

KINETICS AND MECHANISM OF THE AMINOLYSIS OF S-ARYL O-ETHYL DITHIOCARBONATES IN ACETONITRILE

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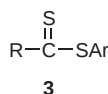
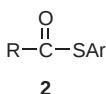
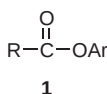
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Dedicated to Professor Otto Exner on the occasion of his 80th birthday in recognition of his outstanding contributions to physical organic chemistry.

The aminolysis of S-aryl O-ethyl dithiocarbonates with benzylamines are studied in acetonitrile at $-25.0\text{ }^{\circ}\text{C}$. The β_X (β_{nuc}) values are in the range 0.67–0.77 with a negative cross-interaction constant, $\rho_{XZ} = -0.24$, which are interpreted to indicate a concerted mechanism. The kinetic isotope effects involving deuterated benzylamine nucleophiles ($\text{XC}_6\text{H}_4\text{CH}_2\text{ND}_2$) are large, $k_{\text{H}}/k_{\text{D}} = 1.41\text{--}1.97$, suggesting that the N–H(D) bond is partially broken in the transition state by forming a hydrogen-bonded four-center cyclic structure. The concerted mechanism is enforced by the strong push provided by the EtO group which enhances the nucleofugalities of both benzylamine and arenethiolate from the putative zwitterionic tetrahedral intermediate.

Keywords: S-Aryl O-ethyl dithiocarbonates; Aminolysis; Concerted mechanism; Cross-interaction constants; Kinetic isotope effects; Reaction mechanisms.

The mechanism of aminolysis of esters and carbonates has been extensively investigated because of its relevance to the enzymatic catalysis of carbonyl group transfer reactions. In many of these nucleophilic substitution reactions curved Brønsted-type plots have been found, which have been attributed to a change in the rate-limiting step from breakdown ($\beta_{\text{nuc}} \approx 0.8\text{--}1.0$) to formation ($\beta_{\text{nuc}} \approx 0.1\text{--}0.3$) of a tetrahedral zwitterionic intermediate, $\text{T}^{\pm}$, in the reaction path as the basicity of the amine nucleophile increases¹. Quite interestingly, however, concerted nucleophilic displacements are found only in the reactions S-aryl O-ethyl thiocarbonates (structure **2** with $\text{R} = \text{EtO}$) with good leaving groups² (**a** $\text{Ar} = 2,4,6\text{-(NO}_2)_3\text{C}_6\text{H}_2$ or **b** $\text{Ar} = 2,4\text{-(NO}_2)_2\text{C}_6\text{H}_3$) and alicyclic secondary amines ($\beta_{\text{nuc}} \approx 0.4\text{--}0.6$)³.



1-3	Ar
a	C ₆ H ₂ -2,4,6-(NO ₂) ₃
b	C ₆ H ₃ -2,4-(NO ₂) ₂
c	C ₆ H ₄ -4-NO ₂

The concerted mechanism is enforced by (i) stronger push provided by R = EtO, which enhances the nucleofugality of both the amine and arylthiolate ion from T[±] relative to other acyl groups (R = alkyl or phenyl) and (ii) much faster expulsion of a given amine and ArS[−] from T[±] formed with **2** than those from T[±] formed with **1** and **3** due to a stronger π -bonding energy of the carbonyl group (C=O) compared with thiocarbonyl (C=S) coupled with a greater nucleofugality of ArS[−] incurred by much less basicity of ArS[−] than ArO[−].

In this work, we carried out kinetic studies of aminolysis of *S*-aryl *O*-ethyl dithiocarbonates, **3** with R = EtO and Ar = C₆H₄Z (Z = 4-Me, H, 4-Cl and 4-Br), using benzylamines (XC₆H₄CH₂NH₂; X = 4-OMe, 4-Me, H, 4-Cl and 3-Cl) in acetonitrile at −25.0 °C. The primary purpose of this work is to examine the effects of (i) amine nature (secondary alicyclic amines versus benzylamines) and (ii) substitution of C=S for C=O on the aminolysis mechanism of *S*-aryl *O*-ethyl carbonates. In addition we are much interested in the mechanistic criteria based on the sign of ρ_{XZ} ⁴ in Eqs (1), where X and Z are substituents in the nucleophile and leaving group, respectively. It has been postulated and experimentally confirmed that in a stepwise acyl transfer

$$\log (k_{\text{XZ}}/k_{\text{HH}}) = \rho_{\text{X}}\sigma_{\text{X}} + \rho_{\text{Z}}\sigma_{\text{Z}} + \rho_{\text{XZ}}\sigma_{\text{X}}\sigma_{\text{Z}} \quad (1a)$$

$$\rho_{\text{XZ}} = \partial\rho_{\text{Z}}/\partial\sigma_{\text{X}} = \partial\rho_{\text{X}}/\partial\sigma_{\text{Z}} \quad (1b)$$

through a tetrahedral intermediate, the sign of ρ_{XZ} is invariably positive and reactivity–selectivity principle (RSP) holds⁵. In contrast, the sign of ρ_{XZ} is normally negative and the RSP is violated⁶ in concerted acyl transfer reactions.

