Article
DOI: 10.1002/bkcs.11242

BULLETIN OF THE
KOREAN CHEMICAL SOCIETY

Kinetic Study on Nucleophilic Substitution Reactions of *O*-Phenyl *O*-Y-substituted-Phenyl Thionocarbonates with 1,8-Diazabicyclo[5.4.0]undec-7-ene in Acetonitrile

Ik-Hwan Um[†,*] **and Kyoung-Ho Park**[‡]

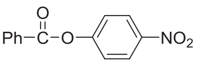
[†]*Department of Chemistry, Ewha Womans University, Seoul 03760, Korea. *E-mail: ihum@ewha.ac.kr*
[‡]*Department of Chemical and Molecular Engineering, Hanyang University, Ansan, Gyeonggi-do, 15588, Korea*
Received June 24, 2017, Accepted August 4, 2017

Second-order rate constants (k_N) for nucleophilic substitution reactions of *O*-phenyl *O*-Y-substituted-phenyl thionocarbonates (**4a–4k**) with 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) in MeCN at 25.0 ± 0.1°C are reported. The reactivity of **4a–4k** decreases as basicity of the leaving group increases except *O*-2,4-dinitrophenyl *O*-phenyl thionocarbonate (**4a**), which is less reactive than *O*-3,4-dinitrophenyl *O*-phenyl thionocarbonate (**4b**) although the former possesses 2 pK_a units less basic nucleofuge than the latter. The Brønsted-type plot for the reactions of **4b–4k** is linear with $\beta_{lg} = -0.50$, a typical β_{lg} value for reactions reported to proceed through a concerted mechanism. The Hammett plot correlated with σ_Y^- constants for the reactions of **4b–4k** results in a better linear correlation than that correlated with σ_Y^o constants. Besides, the Yukawa-Tsuno plot exhibits an excellent linear correlation with $\rho_Y = 2.12$, $r = 0.68$ and $R^2 = 0.990$, indicating that a negative charge develops partially on the O atom of the leaving group in the rate-determining step (RDS). Thus, the reactions have been concluded to proceed through a forced concerted mechanism. Effects of steric hindrance on reactivity and reaction mechanism are also discussed in detail.

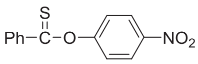
Keywords: *O*-Phenyl *O*-Y-substituted-phenyl thionocarbonates, 1,8-Diazabicyclo[5.4.0]undec-7-ene, Steric hindrance, Forced concerted mechanism, Brønsted-type plot

Introduction

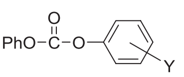
Nucleophilic substitution reaction of esters with amines is one the most important reactions not only in organic syntheses but also in biological processes (*e.g.*, acyl-group transfer from esters to amines in enzyme reactions and peptide biosynthesis).[1–3] Aminolysis of esters has been reported to proceed either through a concerted mechanism or via a stepwise pathway depending on reaction conditions (*e.g.*, nature of the electrophilic center, basicity of the leaving group, electronic nature of the nonleaving-group substituents, type of amines, nature of the reaction medium, etc.).[1–10] Reactions of 4-nitrophenyl benzoate (**1**) with a series of alicyclic secondary amines in 80 mol % H_2O/20 mol % DMSO have been reported to proceed through a stepwise mechanism with a zwitterionic tetrahedral intermediate ($T^{\pm}$) on the basis of a linear Brønsted-type plot with $\beta_{nuc} = 0.81$.[5a] In contrast, the corresponding reactions of *O*-4-nitrophenyl thionobenzoate (**2**) have been concluded to proceed through a stepwise mechanism with two intermediates ($T^{\pm}$ and its deprotonated form T^-) on the basis of the kinetic result that the plots of k_{obsd} vs. amine concentration curved upward.[5b,c] This indicates that the reaction mechanism is dependent on the nature of the electrophilic center (*e.g.*, C=O vs. C=S). On the other hand, reactions of 2,4-dinitrophenyl benzoate (a derivative of **1**) with alicyclic secondary amines in 80 mol % H_2O/20 mol % DMSO have been reported to proceed through a stepwise mechanism, in which the rate-determining step (RDS) changes from breakdown of $T^{\pm}$ to its formation as the incoming amine becomes more basic than the leaving group by 4 ~ 5 pK_a units, on the basis of a curved Brønsted-type plot.[5d] However, the same reactions carried out in MeCN have been concluded to proceed through a concerted mechanism on the basis of a linear Brønsted-type plot with $\beta_{nuc} = 0.4$, implying that nature of the reaction medium (*e.g.*, protic vs. aprotic solvent) controls the reaction mechanism.[5e]



