

- (4) The photolysis of $B_4H_8Fe(CO)_3$ and $C_4H_4Fe(CO)_3$ in the presence of acetylenes yields carboranes and benzenes, respectively: T. P. Fehlner, *J. Am. Chem. Soc.*, **99**, 8355 (1977), and J. S. Ward and R. Pettit, *ibid.*, **93**, 262 (1971).
- (5) The synthesis of a metallocarborane from something other than a carborane is rare. There are five reported instances: the formation of $(B_{10}H_{10}COH)M(CO)_4^-$ from $B_{10}H_{13}^-$ and $M(CO)_6$ ($M = Cr, Mo, W$), P. A. Wegner, L. J. Guggenberger, and E. L. Muettterties, *J. Am. Chem. Soc.*, **92**, 3473 (1970); the formation of $CpCoC_2B_3H_7$ from C_2H_2 and 2- $CpCoB_4H_8$, R. N. Grimes, *Pure Appl. Chem.*, **39**, 455 (1974), and R. Weiss, J. R. Bowser, and R. N. Grimes, *Inorg. Chem.*, in press; the formation of $\mu-C_3H_4(C_6H_5)_2Co_2C_2B_3H_3$ from $B_3H_8^-$, $CoCl_2$, and $C_6H_5^-$, V. R. Miller, R. Weiss, and R. N. Grimes, *J. Am. Chem. Soc.*, **99**, 5646 (1977); the formation of the metal bound hydridoborate ion from Cp_2Co and RBX_2 , G. E. Herberich, G. Greiss, and H. F. Hell, *Angew. Chem., Int. Ed. Engl.*, **9**, 805 (1970); and the formation of metallocarboranes from metal atom reactions, G. J. Zimmerman, R. Wilczynski, L. W. Hall, and L. G. Sneddon, Abstracts of the 174th National Meeting of the American Chemical Society, Chicago, Ill., Aug 1977, INORG 165.
- (6) Pentane has also been used as a solvent; however, the yields are smaller.
- (7) Longer irradiations did not result in an increased yield of this product. Sufficient quantity for characterization was obtained by repetitive photolysis and fractionation.
- (8) The carbonyl bands for $C_4H_4Fe(CO)_3$ were observed at 2065 (s) and 1995 (vs) cm^{-1} .
- (9) The 1H spectrum of $C_4H_4Fe(CO)_3$ was a single sharp line (2-Hz fwhm) at δ 3.23 under these conditions.
- (10) Temperature of 30 °C.
- (11) T. P. Fehlner, J. Ragaini, M. Mangion, and S. G. Shore, *J. Am. Chem. Soc.*, **98**, 7085 (1976).
- (12) R. N. Grimes, *J. Am. Chem. Soc.*, **93**, 261 (1971); D. A. Franz, V. R. Miller, and R. N. Grimes, *ibid.*, **94**, 412 (1972); and J. P. Brennan, R. N. Grimes, R. Schaeffer, and L. G. Sneddon, *Inorg. Chem.*, **12**, 2266 (1973).
- (13) G. E. Herberich, J. Hengesbach, V. Kölle, and W. Oschmann, *Angew. Chem., Int. Ed. Engl.*, **16**, 42 (1977).
- (14) In the ^{11}B spectrum of a closely related compound, 2,3,4,5- $C_4B_2H_6$, the apical boron appears at -60.8 ppm ($J = 202$ Hz), while the basal boron appears at 10.4 ppm ($J = 144$ Hz).
- (15) This is a somewhat unusual structure in that it has a carbon atom in an apical position, i.e. a position of high coordination number. There is precedence for this in carborane chemistry in that $B_3C_2H_7$ has both apical and basal CH units as demonstrated by the 1H NMR (δ 0.79 and 1.8). It is interesting to note that 1,2- $B_3C_2H_7$ is also unstable in solution. D. A. Franz and R. N. Grimes, *J. Am. Chem. Soc.*, **92**, 1438 (1970).
- (16) Note, however, in the case of the thermal reaction of C_2H_2 with 2- $CpCoB_4H_8$ the metal is retained in the product metallocarborane. See ref 5.

