

Figure 1. Proposed structure of $\text{Ph}_4\text{SiW}_{12}\text{O}_{40}$. The central SiO_4 unit is cross-hatched. One of the phenyl rings lies behind the plane of the paper.

$(\text{aryl})_{8-n}\text{XM}_{12}\text{O}_{40}$. For example, addition of hydrated $(\text{H}_3\text{O})_4\text{-SiW}_{12}\text{O}_{40}$ to an acetonitrile solution of $\text{PhN}_2^+\text{PF}_6^-$ yields white, insoluble crystalline $(\text{PhN}_2)_4\text{SiW}_{12}\text{O}_{40}$ (**1**): IR $\nu_{\text{N}=\text{N}}$ 2269 cm^{-1} ; ^{13}C CPMAS NMR 114 (C_{ipso}), 134 (C_{meta} and ortho), 143, 147 (C_{para}) ppm. On heating at 75 °C under vacuum, **1** undergoes rapid, quantitative loss of nitrogen to provide $\text{tan Ph}_4\text{SiW}_{12}\text{O}_{40}$ (**2**).¹⁴ This synthetic method has broad general applicability and has been extended to a wide variety of aryldiazonium salts, readily obtainable from the corresponding anilines, and other molecular metal oxide clusters such as $\text{SiMo}_{12}\text{O}_{40}^{4-}$, $\text{PW}_{12}\text{O}_{40}^{3-}$, and $\text{PMo}_{12}\text{O}_{40}^{3-}$.

Aryldiazonium Keggin ion salts bearing electron-withdrawing ring substituents have significantly higher thermal stability but can be decomposed photochemically. Thus, for example, $(p\text{-CH}_3\text{OPhNHPPhN}_2)_3\text{PW}_{12}\text{O}_{40}$ (**3**) undergoes nitrogen loss at 138 °C. Irradiation into the broad absorption band centered at 450 nm results in elimination of nitrogen and formation of $(p\text{-CH}_3\text{OPhNHph})_3\text{PW}_{12}\text{O}_{40}$ (**4**). The photochemical syntheses are not quantitative, however, because of self-absorption of incident radiation.

The Keggin ion $\text{PMo}_{12}\text{O}_{40}^{3-}$ undergoes monoalkylation by $(\text{CH}_3)_3\text{O}^+\text{BF}_4^-$ and the X-ray structure of $\text{CH}_3\text{PMo}_{12}\text{O}_{40}^{2-}$ disclosed that the methyl group is attached to an oxygen atom which bridges two edge-shared molybdenum octahedra.¹⁵ This compound provides a structural paradigm for $(\text{aryl})_{8-n}\text{XM}_{12}\text{O}_{40}$, and we consider that the aryl substituents are similarly attached to bridging oxygen atoms in the cluster. The ^{13}C CPMAS NMR spectrum of **2** demonstrates peaks at 166 (C_{ipso}), 133 (C_{meta} and C_{para}), and 122 (C_{ortho}) ppm relative to $(\text{CH}_3)_4\text{Si}$. These chemical shift values are typical of oxygen-substituted aryl compounds such as anisole for which the corresponding shifts are 159.9, 129.5, 120.7, and 114.1 ppm¹⁶ and furnish evidence that the aryl groups are in fact covalently bonded to the $\text{SiW}_{12}\text{O}_{40}$ cage, cf. Figure 1. Consistent with this is the observation that the infrared spectra of **1** and **2** in the W-O stretching region are essentially the same which argues against a W=O bonding site.

Compound **2** and its analogues are poorly soluble in nonreactive organic solvents. Typical of inorganic esters, it reacts with aqueous acetonitrile to form phenol, in 97% yield, and $\text{SiW}_{12}\text{O}_{40}^{4-}$. A search for anionic, partially hydrolyzed clusters has not been successful. We consider that the hydrolysis involves nucleophilic attack by hydroxide ion with cleavage of W-O bonds for, when this reaction is carried out with H_2^{18}O , the phenol does not incorporate the ^{18}O label. Remarkably, the hydrolysis also produces a ca. 3% yield of hydroxybiphenyls which also do not contain ^{18}O . The ortho/meta/para isomer ratio is 1:0.24:0.31 which is strongly suggestive of a free radical coupling process.¹⁷ When **2** and $(p\text{-tolyl})_4\text{SiO}_{12}\text{O}_{40}$ are cohydrolyzed, cross-coupling products, viz.,

methylhydroxybiphenyls, are not detected. Similarly, they are not formed when *p*-cresol is added to the hydrolysis mixture. This indicates that the aryl groups which combine to give hydroxybiphenyl are confined to a region close to the surface of the $\text{SiW}_{12}\text{O}_{40}$ cluster and are not freely diffusing in solution.

