

Reactivities of 4-Arylthio-2-azetidinones<sup>1)</sup>

KOICHI HIRAI, HIDEBUMI MATSUDA and YUKICHI KISHIDA

Central Research Laboratories, Sankyo Co., Ltd.<sup>2)</sup>

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Reactivities of 3-methyl-4-arylthio-2-azetidinones (IIIa and IIIb) and their N-chlorosulfonyl derivatives (IIa and IIb) are discussed. Treatment of IIIa with hexamethylphosphoramide (HMPA) gave the acrylonitrile derivative (Va). The arylthio group of IIIa was easily oxidized with *m*-chloroperbenzoic acid to afford the sulfoxide (VII), and further oxidation gave sulfone derivative (IX). Treatment of IIIa with iodine or bromine in methylene chloride gave the disulfide (VI) in high yield. Reaction of IIIa with 2-methylthio-2-thiazoline gave 6-methyl-5-oxo-5H-2,3-dihydrothiazolo[3,2-*a*]pyrimidine (XII) in 16% yield.

In the previous report we described the syntheses of 4-arylthio-2-azetidinones (II) by cycloaddition of CSI ( $\text{ClSO}_2\text{NCO}$ ) with *p*-substituted aryl vinylsulfides (I), followed by the reductive removal of the chlorosulfonyl moiety with thiophenol-pyridine in acetone.<sup>3)</sup>

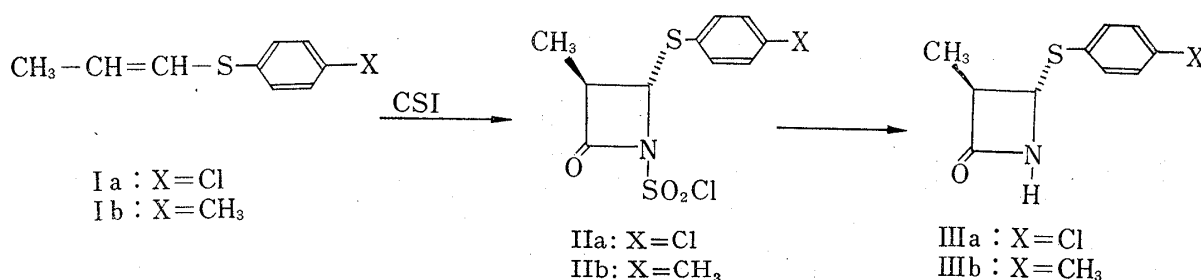


Chart 1

In 1972, T. Durst and M.J. O'Sullivan found a convenient method for the removal of this  $-\text{SO}_2\text{Cl}$  group by the use of an inorganic reducing agent such as sodium sulfite.<sup>4)</sup> Referring to this method we found sodium thiosulfate was also a reducing reagent for the purpose, thus, succeeding in the reductive cleavage of N-chlorosulfonyl group of IIa to IIIa in 22% yield.

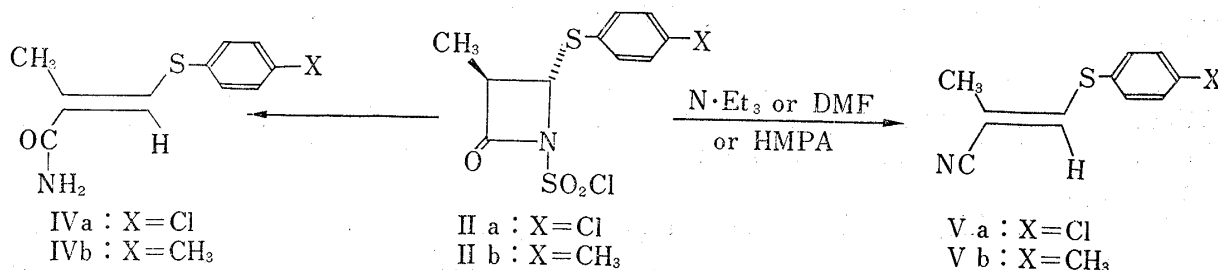


Chart 2

- 1) A part of this work was presented at the 92nd Annual Meeting of Pharmaceutical Society of Japan, Osaka, April, 1972, Abst. p. 89 (Part II).
- 2) Location: 1-2-58, Hiromachi, Shinagawa-ku, Tokyo, 140, Japan.
- 3) K. Hirai, H. Matsuda, and Y. Kishida, *Chem. Pharm. Bull.* (Tokyo), 21, 1090 (1973).
- 4) T. Durst and M.J. O'Sullivan, *J. Org. Chem.*, 35, 2043 (1970).