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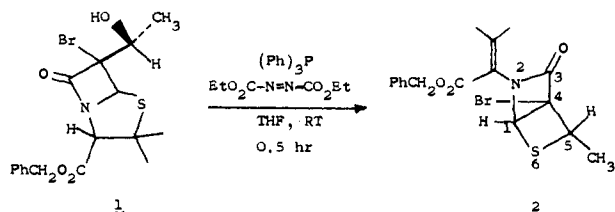
Received January 6, 1978

3-Oxo-6-thia-2-azabicyclo[2.2.0]hexanes: Novel β -Lactams Derived from Penams

Sir:

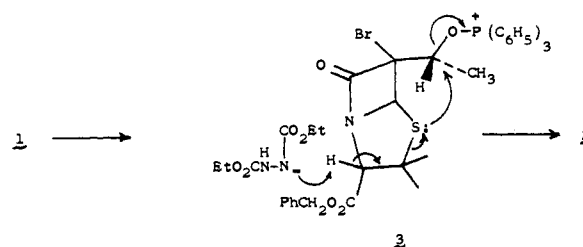
The combination of triphenylphosphine and azodicarboxylate esters has been utilized as an efficient method of in situ hydroxyl activation for nucleophilic displacement reactions.¹ It is of interest to note that, in systems possessing an appropriately situated internal nucleophile, the "DEADCAT" reaction^{1f} facilitates an intramolecular cyclization process.^{1b,c,e} We report herein another example of such a reaction in which a penicillin derivative has been transformed into the first reported example of a 4,4-ring system of the type C_3N-C_3S .^{2,3}

When benzyl 6 α -bromo-6 β -(1-hydroxyethyl)penicillanate (**1**)⁴ was subjected to the DEADCAT reaction (2.5 equiv of $(Ph)_3P$, 2.2 equiv of $EtO_2CN=NCO_2Et$, THF, 25 °C), the novel bicyclic β -lactam **2** was obtained in yields of 20–30%.⁵



The structure of **2** was deduced from an examination of its spectral properties. The IR spectrum ($CHCl_3$) exhibited carbonyl frequencies at 1770 and 1724 cm^{-1} , which were attributed to the β -lactam and ester moieties, respectively. The mass spectrum (MS) showed parent ions at m/e 397 and 395 (FD-MS: calcd for $C_{17}H_{18}NO_3SBr$, 395.0188; found, 395.0187)⁶ and fragmentation peaks at m/e 337 and 335, corresponding to the loss of thioacetaldehyde generated by a cycloversion process typical of thietanes.⁷ The loss of bromine from the latter fragment and the parent ion was also evident by peaks at m/e 256 and 316, respectively. Aside from the base peak, m/e 91 [CH_2Ph]⁺, the next most intense peaks were found at m/e 166 and 164, which correspond to a molecular ion for α -bromothiocrotonaldehyde or its cyclic equivalent, 3-bromo-2-methyl-2H-thiete, another expected reverse cycloaddition fragment. The complementary fragment at m/e 231 was also present. The 300-MHz NMR spectrum ($CDCl_3$) exhibited resonances at δ 1.64 (d, $J = 7$ Hz, CH_3), 2.14 (s, CH_3), 2.3 (s, CH_3), 3.94 (qd, $J = 0.8$ and 7.0 Hz, H-5), 5.17 and 5.23 (dd, $J = 12$ Hz, CO_2CH_2Ph), 5.28 (d, $J = 0.8$ Hz, H-1), and 7.39 (s, ArH).

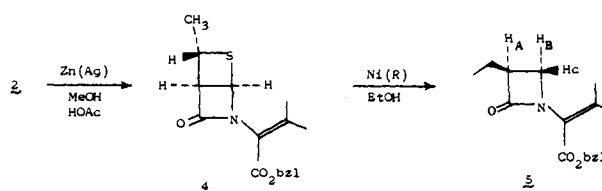
The configuration at C-5 was assigned on the basis of mechanistic considerations and nuclear Overhauser effects. In conformity with the observed stereospecificity¹ of nucleophilic displacement reactions of alcohols mediated by triphenylphosphine and diethyl azodicarboxylate, back-side attack by the sulfur atom in phosphonium ion intermediate **3**



