N-(2-Hydroxyethyl)-*N*-(2-*p*-tolylsulfonylethoxycarbonyl)-*p*-anisidine.—A solution of 10.6 g (0.06 mol) of *N*-2-hydroxyethyl-*p*-anisidine and 6.08 g (0.03 mol) of freshly distilled triethylamine in 40 ml of $CHCl_3$ (purified by percolating through anhydrous alumina) were cooled to 0° in an ice bath (the flask was protected against moisture by means of a drying tube). A solution of 13.75 g (0.06 mol) of 2-(*p*-tolylsulfonyl)ethylchloroformate[22] in 25 ml of $CHCl_3$ was added dropwise with stirring. When addition was complete, the ice bath was removed, and the mixture was stirred at room temperature for 2 hr. With the addition of 50 ml of ethyl ether, a solid formed, and the triethylamine hydrochloride that precipitated was removed. The organic layer was extracted with 5% HCl (three 150-ml portions), washed with 5% $NaHCO_3$, and dried ($NaSO_4$), and the solvent was removed under reduced pressure to yield an oil (XIV), 19.44 g (0.05 mol, 83%). All attempts to crystallize the product failed: ir (neat, KBr) 3490 (OH), 1720 (C=O), and 1320, 1290, and 1420 cm^{-1} (SO_2); nmr ($CDCl_3$) 2.43 (s, 3, CH_3), 3.52 (broad s, 1, OH), 3.39 (t, 2, J = 6 Hz, $-SO_2CH_2$), 3.72 (broad s, 4 NCH_2CH_2O), 3.79 (s, 3, $-OCH_3$), 4.39 ppm (t, 2, J = 6 Hz, CH_2OCO).

N-(2-Tosyloxyethyl)-*N*-(2-tolylsulfonylethoxycarbonyl)-*p*-anisidine.—A solution of 19.4 g (0.05 mol) of XIV (crude oil) in 10 ml of anhydrous pyridine was cooled to 0° in an ice bath. A solution of 9.88 g (0.053 mol) of *p*-toluenesulfonyl chloride was added slowly with stirring and cooling. The mixture was placed in the refrigerator overnight and then poured into 200 ml of cold 1 *N* HCl and extracted with 20 ml of $CHCl_3$. The $CHCl_3$ was washed with 1 *N* HCl (three 150-ml portions) and dried (sodium sulfate), and the solvent was removed under reduced pressure to yield an oil. The oil was placed under vacuum for 10 hr to yield 25.3 g (0.049 mol, 98%) of product XV.

After 2 months, a small amount of product crystallized from benzene. The product, as analyzed by nmr, formed approximately a 1:1 compound with benzene, mp 80–81°. Drying at 75° under high vacuum removed most of the benzene, mp 104–105.5°. An acceptable analysis could not be obtained: ir (KBr) 1720 (C=O), 1320, 1290, and 1140 (SO_2 in SO_2CH_2) and 1370 and 1175 cm^{-1} (SO_2 in SO_2O); nmr (acetone) 2.29 (s, 3, *p*-CH_3–), 2.39 (s, 3, *p*-CH_3–), 3.54 (t, 2, J = 6.4 Hz, $-SO_2CH_2$), 3.64 (t, 2, J = 5.5 Hz, $-NCH_2$), 3.78 (s, 3, *p*-CH_3O–), 4.38 (t, 2, J = 6.4 Hz, $-CH_2OCO$), 4.42 ppm (t, 2, J = 5.5 Hz, $-CH_2CH_2OSO_2$).

3-(*p*-Methoxyphenyl)-2-oxazolidone.—To a solution of 24 g of crude XV in 60 ml of dry THF at 0° under argon, 2.08 g of a 58% NaH mineral oil dispersion (equivalent to 0.05 mol of hydride) was added slowly with stirring and cooling. When addition was complete, the ice bath was removed, and the mixture was stirred at room temperature for 2 hr. The sodium *p*-toluenesulfonate that had precipitated was removed by filtration and the solvent was removed under reduced pressure to yield an oily solid. The solid was recrystallized from benzene to yield 8.7 g (0.045 mol, 91%) of the oxazolidone: mp 108–109° (lit.[26] 109–110);[26] ir (KBr) 1740 cm^{-1} (C=O); nmr (acetone-d_6) 3.80 (s, 3, OCH_3 and 4.28 ppm (m, 4, CH_2CH_2–).