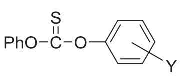
1



2



3a-3k



4a-4k

Y = 2,4-$(NO_2)_2$ (**a**), 3,4-$(NO_2)_2$ (**b**), 4-NO_2 (**c**), 4-CHO (**d**), 4-CN (**e**), 4-COMe (**f**), 4-COOEt (**g**), 3-CHO (**h**), 3-Cl (**i**), 3-COMe (**j**), H (**k**)

Reactions of phenyl Y-substituted-phenyl carbonates (**3a–3k**) with primary and secondary amines in 80 mol % H_2O/

20 mol % DMSO were reported to proceed through a stepwise mechanism with one intermediate ($T^{\pm}$) when the leaving group is weakly basic (*e.g.*, p$K_a \leq 9.02$) but with two intermediates (*e.g.*, $T^{\pm}$ and T^{-}) when the leaving group becomes more basic (*e.g.*, p$K_a > 9.02$).[6a,b] A similar result was reported for the corresponding reactions of *O*-phenyl *O*-Y-substituted-phenyl thionocarbonates (**4a–4k**),[7a,b] indicating that leaving-group basicity also affects the reaction mechanism.

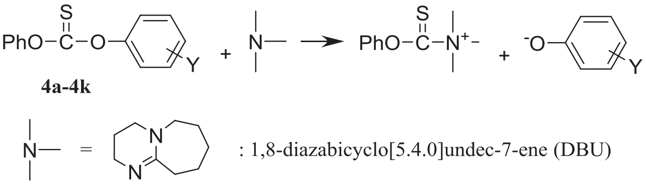
Reactions of esters with tertiary amines (*e.g.*, pyridine, quinuclidine and 1,8-diazabicyclo[5.4.0]undec-7-ene [DBU]) have also been investigated.[8–10] Pyridinolysis of **1** in aqueous medium has been reported to proceed through a stepwise mechanism, in which expulsion of the leaving group from $T^{\pm}$ occurs in the RDS on the basis of a linear Brønsted-type plot with $\beta_{nuc} = 1.06$.[8] In contrast, a curved Brønsted-type plot has been observed for the corresponding reactions of **2**, indicating that the RDS changes from breakdown of $T^{\pm}$ to its formation as the pyridine basicity increases.[8] Similarly, Gresser and Jencks concluded that reactions of **3a** with quinuclidine and its derivatives proceed through a stepwise mechanism with a change in the RDS based on a curved Brønsted-type plot.[9] However, Castro et al. reported that quinuclidinolysis of methyl 2,4-dinitrophenyl carbonate (a derivative of **3a**) proceed through a concerted mechanism on the basis of a linear Brønsted-type plot with $\beta_{nuc} = 0.51$, while the corresponding reactions of methyl 4-nitrophenyl carbonate (a derivative of **3c**) proceed through a stepwise mechanism on the basis of a linear Brønsted-type plot with $\beta_{nuc} = 0.86$.[10]

It is well known that DBU is highly basic (pK_a = 13.5 and 24.34 in H_2O and MeCN, respectively) but is a poor nucleophile due to its bulkiness.[11–15] Accordingly, DBU has often been used as a strong base in E2 reactions but rarely been used as a nucleophile.[12–15] We have recently shown that DBU is much less nucleophilic than piperidine in the reactions of **3a–3g** carried out in 80 mol % H_2O/20 mol % DMSO although the former is ca. 2.5 pK_a units more basic than the latter.[15] Strong steric hindrance has been suggested to be responsible for the low reactivity shown by DBU.[15] However, one cannot exclude a possibility that DBU behaves as a general-base catalyst for the reactions carried out in the aqueous medium, since DBU can generate OH^{-} ion through deprotonation of H_2O molecule.

