

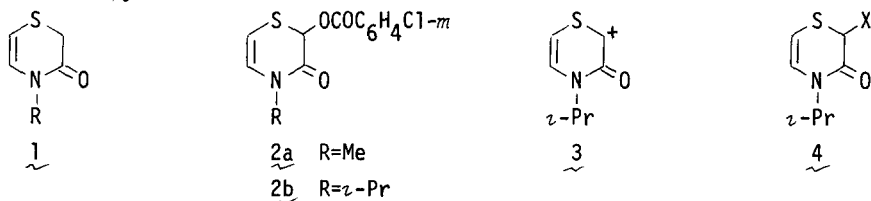
SOLVOLYSIS OF 2-*m*-CHLOROBENZOYLOXY-4-ISOPROPYL-2H-1,4-THIAZIN-3-ONE
 GENERATION OF A STABLE CARBOCATION

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Abstract The title compound 2b undergoes nucleophilic substitution reactions with exclusive alkyl-oxygen bond fission and its rate of solvolysis is highly sensitive toward change in polarity of solvents, as is shown by its highest *m*-value of all reported so far in $\log k - \log k_0 = mY$.

Recently we reported¹ synthesis of 4-alkyl-2H-1,4-thiazin-3-ones 1 (R=Me, Et, *i*-Pr, CH₂Ph) and then communicated² a novel *m*-chlorobenzoyloxylation of 1 (R=Me, *i*-Pr) by *m*-chloroperbenzoic acid, which occurred regioselectively at 2-position of 1 to give 2(a, b) in almost quantitative yields. We have found that alkyl-oxygen bond of ester 2b is highly susceptible to ionize on reactions with nucleophiles, which implies generation of very stable carbocationic species 3.

Dissolution of 2-*m*-chlorobenzoyloxy-4-isopropyl-2H-1,4-thiazin-3-one 2b into ethanol and heating it for 1 hour at reflux temperature gave 2-ethoxy-4-isopropyl-2H-1,4-thiazin-3-one 4a³ (X=OEt) in quantitative yields, instead of the expected product, 2-alcohol 4d (X=OH). Likewise treatment of 2b with isopropylamine (rt, 1 day) afforded corresponding 2-isopropylamino compound 4b⁴ (X=NHPr-*i*) in quantitative yields, instead of the 2-alcohol 4d and *N*-isopropyl-*m*-chlorobenzamide. Toward *N,N*-dimethylaniline, in the presence of a small amount of silica gel as a catalyst⁵, this ester 2b reacted (at rt, for 1 day in CH₂Cl₂) at the para position to give 70% yield of 2-*p*-dimethylanilino phenyl compound 4c⁶ (X=C₆H₄NMe₂-*p*). All these facts clearly show that reactions of the ester 2b with nucleophiles proceed with exclusive alkyl-oxygen bond fission.



These results prompted us to study effects of solvent polarity on the rate of solvolysis of the *m*-chlorobenzoate 2b. In a series of solvents shown in Table I solvolytic reactions were carried out at 25°C and first-order rate constants were determined by following appearance of *m*-chlorobenzoic acid titrimetrically with the use of 0.01 N aqueous solution of sodium hydroxide and phenolphthalein as an indicator. All runs proceed quite cleanly up to 90% reaction and obeyed first-order rate expression well. In Table I are listed these rate data, together with *Y*-value of the respective solvents in Grunwald-Winstein equation⁷, $\log k - \log k_0 = mY$. Plots of $\log k$ versus *Y* (Fig. 1) show satisfactory linear relationship ($r=0.997$), from which $m=1.53$

can be evaluated.

Since by definition $m=1.00$ for *t*-butyl chloride, the value 1.53 means solvolysis of the ester 2b is much more sensitive to the change in polarity of the solvents than *t*-butyl chloride is. To our knowledge, this value is the highest of all reported so far with the use of *ordinary* (not *acidic*) solvents.

The facile and exclusive alkyl-oxygen bond fission of the ester 2b and its high sensitivity toward solvent polarity strongly imply generation of a very stable carbocationic intermediate 3 during solvolyses of the ester 2b. Further works are now in progress in this laboratory regarding a possibility that the cation 3 is a stable aromatic cation as 5.

