Anilinolysis of Reactive Aryl 2,4-Dinitrophenyl Carbonates: Kinetics and Mechanism

ENRIQUE A. CASTRO, CLAUDIA DOMECQ, JOSÉ G. SANTOS

Facultad de Química, Pontificia Universidad Católica de Chile, Casilla 306, Santiago 6094411, Chile

Received 4 November 2010; revised 14 December 2010; accepted 14 December 2010

DOI 10.1002/kin.20544

Published online 3 February 2011 in Wiley Online Library (wileyonlinelibrary.com).

ABSTRACT: The reactions of a series of anilines with phenyl 2,4-dinitrophenyl (1), 4-nitrophenyl 2,4-dinitrophenyl (**2**), and bis(2,4-dinitrophenyl) (**3**) carbonates are subjected to a kinetic investigation in 44 wt% ethanol–water, at $25.0 \pm 0.1^{\circ}$ C and an ionic strength of 0.2 M. Under amine excess pseudo-first-order rate coefficients (k_{obs}) are obtained. Plots of k_{obs} against free amine concentration at constant pH are linear, with slopes k_N . The Brønsted plots (log k_N vs. anilinium pK_a) for the anilinolysis of **1–3** are linear, with slope (β) values of 0.52, 0.61, and 0.63, respectively. The values of these slopes and other considerations suggest that these reactions are ruled by a concerted mechanism. For these reactions, the $k_{\rm N}$ values follow the reactivity sequence: 3 > 2 > 1. Namely, the reactivity increases as the number of nitro groups attached to the nonleaving group increases. Comparison of the reactions of this work with the stepwise pyridinolysis of carbonates 1-3 indicates that the zwitterionic tetrahedral intermediate (T^{\pm}) formed in the pyridinolysis reactions is destabilized by the change of its pyridino moiety by an isobasic anilino group. This is attributed to the superior leaving ability from the T^{\pm} intermediate of anilines, relative to isobasic pyridines, which destabilize kinetically this intermediate. The $k_{\rm N}$ values for the anilinolysis of carbonates 1-3 are similar to those found in the reactions of these carbonates with secondary alicyclic amines. With the kinetic data for the anilinolysis of the title substrates and 4-methylphenyl and 4-chlorophenyl 2,4-dinitrophenyl carbonates, a multiparametric equation is derived for $\log k_{\rm N}$ as a function of the pK_a of the conjugate acids of anilines and nonleaving groups. © 2011 Wiley Periodicals, Inc. Int J Chem Kinet 43: 191–197, 2011

INTRODUCTION

Although the kinetics and mechanisms of the aminolysis of alkyl aryl carbonates are well documented [1–5],

© 2011 Wiley Periodicals, Inc.

less is known on the aminolysis of diaryl carbonates [6–17]. Some of the latter reactions have been described as stepwise, mainly due to the nonlinear Brønsted-type plots obtained, usually consisting of two linear portions (at low and high pK_a values) and a curvature in between. These biphasic plots have been explained by the existence of a zwitterionic tetrahedral intermediate (T[±]) on the reaction pathway, and a change in the rate-determining step, from T[±] formation to its decomposition to products, as the amine basicity increases [6–12]. On the other hand, other aminolysis reactions

Correspondence to: Jose G. Santos; e-mail: jgsantos@uc.cl.

Contract grant sponsor: MECESUP.

Contract grant number: UCH-06011.

Contract grant sponsor: FONDECYT.

Contract grant number: 1060593.

Supporting Information is available in the online issue at wileyonlinelibrary,com.

of diaryl carbonates have been found to be concerted, that is, with no intermediate, in a single step. One of the evidences to reach this conclusion has been the linear Brønsted-type plots of slopes 0.4–0.7 found [13–17].

Examples of the above reactions are the pyridinolysis of phenyl and 4-nitrophenyl 2,4-dinitrophenyl carbonates (**1** and **2**, respectively), bis-(2,4-dinitrophenyl) carbonate (**3**), and 4-methylphenyl and 4-chlorophenyl 2,4-dinitrophenyl carbonates (**4** and **5**, respectively), which were found to be driven by a stepwise mechanism [12]. In contrast, the reactions of secondary alicyclic (SA) amines with the same diaryl carbonates are ruled by a concerted mechanism [13,16,17]. Likewise, the reactions of anilines with carbonates **4** and **5** are also governed by a concerted process [13].