To investigate the role of DBU and the effect of steric hindrance exerted by DBU, our study has been extended to the reactions of **4a–4k** with DBU in MeCN (Scheme 1). It is noted that generation of OH^{-} ion by DBU is not possible for reactions in the aprotic solvent (MeCN). Besides, one might expect that steric hindrance is more significant for the reactions of **4a–4k** than those of **3a–3k** since the S atom in the C=S bond is much larger than the O atom in the C=O bond.

Results and Discussion

Pseudo-first-order conditions (*e.g.*, [DBU] > > [substrate]) were employed for the current reactions. The reactions obeyed pseudo-first-order kinetics in all cases. Pseudo-first-order rate constants (k_{obsd}) were calculated using the well known equation, $\ln (A_{\infty} - A_t) = -k_{obsd} \cdot t + c$. The second-order rate constants (k_N) were calculated from the slope of the linear plots of k_{obsd} vs. [DBU]. Table 1 summarized the k_N values for the reactions of **4a–4k** with DBU together with the pK_a values of the conjugate acid of the leaving Y-substituted-phenoxide ions in MeCN.



Scheme 1. Nucleophilic substitution reactions of **4a–4k** with DBU.

Deduction of Reaction Mechanism. As shown in Table 1, the second-order rate constant (k_N) decreases as the leaving-group basicity increases except for the reaction of *O*-phenyl *O*-2,4-dinitrophenyl thionocarbonate (**4a**), *e.g.*, k_N decreases from 109 $M^{-1}s^{-1}$ to 0.495 and 0.0155 $M^{-1}s^{-1}$ as the pK_a of the leaving group (*i.e.*, Y-substituted-phenoxide) increases from 18.7 to 23.1 and 26.2, in turn. It is noted that **4a** is less reactive than *O*-phenyl *O*-3,4-dinitrophenyl thionocarbonate (**4b**), although the former possesses 2 pK_a units less basic leaving group than the latter. The decreased reactivity of **4a** will be discussed in the subsequent section.

The effect of leaving-group basicity on reactivity is illustrated in Figure 1. The Brønsted-type plot is linear with $\beta_{lg} = -0.50$ when the point for the reaction of **4a** is excluded from the correlation (the negative deviation shown by **4a** will be discussed in the following section). It is well known that the RDS for reactions of esters with

Table 1. Summary of kinetic data for the reactions of *O*-phenyl *O*-Y-substituted-phenyl thionocarbonates (**4a–4k**) with DBU in MeCN at 25.0 ± 0.1°C.

	Y	pK_a	k_N $M^{-1}s^{-1}$
4a	2,4-$(NO_2)_2$	16.7[a]	47.4
4b	3,4-$(NO_2)_2$	18.7[a]	109
4c	4-NO_2	20.9[a]	9.67
4d	4-CHO	22.4[b]	1.63
4e	4-CN	22.8[a]	2.13
4f	4-COMe	23.1[b]	0.495
4g	4-COOEt	23.8[b]	0.380
4h	3-CHO	24.6[b]	0.137
4i	3-Cl	24.7[b]	0.172
4j	3-COMe	25.0[b]	0.0876
4k	H	26.2[b]	0.0155

[a] The pK_a values of Y-substituted phenols in MeCN were taken from ref. 11a.

[b] The pK_a values were calculated from the equation, pK_a (in MeCN) = 1.65 pK_a (in H_2O) + 9.8, which was derived from the pK_a data in ref. 11a.