Table I. Rate Constants for Solvolysis of 2b at $25 \pm 0.05^\circ\text{C}$

Solvent	$k(\text{s}^{-1})$	γ^a
MeOH	4.28×10^{-4}	-1.090
95%EtOH-5% H_2O	3.01×10^{-4}	-1.287
90% Me_2CO -10% H_2O	4.05×10^{-5}	-1.856
EtOH	2.13×10^{-5}	-2.033
<i>i</i> -PrOH	1.40×10^{-6}	-2.73

a) A. H. Fainberg, and S. Winstein, *J. Am. Chem. Soc.*, **78**, 2770 (1956).

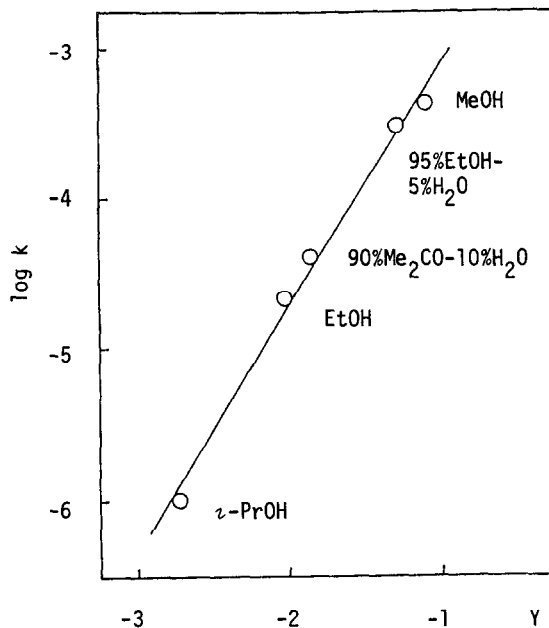
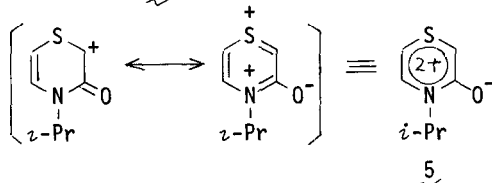


Fig. 1 Plots of $\log k$ versus Y

References and Notes

- (1) M. Hojo, R. Masuda, S. Kosaka, and K. Nagase, *Synthesis*, 1979, 272.
- (2) M. Hojo, R. Masuda, K. Yoshinaga, and S. Munehira, *Synthesis*, 1982, 312, 424.
- (3) Bp $215^\circ\text{C}/5$ torr, $^1\text{H-NMR}(\text{CDCl}_3)$ δ 6.41(d, 7.8Hz, 1H), 5.49(dd, 7.8Hz, 2.4Hz, 1H), 4.90(d, 2.4 Hz, 1H), 4.86(sep, 7.2Hz, 1H), 3.64(m, 2H), 1.25(d, 7.2H, 3H), 1.20(d, 7.2Hz, 3H), and 1.18 (t, 7.2Hz, 3H), IR. 1657 cm^{-1} . Anal. ($\text{C}_9\text{H}_{15}\text{NSO}_2$) C, H, N, S.
- (4) Mp 60°C , $^1\text{H-NMR}(\text{CDCl}_3)$ δ 6.37(d, 7.2Hz, 1H), 5.58(dd, 7.2Hz, 1.8Hz, 1H), 4.84(sep, 7.2Hz, 1H), 4.43(d, 1.8Hz, 1H), 3.10(sep, 7.2Hz, 1H), 2.08(s, 1H), 1.22(d, 7.2Hz, 6H), and 1.09(d, 7.2Hz, 6H), IR(KBr) 1650 cm^{-1} . Anal. ($\text{C}_{10}\text{H}_{18}\text{N}_2\text{SO}$) C, H, N, S.
- (5) M. Hojo, and R. Masuda, *Synth. Commun.*, **5**, 173 (1975).
- (6) Mp 82°C , $^1\text{H-NMR}(\text{CDCl}_3)$ δ 7.20(d, 8.4Hz, 2H), 6.65(d, 8.4Hz, 2H), 6.34(d, 7.2Hz, 1H), 5.62 (dd, 7.2Hz, 1.2Hz, 1H), 4.98(sep, 7.2Hz, 1H), 4.45(d, 1.2Hz, 1H), 2.90(s, 6H), and 1.22(d, 7.2Hz, 6H), IR(KBr) 1670 cm^{-1} . Anal. ($\text{C}_{15}\text{H}_{20}\text{N}_2\text{SO}$) C, H, N, S.
- (7) E. Grunwald and S. Winstein, *J. Am. Chem. Soc.*, **70**, 846 (1948).

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