It is obvious that the mechanism (stepwise vs. concerted) of the above reactions depends on the stability of the T^{\pm} intermediate, which in turn depends on the groups attached to its central carbon atom [6,7]. With the aim to clarify the mechanism of the aminolysis of diaryl carbonates and to assess the effect of the amino and the other groups involved in the T^{\pm} intermediate on its stability, in this work we report a kinetic investigation of the reactions of a series of anilines with carbonates **1–3**.



EXPERIMENTAL

Materials

Anilines were distilled or recrystallized before use. Carbonates **1** [6], **2** [12], and **3** [18], were prepared by the methods described and identified by their melting points and spectroscopic properties.

Kinetic Measurements

These were carried out by means of a Hewlett– Packard 8453 diode array spectrophotometer (300– 500-nm range) in 44 wt% ethanol aqueous solution, at $25.0 \pm 0.1^{\circ}$ C and an ionic strength of 0.2 M (KCl). The reactions were studied by monitoring the appearance of 2,4-dinitrophenoxide anion at 360 nm. The reactions were initiated by the addition of 10 μ L of an acetonitrile substrate solution into the spectrophotometric cell containing 3 mL of a thermostated solution of the corresponding aniline at the desired concentration and pH.

All the reactions were examined under excess of amine over the substrate. The initial substrate concentration was about 5×10^{-5} M, and in most cases the pH was maintained by the use of an external buffer (0.01 M phosphate).

Pseudo-first-order rate coefficients (k_{obs}) were found throughout and determined by means of the kinetics software for first-order reactions of the spectrophotometer. Errors in the k_{obs} values were less than 3%. The experimental conditions of the reactions and the values of k_{obs} are shown in Tables S1–S3 of the Supporting Information.

Product Studies

One of the products of the reactions under scrutiny was identified as 2,4-dinitrophenoxide by comparison of the UV–vis spectra after completion of the reactions with that of an authentic sample under the same experimental conditions.

For the reaction of carbonate **1** with aniline, the other product was identified as phenyl carbamate, by HPLC comparison of a sample at the end of the reaction with that of the product of the reaction of phenyl chloroformate with aniline. HPLC conditions: LiChroCART[®]250-4 HPLC-RP-18e (5 μ m) HPLC Cartridge LiCrhorsphere[®]100 RP 8, mobile phase 50% v/v CH₃CN: phosphate buffer (0.01 M/pH = 7.00), flow rate 1.0 mL/min, r.t. = 19.3 min.

RESULTS AND DISCUSSION

All the reactions studied were carried out under excess aniline over the carbonate, pseudo-first-order coefficients (k_{obs}) being obtained throughout. The values of k_{obs} and the experimental conditions of the reactions are detailed in Tables S1–S3 of the Supporting Information. The ranges of k_{obs} values and aniline concentrations are summarized in Tables I–III.

The rate law obtained for all the reactions investigated is given by Eqs. (1) and (2), where P, S, and [amine] represent the product 2,4-dinitrophenoxide anion, the substrate, and the free aniline concentration, respectively; k_0 is the rate coefficient for solvolysis of the substrate and k_N is the rate coefficient for its aminolysis.

$$\frac{\mathrm{d}[\mathrm{P}]}{\mathrm{d}t} = k_{\mathrm{obs}}[\mathrm{S}] \tag{1}$$

$$k_{\rm obs} = k_0 + k_{\rm N}[\text{amine}] \tag{2}$$

Aniline Substituent	pH	F^b_N	$10^{3}[N]_{tot} (M)^{c}$	$10^3 k_{\rm obs} ({\rm s}^{-1})$	Number of Runs
4-Amino	6.5	0.5287	0.186-1.86	0.894–5.69	7
	7.0	0.7801	0.186-1.86	0.812-6.48	7
4-Methoxy	7.0	0.9800	0.341-3.41	0.482-5.51	7
	7.5	0.9936	0.341-3.41	0.486-3.48	7
	8.0	0.9980	0.341-3.07	0.542-3.17	5
4-Methyl	6.5	0.9755	0.401-4.01	0.328-2.44	6
	7.0	0.9921	0.401-4.01	0.363-2.38	6
	7.5	0.9975	0.401-4.01	0.334-2.33	6
None	6.5	0.9910	0.877-21.9	0.316-4.80	7
	7.0	0.9971	0.877-21.9	0.334-5.72	7
	7.5	0.9991	0.877-21.9	0.416-5.15	7
3-Methoxy	6.5	0.9943	0.450-4.50	0.151-0.658	6
	7.0	0.9982	0.450-4.50	0.151-0.638	7
	7.5	0.9994	0.900-4.50	0.250-0.681	6
3-Acetyl	7.0	0.9999	0.442-4.42	0.148-0.292	7
	7.5	1	0.442-4.42	0.169–0.326	7

Table I Experimental Conditions and k_{obs} Values for the Reactions of Anilines with Phenyl 2,4-DinitrophenylCarbonate $(1)^a$

^aIn 44 wt% ethanol-water, at 25.0°C, ionic strength 0.2 M (KCl), 0.01 phosphate buffer.