RESULTS AND DISCUSSION

The reactions studied in the present work followed the rate law given by Eqs (2) and (3), where [BA] is the concentration of the benzylamine nucleophile.

$$\text{rate} = k_{\text{obs}} [\text{substrate}] \quad (2)$$

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

The values of k_{N} were determined by the slopes of plots of k_{obs} against [BA], and the results are summarized in Table I. In this work, the selectivity parameters obtained as σ and $\text{p}K_{\text{a}}$ dependence of the rate constant, k_{N} (ρ_{X} , β_{X} , ρ_{Z} , β_{Z} and ρ_{XZ}) are also shown. In the determination of Brønsted coefficients, β_{X} and β_{Z} , the $\text{p}K_{\text{a}}$ values in water are used: the $\text{p}K_{\text{a}}$ (CH_3CN) values for structurally similar amines are known to change in parallel with the $\text{p}K_{\text{a}}$ (H_2O) values so that the β_{X} ($= \beta_{\text{nuc}}$) values given are reliable⁷. For the β_{Z} ($= \beta_{\text{lg}}$) values, a factor of 0.62 was used to all the β_{Z} values determined using the $\text{p}K_{\text{a}}$ (H_2O) values⁸.

The rates are extremely faster than those of corresponding reactions of aryl dithioates in acetonitrile. For example, the k_{N} value for the aminolysis of the S-aryl O-ethyl dithiocarbonate is $8.62 \times 10^{-1} \text{ l mol}^{-1} \text{ s}^{-1}$ at -25.0°C whereas those of aryl dithioacetate ($\text{R} = \text{CH}_3$ in **3**) and benzoate ($\text{R} = \text{C}_6\text{H}_5$ in **3**) are $6.99 \times 10^{-1} \text{ l mol}^{-1} \text{ s}^{-1}$ (at 20.0°C)⁹ and $3.82 \times 10^{-1} \text{ l mol}^{-1} \text{ s}^{-1}$ (at 30.0°C)¹⁰, respectively (for $\text{X} = \text{Z} = \text{H}$), with benzylamines in acetonitrile. A strong push provided by the EtO group is due to an efficient charge transfer of the lone pair electrons on the oxygen atom toward the $\sigma_{\text{C-S}}^*$ orbital, $n_{\text{O}} \rightarrow \sigma_{\text{C-S}}^*$ interaction, which leads to a facile bond cleavage of the C–S bond in the transition state (TS). This is especially strong since (i) the n_{O} level is high due to the electron donating effect of Et group and (ii) the $\sigma_{\text{C-S}}^*$ level is low¹¹ relative to $\sigma_{\text{C-O}}^*$. The second-order charge transfer energy¹² is given by $\Delta E^{(2)}_{n \rightarrow \sigma^*} = -2F_{n\sigma^*}^2/\Delta E$, where $\Delta E = E_{\sigma^*} - E_n$ and $F_{n\sigma^*}$ is the matrix element which is proportional to the overlap, $S_{n\sigma^*}$, between the two interacting orbitals.

Another factor that is enhancing the rate is the low $\pi_{\text{C=S}}^*$ level (relative to $\pi_{\text{C=O}}^*$ level)¹¹. Since the initial attack by the lone pair electrons of the nitrogen atom in the benzylamine nucleophile occurs at the $\pi_{\text{C=S}}^*$ orbital, the breaking of the $\pi_{\text{C=S}}^*$ orbital to form a tetrahedral TS or intermediate is facilitated by a strong $n_{\text{N}} \rightarrow \pi_{\text{C=S}}^*$ interaction where n_{N} is the lone pair orbital of the nitrogen atom in benzylamine. Thus the strong rate enhancement is

the combined results of the low $\sigma^*_{\text{C-S}}$ and $\pi^*_{\text{C=S}}$ levels and the high n_{O} and n_{N} levels of the EtO group and amino nitrogen in BA.

