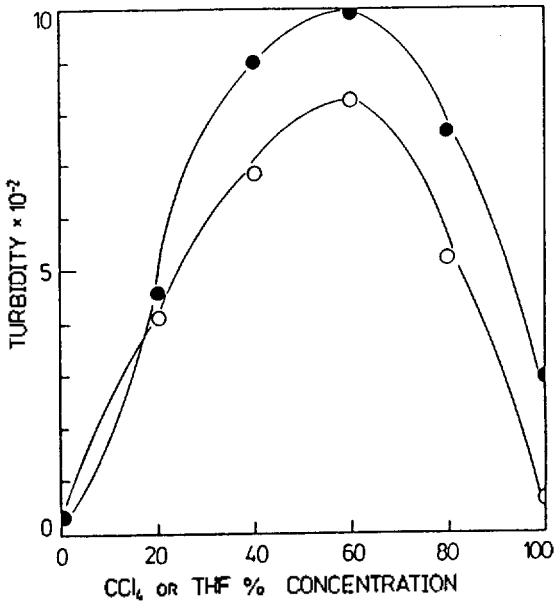

Figure 2. Turbidity change by photopolymerization of acryl amide (10^{-1} M) with harmaline (5×10^{-4} M) as a function of CCl_4 (-○-) or THF (-●-) % concentration in methanol.

The photopolymerization in THF solution may be explained as follows: The aminyl radicals are stable and can abstract hydrogen from solvents such as cyclohexane, THF and alkylbenzene.[14] The photoexcited β-carbolines fragment into 9-β-carbolinyl radical and hydrogen,[4] and the carbolinyl radical abstract hydrogen from THF. Then, the THF radical possibly initiates the polymerization.[15] The details of this reaction will be investigated in this laboratory.

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Conversion of Penicillin to Cephalosporin. Intramolecular Cyclization of a Penicillin-derived 4-mercaptoazetidin-2-one

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Since penicillin sulfoxides underwent an acidic rearrangement to cephalosporins,[1] many researchers have attempted to prepare cephalosporins from readily available penicillins. Azetidinones[2] and thiazolinoazetinones[3] are now well known as the intermediates in the preparation of cephalosporins.

Mercaptoazetinones have been proposed as intermediates on penicillin biosynthesis.[4] Free sulfhydryl compounds have not been directly used in the synthesis of β-lactam antibiotics. Disulfides, instead have often been employed as intermediates, which can be prepared from either penicillin sulfoxides[5] or thiazolinoazetidinones.[6]

Mercapto compounds can be prepared by simple hydrolysis of the corresponding thiazolinoazetidinones.[7,8] Using the sulfur compounds, intramolecular Michael reaction and other cyclizations were carried out in vain.[8]

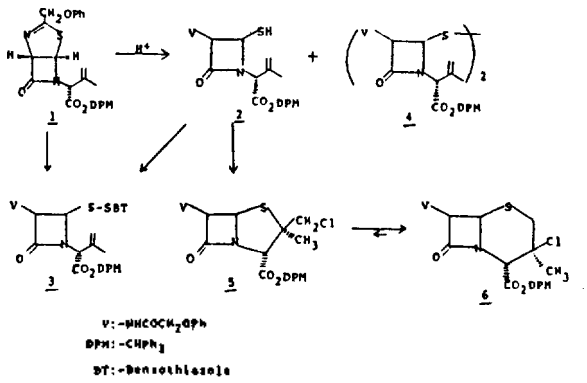
We now wish to report utilization of mercapto compounds for the synthesis of β-lactam antibiotics. Thiazolinoazetidinone **1** was treated with 30% aq $HClO_4$ in the mixture of CH_2Cl_2 and acetone[8] to give mercaptan **2**.[9] By treatment with 2-mercaptobenzothiazole or 2-benzothiazolyl disulfide, the mercaptan could be converted to disulfide **3** which is one of the intermediates in the synthesis of β-lactam antibiotics.[5,6] The mercaptan was treated with 2-mercaptobenzothiazole in the presence of $NaIO_4$ to afford the disulfide in moderate yield. However, the disulfide can be given in higher yield by the known procedure.[5,6]

The mercaptan could not be converted to a β-lactam compound by treatment with m-chloroperoxybenzoic acid or chlorine[5] even in the presence of silver nitrate. The major product was dimer **4**. Photocyclization[10] of the mercaptan us-

ing benzoyl peroxide was not observed.

The ring closure of mercaptan **2** took place with t-BuOCl. Treatment of the mercaptan with t-BuOCl in CCl_4 resulted in chloromethylpenam **5**.[11] When heating in dimethylsulfoxide[12] at 100°, penam **5** was converted to chlorocepham **6**.[11]

Dimer **4** was also the by-product in the reaction with *t*-BuOCl. The reaction gave only the kinetic product,[5,12] the penam. A similar result was obtained by treatment with N-bromosuccinimide or other positive halogen precursors.



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Missing Terms in Semiempirical Evaluation of Molecular Properties

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When molecular properties (meaning electric or magnetic properties which molecules exhibit under the influence of electric or magnetic field) within valence space are desired, the total hamiltonian (H) should be transformed to an effective valence shell Hamiltonian (H^{eff}). H^{eff} acts only within a valence space (P space). In our early work[1], we showed a formal derivation of H^{eff} for properties. That is,

$$H = H^{\circ} + \lambda M \tag{1}$$

$$H^{eff} C_P = (E^{\circ} + \lambda E') C_P \tag{2}$$

$$H^{eff} = H^{\circ,eff} + \lambda M^{eff} - \lambda H^{\circ}_{PQ} (E^{\circ}_{QQ} - H^{\circ}_{QQ})^{-1} E'_{QQ} (E^{\circ}_{QQ} - H^{\circ}_{QQ})^{-1} H^{\circ}_{QP} \tag{3}$$

$$H^{\circ,eff} C^{\circ}_P = E^{\circ} C^{\circ}_P \tag{4}$$

$$H^{\circ,eff} = H^{\circ}_{PP} + H^{\circ}_{PQ} (E^{\circ}_{QQ} - H^{\circ}_{QQ})^{-1} H^{\circ}_{QP} \tag{5}$$

$$M^{eff} = M_{PP} + M_{PQ} (E^{\circ}_{QQ} - H^{\circ}_{QQ})^{-1} H^{\circ}_{QP} + H^{\circ}_{PQ} (E^{\circ}_{QQ} - H^{\circ}_{QQ})^{-1} M_{QP} + H^{\circ}_{PQ} (E^{\circ}_{QQ} - H^{\circ}_{QQ})^{-1} M_{QQ} (E^{\circ}_{QQ} - H^{\circ}_{QQ})^{-1} H^{\circ}_{QP} \tag{6}$$

where H° is molecular electronic Hamiltonian, M is property operator (external field), C_P is true valence wavefunctions in matrix form, E° is molecular energy, and E′ is molecular property value. P denotes a valence space and Q denotes a complementary space. H_{PQ}, H°_{PQ}, M_{PQ} etc. are matrix elements of operators H, H°, M etc. between the state in P space and that in Q space, respectively. The superscript eff means that the operator (H, H° or M) is transformed into effective one. λ is an expansion index.

Semiempirical Hamiltonians consider valence electrons only, which suggests that the semiempirical Hamiltonian (H°)