Next we attempted to know about the reactivities of the 2-azetidinone N-sulfonyl chlorides (IIa and IIb). These labile 2-azetidinone N-sulfonyl chlorides were easily converted into methacryl amides derivatives (IVa and IVb) on exposure to the atmosphere at room temperature. Treatment of IIa or IIb with  $\text{NEt}_3$  or DMF under the reported conditions<sup>5)</sup> gave an acrylonitrile derivative (Va or Vb) in 26% and 53.8% yield, respectively. Further we sought for other methods of the preparation of these nitrile derivatives, and found that the treatment of IIa with hexamethylphosphoramide (HMPA) gave the same nitrile derivative (Va) in 21% yield. The structure of the nitrile derivative was assigned on the basis of the physico-chemical data (see Experimental).<sup>6)</sup> The infrared (IR) spectrum of Va showed the characteristic  $\text{C}\equiv\text{N}$  absorption at  $2200\text{ cm}^{-1}$  with  $\text{C}=\text{C}$  absorption at  $1575\text{ cm}^{-1}$ , and the UV maximum at  $282\text{ nm}$  ( $\epsilon$ , 14000) indicated the presence of  $\alpha,\beta$ -unsaturated nitrile group. The mechanism for the formation of this nitrile (Va) by HMPA-treatment would be analogous to that of DMF-treatment,<sup>5)</sup> and are depicted in Chart 3.

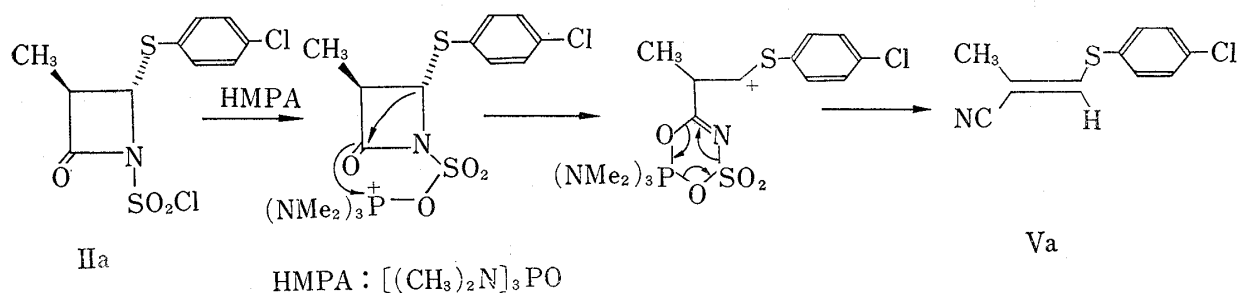


Chart 3

Next we investigated the reactivity of 4-*p*-chlorophenylthio-3-methyl-2-azetidinone (IIIa) and obtained several products due to this labile arylthio-structure. Treatment of IIIa with iodine or bromine in methylene chloride gave disulfide (VI) in high yield which was identical with an authentic specimen of di-*p*-chlorophenylthio-3-methyl-2-azetidinone<sup>7)</sup> and this disulfide was also obtained by the treatment with  $\text{BF}_3$ -etherate, or  $\text{CH}_3\text{I}/\text{NaH}$  in THF, the conditions for the N-methylation. The sulfoxide (VIIa), which was easily prepared from IIIa by oxidation with an equivalent amount of *m*-chloroperbenzoic acid, was treated with iodine or bromine under the same conditions in the formation of the disulfide (VI) to afford the corresponding thiol sulfonate (VIII), mp  $138\text{--}139^\circ$ , in 75.2% yield. This thiol sulfonate (VIII) was also obtained by treatment of VIIa with  $\text{BF}_3\text{-Ac}_2\text{O}$  with concomitant of the formation of the acetate (VIIb). Oxidation of the sulfide (VIIa) with *m*-chloroperbenzoic acid gave the corresponding sulfone (IX). The IR showed the strong  $\text{-SO}_2\text{-}$  absorption at  $1340$  and  $1160\text{ cm}^{-1}$  and other physico-chemical data clearly supported the structure of sulfonyl substituted azetidinone for IX.