Reference to Table I reveals that the β_{X} values are 0.67–0.77, which are in the range of values that have been found for the concerted mechanism^{2a}. The concerted aminolysis reactions normally exhibit the Brønsted slopes in the range 0.4–0.7². However, β values smaller than 0.4¹³ and larger than

TABLE I

The second-order rate constants, k_{N} (in $\text{l mol}^{-1} \text{s}^{-1}$) for the reactions of S-aryl O-ethyl dithiocarbonates ($\text{EtO-C(=S)SC}_6\text{H}_4\text{Z}$) with X-benzylamines ($\text{XC}_6\text{H}_4\text{CH}_2\text{NH}_2$) in acetonitrile at -25.0°C

X	Z				ρ_{Z}^a	β_{Z}^b
	4-Me	H	4-Cl	4-Br		
4-OMe	0.915	1.39	2.52	2.78	1.17 ± 0.06	−0.40
4-Me	1.17^c			3.57		
	0.767	1.15	2.09	2.23	1.14 ± 0.04	−0.29
	0.507^d			1.37		
H	0.581	0.862	1.52	1.64	1.10 ± 0.05	−0.29
4-Cl	0.416	0.602	1.05	1.11	1.05 ± 0.04	−0.27
3-Cl	0.497			1.43		
	0.331	0.483	0.813	0.852	1.01 ± 0.03	−0.26
	0.217			0.512		
ρ_{X}^e	-0.68 ± 0.01	-0.71 ± 0.02	-0.76 ± 0.02	-0.79 ± 0.02	$\rho_{\text{XZ}}^f = -0.24 \pm 0.07$	
β_{X}^g	0.67 ± 0.02	0.70 ± 0.01	0.74 ± 0.02	0.77 ± 0.01		

^a The σ values were taken from Dean J. A.: *Handbook of Organic Chemistry*, Table 7-1, McGraw-Hill, New York 1987. Correlation coefficients were better than 0.997 in all cases.

^b The pK_{a} values were taken from Buckingham J. (Ed.): *Dictionary of Organic Chemistry*, 5th ed., Chapman and Hall, New York 1982. Z = 4-Br was excluded from the Brønsted plot for β_{Z} due to an unreliable pK_{a} values. Correlation coefficients were better than 0.997 in all cases. ^c At -15°C . ^d At -35°C . ^e The σ values were taken from McDaniel D. H., Brown H. C.: *J. Org. Chem.* **1958**, 23, 420. Correlation coefficients were better than 0.999 in all cases.

^f Correlation coefficient was 0.997. ^g The pK_{a} values were taken from Fischer A., Galloway W. J., Vaughan J.: *J. Chem. Soc.* **1964**, 3588. Correlation coefficients were better than 0.999 in all cases. X = 4- CH_3O were excluded from the Brønsted plot for β_{X} (benzylamine) due to an unreliable pK_{a} value listed.

0.7¹⁴ have also been found for concerted processes. The range of β_Z values (−0.26–0.40) is also consistent with the concerted aminolysis reaction^{1b}.

A strong support for the proposed mechanism comes from the negative ρ_{XZ} value (−0.24) obtained in this work. The sign of ρ_{XZ} has been found to be invariably positive ($\rho_{XZ} > 0$) for the stepwise aminolysis reactions⁵. The results of aminolysis of various *S*-aryl *O*-ethyl carbonates in H₂O or in MeCN are collected in Table II. In this table, the reactions in the upper/right region proceed by the concerted mechanism, while those in the lower/left zone proceed by the stepwise mechanism. This is because the amines are arranged in the downward order of increasing kinetic stability rendered to the tetrahedral intermediate^{2,3b}, and the carbonates are ar-

TABLE II
Results of aminolysis reactions of various *S*-aryl *O*-ethyl carbonates in H₂O or in MeCN