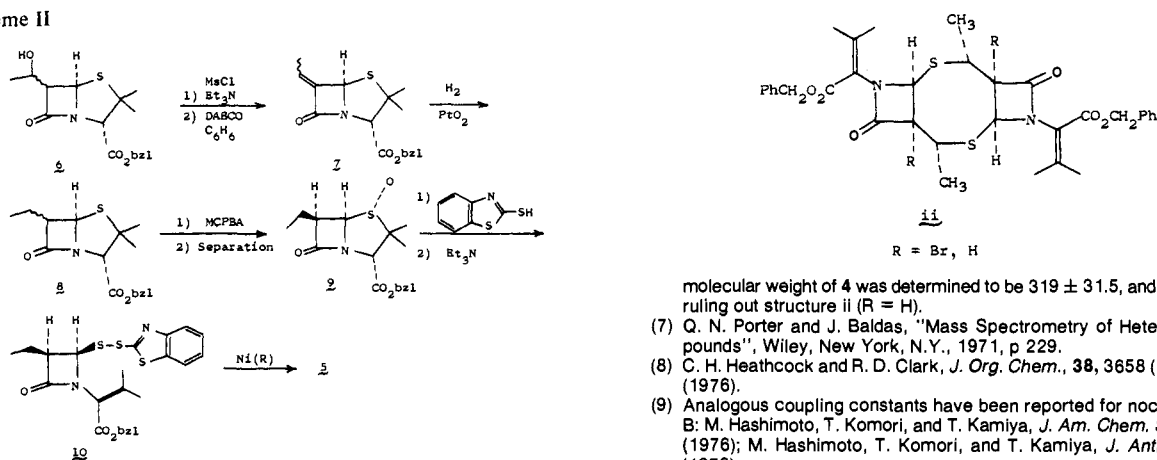
followed by proton abstraction would generate **2** having the *S* configuration at C-5. In support of this postulation was an observed positive effect on H-1 (13.3%) upon irradiation of the C-5 methyl doublet.

To further substantiate the assigned structure, compound **2** was degraded as outlined in Scheme I. Reductive debromination with zinc-silver couple⁸ (MeOH, 3 equiv HOAc, room temperature) provided **4** (60%): IR ($CHCl_3$) 1754 and 1718 cm^{-1} ; NMR ($CDCl_3$) δ 1.64 (d, $J = 6.5$ Hz, CH_3), 2.17 (s, CH_3), 2.28 (s, CH_3), 3.84 (m, $SCHCH_3$), 3.96 (app t, $J = 3$ and 4 Hz, H-4), 5.12 (dd, $J = 1.5$ and 4 Hz, H-1), 5.16 and 5.24 (dd, $J = 12$ Hz, CO_2CH_2Ph), and 7.38 (s, ArH); m/e 317 (M^+).⁶ Compound **4** was desulfurized with Raney nickel (absolute EtOH, 60 °C) to yield 1-(1-benzoyloxycarbonyl-2-methylprop-1-enyl)-3 β -ethylazetid-2-one (**5**): IR ($CHCl_3$) 1733 and 1709 cm^{-1} ; NMR ($CDCl_3$) δ 0.95 (t, $J = 6$ Hz, CH_3), 1.68 (m, $-CH_2CH_3$), 1.94 (s, CH_3), 2.22 (s, CH_3), 3.15 (m, H_A and H_C), 3.52 (app t, $J = 5$ Hz, H_B), 5.18 (s, CO_2CH_2Ph), and 7.26 (s, ArH); m/e 287 (M^+). Owing to the coincident chemical shifts of H_A and H_C of azetidione **5**, a complete assignment of coupling constants for the ring protons was not discernible from the 300-MHz 1H NMR spectra recorded in either $CDCl_3$, C_6D_6 , or 1:1 $C_6D_6-CDCl_3$. However,

Scheme I



Scheme II



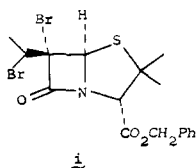
these values were obtained when the spectrum was recorded in $\text{Me}_2\text{CO}-d_6$: δ 3.15 (m, H_A), 3.21 (dd, $J_{AC} = 2.5$ Hz and $J_{BC} = 5$ Hz, H_C),⁹ and 3.55 (t, $J_{AB} = J_{BC} = 5$ Hz, H_B).

Degradation product **5** was independently synthesized in an unequivocal manner as depicted in Scheme II. A mixture of *cis*- and *trans*-(*R*)-hydroxyethylpenicillanates **6**⁴ was quantitatively converted to the corresponding mesylates¹⁰ using the procedure of Crossland and Servis,¹¹ and subsequently eliminated (1,4-diazabicyclo[2.2.2]octane, C_6H_6 , 80 °C, 77%) to a mixture of enelactams.¹⁰ Catalytic hydrogenation (PtO_2 , EtOAc) of **7** provided a mixture of 6-ethylpenicillanates **8** (90%)^{10,12} in which the expected *cis* isomer comprised 90% of the mixture. Sulfoxidation (MCPBA, CH_2Cl_2 , 25 °C) of **8** afforded a mixture of penams (92%) from which the major, crystalline (mp 77–79 °C) α -sulfoxide **9** (80%)^{10,13} was readily separated. Cleavage of the thiazolidine ring of **9** according to the method of Kamiya and co-workers¹⁵ followed by isomerization of the β,γ double bond into conjugation (Et_3N , CH_2Cl_2 , 25 °C) yielded the disulfide azetidinone **10** (85%).¹⁰ Finally, desulfurization of **10** ($\text{Ni}(\text{R})$, EtOH , 60 °C) produced azetidinone **5**, which possessed physical and spectral properties identical with those of the material obtained from the degradation of **2**.

