protonate the products. The organic layer was concentrated to 5 g of a light brown solid. This was chromatographed on 75 g of silica gel eluting with 1600 mL of 0–20% EtOAc in CH_2Cl_2. The most polar of three major bands was isolated from the 15% eluate and concentrated to 0.80 g (20%) of **20** as an off-white solid: NMR ($CDCl_3$) δ 3.72 (2 s, 4, CH_2CN), 5.66 (2 s, 2, CHCN), 7.35 and 7.50 (ab q, 8, Ph), 7.60 (s, 2, pyridazine-H); MS 388 (M^+, bp), 360. Anal. Calcd for $C_{24}H_{16}N_6$: C, 74.21; H, 4.15; N, 21.64. Found: C, 74.51: H, 4.05; N, 21.23.

Acknowledgment. We are indebted to A. M. Mujsce for obtaining mass spectra, and we acknowledge helpful discussions with T. M. Miller and R. C. Haddon.

Registry No. 1, 134881-87-1; 2, 134881-88-2; 3, 134881-89-3; 5, 134881-90-6; 6, 134881-91-7; 7, 134881-92-8; 8, 134881-93-9; 9, 134881-94-0; 10, 134881-95-1; 11 triflate, 134881-97-3; 12 triflate, 134881-99-5; 13·HBr, 134882-00-1; 15, 134882-01-2; 16, 134882-02-3; 17, 134882-03-4; 18, 134882-04-5; 19, 134882-05-6; 20, 134882-06-7; 21, 134882-07-8; DCX, 622-75-3; 2-chloropyridine, 109-09-1; 2-chloropyridine oxide hydrochloride, 20295-64-1; 2-chloropyridine *N*-oxide, 2402-95-1; 3,6-dichloropyridazine, 141-30-0.

Kinetics and Mechanism of the Aminolysis of *O*-Ethyl *S*-Aryl Dithiocarbonates

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The reactions of *O*-ethyl *S*-phenyl dithiocarbonate (**1**) and *O*-ethyl *S*-(*p*-nitrophenyl) dithiocarbonate (**2**) with a series of secondary alicyclic amines, namely, piperidine, piperazine, 1-(β-hydroxyethyl)piperazine, morpholine, 1-formylpiperazine, and (with **2** only) piperazinium ion, are subject to a kinetic study at several pH values. The reaction leads to the corresponding thiocarbamates and thiophenols (measured as thiophenoxide ion by UV–vis spectrophotometry). Pseudo-first-order rate coefficients (k_{obsd}) are found throughout (amine excess). The kinetics are first order in amine for the reactions of **2**. The plots of k_{obsd} vs [amine] for the reactions of **1**, except with 1-formylpiperazine, are linear, but near the origin they are curved, showing a more complex rate equation. The reaction of **1** with 1-formylpiperazine shows a second-order dependence on the amine. No dependence on pH of the second-order rate constant values is observed. The findings are well-accommodated by a mechanistic model involving reversible nucleophilic attack on the thiocarbonyl group, two tetrahedral intermediates, **3** and **4**, and a deprotonation step. The Bronsted-type plots obtained are linear ($\beta_1 = 0.22$) for the reaction of **1** and curved for **2** ($\beta_1 = 0.2$ and $\beta_2 = 0.8$). The Bronsted-type plot obtained with the rate constants for amine expulsion from **3** is linear with $\beta_{-1} = -0.67$ and -0.54 for the reactions of **1** and **2**, respectively.

