.57	6
	7.50	8.0–80	0.33–0.68	6

^a In water at 25.0 °C, ionic strength 0.2 M (KCl), in the presence of phosphate buffer 0.005 M. ^b Total concentration of substituted aniline (acid plus conjugate base).

Table 2. Experimental Conditions and *k*_{obsd} Values for the Reactions of Anilines with *O*-Ethyl *S*-(2,4,6-Trinitrophenyl) Thiocarbonate (TNPTC)^a

aniline substituent	pH	10 ³ [aniline] _{tot} ^b (M)	10 ⁴ <i>k</i> _{obsd} (s ⁻¹)	runs
4-methoxy	7.00	1.0–20	4.4–38	8
	7.20	1.0–20	4.2–39	8
	7.50	1.0–20	4.5–37	8
4-methyl	7.00	6.0–30	7.6–25	6
	7.20	6.0–30	8.3–26	6
	7.50	6.0–30	8.1–26	6
none	7.00	5.0–100	2.6–29	6
	7.20	5.0–100	2.4–30	6
	7.50	5.0–100	2.6–29	6
3-methoxy	7.00	9.0–90	1.8–16	6
	7.20	9.0–90	2.0–16	6
	7.50	9.0–90	2.0–17	6
3-acetyl	7.00	5.0–40	0.6–4.9	7
	7.20	5.0–40	0.7–4.8	7
	7.50	5.0–40	0.8–5.0	7
3-cyano	7.00	8.0–80	0.19–3.1	6
	7.20	8.0–80	0.21–3.5	6
	7.50	8.0–80	0.21–3.8	6
4-acetyl	7.00	5.4–54	0.19–1.6	6
	7.20	5.4–54	0.20–1.6	6
	7.50	5.4–54	0.24–1.6	6

^a In water at 25.0 °C, ionic strength 0.2 M (KCl), in the presence of phosphate buffer 0.005 M. ^b Total concentration of substituted aniline (acid plus conjugate base).

$$\frac{d[\text{ArS}^-]}{dt} = k_{\text{obsd}} [\text{EtOCOSAr}] \quad (1)$$

$$k_{\text{obsd}} = k_0 + k_{\text{N}} [\text{N}] \quad (2)$$

trinitro-phenyl, *k*₀ and *k*_N are the rate constants for hydrolysis and aminolysis of the substrates, respectively, and N represents the substituted aniline free base.

The second-order rate coefficients for aminolysis (*k*_N) were obtained as the slopes of plots of eq 2 at constant pH and were pH independent. These values, together with those of the p*K*_a of the conjugated acids of the anilines, statistically corrected with *q* = 1 and *p* = 3,^{4e,11} are shown in Table 3.

With the data of Table 3, the Brønsted-type plots of Figure 1 were obtained. The slopes of the lines are β =

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Table 3. Values of pK_a of Anilinium Ions and k_N for the Reactions of Anilines with DNPTC and TNPTC^a

aniline	$pK_a + \log(p/q)^b$	$10^3 k_N$ ($s^{-1} M^{-1}$)	
		DNPTC	TNPTC
4-methoxyaniline	6.13	20 ± 1	180 ± 7
4-methylaniline	5.56	6.1 ± 0.1	69 ± 2
aniline	5.21	1.10 ± 0.03	27 ± 1
3-methoxyaniline	4.84	0.59 ± 0.02	17 ± 1
3-aminoacetophenone	4.12	0.38 ± 0.02	12.0 ± 0.3
3-aminobenzonitrile	3.38	0.046 ± 0.002	3.6 ± 0.2
4-aminoacetophenone	2.90		2.8 ± 0.1

^a Both pK_a and k_N values were determined in water at 25.0 °C, ionic strength 0.2 M (KCl). ^b Statistically corrected with $p = 3$ and $q = 1$ (see text).

