HCl (1.0 m*l*) was added, and stirred for 10 min. MeOH and THF were evaporated. The reaction mixture was extracted with ether and washed with water and brine. The ether layer was dried over anhydrous $MgSO_4$. The solvent was evaporated under reduced pressure to give the product in almost quantitative yield. The crude product was purified by preparative TLC (SiO_2, CH_2Cl_2, Rf = 0.40) to afford pure erucyl alcohol (0.169g, 93%).

The resulting procedure is considered to be particularly suitable for large-scale preparation.

References and Notes

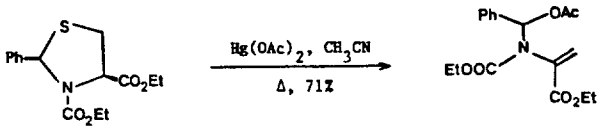
1. S. W. Chaikin and W. G. Brown, *J. Am. Chem. Soc.*, **71**, 122 (1949).
2. H. C. Brown and S. Krishnamurthy, *Tetrahedron*, **35**, 567 (1967).
3. A. T. Costello and D. J. Milner, *Synthetic Communications*, **16**, 1173 (1986).
4. C. A. Henrick, *Tetrahedron*, 1845 (1977).
5. D. A. Carlson, M. S. Mayer, D. L. Silhacek, J. D. James, and B. A. Bierl, *Science*, **174**, 76 (1971).
6. The acid chloride (**11**) was prepared from benzyl cyanide in three steps (68%); (i) dimethylation (NaH, MeI, DMF) (ii) hydrolysis (KOH, ethyleneglycol) (iii) chlorination ($SOCl_2$, heptane).
7. We prepared this compound (**1j**) from 1,9-nonanedioic acid by esterification (EtOH, H^+), partial hydrolysis (KOH, H_2O), followed by chlorination ($SOCl_2$, heptane) in 67% yield.

Selective Cleavage of Thiazolidines I. Mercuric Acetates in Aprotic Media

Jahyo Kang*, Young Ro Choi, Soon-Gyu Choi, Hyung Geun Cho, Daesung Lim, Weon Bin Im, and Jae Hyoung Lee

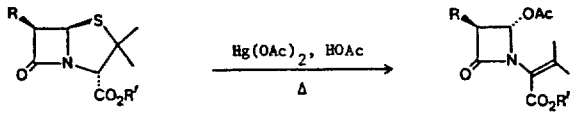
Department of Chemistry, Sogang University, Mapoku, Seoul 121-742. *Received July 1, 1988*

During the course of our attempts to cleave thiazolidines with thiaphilic metal salts in the presence of external nucleophiles, it was found that mercuric salts, expecially mercuric acetate, in acetonitrile was very effective for the cleavage of the compound **1** without incorporation of external nucleophile, which was rather unexpected by two accounts stated below.



1 **2**

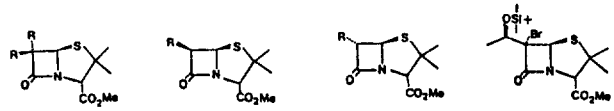
First of all, mercuric acetate is almost insoluble in acetonitrile. Also, the closely related Stoodley fragmentation, which is very useful in penicillin chemistry, is carried out universally in acetic acid where external nucleophiles are present in great excess.[1]



3 **4**

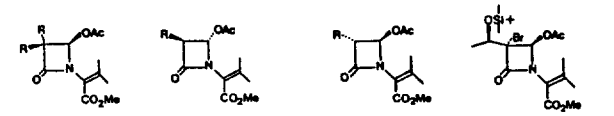
Consequently, a detailed study was undertaken to elucidate the scope and utility of the reaction especially in penams. Thus the following substrates were prepared according to procedures reported elsewhere.

And each substrate was subject to the reaction condition described below for the siloxyethyl derivative **11.** A mixture of mercuric acetate (0.238g, 0.75 mmol), calcium carbonate (as



	R		R		R		
5	H	**7**	PhtN-	**11**		**13**	
6	Br	**8**	$PhCH_2CONH$-	**12**	Br		
		9	$PhOCH_2CONH$-				
		10	Br-				

an acid scavenger, 0.041 g, 0.41 mmol) and the penam **11** (0.140 g, 0.37 mmol) in acetonitrile (1.9 mL) was refluxed for 6 h. After cooling to rt, the white solid was filtered off with aid of methylene chloride. Aqueous work-up followed by chromatography provided the corresponding acetate **20** (0.108 g, 78%). But it was found later that the aqueous work-up could be omitted even for pure product (94%).