Introduction

The chemistry of *O*-alkyl and *O*-aryl dithiocarbonates has been subject to much study because these compounds are widely used in the laboratory and industry. One of the reactions most investigated of these compounds is the thione to thiol Lewis acid catalyzed rearrangement, giving *S,S*-dithiocarbonates; these reactions have been studied from both synthetic[1-4] and mechanistic[5] points of view. A large increase of the reaction rate in going from apolar to polar solvents has been found, suggesting that the rearrangement reaction occurs through highly polar transition states. Another well-investigated reaction is olefin formation from dithiocarbonate pyrolysis (Chugaev reaction).[6] Recently, the kinetics and Arrhenius parameters of the thermal decomposition of *S*-alkyl *O*-phenyl and *O*-alkyl *S*-phenyl dithiocarbonates have been described,[7] leading to a mechanistic proposal for the former reaction, suggesting a more E*i*-like rather than E1-like transition state; but for the latter the rearrangement reaction appears as a competing side reaction, which precludes a meaningful analysis of the rate data. On the other hand, the *O,S*-dithiocarbonates have been much studied as precursors or intermediates in the syntheses of thiols,[8] alkyl halides,[9] S-linked functions,[10] olefins,[11] and 1,3-dithiol-2-ones and 2-thiones,[12] in the deoxygenation of secondary alcohols,[13] in the stereoselective synthesis of allylic sulfides,[14] and recently in obtaining the *S,S*-dithiocarbonates as bidentate ligands in organometallic complexes.[15]

Although a great number of studies on the kinetics and mechanism of nucleophilic reactions on carbonyl compounds have been carried out showing important features affecting the product formation pathway,[16] the same reactions of thiocarbonyl compounds have received little attention. As far as we know no kinetic studies have been carried out on the hydrolysis and aminolysis of *O*-alkyl and *O*-aryl dithiocarbonates.

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Table I. Experimental Conditions and k_{obsd} for the Aminolysis of 1[a]

amine	pH	F_N[b]	$10^2[N]_{tot}$,[c] M	10^3k_{obsd}, s^{-1}	n[d]
piperidine	10.0	0.058	2.00–6.00	0.568–3.11	5
	10.3	0.102	1.00–7.00	0.541–6.78	7
	10.6	0.186	1.00–7.00	1.24–14.5	7
piperazine	9.44	0.24	2.00–7.00	1.18–8.56	6
	9.64	0.33	1.00–7.00	0.615–13.6	7
	9.44	0.50	1.00–7.00	1.24–23.0	7
1-(β-hydroxyethyl)piperazine	9.08	0.33	4.00–10.0	1.73–8.25	7
	9.38	0.50	2.00–8.00	1.12–9.28	7
	9.68	0.667	3.00–9.00	3.12–16.3	7
morpholine	8.48	0.33	3.00–28.0	1.25–23.3	11
	8.78	0.50	4.00–35.0	1.46–48.0	11
	9.08	0.667	4.00–50.0	2.58–113	12
1-formylpiperazine	7.98	0.50	6.00–14.0	0.351–1.60	5
	8.28	0.667	8.00–10.0	0.960–1.62	2
	8.58	0.80	6.00–10.0	0.778–1.77	3

[a] In water, at 25 °C, ionic strength 0.2 M (KCl). [b] Molar fraction of free amine. [c] Total amine concentration. [d] Number of points.

Table II. Experimental Conditions and k_{obsd} for the Aminolysis of 2[a]

amine (pK_a)[b]	pH	F_N[a]	$10^2[N]_{tot}$,[a] M	10^2k_{obsd}, s^{-1}	n[a]
piperidine	10.5	0.15	1.00–7.00	0.341–2.60	7
(11.21)	11.0	0.37	1.00–7.00	0.630–718	7
	11.5	0.64	1.00–7.00	1.94–13.0	7
piperazine	9.50	0.27	2.00–7.00	0.397–3.00	6
(9.94)	10.0	0.53	1.00–7.00	0.783–6.65	7
	10.4	0.74	1.00–6.00	1.11–7.19	7
1-(β-hydroxyethyl)piperazine	8.7	0.17	8.00–23.0	0.441–2.11	7
(9.38)	9.0	0.29	5.00–12.0	0.541–1.71	6
	9.4	0.51	3.00–9.00	0.622–2.46	6
morpholine	9.1	0.667	1.00–5.00	0.119–0.614	5
(8.78)	9.3	0.77	1.00–7.00	0.153–1.43	6
	9.7	0.89	1.00–7.00	0.206–1.79	7
1-formylpiperazine	7.5	0.25	8.00–15.0	0.046–0.151	4
(7.98)	8.0	0.51	6.00–13.0	0.115–0.330	5
	8.5	0.77	5.00–13.0	0.144–0.526	6
piperazium ion	6.6	0.86	2.00–11.0	0.0136–0.0971	7
(5.81)	6.9	0.92	3.00–11.0	0.0211–0.0612	6
	7.2	0.96	5.00–9.00	0.0310–0.0586	4
	7.5	0.98	6.00–15.0	0.0630–0.139	6
	7.8	0.98	3.00–11.0	0.0360–0.121	6