^bFree amine fraction.

^cConcentration of total amine (free base plus protonated forms).

The values of k_0 and k_N for all the reactions were determined as the intercept and slope, respectively, of the linear plots of k_{obs} versus [amine] and were found to be pH independent. The value of k_0 was much lower than that of k_N [amine] in Eq. (2). The k_N values are

presented in Table IV, together with the pK_a values of the conjugate acids of the series of anilines employed. The k_0 values obtained ranged between 3×10^{-2} and 1×10^{-4} s⁻¹. (The individual values are summarized in Table S4 in the Supporting Information.)

Table II Experimental Conditions and k_{obs} Values for the Reactions of Anilines with 4-Nitrophenyl 2,4-Dinitrophenyl Carbonate $(2)^a$

Aniline Substituent	pН	$F^b_{ m N}$	$10^{3}[N]_{tot}(M)^{c}$	$10^3 k_{\rm obs} ({\rm s}^{-1})$	Number of Runs
4-Amino	6.5	0.5287	0.186-1.86	13.3-76.0	7
	7.0	0.7801	0.186-1.86	9.39-88.4	7
	7.5	0.9182	0.186-0.931	11.3-37.1	4
4-Methoxy	6.5	0.9394	0.341-3.41	6.68-38.2	7
	7.0	0.9800	0.341-3.41	6.10-32.0	6
	7.5	0.9936	0.341-3.41	6.72-32.8	6
4-Methyl	6.5	0.9755	0.401-1.20	5.14-10.3	3
	7.0	0.9921	0.401-4.01	4.27-21.3	7
	7.5	0.9975	0.401-4.01	5.41-21.5	7
None	6.5	0.9910	0.877-17.5	4.50-37.3	6
	7.0	0.9971	0.877-21.9	4.36-46.2	6
	7.5	0.9991	0.877-21.9	6.38-48.0	7
3-Methoxy	6.5	0.9943	0.450-4.05	2.71-7.44	6
	7.0	0.9982	0.450-4.50	3.00-8.78	7
	7.5	0.9994	0.450-3.15	3.56-7.36	5
3-Acetyl	6.5	0.9996	0.442-4.42	2.09-3.64	7
	7.5	1	0.442-4.42	2.07-3.66	7

^aIn 44 wt% ethanol-water, at 25.0°C, ionic strength 0.2 M (KCl), 0.01 phosphate buffer.

^bFree amine fraction.

^cConcentration of total amine (free base plus protonated forms).

Aniline Substituent	pH	F^b_N	$10^{3}[N]_{tot}(M)^{c}$	$10^3 k_{\rm obs} ({\rm s}^{-1})$	Number of Runs
4-Amino	6.5	0.5287	0.186-1.30	83.2-412	5
	7.0	0.7801	0.186-0.931	73.8-293	4
4-Methoxy	7.0	0.9800	0.341-3.07	40.6-236	5
	7.5	0.9936	0.341-2.39	51.5-221	5
4-Methyl	6.5	0.9755	0.401-4.01	27.8-164	6
	7.0	0.9921	0.401-4.01	31.3-168	7
	7.5	0.9975	0.401-4.01	36.2-178	7
None	6.5	0.9910	0.439-3.95	21.6-71.0	6
	7.0	0.9971	0.439-4.39	25.4-82.7	7
	7.5	0.9991	0.439-4.39	26.5-81.9	7
3-Methoxy	6.5	0.9943	0.450-4.50	20.0-50.7	6
	7.5	0.9994	0.450-4.50	26.5-57.6	7
3-Acetyl	6.5	0.9996	0.442-4.42	16.0-25.2	7
	7.0	0.9999	0.884-3.98	18.6-25.3	5
	7.5	1	0.442-4.42	15.4–27.4	7

Table III Experimental Conditions and k_{obs} Values for the Reactions of Anilines with Bis-(2,4-dinitrophenyl) Carbonate $(3)^a$

^aIn 44 wt% ethanol-water, at 25.0 °C, ionic strength 0.2 M (KCl), 0.01 phosphate buffer.