The above mentioned evidence indicated that arylthio- or arylsulfinyl groups substituted at  $\text{C}_4$  of 2-azetidinone were very labile and could be excluded easily by treatment with electrophiles such as iodine, bromine or acetic anhydride to give the disulfide or thiol sulfonate, respectively.

These reactivities would be due to that the arylthio groups are substituted at the  $\beta$ -position with respect to the carbonyl group of the 2-azetidinone ring, and hereby a facile leaving of the arylthio group would occur. Although it was reported that reaction of 2-

5) E.J. Moriconi and C.C. Jalandoni, *J. Org. Chem.*, **35**, 3796 (1970).

6) Although the stereochemistry about the double bond in Va could not be determined conclusively from the available data, but it is probably *trans*, the thermodynamically more stable isomer, from the mechanistic standpoint.

7) S.S. B'hatnager and B. Singh, *J. Ind. Chem. Soc.*, **7**, 663 (1930).

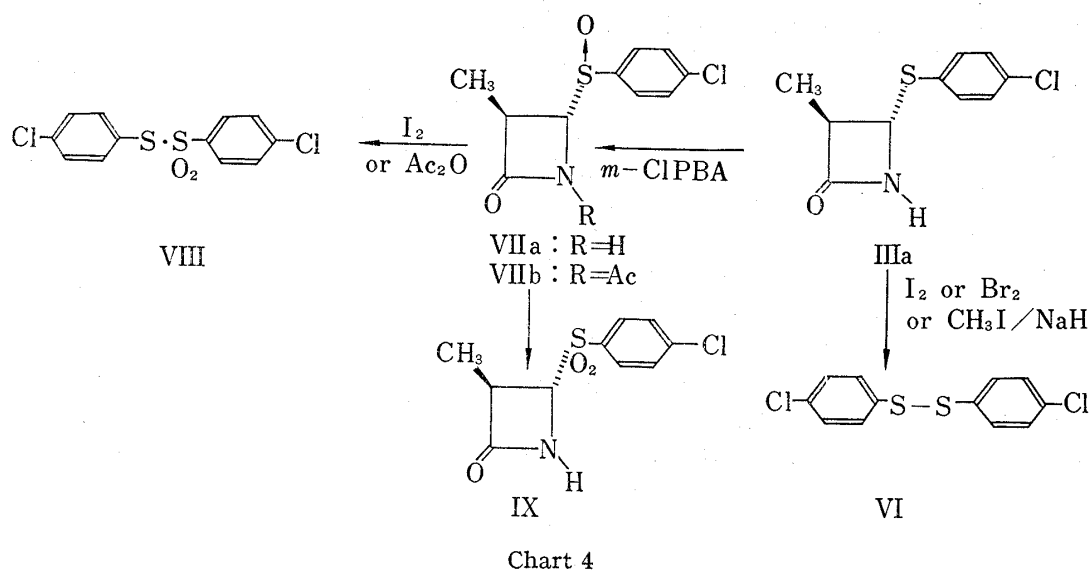


Chart 5

azetidinone with 2-methoxy-1-pyrroline afforded 4-oxo-2,3,4,6,7,8-hexahydropyrrolo[1,2-a]-pyrimidine,<sup>8)</sup> it seemed to be interesting for us to investigate the reactivity of such a 2-azetidinone as **IIIa**, which has an facile leaving group of arylthio, towards cyclic iminoethers.