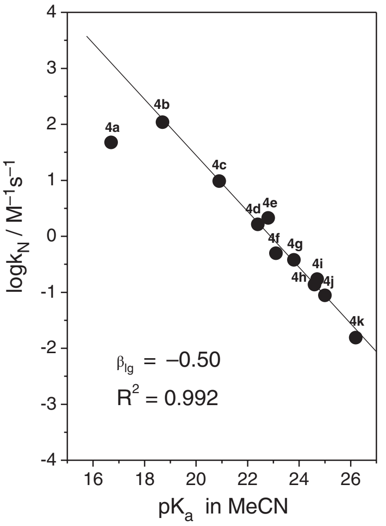


Figure 1. Brønsted-type plot for the reactions of *O*-phenyl *O*-Y-substituted-phenyl thionocarbonates (**4a–4k**) with DBU in MeCN at 25.0 ± 0.1°C.

amines, which proceed through a stepwise mechanism, changes from breakdown of a tetrahdral intermediate ($T^{\pm}$) to its formation as the leaving group becomes 3 ~ 5 pK_a units less basic than the incoming amine.[5–10] It is noted that DBU (pK_a = 24.34 in MeCN)[11b] is 3.4 ~ 5.6 pK_a units more basic than the leaving 4-nitrophenoxide and 3,4-dinitrophenoxide ions in MeCN. Thus, one might expect a curved Brønsted-type plot with a curvature center at pK_a between 19.34 and 21.34, if the current reaction proceeds through a stepwise mechanism. However, the Brønsted-type plot shown in Figure 1 is linear, indicating clearly that no RDS change occurs in the current reactions. Furthermore, a β_{lg} value of −0.6 ± 0.1 has been reported for reactions proceeding through a concerted mechanism.[5–10] In fact, the reactions of **3b–3k** (C═O analogs of **4b–4k**) with DBU in 80 mol % H_2O/20 mol % DMSO have been reported to proceed through a forced concerted mechanism on the basis of a linear Brønsted-type plot with $\beta_{lg} = -0.48$.[15]

More conclusive information on the transition state (TS) structures can be obtained from Hammett plots correlated with σ_Y^- and σ_Y^o constants. If the current reaction proceeds through a concerted mechanism, a negative charge would develop partially on the O atom of the leaving Y-substituted-phenoxide.[5–8] Since such negative charge could be delocalized on the substituent Y through resonance interaction, σ_Y^- constants should result in a better correlation than σ_Y^o constants. On the contrary, if the reactions proceed through a stepwise mechanism with expulsion of the leaving group occurring after the RDS, no negative charge would develop on the O atom of the leaving aryloxide.[5–8] In this case, σ_Y^o constants should exhibit a better linear correlation than σ_Y^- constants.

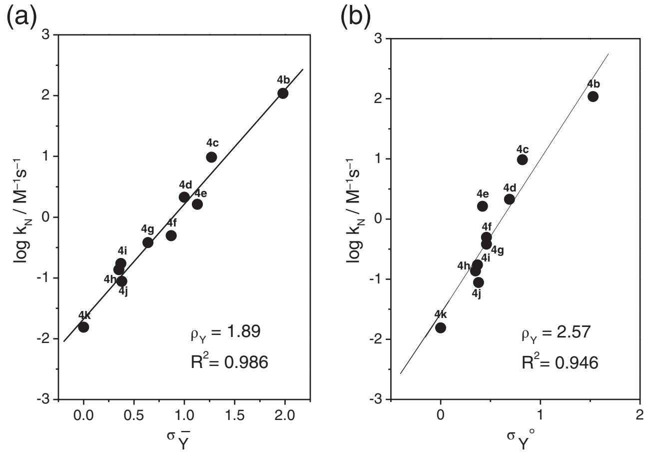


Figure 2. Hammett plots correlated with σ⁻ constants (a) and σ° constants (b) for the reactions of *O*-phenyl *O*-Y-substituted-phenyl thionocarbonates (**4b–4k**) with DBU in MeCN at 25.0 ± 0.1°C.