	R		R		R		
14	H	**16**	PhtN-	**20**		**22**	
15	Br	**17**	$PhCH_2CONH$-				
		18	$PhOCH_2CONH$-	**21**	Br		
		19	Br				

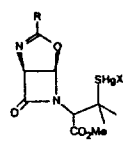
However; extension to other penams revealed the characteristic of the present reaction; although the non-halogenated species, **5, 7** and **11,** gave good yields of the corresponding acetate (**5**→**14,** 81%; **7**→**16,** 56%; **11**→**20,** 78%), halo-

Table 1. Reaction of Penams with Mercuric Acetate in Refluxing Solvent[a]

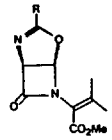
Starting Material	CH_3CN Solvent[b]		AcOH Solvent	
	Time	Product(Yield)[c]	Time	Product(Yield)[c]
5	2h	**14**(81%)	0.5h	**14**(100%)
6	6h	NR[d]	6h	NR[d]
7	5h	**16**[e](56%)	1h	**16**[f](100%)
10	4h	NR[g]	2h	**19**[f](27%)
11	6h	**20**[f](78%)	1h	**20**[f](75%)
12	4h	NR[g]	4h	**21**[h](22%)
13	4h	NR[d]	4h	**22**[i](38%)

[a]Each penam was refluxed with $Hg(OAc)_2$(2.0−4.0 equiv) in anhydrous solvent (concn 0.1−0.2 M). [b]Additonally, $CaCO_3$(2 equiv) was added as an acid scavenger. [c]Isolated yield for pure compound unless specified otherwise. [d]No reaction with >90% recovery of starting material. [e]trans/cis = 4. [f]Almost pure trans. [g]No reaction with >60% recovery of starting material. [h]trans/cis = 2. [i]Chromatographically and spectrochemically homogeneous. Possibly E.

genated penams such as **6, 10, 12** and **13,** regardless of substitution pattern, did not react at all under various conditions. Moreover under the same condition for the successful reactions, methyl esters of penicillin G and V, **8** and **9,** did react to a last trace to afford an array of products, among which oxazolines would be the initial product[2] which may then docompose. Thus, treatment of these esters with more reactive mercuric trifluoroacetate (2.0 equiv) and calcium carbonate in acetonitrile at −30 °C afforded presumably the oxazoline mercaptides **23,** which were treated with DBU (3.0 equiv) under reflux to give the oxazolines, **24** and **25**, in 45 and 51% yields, respectively.



23

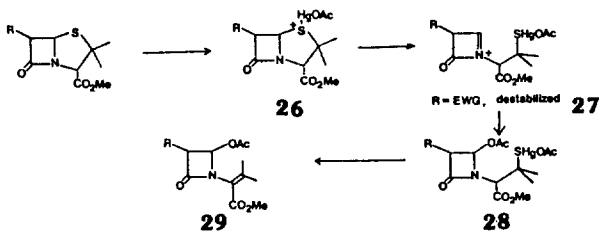


24 R = $PhCH_2$−

25 R = $PhOCH_2$−

These products have been prepared previously in unspecified yields with *t*-butyl hypochlorite.[2] In our hands, the oxazoline **24** could be secured for comparison purpose by the reaction with *t*-butyl hypochlorite only in 17% yield.

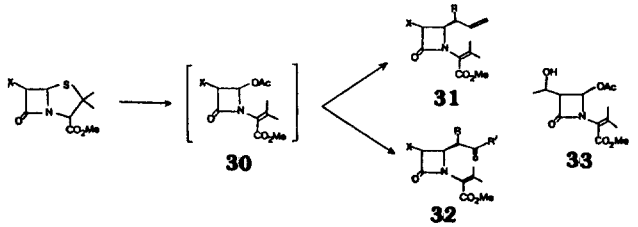
The reactivity of penams with mercuric acetate in acetic acid seems to be higher than in acetonitrile. Comparison of the two reactions was made by carrying out the reactions independently. As can been in Table 1, as bromines are present at 6 position, the reactivities in both systems decrease markedly. Thus the 6,6-dibromo compound **6** would not undergo reaction with recovery of 90% of the starting material even in acetic acid. This would attest the intermediacy of azetidinium ion, **27,** which may be destabilized with electron-withdrawing R groups (R = Br, for the present cases).