We are continuing to investigate the chemistry of these and related hydrocarbyl oxymetalates in an effort to better understand the reaction mechanisms of the pendant aryl groups.

Acknowledgment. We are grateful to W. T. Conway, 3M Analytical and Properties Research Laboratory, for the thermogravimetric analyses.

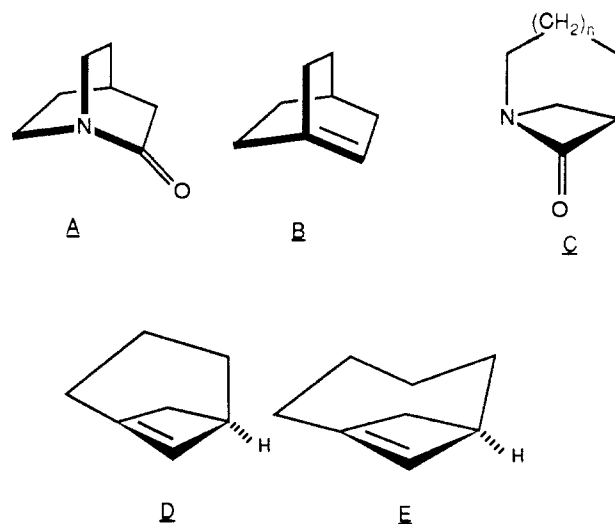
Synthesis of a 1,3-Bridged β -Lactam: A Novel, Anti-Bredt β -Lactam

Robert M. Williams** and Byung H. Lee

Department of Chemistry, Colorado State University
Fort Collins, Colorado 80523

Received May 27, 1986

The β -lactam antibiotics have figured prominently in chemistry due to their desirable medicinal properties as chemotherapeutic agents, their structural novelty, and their attendant rich chemistry.¹ In the past few years, a plethora of structurally novel β -lactam antibiotics have been discovered from natural sources as well as the laboratories of academic and industrial scientists. In conjunction with an ongoing project in our laboratories, we desired the preparation of bicyclic amides containing the amide nitrogen in a bridgehead disposition. Hall² and others³ have employed Bredt's rule, later modified by Wiseman,⁴ Kobrich,⁵ and Schleyer,⁶ as a guide for predicting the stability and attendant isolability of N-bridgehead amides. However, due to the capacity of the nitrogen atom to assume a tetrahedral geometry, several "anti-Bredt amides" have been synthesized⁷ such as 1-aza-bicyclo-[2.2.2]octan-2-one (A); the corresponding olefin B is predicted



to be an unstable olefin⁸ with an olefin strain energy (OS)⁶ of >40

(14) **1**: Anal. Calcd C, 8.7; H, 0.6; N, 3.4. Found C, 8.7; H, 0.6; N, 3.4. **2**: Anal. Calcd C, 9.0; H, 0.6; N, 0.0; found: C, 8.9; H, 0.7; N <0.1. Temperatures required for thermal elimination of N_2 from **1** and further quantitation of N_2 loss was achieved by thermogravimetric analysis.

(15) Knoth, W. H.; Harlow, R. L. *J. Am. Chem. Soc.* **1981**, *103*, 4265.

(16) Sadtler Research Laboratories, Standard Spectrum 526C.

(17) Gould, E. S. *Mechanism and Structure in Organic Chemistry*; Holt, Reinhart and Winston: New York, 1959; p 720.

*Fellow of the Alfred P. Sloan Foundation 1986-1988. NIH Research Career Development Awardee 1984-1989. Eli Lilly Grantee 1986-1988.

(1) For a review, see: *Philos. Trans. R. Soc. London, B* **1980**, *289*, 165-378.

(2) Hall, H. K.; El-Shekeil, A. *Chem. Rev.* **1983**, *83*, 549.