^bFree amine fraction.

^cConcentration of total amine (free base plus protonated forms).

Figure 1 shows the Brønsted plots obtained for the reactions of carbonates **1–3** with the series of anilines. In these plots, the k_N values, as well as those of the pK_a of the conjugate acids of these amines, were statistically corrected with q = 2 for phenylendiamine (q = 1 for the other anilines) and p = 3 for all the conjugate acids of the anilines [13]. The parameter q is the number of equivalent basic sites in the free amine, and p is the number of equivalent dissociable protons in the conjugate acid of the amine [19].

The Brønsted slopes (β) of the linear plots in Fig. 1 are 0.52, 0.61, and 0.63 for the anilinolysis reactions of carbonates **1**, **2**, and **3**, respectively. These β values are in accordance with the values usually obtained (β = 0.4–0.7) for concerted mechanisms in the aminolysis

of carbonates, esters, and their thio analogues [20]. In fact, the concerted reactions of SA amines with carbonates **1**, **2**, **3**, and **5** show β values of 0.39, 0.51, 0.48, and 0.44, respectively [13,16,17]. Similarly, the concerted reactions of quinuclidines with carbonates **4** and **5** exhibit a β value of 0.57 [14]. The linear Brønsted plots found in the reactions of the latter carbonates with anilines show slopes slightly larger ($\beta = 0.68$ and 0.66, respectively) [13], but still within the β range expected for concerted mechanisms.

It is known that the β value alone is not sufficient to conclude that a mechanism is concerted. It is also necessary to make sure that the expected pK_a value at the center of the Brønsted curvature (pK_a^0) for a hypothetical stepwise mechanism is within the pK_a range

Table IV Values of pK_a for the Conjugate Acids of Anilines and k_N Values for the Reactions of Anilines with Phenyl(2,4-dinitrophenyl) Carbonate (1), 4-Nitrophenyl(2,4-dinitrophenyl) Carbonate (2), and Bis(2,4-dinitrophenyl) Carbonate (3)^{*a*,*b*}

Aniline Substituent		$k_{\rm N}({ m s}^1{ m M}^1)$			
	pK _a	1	2	3	
4-Amino	6.45	2.4 ± 0.1	43 ± 1	300 ± 24	
4-Methoxy	5.31	0.98 ± 0.02	9.2 ± 0.5	75 ± 6	
4-Methyl	4.90	0.57 ± 0.01	4.5 ± 0.1	39 ± 1	
None	4.46	0.23 ± 0.01	2.0 ± 0.1	15.0 ± 0.6	
3-Methoxy	4.26	0.12 ± 0.01	1.40 ± 0.08	7.3 ± 0.5	
3-Acetyl	3.1	0.044 ± 0.002	0.36 ± 0.04	2.4 ± 0.2	

^aBoth the p K_a and k_N values were determined in 44 wt% ethanol-water, at 25.0°C, ionic strength 0.2 M (KCl).

^bErrors shown are standard deviations.



Figure 1 Brønsted-type plots for the aminolysis (anilines) of carbonates $1(\bullet)$, 2(o), and $3(\bullet)$ in 44 wt% ethanol–water, $25.0 \pm 0.1^{\circ}$ C, ionic strength 0.2 mol \cdot dm⁻³ (KCl).

employed [21,22]. The pyridinolysis reactions of carbonates 1-3 are stepwise, as judged by the biphasic Brønsted plots obtained, with pK_a^0 values in the range 7.2-8.0 [12]. It is known that anilines are better nucleofuges than isobasic pyridines from the tetrahedral intermediate T^{\pm} [23]. This means that the p K_a^0 value for the reactions of anilines with carbonates 1-3 for a hypothetical stepwise mechanism would be larger than 7.2–8.0 [6], which is outside the pK_a range of the anilines employed. Nevertheless, we are more inclined toward a concerted mechanism for the following reasons: (i) If the studied anilinolysis reactions were stepwise, the slopes of the Brønsted plots in Fig. 1 would correspond to those for rate-determining breakdown of T^{\pm} to products (β_2), since the p K_a^0 value would be larger than that of the most basic aniline [6,7,20]. The experimental values ($\beta = 0.52 - 0.63$) are too small compared with the expected β_2 values for stepwise reactions, which are in the 0.8-1.1 range [6,20]. (ii) The anilinolysis of carbonate 4 is concerted [13]; therefore, the reactions of these amines with carbonate 1 should also be concerted since the change of 4-methylphenyl in 4 by phenyl in 1, as the nonleaving group, should destabilize the putative T^{\pm} intermediate [7,20]. Moreover, the anilinolysis of carbonates 2 and 3 should also be concerted due to the stronger electron-withdrawing substituents in the nonleaving group of these carbonates [7,20]. Therefore, the most likely mechanism for the reactions under the present investigation is the concerted process depicted in Scheme 1.