When a mixture of iminoether such as 2-ethoxy-1-pyrroline or 7-ethoxy-3,4,5,6-tetrahydro-2H-azepine with **IIIa** was heated at 120–130° for 3 hours gave a pyrrolo-pyrimidine derivative (**X**) or a pyrimido-azepine derivative (**XI**) in 34 and 76% yield, respectively.

The product, **X**, had a molecular formula of  $C_8H_{10}ON_2$  ( $M^+$  at  $m/e$  150), which indicated the absence of *p*-chlorophenylthio moiety. The NMR spectrum showed the characteristic triplet like signals at  $\delta$  4.15 (2H,  $-NCH_2-$ ) and 3.11 (2H,  $-SCH_2-$ ). Methylene signals appeared at 2.2–2.54 as multiplet and the vinylic proton appeared at 7.72 which was splitted by long-range coupling with methyl signal at 2.03 with coupling constant of *ca.* 1 Hz. The IR spectrum showed 1660, 1645 and 1600  $cm^{-1}$  due to C=O, C=N and C=C bond absorptions, and the UV spectrum showed maxima absorptions at 228 ( $\epsilon$  6530) and 271.5 ( $\epsilon$ , 6160) nm. These data

8) D. Bormann, *Chem. Ber.*, **103**, 1797 (1970).

coincided well with the proposed structure of 3-methyl-4-oxo-4,6,7,8-tetrahydropyrrolo[1,2-*a*]-pyrimidine (X). The structure assignment of XI was done analogously to that of X.

It is known that the reactivity of 2-alkylthio-2-thiazoline, which was easily prepared from commercially available mercaptothiazoline and alkylhalide, is similar to that of the cyclic iminoether,<sup>9)</sup> and thus 6-methyl-5-oxo-5*H*-2,3-dihydrothiazolo[3.2-*a*]pyrimidine (XII) was obtained in 16% yield by heating a mixture of methylthio-2-thiazoline and IIIa in the presence of a catalytic amount of DABCO (1,4-diazabicyclo[2,2,2]octane). The structure of XII was determined by the usual methods (see Experimental). Especially the nuclear magnetic resonance (NMR) spectrum showed the characteristic A<sub>2</sub>B<sub>2</sub>-pattern signals at  $\delta$  3.33–3.67 (2H almost t.) and 4.32–4.67 (2H, almost t). The rest of the signals were CH<sub>3</sub>-signal at 2.01 (d, *J*=1 Hz) and vinylic proton at 7.61 (q, *J*=1 Hz). Other physico-chemical data are very close to those of X.

Attempts to obtain the hindered four-membered iminoether of IIIa by Meerwein reagent<sup>10)</sup> was unsuccessful and only a intractable mixture was obtained.

### Experimental

**General**—All melting points are uncorrected. NMR spectra were taken using Varian A-60 spectrometer and the chemical shifts were expressed in ppm unit from the internal standard of tetramethylsilane (TMS); s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet. IR spectra were recorded on a Perkin-Elmer Model 137 spectrometer. UV spectra were recorded on a Shimadzu Model IV-50 AL spectrometer. Preparative thin-layer chromatography (preparative TLC) were carried out on Merck TLC-plates silica gel F<sub>254</sub> pre-coated, layer thickness: 2 mm.

**3-Methyl-4-*p*-chlorophenylthio-2-azetidinone (IIIa)**—To a suspension of 1.63 g of 3-methyl-4-*p*-chlorophenylthio-2-azetidinone N-sulfonyl chloride (IIa) in 15 ml of ether was added a solution of sodium thiosulfate (1.5 g) in 7 ml of water at  $-5^\circ$  and then was added 10% aq. NaOH solution to maintain the system to be slightly basic. After 30 min the ether layer was separated and dried and the solvent was evaporated to afford 0.7 g of a residue. Recrystallization from ether gave 0.25 g of pure *trans*-3-methyl-4-*p*-chlorophenylthio-2-azetidinone (IIIa), mp  $115^\circ$  which was identical with an authentic sample prepared by the known method.<sup>3)</sup>