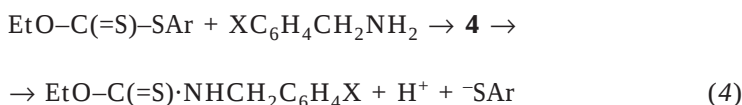
Amines	$\text{EtO}-\overset{\text{O}}{\parallel}{\text{C}}-\text{OAr}$	$\text{EtO}-\overset{\text{O}}{\parallel}{\text{C}}-\text{SAr}$	$\text{EtO}-\overset{\text{S}}{\parallel}{\text{C}}-\text{SAr}$
Benzylamines	MeCN: Stepwise ⁵ $\beta_X = 1.66\text{--}2.38$ $\rho_{XZ} = +1.38$	MeCN: Concerted ⁶ $\beta_X = 0.6\text{--}0.8$ $\rho_{XZ} = -0.47$	MeCN: Concerted ¹⁵ $\beta_X = 0.67\text{--}0.77$ $\rho_{XZ} = -0.24$
Quinuclidines		H ₂ O: concerted ² β_X : a 0.47 b 0.54 c 0.56	
Secondary alicyclic amines		H ₂ O: concerted ³ β_X : a 0.48 b 0.56	H ₂ O: stepwise ¹⁶ β_X : a 0.8 b 0.8
Anilines		H ₂ O: ¹⁹ β_X : a 0.9 b 0.54	MeCN: Concerted ⁶ $\beta_X = 0.50\text{--}0.70$ $\rho_{XZ} = -0.56$
Pyridines		H ₂ O: stepwise ¹⁷ β_X : a 0.80 b 0.90 c 0.80	H ₂ O: stepwise ¹⁸ β_X : a 0.9 b 1.0

a Ar = 2,4,6-(NO₂)₃C₆H₂; **b** Ar = 2,4-(NO₂)₂C₆H₃; **c** Ar = 4-NO₂C₆H₄

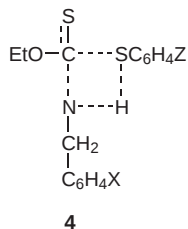
ranged in the order of increasing facility (to the right) of the nucleophilic attack of the substrate¹¹. We note that the sign of ρ_{XZ} is positive for the stepwise aminolysis but is negative for the concerted aminolysis reactions. The mechanism is strongly influenced by (i) facility of the initial attack, (ii) leaving ability of the amine from $T^\pm$, (iii) the nucleofugality of the ArS^- (and ArO^-) group and (iv) effect of solvent. One example is aminolysis of S-aryl O-ethyl carbonates (**2** with $R = EtO$) with quinuclidines². This reaction proceeds concertedly for the substrate with better leaving groups (**a** 2,4,6- $(NO_2)_3C_6H_2$ and **b** 2,4- $(NO_2)_2C_6H_3$) but the mechanism changes to a stepwise reaction with rate-limiting expulsion of the ArS^- group from $T^\pm$ for the substrate with low nucleofugality (**c** $Z = 4-NO_2$).

The secondary alicyclic amines and anilines are in the intermediate range as to the leaving ability from $T^\pm$ so that the mechanism does not follow a simple order, e.g., the secondary alicyclic amines react with **3** ($R = EtO$) in water by the stepwise mechanism¹⁶ but concertedly with **2** ($R = EtO$)³, whereas the reactions of aniline with **3** ($R = EtO$) proceed concertedly⁶.

It is to be noted that the faster rates are accompanied by larger selectivity parameters (Table I) so that the RSP is violated. This also provides support for the concerted mechanism²⁰. We therefore conclude that the reactions studied in the present work proceed via a concerted mechanism, Eq. (4).



The kinetic isotope effects, k_H/k_D , involving deuterated benzylamine nucleophiles²¹ ($XC_6H_4CH_2ND_2$) are shown in Table III. The k_H/k_D values are relatively large, 1.41–1.97, which is an indication that partial N–H(D) bond cleavage is involved in the TS²¹. Thus we propose the TS, **4**, in which the N–H(D) hydrogen is hydrogen bonded to the leaving group with four membered cyclic structure.



Finally the activation parameters, $\Delta H^\ddagger$ and $\Delta S^\ddagger$, are summarized in Table IV. The $\Delta H^\ddagger$ values are relatively low and $\Delta S^\ddagger$ values are large negative, which are consistent with the concerted mechanism²².

TABLE III

The secondary kinetic isotope effects for the reactions of S-aryl O-ethyl dithiocarbonates with deuterated X-benzylamines ($\text{XC}_6\text{H}_4\text{CH}_2\text{ND}_2$) in acetonitrile at -25.0°C

