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Synthesis of New β-Lactam Antibiotics[1]

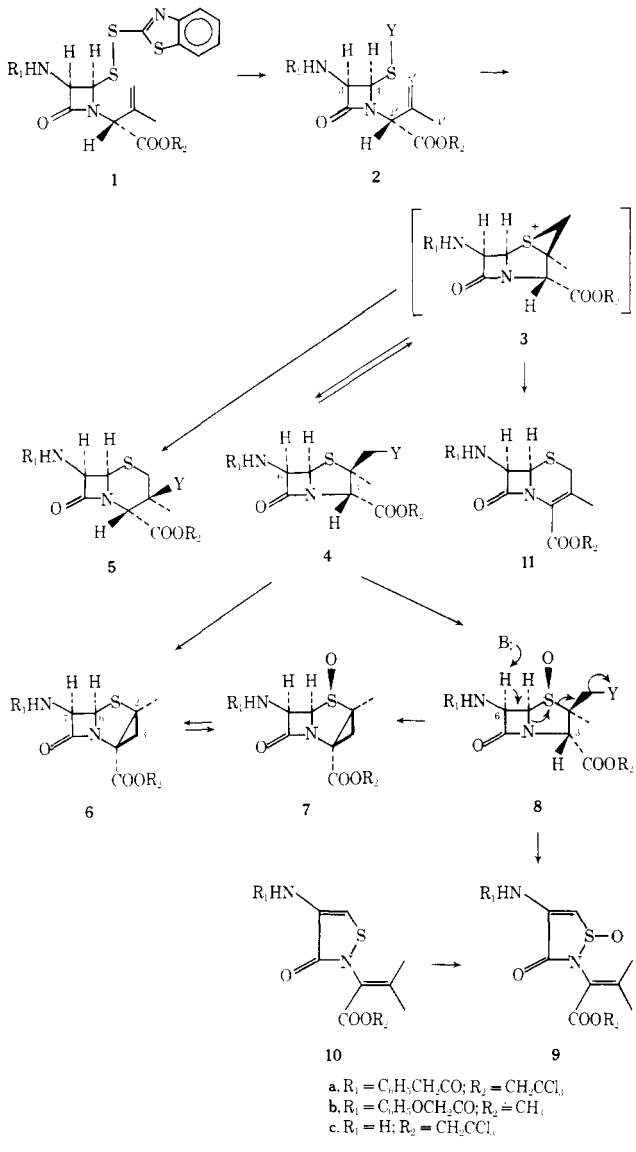
Sir:

In a previous paper[2] we reported the preparations of azetidinone disulfides, **1**, and 2β-halomethylpenicillins, **4** (Y = halogen), which are important precursors for the syntheses of 2β-substituted methylpenicillins **4**, 3β-substituted cephams **5**,[3] and desacetoxycephalosporin **11**.[2] The present communication deals with the isolation of sulfenylanilide **2b** (Y = NHC_6H_5), an intermediate involved in the conversion of **1** into **4** and **5**, and the synthesis of a new tricyclic β-lactam antibiotic **6a** via intramolecular cyclization of **4a** (Y = Br).

We have recently established a method[4] which allows the stereospecific conversion of **1** into **5** as well as **4** (Y = halogen)[2] by treatment with various nucleophiles under the presence of Ag^+. The formation of **4** and **5** presumably proceeds through the sulfenyl derivative **2** which is then transformed into episulfonium ion **3**; we have now secured corroborative evidence for this mechanism by isolation of the sulfenylanilide **2b** (Y = NHC_6H_5). Thus treatment of **1b** with aniline at room temperature in CH_2Cl_2 under the presence of $AgBF_4$ yielded 3β-anilinocepham **5b**[4] (Y = NHC_6H_5), mp 129–130°, $[\alpha]_D$ +58.5° (EtOH), 45% yield. On the other hand, treatment of **1b** with aniline in ethyl acetate under the presence of AgOAc affords **2b** (Y = NHC_6H_5): colorless oil; 90% yield; *m/e* 455; ir 1770 cm^{-1} (β-lactam); NMR ($CDCl_3$), 1.97 (s, 4′-H), 4.78 (s, 2′-H), 5.05 and 5.22 (two br s, 5′-H), 5.08 (d, J = 5 Hz, 4-H), 5.53 (dd, J = 5 and 8 Hz, 3-H). Reaction of **2b** (Y = NHC_6H_5) with BF_3OEt_2 gave **5b** (Y = NHC_6H_5) in 40% yield, thus supporting the intermediacy of **2b** (Y = NHC_6H_5) (Scheme I).

