Table II
Important Data on the Diphenyl-*N*-(substituted)ketenimines

Ketenimines	Isolated Yield,[a] %	Nmr (CCl_4, δ)	Ir (cm^{-1})
6[b]	75–80	1.40 (9 H) s, 7.1–7.4 (10 H) m	2020
7[c]	65–70	4.73 (2 H) s, 7.0–7.4 (15 H) m	2020
8[d]	80–85	1.65 (3 H) d, 4.88 (1 H) q, 7.0–7.4 (15 H) m	2020

[a] After chromatography on alumina. [b] See ref 6 for combustion data. [c] Calcd for $C_{21}H_{17}N$: C, 89.01; H, 6.05; N, 4.94. Found: C, 88.94; H, 6.14; N, 4.90. [d] Calcd for $C_{22}H_{19}N$: C, 88.85; H, 6.44; N, 4.71. Found: C, 88.74; H, 6.52; N, 4.65.

Experimental Section[7]

Alkylaminotriphenylphosphonium Bromides. Into a 300-ml three-necked flask equipped with a pressure-equalized addition funnel, a reflux condenser with a drying tube and an efficient electric stirrer was added 100 ml of benzene (reagent) and 0.1 mol of triphenylphosphine. The solution was cooled in an ice bath and 0.1 mol of bromine was added dropwise to the stirred solution over 0.5 hr. The mixture was stirred for an additional 0.5 hr (bromine color discharged), and a mixture of 0.1 mol of triethylamine and 0.1 mol of primary amine was added dropwise at ice bath temperature over 0.5 hr. The mixture was stirred for 1 hr at ice bath temperature, and the resulting precipitate was collected, washed with ether, and then water. The solid was dissolved in 50 ml of chloroform and crystallized by addition of 500 ml of ethyl acetate. Isolated yields were in excess of 95% in all cases.

Triphenylphosphinalkylimines. Into a 500-ml flask equipped with a reflux condenser fitted at the top with a nitrogen inlet tube, and arranged for magnetic stirring, was placed 20 mmol of the above prepared alkylaminophosphonium bromide, 50 mmol of potassium hydroxide pellets, and 250 ml of anhydrous ether. The mixture was stirred under nitrogen for 20–40 hr at room temperature. The mixture was then filtered and the ether removed *in vacuo*. The resulting solid was crystallized from cyclohexane. The isolated yields of the triphenylphosphinalkylimines were in excess of 75% in all cases.

Diphenyl-*N*-(substituted)ketenimines. Into a 500-ml three-necked flask equipped with a pressure-equalized dropping funnel fitted at the top with a nitrogen inlet tube and an efficient electric stirrer was placed 7 mmol of the above prepared triphenylphosphinalkylimine in 200 ml of anhydrous ether. Diphenylketene[8] dissolved in 30 ml of anhydrous ether was added dropwise to the stirred solution over 0.5 hr at room temperature. The mixture was stirred an additional 1 hr and the ether solution was washed three times with ice–water, dried over anhydrous sodium sulfate, and concentrated *in vacuo*. The resulting residue was chromatographed on basic alumina (Woelm) which had been dried at 125° for 2 hr. The ketenimine was recovered in an early fraction by eluting with ether–petroleum ether (4:1). Ketenimines **6**, **7**, and **8** were prepared in this way.

In the case of the preparation of diphenyl-*N*-(diphenylmethyl)ketenimine (**9**), the characteristic ketenimine band at 2020 cm^{-1} was noted in the ir of the crude reaction mixture. However, after concentration of the ether solution, the 2020-cm^{-1} band was gone. Chromatography yielded a material identified as 2,2,3,3-tetraphenylpropionitrile by comparison with a sample independently prepared by a phase transfer reaction.[9]

(*S*)-(−)-Diphenyl-*N*-(1-phenylethyl)ketenimine. (*S*)-(−)-**8** was prepared by the above procedures starting from (*S*)-(−)-1-phenylethylamine (Norse Chemical Co., Santa Barbara, Calif.). The optical purity of (*S*)-(−)-**8** was demonstrated as follows. (*S*)-(−)-**8** was hydrolyzed to the corresponding amide by a slight modification of a procedure described by Stevens and Singhal.[5] To a solution of 100 mg of (*S*)-(−)-**8** in 5 ml of acetone was added 0.5 ml of 4 *N* hydrochloric acid. The mixture was allowed to stand at room temperature for 2 hr. The solution was then cooled to 5° and water was added slowly until no further white precipitate formed. The mixture was placed in a refrigerator (5°) overnight and then filtered. The solid was collected, dried, and recrystallized from cyclohexane–hexane to give a 95% yield of amide, mp 116.0–116.5°, $[\alpha]^{25}D$ −39.6° (c = 1.2, $CHCl_3$). Amide showing the same properties and specific rotation was prepared by conventional procedures from (*S*)-(−)-1-phenylethylamine and diphenylacetyl chloride.