Registry No.—**2**, 30855-79-9; **3**, 30855-80-2; **5**, 30855-81-3; **6**, 28192-05-4; **7**, 27347-09-7; **9**, 30855-84-6; **10**, 30855-85-7; **11**, 30855-86-8; **12**, 30855-87-9; **13**, 27347-07-5; **17**, 30858-75-4; **18**, 23482-29-3; **19**, 30858-77-6; **20**, 122-98-5; **28**, 30858-79-8; XIV, 30858-80-1; XV, 30858-81-2 *N*-(2-tosyloxyethyl)-*p*-nitroaniline, 30855-86-8; *N*-(2-chloroethyl)-*p*-anisidine HCl, 27347-07-5; 3-(*p*-methoxyphenyl)-2-oxazolidone, 5198-48-1.

(26) A. F. McKay and R. V. Braun, *J. Org. Chem.*, **16**, 1829 (1951).

Aziridines. XXIV. Reactions of Derivatives of 2-Vinylaziridine

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1-(*p*-Nitrocarbobenzoxy)-2-vinylaziridine (**1**) was converted in refluxing decalin into predominantly 1-*p*-nitrocarbobenzoxy)-2-pyrroline (**2**) along with some 1-(*p*-nitrocarbobenzoxy)-3-pyrroline. Reaction of 2-vinylaziridine with phenyl isothiocyanate in ether at 0° gave 2-anilino-4,7-dihydro-1,3-thiazepine (**6**). 2-(*p*-Chlorophenyl)-4,7-dihydro-1,3-thiazepine (**7**) was formed when 2-vinylaziridine was treated with *p*-chlorothiobenzoylthioglycolate.

Previous studies on the thermolysis of aziridines bearing an unsaturated group on the 1 position and a vinyl group on the 2 position of the ring have demonstrated that such compounds undergo ring expansion to either seven-membered or five-membered rings. Thus, 1-[1,2-bis(trifluoromethyl)]vinyl-2-vinylaziridine, 1-*p*-bromophenyl-2-isopropenylaziridine, and 1-*p*-nitrobenzoyl-2-vinylaziridine isomerized upon heating into the seven-membered ring systems, 2,3-bistrifluoromethyl-3,4-dihydro-7*H*-azepine,[1] 7-bromo-4-methyl-2,5-dihydro-1*H*-1-benzazepine,[2] and 2-*p*-nitrophenyl-4,7-dihydro-1,3-oxazepine,[3] respectively. On the other hand, 1-carbethoxy-2-methyl-2-vinylaziridine when subjected to gas chromatography at 100° rearranged into 1-carbethoxy-3-methyl-3-pyrroline.[4] Various 3-(2-vinylaziridinyl)benzoxazolinones although not substituted at the 1 position of the aziridine ring with an unsaturated moiety also, when heated in decalin, rearrange to 3-pyrrolines.[5]

(1) E. L. Stogryn and S. J. Brois, *J. Amer. Chem. Soc.*, **89**, 605 (1967).
(2) P. Scheiner, *J. Org. Chem.*, **32**, 2628 (1967).
(3) P. G. Mente, H. W. Heine, and G. R. Scharoubim, *ibid.*, **33**, 4547 (1968).
(4) A. Mishra, S. N. Rice, and W. Lwowski, *ibid.*, **33**, 481 (1968).

In this paper several new examples of ring expansions of 2-vinylaziridine derivatives into five-membered and seven-membered ring systems are reported. We wish to describe first the thermolysis of 1-(*p*-nitrocarbobenzoxy)-2-vinylaziridine (**1**) in decalin. In contrast to the gas chromatographic behavior of 1-carbethoxy-2-methyl-2-vinylaziridine which rearranges to a 3-pyrroline,[4] compound **1** rearranges predominantly to 1-(*p*-nitrocarbobenzoxy)-2-pyrroline (**2**).