Furthermore, sulfenyl derivative **2b** (Y = NHC_6H_5) may act as an intermediate for introducing other nucleophilic groups. Thus treatment of **2b** (Y = NHC_6H_5) with BF_3OEt_2 in MeOH gave in 80% yield a 1:3 mixture of **4b** (Y = OCH_3) and **5b** (OCH_3).[4] Similarly reaction of **2b** (Y = NHC_6H_5) with HCl yielded **4b** (Y = Cl)[2] in quantitative yield.

Scheme I



We have been able to achieve the conversion of **4a** (Y = Br) into the intramolecularly cyclized product **6a.** Thus base treatment of **4a** (Y = Br) with bases led to the ring-expanded cephem **11a**[2] in high yield, but formation of a minute amount of a by-product was also observed; silica gel chromatography of this gave colorless crystals, mp 140–143°, $[\alpha]_D$ +203.2° ($CHCl_3$). The structure **6a** was assigned on the basis of spectral data: ir, 1795 cm^{-1} (β-lactam); NMR ($CDCl_3$), 1.70 (s, 2-CH_3), 2.06 and 2.27 (ABq, J = 7 Hz, 3-H), 5.47 (dd, J = 4 and 9 Hz, 7-H), 6.19 (d, J = 4 Hz, 6-H). It is reasonable to postulate that in the present case product **6a** is formed directly by an intramolecular nucleophilic displacement in **4a** (Y = Br) and not through an episulfonium ion **3a,** although formation of the latter has been demonstrated in both ring expansion[2,4,5] and nucleophilic substitution[4] reactions of **4.**

Formation of cephem **11a** was avoided by starting from the corresponding sulfoxide **8a** (Y = Br) which would not yield the episulfonium ion **3.** Thus when **8a** (Y = Br) obtained by oxidation of **4a** (Y = Br) with *m*-chloroperbenzoic acid, was treated with Et_3N in acetone at room temperature for 72 hr, a 1:1 mixture of **7a** and **9a** was obtained in ca. 52% yield. The compounds were separated by silica gel

chromatography. The structure of **7a**, mp 148–148.5°, $[\alpha]D$ +22.8° ($CHCl_3$), was established by comparison with a sample synthesized by oxidation of **6a** with *m*-chloroperbenzoic acid. The second product, mp 147–148°, was assigned structure **9a** from spectral data; this was substantiated by an independent synthesis from **10a**[7] by *m*-chloroperbenzoic acid oxidation. It is obvious that compound **7a** is formed by a nucleophilic attack of the C-3 carbanion on the 2β-bromomethyl group, while formation of compound **9a** can be accounted for by the arrows shown in structure **8**, i.e., a rearrangement initiated by formation of the C-6 carbanion.

Cyclization leading to **7a** was best achieved under the following optimum conditions. Namely, treatment of **8a** (Y = Br) with 1,5-diazabicyclo[5.4.0]undec-5-ene (DBU) in DMF at −30° for 1 hr gave **7a** in 80% yield. Similarly, sulfoxide **8c** (Y = Br) derived from **8a** (Y = Br) by a deacylation method[8] gave **7c**, tosylate mp 176–179° dec, in 81% yield. These results indicate that the intramolecular cyclization proceeds faster than the intramolecular rearrangement and also suggest that cyclization of **4a** (Y = Br) would take place preferentially without production of the episulfonium ion **3** if a strong base was employed.

This was corroborated as follows. Treatment of **4a** with DBU under the conditions as described above yielded **6a** in ca. 80% yield; however, this reaction was always accompanied by production of the undesired cephem **11a**, 8%. Tricyclic sulfide **6a** was also derived from **7a** by reduction with PCl_3 in DMF in 76% yield. The synthesis of **6a** from **4a** represents the first intramolecular nucleophilic displacement in the penam system.[9,10]

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(10) Conversion of compound **6** to 2-methylcephem will be reported shortly.