Thus, Hammett plots are constructed using σ_Y^- and σ_Y^o constants. As shown in Figure 2, the Hammett plot correlated with σ_Y^- constants result in a better correlation coefficient ($R^2 = 0.986$) than that correlated with σ_Y^o constants ($R^2 = 0.946$). This implies that a partial negative charge develops on the O atom of the leaving group in the TS.

To get further information on the TS structure, Yukawa-Tsuno plot has been constructed. Although the Yukawa-Tsuno Eq. (**1**) was derived to account for kinetic data obtained from solvolysis of various benzylic systems,[16] Eq. (**1**) has been reported to be highly useful in analyzing resonance effects for S_N reactions of various esters.[5–8] As shown in Figure 3, the Yukawa-Tsuno plot exhibits an excellent linear correlation with $\rho_Y = 2.12$, $r = 0.68$ and $R^2 = 0.990$. Note that the *r* value in Eq. (**1**) represents resonance demand of the reaction center or extent of resonance contribution.[16,17] Thus, an *r* value of 0.68 obtained for the

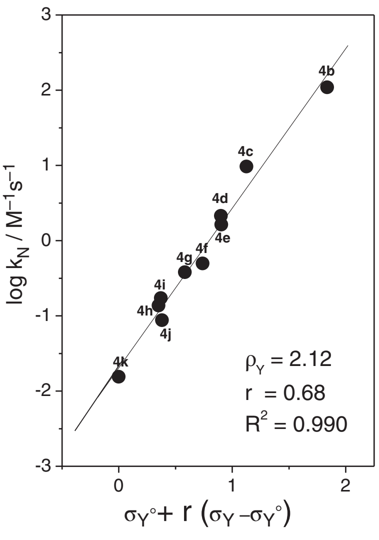


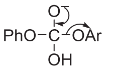
Figure 3. Yukawa-Tsuno plot for the reactions of *O*-phenyl *O*-Y-substituted-phenyl thionocarbonates (**4b–4k**) with DBU in MeCN at 25.0 ± 0.1°C.

current reactions clearly indicates that a negative charge, which can be delocalized on the substituent Y through resonance interactions, develops partially on the O atom of the nucleofuge. This is not possible for reactions which proceed through a stepwise mechanism with expulsion of the leaving group occurring after the RDS. Thus, one can conclude that the current reactions proceed through a concerted mechanism.

$$\log k_N^Y/k_N^H = \rho_Y\left[\sigma_Y^o + r\left(\sigma_Y^- - \sigma_Y^o\right)\right] \qquad (1)$$

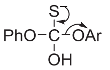
Role of DBU. It is well known that DBU is highly basic but is not a good nucleophile due to its bulkiness.[12] Besides, DBU can generate OH^- ion in aqueous medium through deprotonation of H_2O molecule. Since OH^- ion is a strong nucleophile, DBU might behave as a general-base catalyst for reactions carried out in the aqueous medium. However, generation of OH^- ion by DBU is not possible for the reactions carried out in aprotic solvents. It is noted that the reactions of **4a–4k** with DBU in MeCN proceed with quantitative liberation of Y-substituted-phenoxide ion as one of the reaction products. Thus, the current study demonstrates that DBU behaves as a nucleophile in this study.

Nucleophilic substitution reactions of **3a–3k** with OH^- ion have been reported to proceed through a forced concerted mechanism with a highly unstable intermediate (*e.g.*, I) on the basis of the kinetic result that the Yukawa-Tsuno plot exhibits an excellent linear correlation with $\rho_Y = 1.21$ and $r = 0.33$.[18] In contrast, the corresponding reactions of **4a–4k** have been suggested to proceed via a stepwise mechanism with an addition intermediate (*e.g.*, II), because the Hammett plot correlated with σ^o constants results in a much better linear correlation than that correlated with σ^- constants.[18b] One might expect that II would be less unstable than I, since the ability of the C–S⁻ moiety in II to form a C═S bond is weaker than that of the C—O⁻ moiety in I to form a C═O bond.[19] This idea is consistent with the fact that the overlap between the 2p and 3p orbitals in a C═S bond is weaker than that between the **2p** orbitals in a C═O bond.[19]