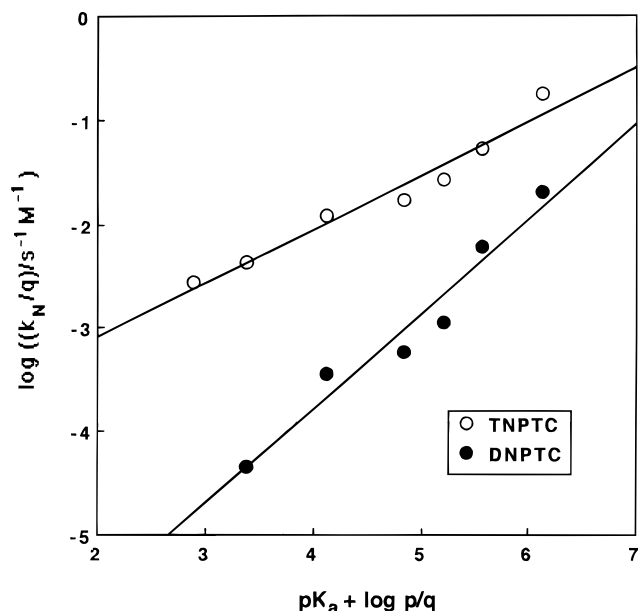
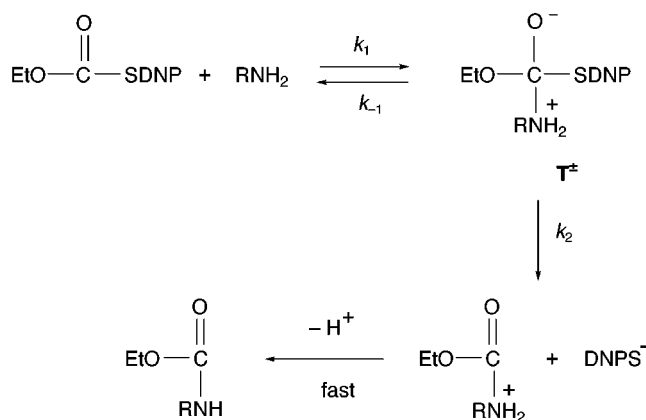


Figure 1. Brønsted-type plots obtained in the reactions of anilines with *O*-ethyl *S*-(2,4-dinitrophenyl) thiocarbonate (DNPTC) and *O*-ethyl *S*-(2,4,6-trinitrophenyl) thiocarbonate (TNPTC) in aqueous solution, at 25.0 °C, ionic strength 0.2 M (KCl).

0.9 ± 0.1 and $\beta = 0.54 \pm 0.05$ for the reactions of DNPTC and TNPTC, respectively.

The magnitude of β for the reaction of DNPTC is in agreement with the values of the Brønsted slopes found in the stepwise aminolysis of similar substrates when the breakdown to products of the zwitterionic tetrahedral intermediate (T^\pm) is the rate-determining step.^{1a,2e,3,4,5a,d,e,6,7c,d,8,9a-c,4e} The mechanism for this reaction is shown in Scheme 1, where DNP is 2,4-dinitrophenyl and R is a substituted phenyl group. The step k_2 should be rate determining for these reactions, and the formation of T^\pm should be an equilibrium step.

In contrast, the value of $\beta = 0.54$ found for the reaction of TNPTC (Figure 1) is in accord with a concerted process in which the structure of the transition state remains constant with the variation of the nucleophile basicity.¹² This β value is in agreement with those found in the concerted reactions of phenoxide anions with 1-acetoxy-8-hydroxynaphthalene ($\beta = 0.48$);¹³ 4-chloro 2-nitrophenyl acetate ($\beta = 0.64 \pm 0.05$);¹⁴ acetic anhydride ($\beta = 0.58 \pm$

Scheme 1

0.05);¹⁵ 2,4-dinitrophenyl acetate ($\beta = 0.57 \pm 0.03$);¹⁵ 3-nitrophenyl, 4-nitrophenyl, and 3,4-dinitrophenyl formates ($\beta = 0.64, 0.51,$ and 0.43 , respectively);¹⁶ and the corresponding acetates ($\beta = 0.66, 0.59,$ and 0.53 , respectively).¹⁶

Nevertheless, concerted phenolysis mechanisms with larger β values are also known, such as those of 4-nitrophenyl, 4-formylphenyl, and 3-nitrophenyl acetates ($\beta = 0.75, 0.79,$ and 1.04 , respectively),¹⁴ although these β values are based on pK_a values at an ionic strength (0.1 M) different than that of the kinetic measurements (1.0 M).¹⁶