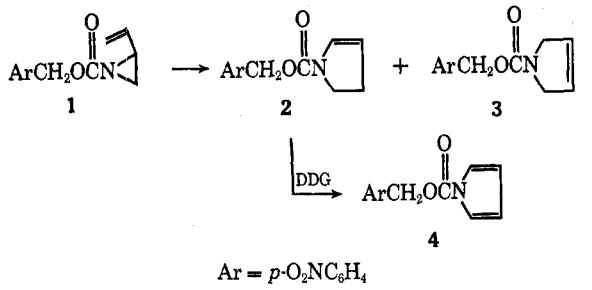
We also wish to describe the reactions of 2-vinylaziridine with phenyl isothiocyanate and sodium *p*-chlorothiobenzoylthioglycolate. Presumably in these reactions 1-thiocarboxanilide-2-vinylaziridine and 1-(*p*-chlorothiobenzoyl)-2-vinylaziridine form and spontaneously isomerize to 4,7-dihydro-1,3-thiazepines.

Results and Discussion

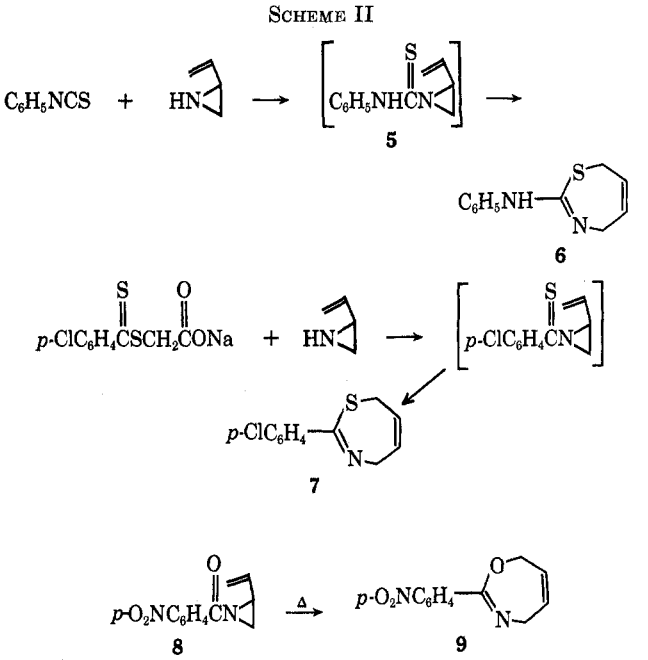
Thermolysis of **1** in refluxing decalin resulted in a mixture of 1-(*p*-nitrocarbobenzoxy)-2-pyrroline (**2**) and 1-(*p*-nitrocarbobenzoxy)-3-pyrroline (**3**) in overall yields of 63–75% (Scheme I).

(5) (a) R. S. Atkinson and C. W. Rees, *Chem. Commun.*, 1232 (1967); (b) R. S. Atkinson and C. W. Rees, *J. Chem. Soc. C*, 778 (1969).

SCHEME I



SCHEME II



Compound **3** was identified by spectral comparison with an authentic sample prepared by the reaction of 3-pyrroline with *p*-nitrocarbobenzoxy chloride. Compound **2** was characterized by nmr spectroscopy (see Experimental Section) and by its oxidation to 1-(*p*-nitrocarbobenzoxy)pyrrole (**4**). An alternate synthesis of **4** was achieved through the reaction of the potassium salt of pyrrole with *p*-nitrocarbobenzoxy chloride.

The relative quantities of **2** and **3** formed in the thermolysis of **1** were estimated by utilizing nmr spectroscopy. The analysis consisted of determining the ratio of the areas under the signals from the vinyl protons of **3** (singlet at δ 5.82) and from the vinyl protons of **2** (multiplets at δ 5.14 and 6.63).

The compositions of the mixtures obtained from the thermolysis of **1** depended upon the pH of the glass surface of the reaction flask. If the reaction flask was acid washed prior to thorough washing with water and then dried, the crude product contained 96% of **2** and 4% of **3**. If the reaction flask was cleaned thoroughly without the benefit of an acid wash the crude product could contain as little as 75% of **2** and as much as 25% of **3**.