(3) Brouillette, W. J.; Einspahr, H. M. *J. Org. Chem.* **1984**, *49*, 5113.

(4) Wiseman, J. R.; Pletcher, W. A. *J. Am. Chem. Soc.* **1970**, *92*, 956.

(5) Kobrich, G. *Angew. Chem., Int. Ed. Engl.* **1973**, *12*, 464.

(6) Maier, W. F.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1981**, *103*, 1891.

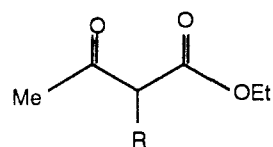
(7) Pracejus, V. H.; Kehlen, M.; Kehlen, H.; Matschiner, H. *Tetrahedron* **1965**, *21*, 2257.

kcal/mol. Indeed, amide **A** displayed unusual properties, such as an anomalously high infrared absorption at $\sim 1750\text{ cm}^{-1}$ for the carbonyl, high pK_a values, and susceptibility to hydrolysis and polymerization. Although several examples of these types of "acylamines" have been reported in the literature, there are no reports of a bicyclic β -lactam bridging the amide nitrogen to the opposite carbon in a 1,3-relationship (i.e., C). The bridgehead disposition of the β -lactam nitrogen atom in such a structure is expected to impart unusual and interesting properties to this system relative to the corresponding traditional monocyclic and bicyclic structures. For comparison purposes, the bicyclo[3.1.1]hept-1-(6)-ene (**D**) and bicyclo[4.1.1]oct-1(7)-ene (**E**) are predicted to be unstable bridgehead olefins with OS values of 39.1 and 37.8 kcal/mol, respectively. In this preliminary account is described a straightforward synthesis of a 1,3-bridged β -lactam⁹ (3,7-dioxo-2-(*tert*-butylcarboxy)-8-methyl-1-azabicyclo[4.1.1]octane).

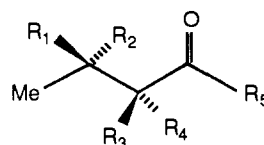
Ethyl acetoacetate is alkylated with 4-bromo-1-butene (NaOEt, EtOH, 50%) to afford the β -keto ester **2**. Sodium borohydride reduction¹⁰ provided an inseparable mixture of the alcohols **3** and **4** (syn/anti, 1:2) which were directly subjected to a Mitsunobu inversion¹¹ (HCO₂H, Ph₃P, DEAD, THF) to furnish the synformate **5** in 20% overall yield from **2**. Hydrolysis to the acid **6** (1 N NaOH, THF) followed by reaction with 1-ethyl-3-(3-(dimethylamino)propyl)carbodiimide hydrochloride (1.3 equiv) and NH₂OCH₃·HCl (1.1 equiv) at pH 4.2 for 1 h at 25 °C furnished the *N*-methoxy amide¹² **7** (94%, mp 64–66.5 °C). Cyclization to the β -lactam **8** according to Miller¹² was accomplished with Ph₃P/DEAD (THF, 25 °C, 75%). Reductive cleavage of the N–O bond¹³ was readily accomplished by dissolving metal reduction (Na⁰, 2.4 equiv, NH₃(l), THF, –40 °C, 10 min) to furnish the desired β -lactam **9** (80%).

Oxidative cleavage of the olefin **9** to the acid **10** could be accomplished in one step by treatment with NaIO₄ in the presence of a catalytic amount of RuCl₃¹⁴ (MeCN, CCl₄, H₂O) but was not practical for the preparation of multigram quantities of **10**. Therefore, a stepwise oxidation proved to be more convenient. Ozonolysis of **9** (MeOH, –78 °C, then Me₂S) followed by Jones oxidation¹⁵ (8 N, acetone, 0 °C) furnished the acid **10** (80%). This material was homologated to the β -keto ester **11** utilizing the procedure of Brooks, Lu, and Masamune.¹⁶ Reaction of **10** with carbonyldiimidazole (THF, 25 °C, 6 h) followed by condensation with Mg(CO₂CH₂CO₂Bu⁺)₂ (0.55 equiv, 12 h, 25 °C) cleanly furnished **11** (20–40%). Diazotization under the standard con-

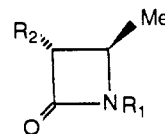
ditions¹⁷ (TsN₃, MeCN, 25 °C) gave the relatively labile diazo β -keto ester **12** (80%). Reaction of **12** with a catalytic amount of Rh₂(OAc)₄ for 1 h in refluxing benzene followed by filtration and evaporation of the solvent and chromatography on silica gel (PTLC, THF/hexane, 1:1) provided the bicyclic compound **13** as a solid in 50% yield.