The reactions of secondary alicyclic amines with DNPTC and TNPTC are concerted, as indicated by the linear Brønsted plots found, with slopes $\beta = 0.56$ and 0.48 , respectively,^{7a,b} and the fact that the predicted Brønsted breaks, had these reactions been stepwise, were not observed.^{7a,b} The β value alone is not sufficient to prove that a reaction is concerted; one must be sure that the hypothetical break (pK_a^0) of the Brønsted-type plot (due to the change in the rate-determining step of a stepwise process) is located at a pK_a value within the pK_a range of the nucleophiles used in the plot.¹² Unfortunately, there are no studies on stepwise reactions of anilines with thiocarbonates and related compounds in which pK_a^0 values have been found experimentally that would allow the estimation of a hypothetical Brønsted break for the reactions of TNPTC with anilines. Nevertheless, the great difference found in the Brønsted slopes for the reactions of the two substrates studied in this work (Figure 1) suggests that the mechanism of the reactions of TNPTC with anilines is concerted.

It has been reported that the reactions of DNPTC and TNPTC with pyridines proceed through the formation of a tetrahedral intermediate (T^\pm).^{7d} The fact that the reactions of the same substrates with secondary alicyclic amines are concerted^{7a,b} was explained by an expulsion rate from T^\pm of the latter amines faster than that for isobasic pyridines. Namely, the alicyclic amines destabilize kinetically the tetrahedral intermediate to the point that it cannot exist.

The fact that the reactions of DNPTC with secondary alicyclic amines are concerted,^{7a} whereas the reactions

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of the same substrate with anilines proceed via a tetrahedral intermediate, indicates that substitution of an aniline by a secondary alicyclic amine implies a substantial destabilization of the tetrahedral intermediate. This is of such magnitude as to prevent the existence of this intermediate, and therefore, the mechanism changes from stepwise to enforced concerted.¹⁷ This destabilization could be due to a faster nucleofugality from the tetrahedral intermediate of a secondary alicyclic amine compared to that of an isobasic aniline, as found in the reactions of methyl 2,4-dinitrophenyl carbonate.^{4e}

On the other hand, the fact that the reactions of TNPTC with pyridines^{7d} are stepwise, whereas those of the same substrate with anilines are concerted, indicates that anilines destabilize kinetically the tetrahedral intermediate (T^\pm) in comparison with pyridines as a result of a greater nucleofugality from T^\pm of the former amines.

In summary, we can conclude that anilines destabilize the tetrahedral intermediate relative to pyridines but stabilize it compared with secondary alicyclic amines. Therefore the sequence: secondary alicyclic amines > anilines > pyridines seems to hold for the rate constants for amine expulsion from the tetrahedral intermediate. This is the same sequence proposed for the reactions of this amine series with methyl 2,4-dinitrophenyl carbonate, where all reactions undergo a stepwise mechanism.^{4b,e}

By comparison of the concerted reactions of TNPTC with the stepwise mechanism for the reactions of DNPTC with the same series of anilines, it can be concluded that there is a remarkable destabilization of the tetrahedral intermediate as a result of the introduction of a third nitro group to the nucleofuge. This destabilization must arise from the lower basicity of TNPS relative to DNPS (pK_a 1.4 and 3.4, respectively),^{6b} which increases its nucleofugality from the intermediate and renders this species highly unstable kinetically. The "intermediate" no longer exists, and the concerted mechanism is enforced.¹⁷

From a comparison of the Brønsted-type plots obtained in the reactions of anilines with DNPTC and methyl 2,4-dinitrophenyl carbonate (DNPC),^{4e} shown in Figure 2, it can be observed that the latter substrate is more reactive toward anilines than the former. Although these substrates possess different "nonleaving" groups (EtO and MeO), it has been found that the change from EtO to MeO as the nonleaving group in similar substrates does not affect the kinetics.^{8c} Therefore, the difference in reactivity between DNPTC and DNPC must arise from the different leaving groups. Because breakdown to products of the corresponding tetrahedral intermediate is the rate-determining step for both reactions, it means that $k_N = K_1k_2$ is greater for DNPC ($K_1 = k_1/k_{-1}$ and k_2 are defined in Scheme 1).