26 **27** **28** **29**

The utility of the present reaction is severalfold: Two of such utility was examined. For example, reduction of the dibromide **6** even with a stoichiometric amount of tributyltin hydride afforded the desired β-bromide **10** contaiminated with the starting material **6** and the completely reduced penam **5.**[4] Separation of the bromide **10** from the non-halogen compound **5** (~15%) was difficult. Thus, exposure of the mixture to $Hg(OAc)_2$ in acetonitrile afforded easily separable mixture, out of which the β-bromide **10** was isolated pure in 68% yield.

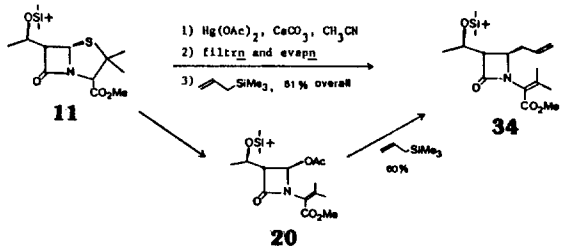
Another potentially useful nature of the present reaction which gives the acetoxylated products is that the acetoxy group in **30** could be replaced *in situ* by an allylic[5] or an β-keto alkyl groups[6], since the acetoxy group can be placed on the azetidinone rings cleanly if the substituents on the ring are not electron-withdrawing.



30 **31** **32** **33**

However, when the reaction was performed together with a variety of Lewis acid and carbon nucleophiles in acetonitrile in the hope of executing two reactions in the same pot[5], desiylated acetate **33** was obtained, which indicated the diminished influence of Lewis acids in a coordinating solvent.

Consequently, the reaction mixture of the penam **11** with $Hg(OAc)_2$(2.5 eq.) and $CaCO_3$(1.1 eq.) in acetonitrile was filtered to remove HgS, $CaCO_3$ and unreacted $Hg(OAc)_2$ and evaporated. This was followed by dissolution in CH_2Cl_2, addition of allyltrimethylsilane (3.0 eq.) and trimethylsilyl triflate (2.0 eq.). Stirring at rt for 3h followed by aq. work-up and chromatography afforded the allylated product and a small amount of the corresponding desilylated alcohol. After silylation of the minor alcohol, the total yield was 61%. Of course, the same product could be obtained from pure **20** in 60% yield. But the direct reaction sequence without isolation should offer some advantage.



11 **34** **20**

In conclusion, a non-acidic and aprotic version of Stoodley fragmentation was developed, which bears some practical ramification.

Acknowledgement. This work is supported by the Korea Science and Engineering Foundation.

References

1. a) R. J. Stoodley and N. R. Whitehouse, *J. Chem. Soc., Perkin I,* 32 (1973) b) *idem, ibid,* 181 (1974) c) H. C. Wang, Y.

Y. Lee and Y. M. Goo, *J. Korean Chem. Soc.*, **30**, 138 (1986)
2. (a) J. C. Sheehan, "Molecular Modification in Drug Design", R. F. Gould, ed., American Chemical Society, 1964, p. 15 (b) D. H. R. Barton, F. Comer and P. G. Sammes, *J. Am. Chem. Soc.*, **91**, 1529 (1969)
3. W. J. Leanza, F. Dininno, D. A. Muthard, R. R. Wikening, K. J. Wildonger, R. W. Ratcliffe and B. G. Christensen, *Tetrahedron*, **39**, 2505 (1983)
4. D. I. John, N. D. Tyrrel and E. J. Thomas, *Tetrahedron*, **39**, 2477 (1983).
5. (a) K. Prasad, K. Adlgasser, R. Sharma and P. Stütz, *Heterocycles*, **19**, 2099 (1982); (b) H. Fliri and C.-P. Mak, *J. Org. Chem.*, **50**, 3438 (1985).
6. (a) A.G.M. Barrett and P. Quayle, *Chem. Commun.*, 1076 (1981); (b) P. J. Reider, R. Rayford, and E. J. J. Grabowski, *Tetrahedron Lett.*, **23**, 379 (1982); (c) P. J. Reider, and E. J. J. Grabowski, *ibid*, **23**, 2293 (1982); (d) R. P. Attrill, A. G. M. Barrett, P. Quayle and J. van derWesthuizen, *J. Org. Chem.*, **49**, 1679 (1984); (e) A. I. Meyers, T. J. Sowin, S. Scholz and Y. Ueda, *Tetrahedron Lett.*, **28**, 5103 (1987).