[a] As in Table I. [b] These are the pK_a values for the conjugate acid of the amine.[21]

In previous studies,[17,18] we have measured the kinetic and thermodynamic parameters of the reactions of some thiocarbonyl compounds with secondary amines and also with thiolate anion nulceophiles, where reaction pathways involving tetrahedral intermediates have been proposed. Following our interest in the reaction mechanism of thiocarbonyl compounds, and in order to shed more light on that of dithiocarbonates, the present work describes the kinetics of the aminolysis of *S*-phenyl and *S*-(*p*-nitrophenyl) *O*-ethyl dithiocarbonates, **1** and **2**, respectively, with piperidine, piperazine, 1-(β-hydroxyethyl)piperazine, morpholine, 1-formylpiperazine, and piperazinium ion.

Experimental Section

Materials. **1** and **2** were prepared by a literature method[19] and identified by ^1H NMR and IR analysis. Piperidinyl- and morpholinylthiocarbamates were prepared as described.[20] The amines were purified as reported.[21]

Kinetic Measurements. These were carried out as described,[21] following spectrophotometrically the appearance of the corresponding thiophenoxide ion. Pseudo-first-order rate coefficients (k_{obsd}) were obtained in all cases, as reported.[21] The experimental conditions of the reactions and the k_{obsd} values are shown in Tables I and II.

Product Studies. The presence of the aryl thiol and/or aryl thiolate ion were determined by comparison of the UV–vis spectra at the end of the reactions with those of the aryl thiol in the same conditions. The presence of the thiocarbamates was determined in two cases by comparison of the retention time at the end of the reactions with that of authentic samples of piperidinyl- and morpholinylthiocarbamates by HPLC in a Knauer Model 64 pump with a C-18 column under the following conditions: eluant, methanol–water (1:1; v/v) in the isocratic mode; flow rate, 1 mL min^{-1}; temperature, ambient; UV detector, Perkin-Elmer LC-15.

Results and Discussion

The overall reactions studied in this work are depicted by eq 1

$$EtOC(S)SAr + HNR^1R^2 \rightarrow ArSH + EtOC(S)NR^1R^2 \quad (1)$$

In the reactions of **1** with amines other than 1-formylpiperazine the k_{obsd} vs [N] plots (*N* is the free amine) are

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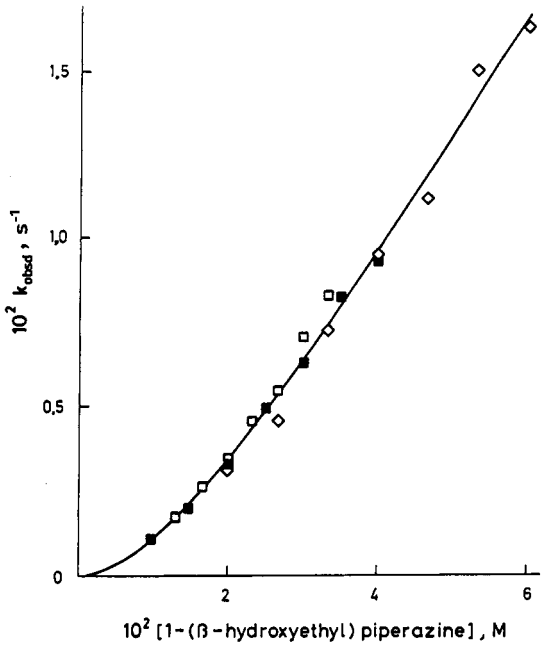
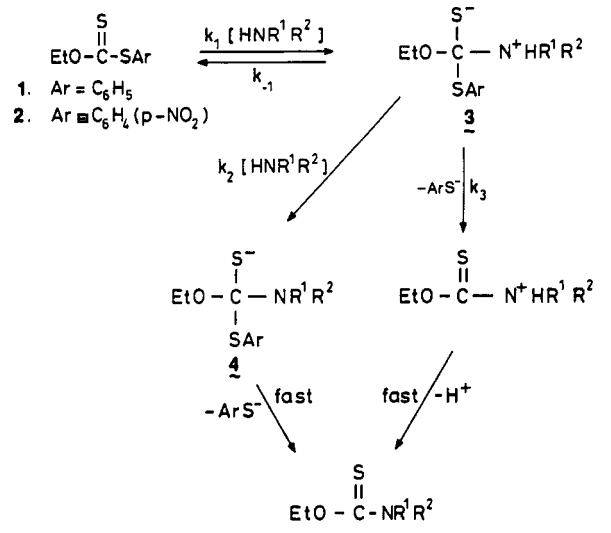