From the k_N values in Table IV and from Fig. 1, the following reactivity sequence can be observed: **3** > **2** > **1**. Namely, the reactivity increases as the num-



Figure 2 Brønsted plots obtained for the reactions of carbonates 1–3 with a series of SA amines (\circ , [16,17]), quinuclidines (Δ , [14]) and anilines (\bullet , this work).

ber of nitro groups attached to the nonleaving group increases. The greater electron-withdrawing power of the nonleaving group as more nitro groups are added leaves the carbonyl carbon of the carbonate more positive and therefore more prone to the aniline attack. The same sequence of reactivity was reported for the concerted reactions of carbonates 1-3 with SA amines [16,17].

Amine Effect

The concerted mechanism for the anilinolysis of 1– 3 is in contrast to the stepwise process found for the pyridinolysis of the same carbonates under the same experimental conditions [12]. This can be attributed to the known fact that anilines are better nucleofuges than isobasic pyridines from a tetrahedral intermediate (T^{\pm}) and, therefore, destabilize this intermediate relative to pyridines. Consequently, the intermediate formed with anilines could not exist, or it could exist, but being so unstable that the concerted process would become of lower free energy of activation relative to that of the stepwise mechanism [24–26].

The reactions of carbonates 1-3 with SA amines and that of 1 with quinuclidines are also concerted [14,16,17]. Figure 2 summarizes the Brønsted plots obtained for the reactions of 1-3 with these series of amines and anilines.

As seen in Fig. 2, SA amines and quinuclidines seem to be more reactive than anilines toward carbonate **1**. Nevertheless, the reactions of the two former series of amines were carried out in water [14,16], whereas those of anilines were performed in aqueous ethanol (this work). Since the reactions of SA amines





and anilines are of similar reactivity toward carbonates 2 and 3 (see Fig. 2, these reactions are both in 44 wt% ethanol-water), it is possible that the apparent greater reactivity of SA amines and quinuclidines toward carbonate 1 is due only to the change of solvent. It is expected that these reactions be faster in water than in aqueous ethanol due to the greater polarity of the transition state compared with reactants [6]. The similar reactivity of these amine series toward carbonates 1-3 is in contrast to the results found for the stepwise reactions of these amines series with 4methylphenyl 4-nitrophenyl carbonate (6) in 44 wt% ethanol-water, whereby SA amines are more reactive than anilines [11]. The similar reactivity of these series of amines toward carbonates 1-3 could be attributed to the lower selectivity shown by the more reactive carbonates (1-3) compared with carbonate 6, according to the reactivity-selectivity principle [27,28].

Multiparametric Study

With the corrected k_N values (k_N/q) obtained for the anilinolysis of carbonates 1–5, all of these reactions corresponding to concerted mechanisms, and the corrected pK_a of the conjugate acids of the anilines, $pK_a + \log(p/q)$, and that of the nonleaving group (pK_{nlg}) , the multiparametric relation shown in Eq. (3) was obtained.

$$\log k_{\rm N/q} = -0.64 + 0.65 \,[{\rm p}K_{\rm a} + \log(p/q)] - 0.33 \,{\rm p}K_{\rm nlg} \qquad (3)$$

Figure 3 shows a log–log plot of the experimental $k_{\rm N}$ values versus those calculated by Eq. (3). The line has unity slope and zero intercept, showing the good fit obtained.

The negative value of the nonleaving group sensitivity ($\beta_{nlg} = -0.33$) is due to the fact that as the



Figure 3 Double logarithmic plot of the experimental k_N/q values against those calculated by means of Eq. (3), for the reactions of anilines with carbonates $(\Delta, \mathbf{1}), (\blacksquare, \mathbf{2}), (\Box, \mathbf{3}), (\circ, \mathbf{4}), \text{ and } (\bullet, \mathbf{5})$. The line has unity slope and zero intercept.

nonleaving group becomes more basic (larger pK_{nlg}) less positive becomes the carbonyl carbon atom of the carbonate and less prone results to the amine attack.