A control run of **3** in refluxing decalin resulted in an almost quantitative recovery of **3**. In another control run of **3** in decalin containing one drop of glacial acetic acid it was possible to recover **3** in 90% yield. In neither control was there any evidence of **2** which establishes that **2** was not produced by isomerization of **3**. Another control established that **2** was not converted to **3** in refluxing decalin. It is interesting to note that the product composition in the thermolysis of 3-(2,2-dimethyl-3-isobutenylaziridinyl)benzoxazolinone was also dependent on the pH of the glass surface of the reaction vessel.[5b]

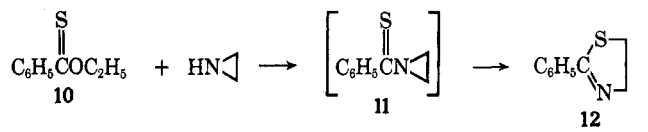
A possible mechanism for the formation of **2** from the thermolysis of **1** may involve a carbon–carbon bond cleavage of the aziridine ring to form a 1,3-diradical or 1,3-dipolar intermediate which subsequently ring closes to the 2-pyrroline. The formation of **3** may be accounted for by scission of the carbon–nitrogen bond of the ring followed by ring closure to the 3-pyrroline.[5b] The reason for the dependency of the ratio of **2** to **3** on the condition of the glass surface of the reaction flask is not clear.

In an attempt to prepare 1-thiocarboxanilide-2-vinylaziridine (**5**), 2-vinylaziridine was treated with phenyl isothiocyanate in ether at 0°. The product however, proved to be 2-anilino-4,7-dihydro-1,3-thiazepine (**6**) (Scheme II). Presumably **5** was generated as an intermediate but rearranged to **6** under the experimental conditions. A similar reaction of 2-vinylaziridine with sodium *p*-chlorothiobenzoylthioglycolate in a stirred ether–water mixture gave the low-melting 2-(*p*-chlorophenyl)-4,7-dihydro-1,3-thiazepine (**7**) (Scheme II). These reactions parallel the previously reported isomerization of 1-*p*-nitrobenzoyl-2-vinylaziridine (**8**) to 2-*p*-nitrophenyl-4,7-dihydro-1,3-oxazepine (**9**)[3] (Scheme II).

Compound **6** seems to be the first example of a 4,7-dihydro-1,3-thiazepine. The structure of **6** was established by nmr spectroscopy and elemental analyses. The nmr spectrum of **6** was quite analogous to the previously characterized **9**. The nmr spectrum of **6** in $CDCl_3$ showed the phenyl group as a complex multiplet centered at *ca.* δ 7.1 ppm (5 H), the NH proton as a broad peak at 6.0 ppm which could be readily eliminated by exchange with D_2O, the two olefinic protons as a multiplet at 5.7 ppm, and the two methylene groups as multiplets at 3.9 (2 H) and 3.4 ppm (2 H). Despite the shift differences, the individual multiplets for the olefinic and methylene protons of **6** are almost superimposable on the corresponding signals of **9**.

Compound **7** was not so stable as **6** and decomposed rapidly on standing. Its structure was inferred by nmr spectroscopy. As anticipated, the spectra of **6** and **7** were nearly the same.

The greater nucleophilicity of the thiocarbonyl sulfur of the presumed intermediate **5** relative to the carbonyl oxygen of **8** is probably responsible for the rapid formation of **6**. The contrast in nucleophilicity between thiocarbonyl sulfur and carbonyl oxygen has recently been demonstrated. For example, treatment of the thio



ester **10** with aziridine did not give the expected thioacylaziridine **11** but instead the thiazoline **12**.[6] An-

(6) P. Reynaud, R. C. Moreau, and P. Fodor, *C. R. Acad. Sci., Ser. C*, **266**, 632 (1968).

other example is the conversion of 1-thiobenzoylazetidine in concentrated hydrochloric acid for 10 days at room temperature into 2-phenyl-4,5-dihydro-6*H*-1,3-thiazine while under identical conditions 1-benzoylazetidine gave only *N*-(3-chloropropyl)benzamide.[7]