Figure 1. Dependence of k_{obsd} on the concentration of free 1-(β-hydroxyethyl)piperazine, in reaction with 1: □, pH 9.08; ■, pH 9.38; ◇, pH 9.68. The line was calculated through eq 4, wit the values of k_1 and k_{-1} from Table III and $k_2 = 10^{10}\ s^{-1}\ M^{-1}$.

Scheme I



linear at high concentrations but the intercepts of these lines are negative, exhibiting a curve toward the origin as shown in Figure 1. The second-order rate coefficients (k_N) were determined from the reciprocal of the intercepts of the linear $[N]/k_{obsd}$ vs $[N]^{-1}$ plots. For the reaction of 1 with 1-formylpiperazine the plot k_{obsd} against $[N]^2$ is linear under the amine concentration range used. In the aminolysis of 2 (except piperazinium ion) the plots k_{obsd} vs [N] are linear with zero intercepts, and the k_N values were obtained as the slopes. The k_N value for the reaction of 2 with piperazinium ion was determined as the slope of the m/F_N vs F_{NH}/F_N plot or as the intercept of m/F_{NH} vs F_N/F_{NH} plot, where m is the slope of a k_{obsd} vs $[N]_{tot}$ (total amine concentration) plot and F_N and F_{NH} are the free piperazine and piperazinium ion fractions, respectively.[21]

For all the reactions studied it is noticeable that no significant differences in the kinetic behavior were observed at the different pH values used (e.g., Figure 1).

Scheme I shows a plausible mechanism for the reactions studied, which is similar to that proposed by Satterthwait and Jencks for the aminolysis of esters.[22]

Table III. Values of the Microconstants Obtained in the Aminolysis of 1

amine	k_1, $s^{-1}\ M^{-1}$	(k_2/k_{-1}), M^{-1}	$10^{-6}k_{-1}$, s^{-1}
piperidine	1.08	788	0.127
piperazine	0.82	84.6	1.18
1-(β-hydroxyethyl)piperazine	0.401	36.7	2.7
morpholine	0.37	18.1	5.5

In Scheme I the 4 → 3 reaction was disregarded since it is thermodynamically unfavorable due to the lower basicity of the amine moiety in 3 relative to the free amine[17] (see below), and as mentioned above, no kinetic dependence on pH was found. With this assumption and applying the steady-state condition to intermediate 3, eq 2 can be derived. The differences found in the empirical rate equations depend on the relative importance of the intermediate decomposition rates in Scheme I.

$$k_{obsd} = k_1[N](k_2[N] + k_3)(k_{-1} + k_2[N] + k_3)^{-1} \quad (2)$$

As we will discuss later, the k_2 value is the same for all the reactions since this step is the favorable deprotonation by the amine of the corresponding protonated amine moiety, so the differences in the rate equations can be attributed to the k_{-1} and k_3 values and to the amine concentration range.