$\mathrm{PhO{-}\overset{O^-}{\underset{OH}{C}}{-}OAr}$

I



$\mathrm{PhO{-}\overset{S^-}{\underset{OH}{C}}{-}OAr}$

II

One might suggest that the intermediate formed from the reactions of C═S compounds would be less unstable than that formed from the corresponding reactions of C═O compounds when steric hindrance is not significant (*e.g.*, reactions with OH^- ion). However, the reactions with DBU would experience strong steric hindrance due to the bulkiness of DBU. Furthermore, the intermediate formed from the reactions of C═S centered esters (*e.g.*, **4a–4k**) with DBU would experience much stronger steric hindrance than that formed from the corresponding reactions of C═O centered esters (*e.g.*, **3a–3k**) since the S atom in the C═S bond is much larger than the O atom in the C═O bond. Such strong steric hindrance could be relieved as the leaving group departs from the sp^3-hybridized intermediate to form an sp^2-hybridized product. This is because the bond angle increases from 109° to 120° upon expulsion of the leaving group from the intermediate. In fact, the reactions of **3a–3k** with DBU in 80 mol % H_2O/20 mol % DMSO were reported to proceed through a forced concerted mechanism to decrease the steric hindrance.[15] Thus, one can conclude that the current reactions of **4a–4k** proceed also through a forced concerted mechanism to reduce the strong steric hindrance.

As mentioned earlier, **4a** is less reactive than **4b** although the former possesses 2 pK_a units less basic nucleofuge than the latter. Consequently, **4a** deviates negatively from the linear Brønsted-type plot (Figure 1). It is apparent that the negative deviation is not due to a change in the RDS, since the current reactions proceed through a concerted mechanism. Note that steric hindrance is an important factor that affects reactivity. Furthermore, presence of a NO_2 group at the 2-position of the leaving group (*e.g.*, 2,4-dinitrophenoxide) would increase steric hindrance significantly as the reaction progresses from the sp^2-hybridized ground state (GS) to the sp^3-hybridized TS (or $T^{\pm}$). Thus, one can attribute the negative deviation shown by **4a** from the linear Brønsted-type plot to the enhanced steric hindrance caused by the NO_2 group at the 2-position of the leaving group.

Conclusion

We have shown that DBU behaves as a nucleophile in the current reactions and have drawn the following conclusions: (1) The Brønsted-type plot for the reactions of **4b–4k** with DBU is linear with $\beta_{lg} = -0.50$, a typical β_{lg} value for reactions proceeding through a concerted mechanism. (2) The σ_Y^- constants result in a better Hammett correlation than σ_Y^o constants. Besides, the Yukawa-Tsuno plot exhibits an excellent linear correlation with $\rho_Y = 2.12$, $r = 0.68$ and $R^2 = 0.990$. These indicate that a partial negative charge develops on the O atom of the leaving group in the TS and are consistent with a concerted mechanism. (3) Presence of a NO_2 group at the 2-position of the leaving group destabilizes the TS (or a plausible intermediate) by increasing steric hindrance. The enhanced steric hindrance is responsible for the decreased reactivity of **4a** toward DBU. (4) Strong steric hindrance exerted by DBU in the plausible intermediate forces the reaction to proceed through a concerted mechanism.

Experimental

Materials. *O*-Phenyl *O*-Y-substituted-phenyl thionocarbonates (**4a–4k**) were prepared from reactions of *O*-phenyl chlorothionoformate with the respective Y-substituted phenol as reported previously.[18b] The crude products were purified by a column chromatography method. DBU and other chemicals used were of the highest quality available.

Kinetics. The kinetic study was performed using a UV–vis spectrophotometer equipped with a constant temperature circulating bath to maintain the reaction mixture at 25.0 ± 0.1°C. The reactions were followed by monitoring appearance of the leaving Y-substituted phenoxide ion. All the reactions were carried out under pseudo-first-order conditions in which the DBU concentration was at least 20 times greater than the substrate concentration. Detailed kinetic methods are as reported previously.[5–8]

Product Analysis. Y-Substituted phenoxide ion was liberated quantitatively and identified as one of the products by comparison of the UV–vis spectra after completion of the reaction with the authentic sample under the same reaction conditions.