Experimental Section

1-(*p*-Nitrocarbobenzoxy)-2-vinylaziridine (1).—A solution of 2.2 g of *p*-nitrocarbobenzoxy chloride in 45 ml of ether was added dropwise to a stirred solution of 1.0 g of 2-vinylaziridine[8] and 1.2 g of triethylamine in 100 ml of ether. The reaction mixture was stirred for 4 hr and then filtered free of the precipitated triethylamine hydrochloride. The filtrate was evaporated to give 2.5 g of a yellow oil. The oil was dissolved in 2-propanol and the solution was kept at −10° for 6 hr. The supernatant was decanted and the residue was washed with petroleum ether (bp 60–110°). Repetition of the purification procedure gave 1.11 g (46%) of **1** melting at 56–58°.

Anal. Calcd for $C_{12}H_{12}N_2O_4$: C, 58.07; H, 4.87; N, 11.28. Found: C, 57.81; H, 4.81; N, 11.43.

Rearrangement of 1 to 2.—A round-bottomed flask cleaned with chromic acid solution and repeatedly washed with distilled water and dried was charged with 249 mg of **1** and 10 ml of decalin. The reaction mixture was refluxed for 1 hr and then cooled to −10° and filtered. The crude product weighed 157 mg (63%) and as determined by nmr spectroscopy was 96% compound **2** and 4% compound **3**. Recrystallization four times from petroleum ether (bp 100–115°) gave **2** melting at 117.5–119.5°. The nmr spectrum of **2** is comparable to that of 2,3-dihydrofuran:[9] nmr ($CDCl_3$) δ 2.70 (t, 2, $=CHCH_2$), 2.84 (t, 2, NCH_2), 5.14 (m, 1, $=CHCH_2$), 5.29 (s, 2, CH_2O), 6.63 (q, 1, $NCH=$), 7.55 and 8.24 (m, 4, C_6H_4).

Anal. Calcd for $C_{12}H_{12}N_2O_4$: C, 58.07; H, 4.87; N, 11.28. Found: C, 58.41; H, 4.89; N, 11.08.

1-(*p*-Nitrocarbobenzoxy)-3-pyrroline (3).—A solution of 2.2 g of *p*-nitrocarbobenzoxy chloride in 30 ml of ether was added over 10 min to a stirred and cooled (ice bath) solution of 0.70 g of 3-pyrroline in 100 ml of ether. The reaction mixture was stirred for 2.5 hr and then filtered. Evaporation of the filtrate gave 1.6 g of crude **3**. Three recrystallizations from petroleum ether gave **3** melting at 129.5–131°: nmr ($CDCl_3$) 4.22 (s, 4, CH_2NCH_2), 5.26 (s, 2, CH_2O), 5.82 (s, 2, CH=CH).

Anal. Calcd for $C_{12}H_{12}N_2O_4$: C, 58.07; H, 4.87; N, 11.28. Found: C, 58.00; H, 4.84; N, 10.81.

1-(*p*-Nitrocarbobenzoxy)pyrrole (4).—To a solution of 0.50 g of pyrrole in 40 ml of C_6H_6 was added 0.80 g of potassium *tert*-butoxide. The mixture was stirred for 0.5 hr and then 1.20 g of *p*-nitrocarbobenzoxy chloride in 15 ml of C_6H_6 was added and the stirring was continued for an additional 2 hr. The reaction mixture was filtered and the filtrate was evaporated to give 1.35 g of yellow solid. The solid was dissolved in a little petroleum ether (bp 100–115°) and the solution was cooled and filtered. Repeated recrystallization from petroleum ether (bp 70–100°) and finally 2-propanol gave an analytical sample of **4** melting at 99–101°.

Anal. Calcd for $C_{12}H_{10}N_2O_4$: C, 58.53; H, 4.09; N, 11.38. Found: C, 58.36; H, 3.94; N, 11.20.

Oxidation of 2 to 4.—A mixture of 87 mg of **2** containing 2% **3** and 200 mg of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone in 15 ml of toluene was refluxed for 5.5 hr. The solvent was evaporated to dryness and the residue extracted with chloroform. The chloroform extract was washed with 2% NaOH solution, dried over K_2CO_3, and decolorized with charcoal. The solution was evaporated to dryness to give 64 mg of crude **4** which had an infrared spectrum identical with that of authentic **4**.

