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

[Ik-Hwan Um](#)

Corresponding Author

E-mail address: [ihum@ewha.ac.kr](mailto:ihum@ewha.ac.kr)

Department of Chemistry, Ewha Womans University, Seoul 03760, Korea

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[Kyoung-Ho Park](#)

Department of Chemical and Molecular Engineering, Hanyang University, Ansan, Gyeonggi-do, Korea

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[Ik-Hwan Um](#)

Corresponding Author

E-mail address: [ihum@ewha.ac.kr](mailto:ihum@ewha.ac.kr)

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Department of Chemistry, Ewha Womans University, Seoul 03760, Korea

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[Kyoung-Ah Park](#)

Department of Chemical and Molecular Engineering, Hanyang University, Ansan,  
Gyeonggi-do, Korea

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## Abstract

Second-order rate constants ( $k_N$ ) for nucleophilic substitution reactions of *O*-phenyl *O*- $\gamma$ -substituted-phenyl thionocarbonates (**4a**–**4k**) with

1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) in MeCN at 25.0 °C are reported. The reactivity of **4a** decreases as basicity of the leaving group increases except O-phenyl thionocarbonate (**4a**), which is less reactive than O-phenyl thionocarbonate (**4b**) although the former possesses 2 pK<sub>a</sub> units less basic nucleofuge than the latter. The Brønsted-type plot for the reactions of **4b** is linear with  $\rho = -0.50$ , a typical  $\rho$  value for reactions reported to proceed through a concerted mechanism. The Hammett plot correlated with  $\sigma_p$  constants for the reactions of **4b** results in a better linear correlation than that correlated with  $\sigma$  constants. Besides, the Yukawa-Tsuno plot exhibits an excellent linear correlation with  $\sigma_p^+$  constants ( $r = 0.990$ ), 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.

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