Registry No.—**6**, 26149-14-4; **7**, 52826-48-9; (*S*)-(−)-**8**, 52826-49-0; (*S*)-(−)-**8** amide derivative, 52826-50-3; **9**, 52826-51-4; benzylamine, 100-46-9; (±)-1-phenylethylamine, 618-36-0; (*S*)-(−)-1-phenylethylamine, 2627-86-3; diphenylmethylamine, 91-00-9; *tert*-butylamine, 75-64-9; triphenylphosphine, 603-35-0; bromine, 7726-95-6; diphenylketimine, 52826-52-5.

References and Notes

(1) L. A. Singer and K. W. Lee, *Chem. Commun.*, in press.
(2) H. Staudinger and E. Hauser, *Helv. Chim. Acta*, **4**, 887 (1921).
(3) H. Zimmer and G. Singh, *J. Org. Chem.*, **28**, 483 (1963).
(4) See G. R. Krow, *Angew. Chem., Int. Ed. Engl.* **10**, 435 (1971), for a review of synthetic procedures of ketenimines. We believe our present work is the first synthesis of an optically active ketenimine.
(5) C. L. Stevens and G. H. Singhal, *J. Org. Chem.*, **29**, 34 (1964).
(6) J. A. Green, II, and L. A. Singer, *Tetrahedron Lett.*, 5093 (1969).
(7) Melting points are uncorrected. Combustion analyses were done by Elek Microanalysis Laboratory, Torrance, Calif. All nmr spectra were obtained on a Varian T-60 NMR Spectrometer. All infrared spectra were recorded on a Perkin-Elmer 337 spectrometer. Optical rotations were obtained on a Perkin-Elmer 141 polarimeter. Concentration units are g/100 ml.
(8) E. C. Taylor, A. Mc Killop, and G. H. Hawks, *Org. Syn.*, **52**, 36 (1973).
(9) M. Makosza and B. Serafin, *Rocz. Chem.*, **39**, 1799 (1965); *Chem. Abstr.*, **64**, 17475g (1966).

A New Route to 2-Vinylaziridines and an Unusual Intramolecular Analog of the SN2′ Reaction Leading to Aziridine Ring Formation

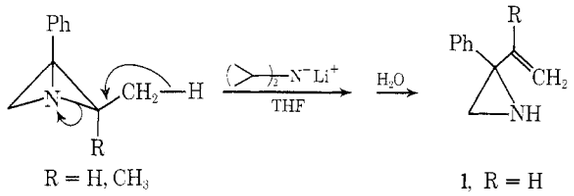
Alfred G. Hortmann* and Ja-young Koo

Department of Chemistry, Washington University, St. Louis, Missouri 63130

Received July 22, 1974

N-Unsubstituted 2-vinylaziridines have been obtained from butadiene[1a] and isoprene[1b] by modification of the Wenker aziridine synthesis, and as by-products in hydride reductions of isophorone oxime.[1c] N-Substituted 2-vinylaziridines have been synthesized *via* nitrene precursors and butadienes[2]

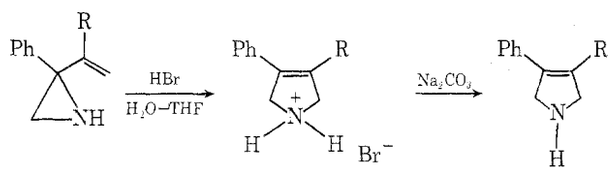
We report here a new method for the synthesis of certain N-unsubstituted 2-vinylaziridines by treatment of 2-methyl-substituted 1-azabicyclobutanes with strong base. Thus we have obtained 2-phenyl-2-vinylaziridine (**1**) and 2-phenyl-2-(2-propenyl)aziridine (**2**) from the reaction of *exo*-2-methyl-3-phenyl-1-azabicyclobutane[3] and 2,2-dimethyl-3-phenyl-1-azabicyclobutane,[3] respectively, with lithium diisopropylamide in THF.