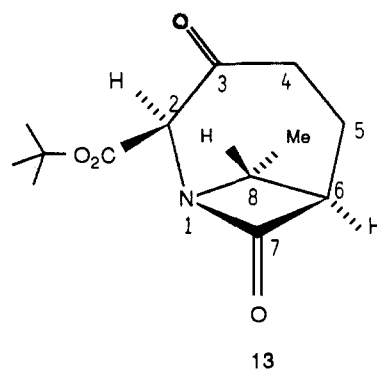
- 1, R=H
- 2, R=CH₂CH₂CH=CH₂



- 3, R₁=OH, R₂=H, R₃=CH₂CH₂CH=CH₂, R₄=H, R₅=OEt
- 4, R₁=OH, R₂=H, R₃=H, R₄=CH₂CH₂CH=CH₂, R₅=OEt
- 5, R₁=H, R₂=OCHO, R₃=H, R₄=CH₂CH₂CH=CH₂, R₅=OEt
- 6, R₂=OH, R₁=R₃=H, R₄=CH₂CH₂CH=CH₂, R₅=OH
- 7, R₂=OH, R₁=R₃=H, R₄=CH₂CH₂CH=CH₂, R₅=NHCOCH₃



- 8, R₁=OCH₃, R₂=CH₂CH₂CH=CH₂
- 9, R₁=H, R₂=CH₂CH₂CH=CH₂
- 10, R₁=H, R₂=CH₂CH₂CO₂H
- 11, R₁=H, R₂=CH₂CH₂COCH₂CO₂Bu⁺
- 12, R₁=H, R₂=CH₂CH₂COC(N₂)CO₂Bu⁺

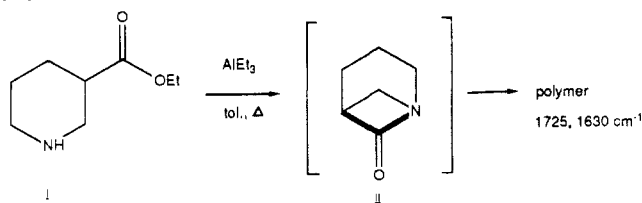


13

The structure of **13** was evident by examination of the spectroscopic properties.^{18,19} The infrared exhibited carbonyl ab-

(8) Maier and Schleyer have proposed the following empirical rule regarding the relationship between the calculated olefinic strain (OS) and predicted experimental observability: (a) isolable bridgehead olefins OS ≤ 17 kcal/mol; (b) observable bridgehead olefins $17\text{ kcal/mol} \leq \text{OS} \leq 21\text{ kcal/mol}$; (c) unstable bridgehead olefins OS $\geq 21\text{ kcal/mol}$.

(9) Attempts at synthesizing a bicyclo[3.1.1] β -lactam **ii** from **i** afforded an unstable product (IR (neat) 1935, 1850, 1795, 1725 cm^{-1}) that rapidly polymerized (IR (neat) 1725, 1630 cm^{-1}).



(10) Lee, B. H.; Biswas, A.; Miller, M. *J. Org. Chem.* **1986**, *51*, 106.

(11) (a) Mitsunobu, O. *Synthesis* **1981**, 1. (b) Georg, G. I.; Gill, H. S.; Gerhardt, C. *Tetrahedron Lett.* **1985**, *26*, 3903.

(12) (a) Miller, M. J.; Mattingly, P. G.; Morrison, M. A.; Kerwin, J. F., Jr. *J. Am. Chem. Soc.* **1980**, *102*, 7026. (b) Bajwa, J. S.; Peterson, K. P.; Mattingly, P. G.; Miller, M. J. *J. Org. Chem.* **1982**, *47*, 4928. (c) Miller, M. J.; Biswas, A.; Krook, M. A. *Tetrahedron* **1983**, *39*, 2571. (d) Miller, M. J.; Mattingly, P. G.; Copper, R. D. G.; Daugherty, B. W. *J. Org. Chem.* **1983**, *48*, 3556. (e) Morrison, M. A.; Miller, M. J. *J. Org. Chem.* **1983**, *48*, 4221.