**$\beta$ -*p*-Chlorophenylthio-methacrylamide (IVa) and  $\beta$ -*p*-Tolylthio-methacrylamide (IVb)**—A pure sample of 3-methyl-4-*p*-chlorophenylthio-2-azetidinone N-sulfonyl chloride (IIa) (165 mg) or *p*-tolylthio-2-azetidinone N-sulfonylchloride (IIb) (150 mg) was left standing at room temperature, to be exposed to the atmosphere for one week. The contents turned to red syrup. Recrystallization from ether gave 20 mg of IVa (mp  $143^\circ$ ) and 25 mg of IVb (mp  $132^\circ$ ), each of which was identical with the corresponding authentic sample.<sup>3)</sup>

**$\beta$ -*p*-Chlorophenylthio-methacrylonitrile (Va)**—a) A solution of 300 mg of 3-methyl-4-*p*-chlorophenylthio-2-azetidinone-N-sulfonyl chloride (IIa) in 1 ml of DMF was heated at  $60^\circ$  for one hour. After cooling the mixture was poured into ice-water and extracted with ether. After removal of the solvent the product was separated by preparative TLC with a solvent system of benzene: *n*-hexane (1:1) to give 50 mg of the title compound. *Rf*=0.3. mp  $84-86^\circ$  (recrystallized from *n*-hexane and ether). IR  $\nu_{\text{max}}^{\text{Nujol}}$  cm<sup>-1</sup>: 2220 (C $\equiv$ N), 1575 (C=C). UV  $\lambda_{\text{max}}^{\text{EtOH}}$  nm: 240 (sh), 282 (14000). Anal. Calcd. for C<sub>10</sub>H<sub>8</sub>NSCl: C, 57.25; H, 3.85; N, 6.68; S, 15.29. Found: C, 57.43; H, 3.81; N, 6.81; S, 15.39. Mass Spectrum *m/e*: 209 and 211 (M<sup>+</sup>, 3:1), 194 and 196 (M<sup>+</sup>-CH<sub>3</sub>, 3:1), 183 and 185 (M<sup>+</sup>-CN, 3:1).

b) A solution of 300 mg IIa in 1 ml of HMPA was kept at room temperature for 20 hours. The product was separated directly by preparative TLC to give 40 mg of the title compound. mp  $84-86^\circ$ .

**$\beta$ -*p*-Tolylthio-methacrylonitrile (Vb)**—A solution of 300 mg of 3-methyl-4-*p*-tolylthio-2-azetidinone-N-sulfonyl chloride (IIb) in 1 ml of DMF was kept at room temperature for two days. The product was separated by the preparative TLC (benzene: *n*-hexane, *Rf*=0.3) to give 100 mg of the oily title compound. IR  $\nu_{\text{max}}^{\text{film}}$  cm<sup>-1</sup>: 2200 (C=N). Mass Spectrum *m/e*: 189 (M<sup>+</sup>, C<sub>11</sub>H<sub>11</sub>NS), 163 (M<sup>+</sup>-CN).

**Di-*p*-chlorophenyl Disulfide (VI)**—a) To a stirred solution of 455 mg of 3-methyl-4-*p*-chlorophenylthio-2-azetidinone (IIIa) in 3 ml of methylene chloride was added dropwise a solution of I<sub>2</sub> (254 mg) in methylene chloride (12 ml) at room temperature. After 5 hrs the viscous materials were removed off by decantation and the solvent was washed with 3% aq. sodium thiosulfate and water. After removal of the solvent the crude product was recrystallized from *n*-hexane to give 220 mg of pure di-*p*-chlorophenyl disulfide (VI), mp  $71^\circ$  which was identical with the authentic sample of di-*p*-chlorophenyl disulfide in all respects.

9) K. Hirai, H. Matsuda, and Y. Kishida, *Chem. Pharm. Bull.* (Tokyo), **20**, 97 (1972).