The good correlation shown by the concerted anilinolysis of carbonates 4 and 5 with the anilinolysis of carbonates 1-3 (Fig. 3) indicates that the latter reactions are also concerted.

CONCLUSIONS

- i. The kinetic results for the anilinolysis reactions of carbonates **1–3** are in accordance with a concerted mechanism.
- ii. The greater k_N values as more nitro groups are attached to the nonleaving group of the carbonate is due to the greater electron withdrawal from this group, which leaves the carbonyl carbon more

positive and, therefore, more prone to amine attack.

- iii. The T[±]intermediate formed in the pyridinolysis reactions is destabilized by the change of its pyridino moiety by an isobasic anilino group, due to the superior leaving ability of anilines, relative to isobasic pyridines.
- iv. The $k_{\rm N}$ values for the anilinolysis of carbonates **1–3** are similar to those found in the reactions of these carbonates with SA amines.

We thank the program "Mejoramiento de la calidad y la equidad de la Educación Superior" (MECESUP) of Chile (project UCH-06011) and Fondo Nacional de Desarrollo Científico y Tecnológico (FONDECYT) of Chile (project 1060593) for financial support.

BIBLIOGRAPHY

- 1. Bond, P. M.; Moodie, R. B. J Chem Soc, Perkin Trans 2 1976, 679–682.
- Castro, E. A.; Gil, F. J. J Am Chem Soc 1977, 99, 7611– 7612.
- Fife, T. H.; Hutchins, J. E. C. J Am Chem Soc 1981, 103, 4194–4199.
- Koh, H. J.; Lee, J. W.; Lee, H. W.; Lee, I. Can J Chem 1998, 76, 710–716.
- Tundo, P.; Rossi, L.; Loris, A. J Org Chem 2005, 70, 2219–2224.
- Gresser, M. J.; Jencks, W. P. J Am Chem Soc 1977, 99, 6963–6970.
- Gresser, M. J.; Jencks, W. P. J Am Chem Soc 1977, 99, 6970–6980.

- Um, I.-H.; Kim, E. Y.; Park, H.-R.; Jeon, S.-E. J Org Chem 2006, 71, 2302–2306.
- Um, I.-H.; Yoon, S.; Park, H.-R.; Han, H.-J. Org Biol Chem 2008, 6, 1618–1624.
- Castro, E. A.; Andujar, M.; Toro, A.; Santos, J. G. J Org Chem 2003, 68, 3608–3613.
- Castro, E. A.; Gazitúa, M.; Santos, J. G. J Org Chem 2005, 70, 8088–8092.
- Castro, E. A.; Acuña, M.; Soto, C.; Trujillo, C.; Vásquez, B.; Santos, J. G. J Phys Org Chem 2008, 21, 816–822.
- Castro, E. A.; Campodónico, P.; Toro, A.; Santos, J. G. J Org Chem 2003, 68, 5930–5935.
- Castro, E. A.; Campodónico, P.; Contreras, R.; Fuentealba, P.; Santos, J. G.; Leis, J. R.; García-Río, L.; Saez, J. A.; Domingo, L. Tetrahedron 2006, 62, 2555– 2562.
- Castro, E. A.; Ramos, M.; Santos, J. G. J Org Chem 2009, 74, 6374–6377.
- Castro, E. A.; Aliaga, M.; Campodónico, P.; Santos, J. G. J Org Chem 2002, 67, 8911–8916.
- Castro, E. A.; Soto, C.; Vásquez, B.; Santos, J. G. Arkivoc 2008, X, 151–160.
- El Seoud, O. E.; El Seoud, M. I.; Farah, J. P. S. J Org Chem 1997, 62, 5928–5933.
- 19. Bell, R. P. The Proton in Chemistry; Methuen: London, 1959; p. 159.
- 20. Castro, E. A. Chem Rev 1999, 99, 3505-3524.
- 21. Chystiuk, E.; Wiliams, A. J Am Chem Soc 1987, 109, 3040–3046.
- 22. Williams, A. Acc Chem Res 1989, 22, 387-392.
- Castro, E. A.; Muñoz, P.; Santos, J. G. J Org Chem 1999, 64, 8298–8301.
- 24. Jencks, W. P. Acc Chem Res 1980, 13, 161-169.
- 25. Jencks, W. P. Chem Soc Rev 1981, 10, 345–375.
- 26. Williams, A. Chem Soc Rev 1994, 23, 93–100.
- 27. Pross, A. J Am Chem Soc 1976, 98, 776–778.
- 28. Hammond, G. S. 1955, 77, 334-338.