(13) Floyd, D. M.; Fritz, A. W.; Pluscec, J.; Weaver, E. R.; Cimarrusti, C. *J. Org. Chem.* **1982**, *47*, 5160.

(14) Carlsen, P. H. J.; Katsuki, T.; Martin, V. S.; Sharpless, K. B. *J. Org. Chem.* **1981**, *46*, 3936.

(15) Kametani, T.; Huang, S. P.; Nagahara, T.; Yokohama, S.; Ihara, M. *J. Chem. Soc., Perkin Trans. 1* **1981**, 964.

(16) Brooks, D. W.; Lu, L. D.-D.; Masamune, S. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 72.

(17) (a) Salzmann, T. N.; Ratcliffe, R. W.; Cristensen, B. G.; Bouffard, F. A. *J. Am. Chem. Soc.* **1980**, *102*, 6161. (b) Karady, S.; Amato, J. S.; Reamer, R. A.; Weinstock, L. M. *J. Am. Chem. Soc.* **1981**, *103*, 6765.

(18) ¹H NMR (270 MHz, CDCl₃) δ (Me₄Si) 1.50 (9 H, s), 1.53 (3 H, d, $J = 6.0\text{ Hz}$), 2.3–2.5 (2 H, m), 2.51–2.80 (2 H, m), 2.93 (1 H, dq, $J \sim 1$, $J = 6.0\text{ Hz}$), 3.13 (1 H, dd, $J = 4.0$, $J = 1.3\text{ Hz}$), 4.68 (1 H, s).

(19) The corresponding *p*-nitrobenzyl ester series was also synthesized and cyclized to the 1,3-bridged β -lactams as a 1:1 mixture of diastereomers epimeric at the β -keto ester methine position. The *tert*-butyl ester reported herein gave a single diastereomer that has been tentatively assigned the indicated stereochemistry.

sorptions at 1795, 1750, and 1730 cm^{-1} (NaCl, neat) for the β -lactam, ester, and ketone moieties, respectively. The mass spectrum (CH_4 , CI) gave peaks at m/z 254 and 198 for ($M^+ + 1$) and ($M^+ - \text{C}_4\text{H}_9$), respectively. The ^1H NMR exhibited the characteristic one-proton singlet at δ 4.7 for the C-2 methine; a multiplet centered at δ 2.9 for the C-8 methine reflects a 0.6 ppm upfield shift of this resonance from the monocyclic precursors **9-12** and probably reflects both increased sp^3 character on nitrogen as well as shielding by the C-3 carbonyl.

The relatively surprising stability of **13** opens the possibility that numerous, stable "anti-Bredt" β -lactams can be synthesized and studied for novel chemical and possibly biological properties. Investigations along these lines are in progress in these laboratories and shall be reported on in due course.

Acknowledgment. We acknowledge the National Institutes of Health and the National Science Foundation for their generous support of our programs.

Supplementary Material Available: Physical data for all new compounds (2 pages). Ordering information is given on any current masthead page.

Oxazoline Route to Azomethine Ylides

Edwin Vedejs* and Janet Wisniewski Grissom

S.M. McElvain Laboratory of Organic Chemistry
Chemistry Department, University of Wisconsin
Madison, Wisconsin 53706
Received January 13, 1986

Recent progress^{1,2} in generation of nonstabilized azomethine ylides allows synthesis of relatively simple five-membered nitrogen rings by 2 + 3 dipolar cycloaddition. Acyl-stabilized analogues **3** can be similarly used to prepare more complex cycloadducts,^{3,4} but the most practical method to date for their generation via aziridine pyrolysis has limitations. Only the most reactive dipolarophiles can trap aziridine-derived dipoles stereospecifically,³ and the behavior of alkyl-substituted aziridines (**2**, $R^1 = \text{CH}_3$, etc.) is surprisingly complex in certain systems.^{5,6}

An alternative route to **3** from 4-oxazolines **4** has been contemplated⁷ ever since the reverse reaction was demonstrated in

(1) Vedejs, E.; Martinez, G. R. *J. Am. Chem. Soc.* **1979**, *101*, 6452. Vedejs, E.; Larsen, S.; West, F. G. *J. Org. Chem.* **1985**, *50*, 2170 and references therein.