10) D. Bormann, *Ann. Chem.*, **725**, 124 (1969).

b) To a stirred solution of 114 mg of IIIa in 1 ml of methylene chloride was added dropwise a solution of 80 mg of Br<sub>2</sub> in 1 ml of methylene chloride at room temperature. After stirring for 45 min the appeared viscous polymeric materials were removed off by decantation, and removal of the solvent gave 700 mg of di-*p*-chlorophenyl disulfide, mp 71°.

c) To a solution of 228 mg of IIIa in acetic anhydride (2 ml) was added two drops of BF<sub>3</sub>-etherate and the mixture was heated at 90° for one hour. Ethanol was added and the solvent was removed off *in vacuo*. The products were separated by preparative TLC (solvent system, benzene: acetone=5:1) and a portion of R<sub>f</sub>=0.7 was extracted with methylene chloride to give 60 mg of di-*p*-chlorophenyl disulfide, mp 71° (recrystallized from *n*-hexane).

d) To a solution of 100 mg of IIIa in 0.5 ml of dry THF was added 21 mg of 50% NaH in mineral oil at -40° and then was added 62.5 mg of methyl iodide. After stirring for 30 min at -40° the temperature of the reaction mixture was gradually raised to room temperature. The product was separated by the preparative TLC to give 114 mg of di-*p*-chlorophenyl disulfide, mp 71°.

**3-Methyl-4-*p*-chlorophenylsulfinyl-2-azetidinone (VIIa)**—To a solution of 4.1 g of IIIa in 240 ml of methylene chloride was added 3.72 g of *m*-chloroperbenzoic acid at -30° over one hour. After stirring for 1.5 hours at -30° the crystals formed were filtered off and the organic solvent was washed with saturated aq. NaHCO<sub>3</sub> solution and water, and dried over MgSO<sub>4</sub>. After removal of the solvent the product was recrystallized from methylene chloride to give colorless plates. (2.6 g). mp 141–143°. IR  $\nu_{\text{max}}^{\text{Nujol}}$  cm<sup>-1</sup>: 3150 (N-H), 1780 and 1760 (C=O), 1035 (S-O). UV  $\lambda_{\text{max}}^{\text{EtOH}}$  nm ( $\epsilon$ ): 248.5 (8350), 295 (sh). NMR (CDCl<sub>3</sub>)  $\delta$ : 7.57 (4H, s, arom.), 4.08 (1H, d, *J*=2 Hz), 3.62 (1H, d, of q, *J*=8 and 2 Hz), 1.16 (3H, d, *J*=8 Hz). Anal. Calcd. for C<sub>10</sub>H<sub>10</sub>O<sub>2</sub>NSCl: C, 49.27; H, 4.14; N, 5.75; S, 13.16. Found: C, 49.41; H, 4.09; N, 5.70; S, 13.46. Mass Spectrum *m/e*: 243 and 245 (M<sup>+</sup>, 3:1), 200 and 202 (M<sup>+</sup>-NHCO, 3:1), and 84.

**Acetyl 3-Methyl-4-*p*-chlorophenylsulfinyl-2-azetidinone (VIIb)**—A solution of 510 mg of 3-methyl-4-*p*-chlorophenylsulfinyl-2-azetidinone (VIIa) in 270 mg of acetic anhydride and 4 ml of benzene was refluxed in the presence of a catalytic amount of BF<sub>3</sub>-etherate for one hour. 3 ml of ethanol was added and the solvent was removed off *in vacuo*. The products were separated by preparative TLC (solvent system of benzene: acetone=3:1). A portion of R<sub>f</sub>=0.7 was extracted with methylene chloride to give 370 mg of *p*-chlorophenylthio-*p*-chlorophenylsulfonate (VIII), mp 138–139°, and a portion of R<sub>f</sub>=0.35 gave 9 mg of the N-acetate (VIIb), mp 122–126° (recrystallization from ether). IR  $\nu_{\text{max}}^{\text{Nujol}}$  cm<sup>-1</sup>: 1797 and 1715 (C=O). 1042 (S-O). UV  $\lambda_{\text{max}}^{\text{EtOH}}$  nm ( $\epsilon$ ): 248 (4380). NMR (CDCl<sub>3</sub>)  $\delta$ : 7.55 (4H, s, arom.), 4.32 (1H, d, *J*=3.0 Hz), 3.77 (1H, d, of q, *J*=3.0 and 7.5 Hz), 2.44 (3H, s, COCH<sub>3</sub>), 0.95 (3H, d, *J*=7.5 Hz). Mass Spectrum *m/e*: 285 and (M<sup>+</sup>, 3:1), 126.