Acknowledgments. This research was supported by Basic Science Research Program through the National Research Foundation of Korea funded by the Ministry of Education (2015-R1D1A1A-01059624).

References

1. (a) E. V. Anslyn, D. A. Dougherty, *Mordern Physical Organic Chemistry*, University Science Books, Sausalito, CA, **2006**, Chapter 10; (b) E. A. Castro, *Pure Appl. Chem.* **2009**, *81*, 685; (c) E. A. Castro, *J. Sulfur Chem.* **2007**, *28*, 401; (d) E. A. Castro, *Chem. Rev.* **1999**, *99*, 3505; (e) W. P. Jencks, *Chem. Rev.* **1985**, *85*, 511.
2. (a) G. B. Desmet, D. R. D'hooge, M. K. Sabbe, M. F. Reyniers, G. B. Marin, *J. Org. Chem.* **2016**, *81*, 11626; (b) P. Pavez, D. Millan, M. Rojas, J. I. Morales, J. G. Santos, *Int. J. Chem. Kinet.* **2016**, *48*, 337; (c) P. Pavez, D. Millan, J. Morales, M. Rojas, D. Cespedes, J. G. Santos, *Org. Biomol. Chem.* **2016**, *14*, 1421; (d) S. Dey, *Am. J. Chem.* **2015**, *5*, 55; (e) S. Dey, *Sci. J. Chem.* **2015**, *3*, 57.
3. (a) E. A. Castro, M. E. Aliaga, M. Gazitua, P. Pavez, J. G. Santos, *J. Phys. Org. Chem.* **2014**, *27*, 265; (b) P. Pavez, D. Millan, J. I. Morales, E. A. Castro, *J. Org. Chem.* **2013**, *78*, 9670; (c) R. Aguayo, F. Arias, A. Canete, C. Zuniga, E. A. Castro, P. Pavez, J. G. Santos, *Int. J. Chem. Kinet.* **2013**, *45*, 202; (d) E. A. Castro, D. Ugarte, M. F. Rojas, P. Pavez, J. G. Santos, *Int. J. Chem. Kinet.* **2011**, *43*, 708.
4. (a) I. H. Um, M. Y. Kim, A. R. Bae, J. Dust, E. Buncel, *J. Org. Chem.* **2015**, *80*, 217; (b) I. H. Um, A. R. Bae, *J. Org. Chem.* **2011**, *76*, 7510; (c) I. H. Um, E. H. Kim, J. H. Shin, *Org. Biomol. Chem.* **2010**, *8*, 3801; (d) I. H. Um, J. Y. Lee, S. H. Ko, S. K. Bae, *J. Org. Chem.* **2006**, *71*, 5800.
5. (a) I. H. Um, J. S. Min, J. A. Ahn, H. J. Hahn, *J. Org. Chem.* **2000**, *65*, 5659; (b) I. H. Um, S. J. Hwang, S. R. Yoon, S. E. Jeon, S. K. Bae, *J. Org. Chem.* **2008**, *73*, 7671; (c) I. H. Um, J. A. Seok, H. T. Kim, S. K. Bae, *J. Org. Chem.* **2003**, *68*, 7742; (d) I. H. Um, E. K. Chung, S. M. Lee, *Can. J. Chem.* **1998**, *76*, 729; (e) I. H. Um, S. E. Jeon, J. A. Seok, *Chem. Eur. J.* **2006**, *12*, 1237.
6. (a) J. S. Kang, Y. J. Song, I. H. Um, *Bull. Korean Chem. Soc.* **2013**, *34*, 2023; (b) Y. J. Song, M. Y. Kim, I. H. Um, *Bull. Korean Chem. Soc.* **2013**, *34*, 1722.