The k_2 values found for the expulsion of DNPS and DNPO from the tetrahedral intermediates formed in the reactions of 2,4-dinitrophenyl thiolacetate and acetate with secondary alicyclic amines are closely similar, 2.4×10^9 and 3.0×10^9 s⁻¹, respectively.^{6b,18} This is so because the difference in basicity of these two groups ($pK_a = 3.4$ and 4.0 for 2,4-dinitrobenzenethiol and 2,4-dinitrophenol, respectively),^{6b} is compensated by the fact that

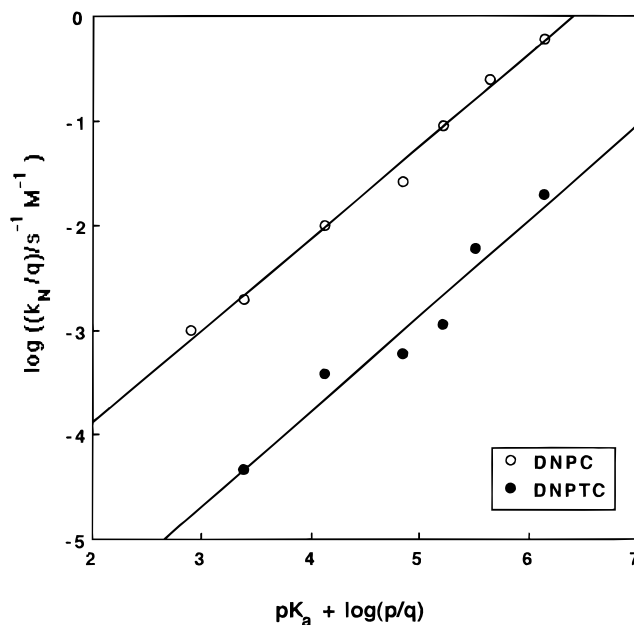
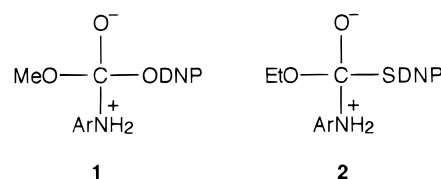


Figure 2. Brønsted-type plots obtained in the reactions of anilines with *O*-ethyl *S*-(2,4-dinitrophenyl) thiocarbonate (DNPTC) and methyl 2,4-dinitrophenyl carbonate (DNPC) in aqueous solution, at 25.0 °C, ionic strength 0.2 M (KCl).

phenoxide anions are better leaving groups from a tetrahedral intermediate than *isobasic* benzenethiolate anions.¹⁹ If it is assumed that the greater push due to the change of methyl by an ethoxy or methoxy group in T^\pm enlarges the k_2 values by the same factor,^{3,7a} the greater reactivity toward anilines of DNPC compared with DNPTC, when breakdown of T^\pm is rate limiting, must be due to K_1 .

From eqs 7 and 8 of ref 18 and eqs 15 and 16 of ref 6b, the values of k_{-1} (expulsion of secondary alicyclic amines and pyridines from the corresponding tetrahedral intermediates) can be determined for the reactions of 2,4-dinitrophenyl acetate¹⁸ and 2,4-dinitrophenyl thiolacetate.^{6b} It is found that the k_{-1} value for a given amine is 2 to 4 times greater for the former reaction. This is in line with the known superior push provided by a ArO group from T^\pm to expel other groups, compared to the push from ArS.²⁰ Therefore, the value of k_{-1} (expulsion of an aniline) should be greater from the intermediate **1** than from **2** in view of the stronger push exerted by DNPO in **1**.



Therefore, the larger value of K_1k_2 for the reactions of anilines with DNPC relative to that with DNPTC (Figure 2) can only be explained by a larger k_1 value for DNPC to more than compensate for its larger value of k_{-1} . A greater value of k_1 in the reactions of anilines with DNPC, relative to DNPTC, can be explained on the basis

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of the "hard and soft acids and bases" principle:²¹ anilines, which are considered borderline bases, react faster with the carbonyl group of carbonate, considered relatively hard, than the relatively soft carbonyl group of thiolcarbonate.²¹ Pyridines, whose absolute hardness is similar to that of anilines,²¹ react faster toward the carbonyl

group of methyl 2,4-dinitrophenyl carbonate compared to the softer thiocarbonyl group of ethyl 2,4-dinitrophenyl thionocarbonate.^{8c}

Acknowledgment. We thank FONDECYT of Chile for financial assistance to this work.

JO982063U

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