X	Z	$k_{\text{H}}, \text{mol l}^{-1} \text{s}^{-1}$	$k_{\text{D}}, \text{mol l}^{-1} \text{s}^{-1}$	$k_{\text{H}}/k_{\text{D}}$
4-OMe	4-Me	0.915 (± 0.008)	0.464 (± 0.005)	1.97 ± 0.03^a
4-OMe	H	1.39 (± 0.01)	0.808 (± 0.006)	1.72 ± 0.02
4-OMe	4-Cl	2.52 (± 0.04)	1.52 (± 0.02)	1.65 ± 0.03
4-OMe	4-Br	2.78 (± 0.05)	1.87 (± 0.03)	1.49 ± 0.04
4-Cl	4-Me	0.416 (± 0.004)	0.227 (± 0.002)	1.83 ± 0.02
4-Cl	H	0.602 (± 0.007)	0.358 (± 0.003)	1.68 ± 0.02
4-Cl	4-Cl	1.05 (± 0.01)	0.669 (± 0.006)	1.57 ± 0.02
4-Cl	4-Br	1.11 (± 0.02)	0.787 (± 0.007)	1.41 ± 0.03

^a Standard deviations.

TABLE IV

Activation parameters^a for the reactions of S-aryl O-ethyl dithiocarbonates with X-benzylamines in acetonitrile

X	Z	$\Delta H^\ddagger, \text{kcal mol}^{-1}$	$-\Delta S^\ddagger, \text{cal mol}^{-1} \text{K}^{-1}$
4-Me	4-Me	4.6	40
4-Me	4-Br	5.2	35
3-Cl	4-Me	4.5	41
3-Cl	4-Br	5.6	36

^a Calculated using the Eyring equation. The maximum errors calculated (Wiberg K. B.: *Physical Organic Chemistry*, p. 378, Wiley, New York 1964.) are $\pm 0.4 \text{ kcal mol}^{-1}$ and $\pm 2 \text{ e.u.}$ for $\Delta H^\ddagger$ and $\Delta S^\ddagger$, respectively.

EXPERIMENTAL

Materials

GR grade acetonitrile was used after three distillations. The benzylamine nucleophiles, GR grade, were used without further purification.

Substrates

The dithiocarbonates were prepared by the known method in the literature²³.

Kinetic Measurement

Rates were measured conductometrically at -25.0 ± 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 with large excess of benzylamine. Second-order rate constants, k_{N} , were obtained from the slope of a plot of k_{obs} vs benzylamine with more than five concentrations of more than three runs and were reproducible within $\pm 3\%$.

Product Analysis

Substrate (0.05 mol) and 4-methoxybenzylamine (0.5 mol) were added to acetonitrile and reacted at -25.0 °C under the same conditions as in kinetic measurements. After more than 15 half-lives, solvent was removed under reduced pressure and product was separated by column chromatography (silica gel, 10% ethyl acetate–hexane). Analysis of the product gave the following results.

$\text{CH}_3\text{CH}_2\text{OC}(=\text{S})\text{NHCH}_2\text{C}_6\text{H}_4\text{-4-OCH}_3$: liquid. IR (KBr): 3315 (N–H); 2972 (C–H, benzyl); 2963 (C–H, CH_2); 2946 (C–H, CH_3); 1683 (C=O); 1549 (C=C, aromatic ring); 1522 (N–H); 1260, 1038 (C–O). ^1H NMR (400 MHz, CDCl_3): 1.26 (3 H, t, CH_3); 2.04 (2 H, d, $J = 5.86$, $\text{CH}_2\text{-N}$); 3.90 (3 H, s, OCH_3); 4.19 (2 H, q, $J = 7.08$, OCH_2); 5.55 (1 H, s, NH); 6.97–7.85 (4 H, m, $J = 8.30$, aromatic ring). ^{13}C NMR (100.4 MHz, CDCl_3): 198.1 (C=S); 162.4, 134.2, 128.2, 113.9 (aromatic ring); 60.7, 55.9 (OCH_3); 36.3 (CH_2); 14.5 (CH_3). MS, m/z : 225 (M^+). For $\text{C}_{11}\text{H}_{15}\text{NO}_2\text{S}$ (225.3) calculated: 58.6% C, 6.71% H; found: 58.4% C, 6.73% H.

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REFERENCES AND NOTES

1. a) Jencks W. P.: *Chem. Rev.* **1985**, *85*, 511; b) Gresser M., Jencks W. P.: *J. Am. Chem. Soc.* **1977**, *99*, 6963; c) Gresser M., Jencks W. P.: *J. Am. Chem. Soc.* **1977**, *99*, 6970; d) Castro E. A., Ureta C.: *J. Org. Chem.* **1989**, *54*, 2153; e) Castro E. A., Ureta C.: *J. Org. Chem.* **1990**, *55*, 1676; f) Koh H. J., Han K. L., Lee I.: *J. Org. Chem.* **1999**, *64*, 4783; g) Oh H. K., Ku M. H., Lee H. W., Lee I.: *J. Org. Chem.* **2002**, *67*, 3874.
2. Castro E. A., Munoz P., Santos J. G.: *J. Org. Chem.* **1999**, *64*, 8298.
3. a) Castro E. A., Ibanez F., Salas M., Santos J. G.: *J. Org. Chem.* **1991**, *56*, 4819; b) Castro E. A., Salas M., Santos J. G.: *J. Org. Chem.* **1994**, *59*, 30.