7. (a) I. H. Um, S. R. Yoon, H. R. Park, H. J. Han, *Org. Biomol. Chem.* **2008**, *6*, 1618; (b) I. H. Um, E. Y. Kim, H. R. Park, S. E. Jeon, *J. Org. Chem.* **2006**, *71*, 2302.
8. I. H. Um, S. J. Hwang, M. H. Baek, E. J. Park, *J. Org. Chem.* **2006**, *71*, 9191.
9. M. Gresser, W. P. Jencks, *J. Am. Chem. Soc.* **1977**, *99*, 6963.
10. (a) E. A. Castro, M. Aliaga, P. Campodonico, J. G. Santos, *J. Org. Chem.* **2002**, *67*, 8911; (b) E. A. Castro, M. Anduja, A. Toro, J. G. Santos, *J. Phys. Org. Chem.* **2006**, *19*, 683.
11. (a) A. Trummal, A. Rummel, E. Lippmaa, P. Burk, I. Koppel, *J. Phys. Org. Chem.* **2009**, *113*, 6206; (b) I. Kaljurand, A. Kütt, L. Sooväli, T. Rodima, V. Mäemets, I. Leito, I. A. Koppel, *J. Org. Chem.* **2005**, *70*, 1019.
12. J. G. Smith, *Organic Chemistry*, 3rd ed., McGraw Hill, Singapore, **2011**, p. 286.
13. (a) E. Shahbazali, M. Spapens, H. Kobayashi, S. Ookawara, T. Noël, V. Hessel, *Chem. Eng. J.* **2015**, *281*, 144; (b) L. L. Fershtat, M. A. Epishina, A. S. Kulikov, N. N. Makhova, *Mendel. Commun.* **2015**, *25*, 36; (c) X. Huang, B. Fulton, K. White, A. Bugarin, *Org. Lett.* **2015**, *17*, 2594.
14. (a) J. Chen, K. Natte, H. Neumann, X.-F. Wu, *Chem. Eur. J.* **2014**, *20*, 16107; (b) E. Quaranta, A. Angelini, M. Carafa, A. Dibenedetto, V. Mele, *ACS Catal.* **2014**, *4*, 195.
15. K. H. Park, M. Y. Kim, I. H. Um, *Bull. Korean Chem. Soc.* **2016**, *37*, 77.
16. (a) Y. Tsuno, M. Fujio, *Adv. Phys. Org. Chem.* **1999**, *32*, 267; (b) Y. Tsuno, M. Fujio, *Chem. Soc. Rev.* **1996**, *25*, 129; (c) Y. Yukawa, Y. Tsuno, *Bull. Chem. Soc. Jpn.* **1959**, *32*, 965.
17. (a) M. Mishima, J. L. M. Abboud, M. Fujio, M. Suenaga, H. F. Koch, G. Judith, *J. Phys. Org. Chem.* **2016**, *29*, 523; (b) M. Mishima, J. L. M. Abboud, *J. Phys. Org. Chem.* **2016**, *29*, 77; (c) M. M. R. Badal, M. Zhang, S. Kobayashi, M. Mishima, *Bull. Chem. Soc. Jpn.* **2013**, *86*, 856; (d) M. Zhang, M. M. R. Badal, I. A. Koppel, M. Mishima, *Bull. Chem. Soc. Jpn.* **2013**, *86*, 813.
18. (a) S. I. Kim, S. J. Hwang, I. H. Um, *Bull. Korean Chem. Soc.* **2010**, *31*, 2015; (b) S. I. Kim, H. R. Baek, I. H. Um, *Bull. Korean Chem. Soc.* **2011**, *32*, 179.
19. (a) S. V. Hill, S. Thea, A. Williams, *J. Chem. Soc., Perkin Trans. 2* **1983**, 437; (b) H. K. Oh, S. K. Kim, H. W. Lee, I. Lee, *New J. Chem.* **2001**, *25*, 313; (c) H. K. Oh, S. K. Kim, H. W. Lee, I. Lee, *J. Chem. Soc., Perkin Trans. 2* **2001**, 1753.