The E2 or E1cB type of elimination which is occurring here involves the formation of an aziridinamide anion as a leaving group. It is noteworthy that such loss of a strongly basic amide anion is probably unknown to occur in elimination reactions.[4] The concommitant relief of ring strain is probably an important factor which allows the above reaction to proceed; in addition, coordination of Li^+ to the N of the azabicyclobutane may play an important role in giving the nitrogen more leaving-group character akin to that of the positively charged N in ammonium salts which can undergo Hofmann-type elimination.

2-Vinylaziridines are of interest as possible substrates for conversion to Δ^3-pyrrolines *via* thermal isomerization[5]

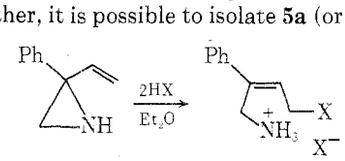
in analogy to the vinylcyclopropane–cyclopentene rearrangement.[6] Hence we examined the pyrolysis of **1** and **2** in high-boiling solvents. Heating **1** in decalin at 160–170° for periods of 1–3 hr led to partial decomposition of **1**, but no peaks corresponding to Δ^3-pyrroline **3** were observed in the nmr spectrum of the crude product. Similarly, heating **2** in decalin at 175–180° (2 hr under N_2) and in refluxing phenetol [bp 171–174° (3 hr, N_2)] led to complete decomposition of **2**, but no formation of Δ^3-pyrroline **4** was observed as evidenced by lack of absorption for $-CH_2N-$ in the δ 2.5–4.0 region of the nmr spectra of the crude products. No change occurred when **2** was heated in refluxing xylene (~140°) for 2 hr.



1, 2 3·HBr, R = H 3, R = H; 4, R = CH_3

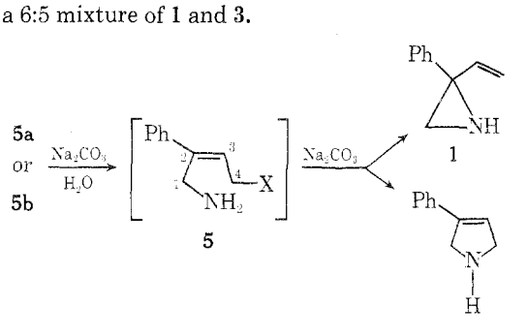
A simple procedure was finally developed whereby **1** could be converted to **3** in fairly high yield. Treatment of **1** with HBr–H_2O in THF for 6 hr at 25–30° led to the formation of the hydrobromide salt of **3** in 70% yield. Treatment of **3** · HBr with Na_2CO_3 afforded the free Δ^3-pyrroline **3**. Attempts to develop a similar route to **4** by way of a clean conversion of **2** to **4** · HBr or **4** · HCl came to naught.

In considering the reaction of **1** with HBr–H_2O–THF which led directly to **3** · HBr, it was presumed that **5a** was a likely intermediate. Indeed, in subsequent work it was found that when **1** is treated with gaseous HBr (or HCl) in anhydrous ether, it is possible to isolate **5a** (or **5b**) directly.



1 **5a**, X = Br; **b**, X = Cl

Neutralization of **5a** with Na_2CO_3 in H_2O led, surprisingly, to a mixture of **1** and **3** in a ratio of 1:1. Similarly, **5b** gave a 6:5 mixture of **1** and **3**.



The formation of **3** is taken as proof of the *Z* stereostructures drawn for **5a** and **5b**. The concommitant formation of **1** as a major product suggests that the approach of N in bonding to C-2 from above the plane of the carbon skeleton of **5** can be, with the aid of the C-2–C-3 π system, synchronous with the departure of X^- from above or below the plane of the carbon skeleton. Whereas the π system can be intimately involved in the stabilization of the transition state of this process leading to **1**, which has its intermolecular analogy in the SN2′ reaction, it is orthogonal to the collinear N---C---X system involved in the transition state leading to **3** which has its intermolecular analogy in the SN2 process. Hence, the stabilization afforded by the involvement of the π system in the former SN2′-like process apparently can compensate for the appreciable strain energy which must be introduced during the simultaneous formation of the three-membered ring system, and thus allows this SN2′-like process leading to aziridine ring formation to compete effectively with five-membered pyrroline ring formation which would normally appear to be the transformation more likely to occur.[7,8]

Experimental Section[9]