4. a) Lee I.: *Adv. Phys. Org. Chem.* **1992**, 27, 57; b) Lee I.: *Chem. Soc. Rev.* **1990**, 19, 317; c) Lee I., Lee H. W.: *Collect. Czech. Chem. Commun.* **1999**, 64, 1529.
5. Koh H. J., Lee J.-W., Lee H. W., Lee I.: *Can. J. Chem.* **1998**, 76, 710.
6. a) Oh H. K., Lee Y. H., Lee I.: *Int. J. Chem. Kinet.* **2000**, 32, 131; b) Oh H. K., Lee J.-Y., Park Y. S., Lee I.: *Int. J. Chem. Kinet.* **1998**, 30, 419.
7. a) Coetzee J. F.: *Prog. Phys. Org. Chem.* **1965**, 4, 45; b) Spillane W. J., Hogan G., McGrath P., King J., Brack C.: *J. Chem. Soc., Perkin Trans. 2* **1996**, 2099; c) Lee I., Kim C. K., Han I. S., Lee H. W., Kim W. K., Kim Y. B.: *J. Phys. Chem. B* **1999**, 103, 7302.
8. Assuming $\text{pK}_a(\text{H}_2\text{O})$ vs σ^- plots for phenols and thiophenols have similar slopes ($\rho^- \approx 2.0$), β_Z (with $\text{pK}_a(\text{MeCN})$)/ β_Z (with $\text{pK}_a(\text{H}_2\text{O})$) ≈ 0.62 . Literature^{1c} and Oh H. J., Park J. E., Sung D. D., Lee I.: *J. Org. Chem.* **2004**, 69, 3150.
9. Oh H. K., Woo S. Y., Shin C. H., Park Y. S., Lee I.: *J. Org. Chem.* **1997**, 62, 5780.
10. Oh H. K., Shin C. H., Lee I.: *Bull. Korean Chem. Soc.* **1995**, 16, 657.
11. Lee I., Kim C. K., Li H. G., Sohn C. K., Kim C. K., Lee H. W., Lee B.-S.: *J. Am. Chem. Soc.* **2000**, 122, 11162.
12. a) Reed A. E., Curtiss L. A., Weinhold F.: *Chem. Rev.* **1988**, 88, 899; b) Epiotis N. D., Cherry W. R., Shaik S., Yates R., Bernardi F.: *Structural Theory of Organic Chemistry*, Part I. Springer-Verlag, Berlin 1977; c) Lee I.: *Int. Rev. Phys. Chem.* **2003**, 22, 263.
13. a) Skoog M. T., Jencks W. P.: *J. Am. Chem. Soc.* **1984**, 106, 7597; b) Bourne N., Williams A.: *J. Am. Chem. Soc.* **1984**, 106, 7591.
14. Ba-Saif S., Luthra A. K., Williams A.: *J. Am. Chem. Soc.* **1989**, 111, 2647.
15. This work.
16. Castro E. A., Ibanez F., Salas M., Santos J. G., Sepulveda P.: *J. Org. Chem.* **1993**, 58, 459.
17. Castro E. A., Pizarro M. I., Santos J. G.: *J. Org. Chem.* **1996**, 61, 5982.
18. Castro E. A., Araneda C. A., Santos J. G.: *J. Org. Chem.* **1997**, 62, 126.
19. Castro E. A., Leandro L., Millan P., Santos J. G.: *J. Org. Chem.* **1999**, 64, 1953.
20. a) Lee I., Sung D. D.: *Curr. Org. Chem.* **2004**, 8, 557; b) Oh H. K., Kim I. K., Sung D. D., Lee I.: *Org. Biomol. Chem.* **2004**, 2, 1213.
21. Lee I.: *Chem. Soc. Rev.* **1995**, 24, 223.
22. Isaacs N. S.: *Physical Organic Chemistry*, 2nd ed., Chap. 10. Longman, Harlow 1995.
23. Castro E. A., Cubillos M., Ibanez F., Moraga I., Santos J. G.: *J. Org. Chem.* **1993**, 58, 5400.