If the amine is poorly basic, its expulsion from 3 is fast and it is possible that $k_{-1} \gg (k_2[N] + k_3)$, and if the nucleofuge is relatively poor, $k_2[N] \gg k_3$ and eq 3 can be obtained. Probably this is the case in the reaction of 1 with 1-formylpiperazine.

$$k_{obsd} = (k_1k_2/k_{-1})[N]^2 \quad (3)$$

On the other hand, if the nucleofuge of the substrate is relatively poor, and if at the amine concentration range $k_2[N]$ and k_{-1} are comparable, eq 4 is obtained, which accounts for a first order in amine at high amine concentrations and a curve at low concentrations. Equation 4 can

$$k_{obsd} = k_1k_2[N]^2(k_{-1} + k_2[N])^{-1} \quad (4)$$

$$[N]/k_{obsd} = k_{-1}(k_1k_2)^{-1}[N]^{-1} + k_1^{-1} \quad (5)$$

be rewritten as eq 5, which explains the linear plots of $[N]/k_{obsd}$ vs $[N]^{-1}$. This is the case of the reactions of 1 with the amines, except 1-formylpiperazine. The values of k_1 and k_2/k_{-1} can be obtained from the intercepts and slopes of plots of eq 5.

If the amine is basic, its expulsion from 3 is slow, so that $k_{-1} \ll (k_2[N] + k_3)$, leading to eq 6. On the other hand, if there is a good nucleofuge in the substrate, it is possible that $k_3 \gg k_2[N]$ and if $k_3 \approx k_{-1}$, eq 2 leads to eq 7, which depending on the amine basicity ($k_3 \gg k_{-1}$) can also be transformed to eq 6.

$$k_{obsd} = k_1[N] \quad (6)$$

$$k_{obsd} = k_1k_3[N](k_{-1} + k_3)^{-1} \quad (7)$$

The rate equation for the aminolysis of 2 is first order in amine, in accord with eqs 6 and 7, and we found this behavior even for the least basic amine. This indicates that eq 7 is valid at least for the less basic amines.

Table III summarizes the values of k_1 and k_2/k_{-1} obtained for the reactions of 1. Before plotting the Bronsted-type equation the pK_a and k_1 values must be statistically corrected, with $q = 1$ (except piperazine with

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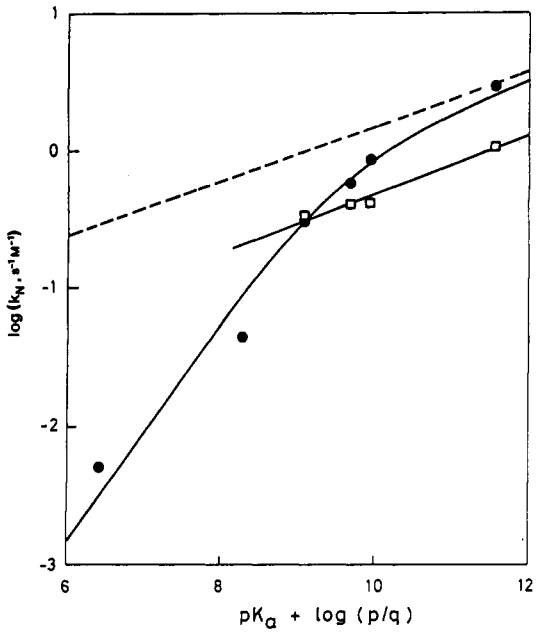
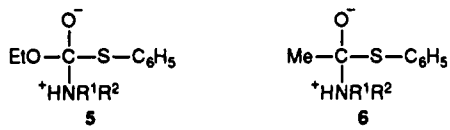


Figure 2. Bronsted-type plots for the aminolysis of □ phenyl O-ethyl dithiocarbonate and of ● *p*-nitrophenyl *O*-ethyl dithiocarbonate.

q = 2) and p = 2 (except piperazinium ion with p = 4).[21,23,24] The plot for k_1 is linear (Figure 2) with β = 0.22 ± 0.05, which is in accord with the value expected for amine attack to thiocarbonyl as the rate-determining step.[25,26]

In order to evaluate the pK_a of **3** in Scheme I we will estimate first the pK_a of **5**, analogue of **3**.



