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- (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 B₂C₂H₇ 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,-B₃C₂H₇ is also unstable in solution. D. A. Franz and R. N. Grimes, J. Am. Chem. Soc., 92, 1438 (1970).
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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 C₃N- $C_3S.^{2,3}$

When benzyl 6α -bromo- 6β -(1-hydroxyethyl)penicillanate $(1)^4$ was subjected to the DEADCAT reaction (2.5 equiv of (Ph)₃P, 2.2 equiv of EtO₂CN=NCO₂Et, 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 (CHCl₃) 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 cycloreversion 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 [CH₂Ph]⁺, 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/e231 was also present. The 300-MHz NMR spectrum (CDCl₃) exhibited resonances at δ 1.64 (d, J = 7 Hz, CH₃), 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 (CHCl₃) 1754 and 1718 cm^{-1} ; NMR (CDCl₃) δ 1.64 (d, J = 6.5 Hz, CH₃), 2.17 (s, CH_3), 2.28 (s, CH_3), 3.84 (m, $SCHCH_3$), 3.96 (app t, J = 3and 4 Hz, H-4), 5.12 (dd, J = 1.5 and 4 Hz, H-1), 5.16 and 5.24 (dd, J = 12 Hz, CO₂CH₂Ph), 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-benzyloxycarbonyl-2methylprop-1-enyl)- 3β -ethylazetidin-2-one (5): IR (CHCl₃) 1733 and 1709 cm⁻¹; NMR (CDCl₃) δ 0.95 (t, J = 6 Hz, CH₃), 1.68 (m, -CH₂CH₃), 1.94 (s, CH₃), 2.22 (s, CH₃), 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 azetidinone 5, a complete assignment of coupling constants for the ring protons was not discernible from the 300-MHz ¹H NMR spectra recorded in either CDCl₃, C₆D₆, or 1:1 C₆D₆-CDCl₃. However,







these values were obtained when the spectrum was recorded in Me₂CO- d_6 : δ 3.15 (m, H_A), 3.21 (dd, J_{AC} = 2.5 Hz and J_{BC} = 5 Hz, Hc),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, C₆H₆, 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, CH₂Cl₂, 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 (Et₃N, CH_2Cl_2 , 25 °C) yielded the disulfide azetidinone 10 (85%).¹⁰ Finally, desulfurization of 10 (Ni(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.

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= Br, H R

molecular weight of 4 was determined to be 319 ± 31.5 , and thereby further

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Reactions of Platinum Metal Complexes with Strained-Ring Compounds: $IrClH(\eta^{3}-C_{3}H_{4}C_{6}H_{5})[P(C_{6}H_{5})_{3}]_{2}$, 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 NiH(η^3 -C₃H₅)(PPh₃) and NiH(η^3 -C₃H₅)(PF₃),⁸ prepared at low temperatures, were found to decompose irreversibly above -30 °C. Between -40and -50 °C, the PF₃ 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 $MoH(\eta^3-C_3H_5)(Ph_2PCH_2CH_2PPh_2)_2$ and have shown that this complex exhibits similar dynamic behavior. In an attempt to prepare an iridium metallocyclobutane, i.e., A in Scheme I, we have isolated an η^3 -allyl metal hydride complex of formula $IrClH(\eta^3-C_3H_4Ph)(PPh_3)_2$. 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.

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