2-Anilino-4,7-dihydro-1,3-thiazepine (6).—To a solution of 2.3 g of 2-vinylaziridine in 20 ml of ether cooled to 0° was added dropwise 4.5 g of phenyl isothiocyanate. A white solid precipitated. About 3 ml of petroleum ether (bp 30–60°) was added to complete the precipitation of **6**. The crude **6** was filtered and washed with a 1:1 mixture of ether–petroleum ether (bp 30–60°) giving 4.0 g (59%) of crude **6**; recrystallization from 4:1 petroleum ether (bp 100–115°)–1-propanol, gave **6**, mp 138–141°.

Anal. Calcd for $C_{11}H_{12}N_2S$: C, 64.67; H, 5.92; N, 13.71. Found: C, 64.63; H, 6.11; N, 13.56.

2-(*p*-Chlorophenyl)-4,7-dihydro-1,3-thiazepine (7).—To a slurry of 7.4 g of *p*-chlorothiobenzoylthioglycolic acid in 75 ml of water was added 3.1 g of sodium bicarbonate in small portions with shaking. About 100 ml of ether and 2.2 g of vinylaziridine was added to the reaction mixture which was then stirred for 1.5 hr. The ether layer was separated, the solvent evaporated, and the residue dissolved in hexane. The hexane solution was chromatographed on alumina using hexane as the eluent giving 3.4 g of crude **7**. Dissolution in hexane and cooling to −10° gave white crystals which melted at room temperature.

Registry No.—**1**, 31417-81-9; **2**, 31417-82-0; **3**, 31417-83-1; **4**, 31417-84-2; **6**, 31417-85-3; **7**, 31417-86-4.

Acknowledgment.—This investigation was supported by Public Health Research Grant CA 10015.

(7) Y. Iwakura, A. Nabeya, T. Nishiguchi, and K. H. Ohkawa, *J. Org. Chem.*, **31**, 3352 (1966).

(8) E. L. Stogryn and S. J. Brois, *J. Amer. Chem. Soc.*, **89**, 605 (1967).

(9) L. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press, London, 1959, pp 62, 88.

Reactions of 2-*p*-Nitrophenyl-4,7-dihydro-1,3-oxazepine

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Reactions of 2-*p*-nitrophenyl-4,7-dihydro-1,3-oxazepine (**1**) with electrophilic reagents such as bromine or iodine form the ring-contracted products 2-*p*-nitrophenyl-5-(1,2-dibromoethyl)-2-oxazoline (**2**) and 2-*p*-nitrophenyl-5-vinyl-2-oxazoline (**3**), respectively. Compound **1** is also isomerized by sulfuric acid, iodide ion, and bromide ion into **3** but with methoxide ion, cyanide ion, triethylamine, and thiocyanate ion **1** is rearranged into *cis*-1-*p*-nitrobenzamido-1,3-butadiene (**5**). Treatment of *N*-(4-iodo-2-butenyl)-*p*-nitrobenzamide (**4a**) and *N*-(2-iodo-3-butenyl)-*p*-nitrobenzamide (**12**) with sodium hydride gave *N*-*p*-nitrobenzoyl-3-pyrroline (**13**) and **3**, respectively.

The synthesis and rearrangement of 1-*p*-nitrobenzoyl-2-vinylaziridine into 2-*p*-nitrophenyl-4,7-dihydro-1,3-oxazepine (**1**) has been recently reported.[1] In this paper the ring openings and rearrangements of **1** by various electrophiles, nucleophiles, and bases are described.

(1) P. G. Mente, H. W. Heine, and G. R. Scharoubim, *J. Org. Chem.*, **33**, 4547 (1968).

Results

Treatment of **1** with bromine formed 2-*p*-nitrophenyl-5-(1,2-dibromoethyl)-2-oxazoline (**2**) in 48% yield (Scheme I). The structure of **2** was established by an alternate synthesis involving the addition of bromine to the known 2-*p*-nitrophenyl-5-vinyl-2-oxazoline (**3**)[1] and by nmr spectroscopy. Other electrophilic reagents also caused the ring contraction of **1**. For example,