The pK_a value of **6** has been estimated equal to that of the parent aminium ion,[21] based on Jencks' procedure.[27-29] Substitution of the methyl group of **6** by ethoxy (σ_I = −0.05 and 0.27,[30] respectively) lowers the pK_a of **6** by (−0.05–0.27) 7.3 = −2.3 units.[17,21,28] Therefore, the pK_a of **5** is 2.3 units lower than that of the parent aminium ion.

It has been asserted that there is a pK_a lowering of 3.5 units when going from N-protonated *N*-alkylcarbamates to the corresponding thiocarbamates.[31] Obviously, the pK_a lowering in going from **5** to **3** cannot be as large since the delocalization of the N positive charge is much larger in the thiocarbamate system than in the intermediates **3** or **5**.[17] The quantification of the pK_a lowering is difficult, and we can only state that the pK_a value of **3** for a given amine should be smaller than that of **5**.

According to the discussion above the proton transfer from **3** to the corresponding amine is thermodynamically favorable and for the reactions under study we can estimate k_2 as 10^{10} s^{-1} M^{-1}.[32]

Table IV. Values of k_N and the Microconstants Obtained in the Aminolysis of 2

amine	(k_N/q), s^{-1} M^{-1}	(k_1/q), s^{-1} M^{-1}	(k_{-1}/k_3)
piperidine	3.03	3.03	
piperazine	0.85	1.45	0.7
1-(β-hydroxyethyl)piperazine	0.57	1.29	1.26
morpholine	0.30	0.977	2.26
1-formylpiperazine	0.06	0.676	10.26
piperazinium ion	0.005	0.286	57.2

With the k_2/k_{-1} values for the reaction of **1** (Table III) and the value of k_2 we can estimate the k_{-1} values in the aminolysis of **1**. Table III also summarizes these values, which give a linear Bronsted-type plot (not shown), with slope β_{-1} = −0.67 ± 0.05. This value is similar to that reported in the aminolysis of aryl acetates,[23] carbonates,[33] and thiolacetates,[34] but there are no values reported for thiocarbonyl compounds such as the ones under study.

The extrapolated value (from the Bronsted-type plot) for the expulsion of 1-formylpiperazine from **3** is ca. 2 × 10^9 s^{-1}. This means that in the reaction of **1** with this amine, $k_{-1} \gg k_2[N]$ over all the amine concentration range (Table I) and explains why kinetics second order in amine were found for this reaction.

With the k_1 and k_{-1} values of Table III for the aminolysis of **1** and with k_2 = 10^{10} s^{-1} M^{-1}, we can calculate the curves k_{obsd} against [N] through eq 4, which agree well with the experimental points. Figure 1 is an example of the fit.

Figure 2 shows the statistically corrected Bronsted-type plot for the aminolysis of **2** using the k_N/q values of Table IV. The points are experimental, and the line calculated through a semiempirical equation based on the existence of a tetrahedral intermediate **3** in the reaction path and a change in the rate-determining step from breakdown of **3** to its formation as the basicity of the amine increases.[35] The curve fits the experimental data with the slopes β_1 = 0.2, β_2 = 0.8 for the formation and breakdown of **3**, respectively. The values used for the other adjustable parameters are $pK_a°$ = 9.6 and log $k_N°$ = −0.25. The $pK_a°$ and log $k_N°$ are the coordinates at the center of curvature and refer to an (hypothetical) amine for which k_{-1} equals k_3 in Scheme I.[35]

The described behavior is in accord with eq 7 and Scheme I, with $k_N = k_1k_3/(k_{-1} + k_3)$. Since $k_N°$ is the value of k_N when $k_{-1} = k_3$ we can determine $k_1° = k_N°/2$ = 1.12 s^{-1} M^{-1} for the reaction of **2** with a hypothetical amine of pK_a = 9.6. For an amine as basic as piperidine (corrected pK_a = 11.54), $k_N = k_1$. Drawing a straight line of slope 0.2 through the experimental piperidine point (dotted line in Figure 2), we can estimate values for k_1 and the k_{-1}/k_3 ratio; no differences in the estimated values are found if the straight line is drawn through the $k_1°$ value. Table IV summarizes these estimations.