***p*-Chlorophenylthio-*p*-chlorophenylsulfonate (VIII)**—To a solution of 121 mg of IIIa was added a solution of I<sub>2</sub> (61 mg) in 6 ml of methylene chloride at room temperature. After stirring for 20 hr the organic solvent was washed with 3% aq. thiosulfate solution and water, and dried over MgSO<sub>4</sub>. After removal of the solvent the products were separated by preparative TLC (solvent system of benzene: acetone=3:1). Extraction of a portion of R<sub>f</sub>=0.7 with methylene chloride gave 60 mg of colorless plates. mp 138–139° (recrystallization from ether-*n*-hexane). UV  $\lambda_{\text{max}}^{\text{EtOH}}$  nm ( $\epsilon$ ): 239.5 (20700). NMR (CDCl<sub>3</sub>)  $\delta$ : 7.15–7.53 (8H, m). Anal. Calcd. for C<sub>12</sub>H<sub>8</sub>O<sub>2</sub>S<sub>2</sub>Cl: C, 45.10; H, 2.52; S, 20.07; Cl, 22.20. Found: C, 45.16; H, 2.22; S, 19.89; Cl, 22.40. Mass Spectrum *m/e*: 318, 320 and 322 (M<sup>+</sup>, 9:6:1), 175 and 177 (M<sup>+</sup>-ClC<sub>6</sub>H<sub>5</sub>S), 143 and 145 (M<sup>+</sup>-ClC<sub>6</sub>H<sub>5</sub>SO<sub>2</sub>).

**3-Methyl-4-*p*-chlorophenylsulfonyl-2-azetidinone (IX)**—To a stirred solution of 240 mg of 3-methyl-4-*p*-chlorophenylsulfinyl-2-azetidinone (VIIa) was added 200 mg of *m*-chloroperbenzoic acid at -30°. The temperature of the reaction mixture was gradually raised to room temperature over 30 min and then the solvent was washed with saturated aq. NaHCO<sub>3</sub> solution and water, and dried over MeSO<sub>4</sub>. After removal of the solvent the product was recrystallized from ether-acetone to give plates (136 mg). mp 176–181°. IR  $\nu_{\text{max}}^{\text{Nujol}}$  cm<sup>-1</sup>: 3250 (NH), 1780 and 1760 (C=O), 1340 and 1160 (SO<sub>2</sub>). UV  $\lambda_{\text{max}}^{\text{EtOH}}$  nm ( $\epsilon$ ): 231.5 (16700). NMR (CDCl<sub>3</sub>)  $\delta$ : 7.53–8.0, (4H, A<sub>2</sub>B<sub>2</sub>-part of *p*-chlorophenyl), 6.75 (1H, NH), 4.4 (1H, d, *J*=2 Hz), 3.52 (1H, d, of q, *J*=8 and 2 Hz), 1.4 (3H, d, *J*=8 Hz). Anal. Calcd. for C<sub>10</sub>H<sub>10</sub>O<sub>3</sub>NSCl: C, 46.24; H, 3.38; N, 5.39; S, 12.35. Found: C, 46.20; H, 3.78; N, 5.56; S, 12.21. Mass Spectrum *m/e*: 259 (M<sup>+</sup>).