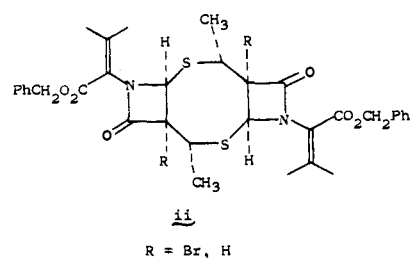
Acknowledgment. We thank Mr. J. Smith for mass spectral measurements, Mr. H. Flynn for recording the 300-MHz NMR spectra and performing the NOE experiments, and Dr. J. A. McCauley for the vapor phase osmometric molecular weight determinations.

References and Notes

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- It should be noted that, during the preparation of this manuscript, a report of another 3-oxo-2-azabicyclo[2.2.0]hexane appeared: P. K. Sen, C. J. Veal, and D. W. Young, *J. Chem. Soc., Chem. Commun.*, 678 (1977). The compound reported therein is more appropriately a tricyclic 4,4,5 ring system.
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- The other identifiable products were a mixture of enelactams **7** and the dibromopenicillanate **i**.



- The exact mass of **2** was supported by a vapor phase osmotic molecular weight determination of 414 ± 20.7 . This determination eliminated the possibility of a dimeric structure **ii** ($\text{R} = \text{Br}$) for this material. Similarly, the



molecular weight of **4** was determined to be 319 ± 31.5 , and thereby further ruling out structure **ii** ($\text{R} = \text{H}$).

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- All new materials gave satisfactory spectroscopic analyses.
- Q. N. Porter and K. L. Servis, *J. Org. Chem.*, **35**, 3195 (1970).
- For similar reductions see J. C. Sheehan and Y. S. Lo, *J. Org. Chem.*, **38**, 3227 (1973), and R. W. Ratcliffe et al., *J. Am. Chem. Soc.*, in press.
- The sulfoxide configuration was determined by ¹³C NMR utilizing the method of Harrison and Hodge.¹⁴ Pertinent to this assignment, the $2\beta\text{-CH}_3$ resonated at δ 24.4 ppm and the $2\alpha\text{-CH}_3$ at δ 15.6 ppm downfield from Me_4Si in CDCl_3 .
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- T. Kamiya, T. Teraji, Y. Saito, M. Hashimoto, O. Nakaguchi, and T. Oku, *Tetrahedron Lett.*, 3001 (1973).

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Reactions of Platinum Metal Complexes with Strained-Ring Compounds: $\text{IrCl}(\eta^3\text{-C}_3\text{H}_4\text{C}_6\text{H}_5)[\text{P}(\text{C}_6\text{H}_5)_3]_2$, an Isolable η^3 -Allyl Metal Hydride Complex

Sir:

Transition-metal catalyzed rearrangements of strained-ring systems have received much attention in recent years.¹ One of the most widely studied reactions has been the ring opening of a cyclopropyl fragment to yield an isomeric olefin.²⁻⁴ An η^3 -allyl metal hydride intermediate (**B** in Scheme I) is often invoked in the mechanism, as it accounts for the variety and distribution of the olefinic products found, but it has never been directly observed in these reactions. In other important metal-catalyzed olefinic transformations (e.g., olefin metathesis,⁵ isomerization,⁶ and oligomerization⁷) the existence of an allyl metal hydride intermediate is strongly, but indirectly, suggested. We know of only three brief reports concerning the characterization of allyl metal hydride complexes.⁸⁻¹⁰ The compounds $\text{NiH}(\eta^3\text{-C}_3\text{H}_5)(\text{PPh}_3)$ and $\text{NiH}(\eta^3\text{-C}_3\text{H}_5)(\text{PF}_3)$,⁸ prepared at low temperatures, were found to decompose irreversibly above -30 °C. Between -40 and -50 °C, the PF_3 complex was shown to be in dynamic equilibrium with the corresponding nickel(0)- η^2 -propene complex. Byrne et al.⁹ have reported the ¹H NMR characterization of $\text{MoH}(\eta^3\text{-C}_3\text{H}_5)(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)_2$ and have shown that this complex exhibits similar dynamic behavior. In an attempt to prepare an iridium metalocyclobutane, i.e., **A** in Scheme I, we have isolated an η^3 -allyl metal hydride complex of formula $\text{IrClH}(\eta^3\text{-C}_3\text{H}_4\text{Ph})(\text{PPh}_3)_2$. This complex is very stable and does not exhibit dynamic behavior at ambient temperatures. We believe that this represents the first example of a stable, fully characterized, η^3 -allyl metal hydride complex.