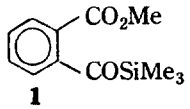
Acylsilanes in Aromatic Annulation for Hydroquinones

Jahyo Kang*, Jae Hyoung Lee, Jong Gil Rim, and Chongsuh Pyun

Department of Chemistry, Sogang University Mapoku, Seoul 121-742. *Received July 8, 1988*

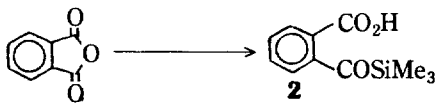
Michael addition followed by base-induced cyclization is a versatile method for the construction of carbocyclic 6-membered rings. Generally, the Michael acceptors supply 4 carbons out of 6 carbons (e.g. Robinson annulation[1]). Another useful variant is one in which 4 carbons are supplied by Michael donors. And this has been a major impetus for the ready construction of hydroquinon-quinone subunits which are present in anthracycline antibiotics[2] and potentially other naphthazarin natural products such as chrysophanol and fredericamycins. The Michael donors which act as 1,4-dipoles are typified by the presence of the o-carboalkoxybenzylic anion. These include anions of dimethyl homophthalate[3] 3-phenylsulfonyl- and 3-cyano-phthalide[4], o-toluoyl esters[5] and homophthalic anhydrides[6].

In this paper, we wish to introduce another 1,4-dipole, o-carbomethoxybenzoyltrimethylsilane (**1**), which is conceptually related but functionally different, and its behavior toward Michael acceptors.



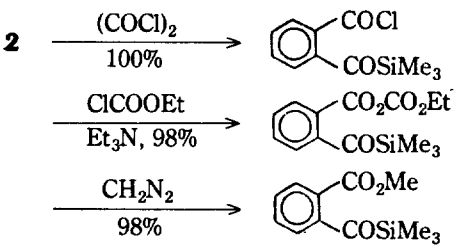
1

Acylsilanes are a versatile class of compounds which undergo a variety of interesting reactions[7,8]. A facile method for the preparation of multi-functional acylsilanes is lacking even though there are available in literature a number of preparatively useful methods, most of which utilize acyl anion equivalents[9], due to the difficulties associated with generation of silyl anions under mild conditions[10,11]. Consequently, a new methodology was developed[12] using the readily available $LiAl(SiMe_3)_4$ and $Al(SiMe_3)_3$[13]. Thus, phthalic anhydride could be converted, in the presence of CuCN, to the corresponding acylsilane **2** using either $LiAl(SiMe_3)_4$ or $LiMeAl(SiMe_3)_3$ in 80-90% yield[12].

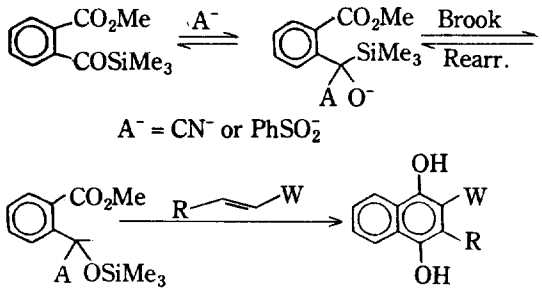


2

Having accomplished the preparation of o-carboxybenzoyltrimethylsilane **2**, it was further converted to the corresponding acid derivatives.



Subsequently, among the 3 derivatives, only o-carbomethoxybenzoyltrimethylsilane **1** was found to behave properly as a 1,4-dipole. Thus, ester **1** was treated with a variety of anions in the presence of dimethyl maleate as a representative Michael acceptor. Cyanide and benzenesulfinate were added in anticipation of the reaction path shown below.



However, under no circumstance did the reaction proceed. The starting material either remained intact below 23 °C or decomposed to an array of products at higher temperature. But soluble fluoride sources, especially cesium fluoride and tetrabutylammonium fluoride, gave acceptable results; here the fluoride had to be vigorously dried, otherwise the corresponding aldehyde was obtained[7] (Table 1).