

HCl (1.0 ml) 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 , $R_f = 0.40$) 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).

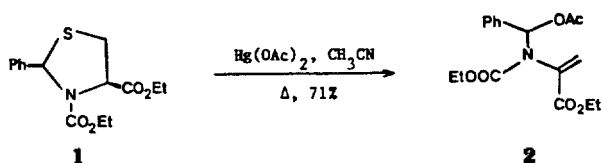
- H. C. Brown and S. Krishnamurthy, *Tetrahedron*, **35**, 567 (1967).
- A. T. Costello and D. J. Milner, *Synthetic Communications*, **16**, 1173 (1986).
- C. A. Henrick, *Tetrahedron*, 1845 (1977).
- D. A. Carlson, M. S. Mayer, D. L. Silhacek, J. D. James, and B. A. Bierl, *Science*, **174**, 76 (1971).
- 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).
- We prepared this compound (**11**) 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

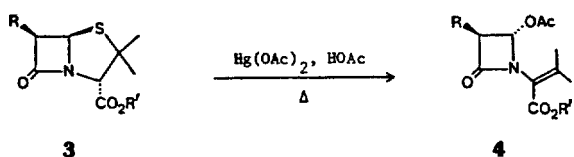
Jahyo Kang*, Young Ro Choi, Soon-Gyu Choi, Hyung Geun Cho,
Daesung Lim, Weon Bin Im, and Jae Hyung Lee

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

During the course of our attempts to cleave thiazolidines with thiophilic metal salts in the presence of external nucleophiles, it was found that mercuric salts, especially 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.

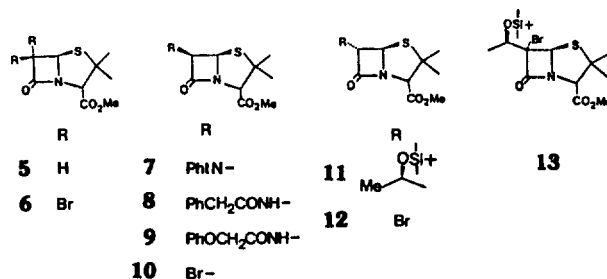


First of all, mercuric acetate is almost insoluble in acetonitrile. Also, the closely related Stodley fragmentation, which is very useful in penicillin chemistry, is carried out universally in acetic acid where external nucleophiles are present in great excess.¹

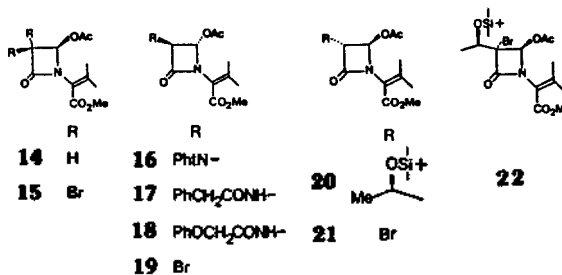


Consequently, a detailed study was undertaken to elucidate the scope and utility of the reaction especially in penams. Thus the following substrates were prepared according to procedures reported elsewhere.

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



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%).



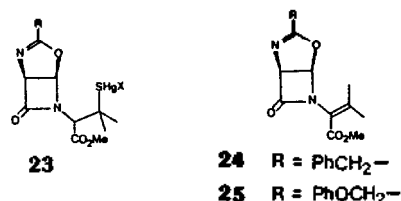
However; extension to other penams revealed the characteristic of the present reaction; although the non-halogenated species, **5**, **7** and **11**, gave good yields of the corresponding acetate (**5**→**14**, 81%; **7**→**16**, 56%; **11**→**20**, 78%), halo-

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

Starting Material	CH ₃ CN 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 (56%)	1h	16 (100%)
10	4h	NR ^e	2h	19 (27%)
11	6h	20 (78%)	1h	20 (75%)
12	4h	NR ^e	4h	21 ^h (22%)
13	4h	NR ^d	4h	22 (38%)

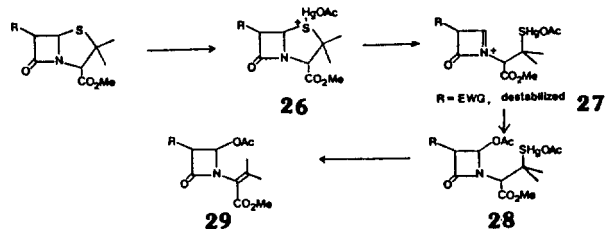
^aEach penam was refluxed with Hg(OAc)₂(2.0–4.0 equiv) in anhydrous solvent (concn 0.1–0.2 M). ^bAdditionally, CaCO₃(2 equiv) was added as an acid scavenger. ^cIsolated yield for pure compound unless specified otherwise. ^dNo reaction with >90% recovery of starting material. ^etrans/cis = 4. ^fAlmost pure trans. ^gNo reaction with >60% recovery of starting material. ^htrans/cis = 2. ⁱChromatographically and spectrochemically homogeneous. Possibly E.

generated 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 product² which may then decompose. 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.