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Evidence for S(^{1}D) Atom Reactions Involving $^{34}S(n,\gamma)^{35}S$ Nuclear Recoil Generated Sulfur

Sir:

Reactions of recoil sulfur atoms produced by both the $^{35}Cl(n,p)^{35}S$ and $^{34}S(n,\gamma)^{35}S$ nuclear processes in the gas phase are known to be quite complex[1] due primarily to the polyvalent nature of the atom. In addition the propensity for sulfur species to undergo oxidation reduction processes further complicates the identification and characterization of primary reaction channels. Earlier accounts of nuclear recoil sulfur reactions have, in general, ignored the role of electronic excitation, or, as reported in one case, the contribution of S(^{1}D) has been discounted as being unimportant.[2]

Table I. Data for $^{35}S + CS_2$ Exchange Reaction as a Function of Gaseous Additives

Additives M	Additives N	Sample composition (Torr) P_{CS_2}	P_M	P_N	Yield $CS^{35}S$ normalized activity[a]
		200			490 ± 10
H_2		200	100		350 ± 10
H_2		200	200		256 ± 10
H_2		200	400		153 ± 5
H_2	Ar	200	100	1077	235 ± 10
C_2H_6		200	400		49 ± 3
C_2H_4		200	400		41 ± 2

[a] The yield of $CS^{35}S$ is the normalized activity per Torr of S available. Results reported are the average of two or more determinations and the errors are based upon the statistical errors in the aliquots counted.

The differences in reactivity for the low lying electronic states of sulfur atoms have been extensively characterized in systems where the atoms are photochemically generated.[3] In particular, changes in both reaction mechanisms and reaction rates are known to be associated with S(^{1}D) and S(^{3}P) reactions. Direct use of the techniques employed in photochemical systems, however, has not led to an unambiguous interpretation of nuclear recoil systems.[2] We have obtained evidence for the gas phase reactions of singlet sulfur atoms, S(^{1}D), generated by the $^{34}S(n,\gamma)^{35}S$ nuclear recoil reaction in the presence of CS_2.

The recoil sulfur species were generated by thermal neutron irradiation for 10 min to 1 hr at a flux of 10^{12} (n/cm^2)/sec on a rotating multiple sample holder at the Washington State Nuclear Radiation Center. All samples were prepared by standard high vacuum techniques and flame sealed in 15-cm^3 cylindrical quartz irradiation vessels. Carbon disulfide (Matheson Coleman and Bell) was thoroughly degassed and vacuum distilled before use. No impurities were detected by gas chromatography. Research grade C_2H_4 and C_2H_6 (Phillips) and H_2 and Ar (Matheson) additives were used directly from gas cylinders. Product analysis was carried out by radio gas chromatography incorporating an internal flow proportional detector.

The reactions between both triplet and singlet sulfur atoms and CS_2 are known to occur in the gas phase and have been discussed previously.[4] In this study the effect of various gas additives on the total production of $CS^{35}S$ from nonlabeled CS_2 has been determined in order to investigate the role of various forms of recoil atom excitation in driving the exchange reaction. In Table I, the $CS^{35}S$ produced as a function of H_2 dilution and at fixed dilution with C_2H_4, C_2H_6, and Ar is tabulated. The activity of the labeled CS_2 is reported as specific activity per Torr of CS_2 originally present in the sample mixture.[5]

The results indicate that the efficiency of the sulfur atom exchange reaction with CS_2 rises linearly within experimental error as the mole fraction of CS_2 increases. This behavior suggests that the hydrogen additive is competing effectively for the reactive sulfur atoms or sulfur containing intermediates.[6] Such competition might arise from a moderating effect on a hot reaction, an exchange reaction between an excited intermediate and CS_2, or a quenching effect which eliminates electronically excited states of atomic sulfur. The reaction of ground electronic state sulfur atoms with H_2, if it occurs at all, cannot compete with the reaction