(2) Padwa, A.; Chen, Y.-Y.; Dent, W.; Nimmegern, H. *J. Org. Chem.* **1985**, *50*, 4006. Imai, N.; Terao, Y.; Achiya, K.; Sekiya, M., *Tetrahedron Lett.* **1984**, *25*, 1579. Tsuge, O.; Kanemasa, S.; Hatada, A.; Matsuda *Chem. Lett.* **1984**, 801. Chastanet, J.; Roussi, G. *J. Org. Chem.* **1985**, *50*, 2910. Smith, R.; Livinghouse, T. *J. Org. Chem.* **1983**, *48*, 1554 and references therein.

(3) (a) *1,3-Dipolar Cycloaddition Chemistry*; Padwa, A., Ed.; Wiley-Interscience: New York, 1984. (b) Hermann, H.; Huisgen, R.; Mader, H. *J. Am. Chem. Soc.* **1971**, *93*, 1779. (c) Woller, P. B.; Cromwell, N. H. *J. Org. Chem.* **1970**, *35*, 888. (d) Deyrup, J. A. *J. Org. Chem.* **1969**, *34*, 2724. (e) Lown, J. W. *Can. J. Chem.* **1972**, *50*, 2236.

(4) Selected recent applications: (a) DeShong, P.; Kell, D. A.; Sidler, D. *R. J. Org. Chem.* **1985**, *50*, 2309. (b) Porter, A. E. A.; Husinec, S.; Roberts, J. S.; Strachan, C. H. *J. Chem. Soc., Perkin Trans 1*, **1984**, 2517. (c) Wenkert, D.; Ferguson, S. B.; Porter, B.; Qvanstrom, A.; McPhail, A. T. *J. Org. Chem.* **1985**, *50*, 4114.

(5) Gelas-Mialhe, Y.; Hierle, R.; Vessiere, R. *Bull. Chim. Soc. Fr.* **1974**, 709.

(6) (a) Schmidt, G.; Stracke, H.-V.; Winterfeldt, E. *Chem. Ber.* **1970**, *103*, 3196. (b) Dowd, P.; Kang, K. *J. Chem. Soc., Chem. Commun.* **1974**, 258. (c) Padwa, A.; Dean, D.; Oine, T. *J. Am. Chem. Soc.* **1975**, *97*, 2822. (d) Dopp, D.; Nour-El-Din, A. M. *Tetrahedron Lett.* **1978**, 1463.

(7) (a) Lown, J. W. *Rec. Chem. Prog.* **1971**, *32*, 51 and references therein. (b) Texier, F.; Carrie, R. C. *Acad. Sci.* **1970**, C271, 958. (c) Vaultier, M.; Mullick, G.; Carrie, R. *Can. J. Chem.* **1979**, *57*, 2876 and references therein. (d) Freeman, J. P. *Chem. Rev.* **1983**, *83*, 241. (e) See also ref 4c. (f) Texier, F.; Carrie, R. *Bull. Chim. Soc. Fr.* **1971**, 4119. (g) Sannier, Y. M.; Danion-Bougout, R.; Carrie, R. *Tetrahedron* **1976**, *32*, 1995. Kobayashi, Y.; Kumadaki, I.; Yoshida, T. *Heterocycles* **1977**, *8*, 387. (h) Niklas, K. Ph.D. Dissertation, University Munich, cited in ref 7d. (i) For a stable *N*-carboethoxy-4-oxazoline, see: Hiyama, T.; Taguchi, H.; Nozaki, H. *Bull. Chim. Soc. Jpn.* **1974**, *47*, 2909. (j) Spry, D. O. *J. Org. Chem.* **1975**, *40*, 2411. (k) Nour-El-Din, A. M.; El Said, M.; Medamer, R. *Heterocycles* **1985**, *23*, 1155.