**3-Methyl-4-oxo-4,6,7,8-tetrahydropyrrolo[1,2-*a*]pyrimidine (X) and 3-Methyl-4-oxo-4,6,7,8,9,10-hexahydropyrimido[1,2-*a*]azepine (XI)**—A mixture of 246 mg of 2-ethoxy-1-pyrroline (or 339 mg of 7-ethoxy-3,4,5,6-tetrahydro-2H-azepine) and 500 mg of IIIa was heated at 120–130° for 3 hr under a nitrogen atmosphere. After cooling the product was separated by preparative TLC (benzene: acetone=2:1) and a portion of R<sub>f</sub>=0.2 was extracted with methylene chloride to give 239 mg of X (or 301 mg of XI). 3-Methyl-4-oxo-4,6,7,8-tetrahydropyrrolo[1,2-*a*]pyrimidine (X), mp 77–79°. Anal. Calcd. for C<sub>8</sub>H<sub>10</sub>ON<sub>2</sub>: C, 63.98; H, 6.71; N, 18.66. Found: C, 63.93; H, 6.75; N, 18.73. Mass Spectrum *m/e*: 150 (M<sup>+</sup>), 135 (M<sup>+</sup>-CH<sub>3</sub>), 122 (M<sup>+</sup>-CO). 3-Methyl-4-oxo-4,6,7,8,9,10-hexahydropyrimido[1,2-*a*]azepine (XI), mp 57°. IR  $\nu_{\text{max}}^{\text{Nujol}}$  cm<sup>-1</sup>: 1675 (C=O), 1655 (C=N), 1600 (C=C). UV  $\lambda_{\text{max}}^{\text{EtOH}}$  nm ( $\epsilon$ ): 227 (5900), 279 (6300), 300 (sh.). NMR (CDCl<sub>3</sub>)  $\delta$ : 7.65 (1H, q, *J*=1 Hz), 4.1–4.56 (2H, m, C<sub>6</sub>-H<sub>2</sub>), 2.77–3.17 (2H, m, C<sub>10</sub>-H<sub>2</sub>), 2.03 (3H, d, *J*=1 Hz), 1.59–1.95 (6H, m), Anal. Calcd. for C<sub>10</sub>H<sub>14</sub>ON<sub>2</sub>: C, 67.38; H, 7.92; N, 15.72. Found: C, 67.57; H, 7.89; N, 16.05. Mass Spectrum *m/e*: 178 (M<sup>+</sup>), 163 (M<sup>+</sup>-CH<sub>3</sub>), 150 (M<sup>+</sup>-CO).

**6-Methyl-5-oxo-5H-2,3-dihydrothiazolo[3,2-*a*]pyrimidine (XII)**—A mixture of 500 mg of 3-methyl-4-*p*-chlorophenylthio-2-azetidinone (IIIa) and 400 mg of 2-methylthio-2-thiazoline was heated at 120° for three hours in the presence of a catalytic amount of DABCO under a nitrogen atmosphere. After cooling the product was separated by preparative TLC (benzene:acetone=5:1). Extraction of a portion of *R<sub>f</sub>*=0.2 with methylene chloride gave 61 mg of the title compound (XII), mp 120—126° (recrystallized from ether). IR  $\nu_{\text{max}}^{\text{Nujol}}$  cm<sup>-1</sup>: 1663 (C=O), 1595 (C=N). UV  $\lambda_{\text{max}}^{\text{EtOH}}$  nm ( $\epsilon$ ): 232 (6500), 289 (8600), 297 (sh.). NMR (CDCl<sub>3</sub>)  $\delta$ : 7.61 (1H, q, *J*=1 Hz), 4.32—4.67 (2H, almost t), 3.33—3.67 (2H, almost t), 2.01 (3H, d, *J*=1 Hz). *Anal.* Calcd. for C<sub>7</sub>H<sub>8</sub>ON<sub>2</sub>S: C, 49.98; H, 4.79; N, 16.67; S, 19.09. Found: C, 50.09; H, 4.80; N, 16.66; S, 19.11. Mass Spectrum *m/e*: 168 (M<sup>+</sup>), 140 (M<sup>+</sup>-CO).