Table 3. Hammett Reaction Constants ρ_X and ρ_Z, for the Elimination from 2-Substituted (*Z*)-Phenyletyl Substituted (*X*)-Benzenesulfonates with *tert*-BuO$^-$ in *tert*-Butyl alcohol at 40℃ [5a]

Z	ρ_X	*R*	*X*	ρ_Z	*R*
p-CH_3O	1.24± 0.02	0.999	*p*-CH_3	2.49± 0.03	0.998
p-CH_3	1.24± 0.05	0.997	H	2.50± 0.02	0.998
H	1.08± 0.03	0.999	*p*-Br	2.36± 0.02	0.999
m-CH_3O	1.06± 0.04	0.999	*p*-NO_2	2.03± 0.04	0.998
p-Cl	1.01± 0.04	0.996			
m-Cl	0.94± 0.02	0.997			

tion between *Z* and *X*.

Banger *et al.*[5a] reported that ρ_Z values decrese linearly with increase of the electron-withdrawing power of the leaving group *X* (see Table 3), which indicates the shift to transition state of less carbanion character. The ρ_X values become less positive as *Z* becomes more electron-withdrawing (Table 3), suggesting that increased C_β-H bond-breaking is accompanied by decreased C_α-O bond-breaking, and the shift to transition state with greater carbanion character.

We also examined the plot of ρ_Z *vs.* σ_X to give a linear correlation with a slope of -0.51 ($r=0.979$), and that of ρ_X *vs.* σ_Y to give the same slope of -0.50 ($r=0.979$). Therefore, within these series of substituents of *Z* and *X*, the rate constants of the elimination reaction are correlated with general Eq. (6), and it can be written as

$$\log k_{ZX}/k_{oo}=2.45\sigma_Z-0.51\,\sigma_Z\sigma_X+1.12\,\sigma_X \quad (8)$$

In the presence of a base, 2-phenylethyl arensulfonates undergoes E2 elimination reaction (Eq. 3).[5a] The same interaction coefficient of -0.51 which derived from either ρ_Z and ρ_X, probably indicates that the deprotonation of C_β-H and C_α-O bond-breaking in these elimination reaction are concerted in the E2 transition state within the range of variations of substituents *Z* and *X*. From these results, it was possible to apply the multiple Hammett equation to the bimolecular elimination reaction (E2 reaction). In conclusion, cross interaction term, ρ_{XY}, ρ_{YZ}, and ρ_{ZX}, in the substituent effects are useful tool in elucidating not only an S_N2 reaction mechanism but also an E2 reaction.

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Photoinitiated Radical Cyclization of a Penicillin-derived 4-mercaptoazetidin-2-one

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Many researchers have attempted to prepare cephalosporins from readily available penicillins. The efficient methods of the penam-cepham conversion involve primarily interaction between an electrophilic sulfur or its equivalent groups and an appropriately situated isopropenyl double bond of the N-side chain in the azetidinone intermediates.[1]

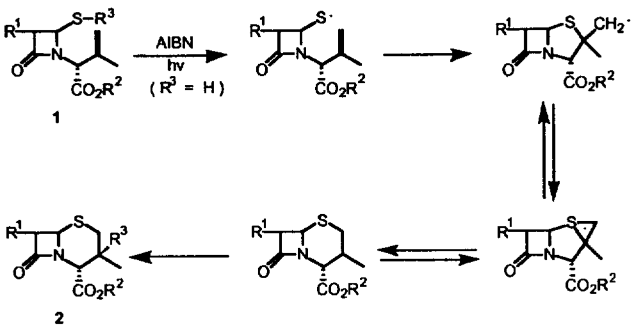
Mercaptoazetidinones have been proposed as intermediates on penicillin biosynthesis,[2] but free mercapto compounds have not been directly used in the biosynthesis of β-lactam antibiotics.[3] Mercapto compounds can be prepared by simple hydrolysis of the corresponding thiazolinoazetidinones.[4,5] The intramolecular cyclization of mercaptan **1b** was reported by us.[6] Treatment of mercaptan **1b** with *t*-BuOCl yielded chloromethyl penam which was converted to 3-chlorocepham **2c** upon heating in DMSO. A similar result was obtained in the reaction with NBS or other positive halogen precursors.