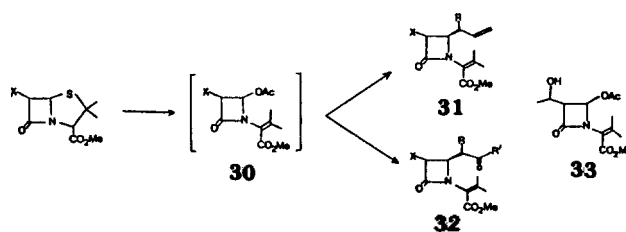
These products have been prepared previously in unspecified yields with *t*-butyl hypochlorite.² In our hands, the oxazoline **24** could be secured for comparison purpose by the reaction with *t*-butyl hypochlorite only in 17% yield.

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 be seen in Table I, 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).



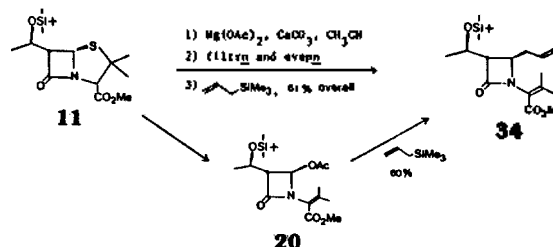
The utility of the present reaction is severalfold: Two of such utility was examined. For example, reduction of the dibromide **6** even with a stoichiometric amount of tributyltin hydride afforded the desired β -bromide **10** contaminated with the starting material **6** and the completely reduced 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 acetoxyated products is that the acetoxy group in **30** could be replaced *in situ* by an allylic⁵ or an β -keto alkyl groups⁶, since the acetoxy group can be placed on the azetidione rings cleanly if the substituents on the ring are not electron-withdrawing.



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 pot⁵, desilylated 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 CaCO₃(1.1 eq.) in acetonitrile was filtered to remove HgS, CaCO₃ and unreacted Hg(OAc)₂ and evaporated. This was followed by dissolution in CH₂Cl₂, 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.



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. Wikenning, 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).

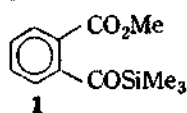
Acylsilanes in Aromatic Annulation for Hydroquinones

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

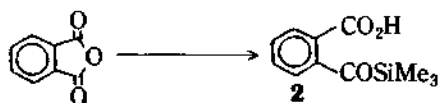
Department of Chemistry, Sogang University Mapo, Seoul 121-742. Received July 8, 1988

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 annulation¹). 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 antibiotics² 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 homophthalate³ 3-phenylsulfonyl- and 3-cyano-phthalide⁴, *o*-toluoyl esters⁵ and homophthalic anhydrides⁶.

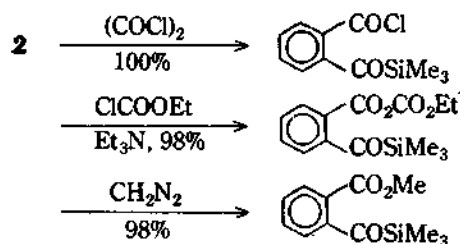
In this paper, we wish to introduce another 1,4-dipole, *o*-carbomethoxybenzoyltrimethylsilane (**1**), which is conceptually related but functionally different, and its behavior toward Michael acceptors.



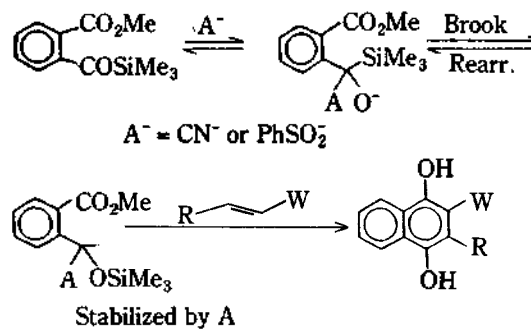
Acylsilanes are a versatile class of compounds which undergo a variety of interesting reactions^{7,8}. A facile method for the preparation of multi-functional acylsilanes is lacking even though there are available in literature a number of preparatively useful methods, most of which utilize acyl anion equivalents⁹, due to the difficulties associated with generation of silyl anions under mild conditions^{10,11}. Consequently, a new methodology was developed¹² using the readily available LiAl(SiMe₃)₄ and Al(SiMe₃)₃¹³. Thus, phthalic anhydride could be converted, in the presence of CuCN, to the corresponding acylsilane **2** using either LiAl(SiMe₃)₄ or LiMeAl(SiMe₃)₃ in 80-90% yield¹².



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 obtained⁷ (Table 1).