Table I. 2 + 2 Cycloadducts from 4-Substituted 4-Oxazolines ($R = \text{CH}_3$)

entry	R'	R''	R'''	product	yield
a	CH ₃	Ph	Ph	6a	70%
b	CH ₃	CH ₃	CH ₃	6b	82%
c	Ph	CH ₃	Ph	6c	81%

Table II. 2 + 3 Cycloadducts from 4-Unsubstituted 4-Oxazolines ($R = \text{CH}_3$)

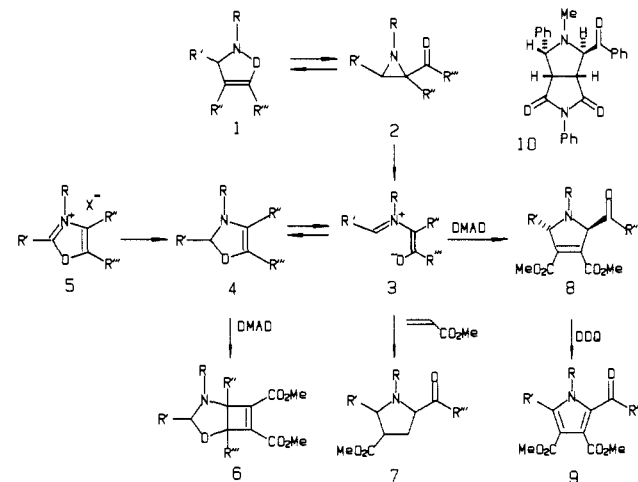
entry	R'	R''	R'''	yields	
				7	9^a
d	Ph	H	Ph	55% ^b	95%
e	Ph	H	CH ₃	87%	90%
f	Ph	H	OC ₂ H ₅	63% ^b	93%
g	Ph	H	H	57%	
h	CH ₃	H	OC ₂ H ₅	61%	64%
i	CH ₃	H	Ph	40% ^b	85%

^a After DDQ oxidation of the crude product. ^b The other regioisomer (single stereoisomer) is formed in (d) 9%, (f) 10%, (i) 20%.

a study of the valence bond tautomers **1-4**.⁸ However, we can find only one example where pyrolysis of **4** with a dipolarophile is claimed to result in adduct formation.^{7f} The other known 4-oxazolines **4**^{7,8} are remarkably resistant to this process. They are also relatively inaccessible, and so far, all have been made directly or indirectly by acylaziridine pyrolysis, as in **2** \rightarrow **3** \rightarrow **4**.

We have developed an independent route to 4-oxazolines **4** by reduction of oxazolium salts **5** with $\text{PhSiH}_3/\text{CsF}$.⁹ This reagent provides active hydride under aprotic, essentially neutral conditions, and overreduction of **4** is easily avoided. Most important, the silane/fluoride reagent selectively reduces oxazolium salts in the presence of dipolarophiles such as acrylate or acetylenedicarboxylate and permits in situ trapping of unstable oxazolines.

Isolation of the 4-oxazolines from oxazolium salt reductions has not been achieved due to their hydrolytic sensitivity but the 4,5-diphenyl derivative **4a** is stable in solution at room temperature (NMR, CD_3CN , CH_3CH , 5.02 ppm, quartet, $J = 5.5$ Hz). Addition of dimethyl acetylenedicarboxylate (DMAD) results in conversion into a 1:1 cycloadduct to which we assign the bicyclic structure **6** based on NMR evidence.¹⁰ Similar adducts are obtained from other 4,5-disubstituted 4-oxazolines made in situ (Table I).



In contrast, several oxazolium salts having no substituent at C₄ are reduced by the in situ method ($\text{PhSiH}_3/\text{CsF}$ /dipolarophile)

(8) Baldwin, J. E.; Pudussery, R. G.; Qureshi, A. K.; Sklarz, B. *J. Am. Chem. Soc.* **1968**, *90*, 5325.

(9) Corriu, R. J. P.; Perez, R.; Reye, C. *Tetrahedron* **1983**, *39*, 999.

(10) For example, **6b**: ^1H NMR (CDCl_3 , ppm) 3.94 (1 H, q, $J = 5.2$ Hz), 3.78 (6 H, s), 1.43 (3 H, s), 1.33 (3 H, s), 1.31 (3 H, d, $J = 5.2$ Hz); ^{13}C NMR (CDCl_3 , ppm) 167.2 (s), 162.6 (s), 142.9 (s), 140.8 (s), 89.0 (d), 85.7 (s), 74.5 (s), 52.0 (q), 51.9 (q), 31.6 (q), 17.9 (q), 16.1 (q), 15.9 (q).