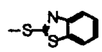
Photoirradiation of disulfide **1a** in acetonitrile gave cepham **2a**, and other cephalosporins and penams.[7] The photoreaction was significantly concentration dependent; irradiation at lower concentration resulted in the predominant formation of cephalosporin derivatives.[8] Recently cepham **2d** was prepared from mercaptan **1d** *via* metal promoted thinyl radical cyclization.[9]

We now wish to report the photoreaction of a penicillin-derived 4-mercaptoazetidin-2-one (**1e**).[10] Free radical addition of thiols to unsaturated compounds has been reported.[11] The mercaptan **1d** was prepared by Baldwin's procedure.[4] Using 2,2'-azobisisobutyronitrile (AIBN) as an initiator, irradiation of mercaptan **1e** afforded cepham **2e** and small amount of few unknown compounds.

A solution of mercaptan **1e** (100 mg, 0.23 mmol) and AIBN (50 mg, 0.3 mmol) in ethyl acetate (10 mL) in a quartz vessel was degassed with nitrogen for 15 min and then irradiated with 2539 Å U.V. lamp at room temperature for 3 hr. After removal of the solvent the residue was chromatographed on a silica gel column with ethyl acetate-hexane (2 : 3) as an eluent.

The major component (50%, mp. 116-119°) was assigned structure **2e** based on spectroscopic evidence.[12] Any cyclized products were not given in the reaction without AIBN.[13]



	R^1	R^2	R^3
a:	-NHCOCH$_2$Ph	CH$_2$CCl$_3$	
b:	-NHCOCH$_2$OPh	-CH(Ph)$_2$	H
c:	-NHCOCH$_2$OPh	-CH(Ph)$_2$	Cl
d:	-NHCOCH$_2$OPh	CH$_2$CCl$_3$	H
e:	-NHCOCH$_2$OPh	CH$_2$Ph	H

Scheme 1.

The formation of the 6-membered cepham was rationalized by intramolecular addition to a double bond in 5-exo fashion,[14] rearrangement and hydrogen abstraction.[9]

Further studies in order to stop the reaction in penam stages are under way.[15]

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10. Mercaptan **1d** was obtained in solid and other mercapto compounds were not. Therefore mercaptan **1d** was recrystallized and examined.
11. K. Takabe, T. Katogiri, and J. Tanaka, *Tetrahedron Lett.*, 4805 (1970).
12. Cepham **2e**: ^{1}H-NMR (CDCl$_3$) δ 0.92 (d, J=7 Hz, 3H), 1.25 (m, 1H), 2.37, 2.93 (AX, J=13 Hz, 2H), 4.46 (s, 2H), 4.56 (d, 1H), 5.0-5.5 (m, 4H), 6.77-7.50 (m, 11H); IR (KBr) 3400, 1763, 1728, 1666 cm^{-1}; MS (m/z) 440.
13. Cepham **2e** was given in low yield using other U.V. lights such as 3014 Å and 3467 Å. Mercaptan **1e** was unstable at higher temperature.[4]
14. B. Giese, "Radicals in Organic Synthesis", Pergamon Press, Oxford, 1986, p. 141.
15. In fact, we once obtained a penam but failed to reproduce.

Unusual Stability Increment of Ag(I)-Podand Complexes

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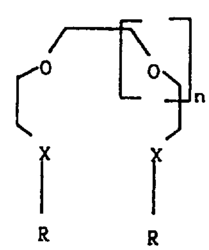
The oligoethylene glycol derivatives with aromatic donor groups at both ends, called podands can be obtained simply and cheaply.[1-3] Some podands containing larger aromatic groups with heterodonor atoms wrap themselves around the cations such as Na^+ and Rb^+ ion in a helical manner to make pseudocavity in solid and solution states.[1,2] But no experimental evidence was observed that the simple aromatic groups, such as phenyl group, take place in such a stacking interaction to enhance the selectivity for given cations. Furthermore, the podands possessing the sulfur-oxygen mixed donor atoms have been much less frequently studied.[3] Under these circumstances, we have designed some podands possessing sulfur donor atoms in ether chain and simple aromatic moieties, such as phenyl (Ph) or benzyl (Bz) groups at both ends, which could be expected as the strong ionophores for Ag(I) ion rather than alkali metal ions.

The influence of the flexibility of aromatic end groups on the stacking interaction have not investigated carefully. Thus, in this study we confirm the conformational change by incorporation of methylene spacing groups to the aromatic end groups, which favors the formation of pseudocavity and increases the stability.



Ph$_2$O$_4$; n=1; X=O; R=phenyl, Ph$_2$O$_2$S$_2$; n=1; X=S; R=phenyl
Bz$_2$O$_2$S$_2$; n=1; X=S; R=benzyl, Ph$_2$O$_5$; n=2; X=O; R=phenyl
Ph$_2$O$_3$S$_2$; n=2; X=S; R=phenyl, Bz$_2$O$_3$S$_2$; n=2; X=S; R=benzyl