A comparison between the k_1 values for the reactions of both substrates (Tables III and IV) shows that the reactivity of **2** is about three times greater than that of **1**. This difference can be attributed to the electron-withdrawing effect of the *p*-NO_2 group in **2** that makes this thiocarbonyl carbon more electrophilic.

On the other hand, assuming that k_3 is independent of the amine basicity, since there is little or no electron do-

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nation from the cationic amine moiety of **3** to exert the push,[21,23,33] the slope of a Bronsted-type plot for k_{-1}/k_3 must be β_{-1}. For the reaction of **2** the value found of the slope of this plot (not shown) is −0.54, lower than that determined for **1**. Nevertheless this value must be taken with care due to the errors involved in both the determination of k_1 (and therefore k_{-1}/k_3) and the estimation of β_N (=0 ± 0.1) for k_3.[33] Assuming β_{-1} is ca. −0.7, one concludes that the effective charge on the nitrogen atom of **3** is $(\beta_1 - \beta_{-1}) = +0.9$[33] and that on the nitrogen atom of the transition state for the first step is +0.2.

The rate equations, the reactivity difference found in the aminolysis of both substrates, and the structure–reactivity relations are in accord with the proposed reaction scheme, but probably more data are needed to confirm this mechanism.

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Registry No. 1, 3278-38-4; 2, 99358-06-2; piperidine, 110-89-4; piperazine, 110-85-0; 1-(β-hydroxyethyl)piperazine, 103-76-4; morpholine, 110-91-8; 1-formylpiperazine, 7755-92-2; piperazinium ion, 22044-09-3.

Synthesis of Substituted Tetrahydronaphthalenes by Mn(III), Ce(IV), and Fe(III) Oxidation of Substituted Diethyl α-Benzylmalonates in the Presence of Olefins

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The oxidation of substituted diethyl α-benzylmalonates (**1a–m**) by manganese(III) acetate in acetic acid, cerium(IV) ammonium nitrate in methanol, or iron(III) perchlorate in acetonitrile in the presence of substituted olefins **2a–u** was investigated. The results are consistent with a common mechanism. It involves selective generation of malonyl radicals from high-valent metal malonyl complexes, their addition to the olefin, and competition of the adduct radical between intramolecular cyclization to produce highly functionalized tetrahydronaphthalenes (**3**) and oxidation by metal salt to give mainly γ-lactones (**5**). Several electron-withdrawing and releasing substituents on the aromatic ring and on the olefin can be successfully used in the synthesis of **3** without olefin telomerization. The influence of metal and olefin or aromatic substituents on the homolytic addition and intramolecular aromatic substitution is discussed.

The oxidation of carbonyl compounds by high-valent metal salts (Fe(III),[1] Ce(IV),[2] and mainly Mn(III))[3,4] has attracted the attention of synthetic organic chemists as a tool to obtain efficiently highly functionalized derivatives. In particular, we[1,4] and others[5,6] have recently reported examples for homolytic aromatic alkylation by these radical sources showing high yield and selectivity. In an attempt to extend further the potentiality of these oxidations, we were interested to know the limit of application of the previously reported intramolecular aromatic substitution by oxidative addition of carbonyl compounds to olefins.[6,7] In his pioneering work,[7] Heiba reported moderate yields of tetralones when acetophenones were oxidized by Mn(III) acetate in the presence of monosubstituted or 1,2-disubstituted alkenes in excess. More re-

Table I. Oxidative Addition of X-Substituted Benzylmalonates (1a–m) to 1-Octene Induced by Mn(III) Acetate (AcOH, 60 °C, 12 h)

1	1 (conv, %)	3 (yield, %)
1a	95	90
1b	96	86
1c	90	85
1d	91	85
1e	93	89[a]
1f	90	83[b]
1g	88	80[c]
1h	95	85[d]
1i	88	79
1j	98	91
1k	93	trace
1m	55	48[e]

[a] Ortho/para ratio of addition–cyclization isomers: **3eb′/3eb** = 1.64; [b] **3fb′/3fb** = 1.33; [c] **3gb′/3gb** = 0.62; [d] **3hb′/3hb** = 0.88. [e] After 48 h.

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