2-Phenyl-2-vinylaziridine (1). *n*-Butyllithium (0.036 mol; 15.3 ml of a 21.3% solution in hexane; Alfa Inorganics) was added dropwise to a solution of *exo*-2-methyl-3-phenyl-1-azabicyclobutane[3] (3.0 g, 0.021 mol) and diisopropylamine (3.6 g, 0.036 mol) in 65 ml of anhydrous THF during a period of 6–10 min under N_2 while stirring vigorously. The temperature of the reaction was maintained at 35° for 5 hr. Water (40 ml) was added and the resulting mixture was extracted with CH_2Cl_2; the extracts were combined and dried over anhydrous K_2CO_3. Evaporation of the solvent *in vacuo* left an orange oil. Distillation afforded 1.45 g (48%) of 2-phenyl-2-vinylaziridine (**1**), bp 58–60° (0.4 mm), which was pure enough for most purposes. A sample of analytically pure **1** was obtained by evaporative distillation: bp 55–60° (0.4 mm); nmr ($CDCl_3$) δ 0.90 (br s, 1), 2.07 (s, 1), 2.13 (s, 1), 4.93 (dd, 1, J = 17, 1.5 Hz), 5.12 (dd, 1, J = 10, 1.5 Hz), 5.85 (dd, 1, J = 17, 10 Hz), 7.33 (m, 5); ir (CCl_4) 3310, 1632, 1220, 1139, 1108, 918, 890, 692 cm^{-1}; uv max (cyclohexane) 198 nm (ϵ 24,000), 243 (1300 sh). *Anal.* Calcd for $C_{10}H_{11}N$: C, 82.72; H, 7.64; N, 9.65. Found: C, 82.80; H, 7.62; N, 9.62.

2-Phenyl-2-(2-propenyl)aziridine (2). *n*-Butyllithium in hexane (0.038 mol; 16.2 ml of a 21.3% solution) was added dropwise to a solution of 2,2-dimethyl-3-phenyl-1-azabicyclobutane[3] (3.0 g, 0.019 mol) and diisopropylamine (3.8 g, 0.038 mol) in 40 ml of anhydrous THF during a period of 6–10 min at room temperature and under N_2 while stirring vigorously. Stirring was continued for 7 hr at 47°. Workup as described for **1** afforded 1.55 g (52%) of 2-phenyl-2-(2-propenyl)aziridine (**2**) [bp 60–63° (0.3 mm)]. Redistillation afforded analytically pure **2**: bp 60–63° (0.3 mm); nmr ($CDCl_3$) δ 0.98 (br s, 1), 1.74 (m, 3), 2.05 (s, 1), 2.18 (s, 1), 4.98 (m, 1), 5.05 (m, 1), 7.33 (m, 5); ir (CCl_4) 3310, 1645, 1230, 1190, 1140, 910-870, 690 cm^{-1}; uv max (cyclohexane) 198 nm (ϵ 26,000), 215 (8600sh), 258 (366). *Anal.* Calcd for $C_{11}H_{13}N$: C, 82.97; H, 8.23; N, 8.80. Found: C, 82.65; H, 8.29; N, 8.78.

Δ^3-3-Phenylpyrroline Hydrobromide (3 · HBr). A solution of 48% HBr (sp. gr. 1.5; 0.42 g, 0.0025 mol) in 10 ml THF was slowly added during *ca.* 30 min to a solution of 2-phenyl-2-vinylaziridine (**1**) (0.30 g, 0.00207 mol) in 15 ml of THF while stirring under N_2. Stirring was continued for 6 hr at 25–30° under N_2. Upon reduction of the volume of the solution to *ca.* 8 ml, small needle-like crystals separated. The crystals were filtered and washed with THF–ether (1:1). Reduction of the volume of the combined mother liquor and washings and addition of ether caused further precipitation. The total yield of crystalline **3** · HBr was 0.32 g (70%) which was pure by nmr assay. Recrystallization from acetonitrile gave analytically pure **3** · HBr: mp 159.5–160.5°; nmr (D_2O) δ 4.18 (m, 2), 4.32 (m, 2), 6.13 (quintet, 1, J = 2 Hz), 7.32 (s, 5); ir (KBr pellet) 3000–2580, 1575, 1400, 1150, 1040, 750, 690 cm^{-1}; uv max (EtOH) 250 nm (ϵ 13,300). *Anal.* Calcd for $C_{10}H_{12}NBr$: C, 53.12; H, 5.35; N, 6.19. Found: C, 52.95; H, 5.31; N, 6.17.

Δ^3-3-Phenylpyrroline (3). A solution of **3** · HBr (140 mg, 0.62 mmol) in 5 ml of H_2O was added dropwise to a stirred solution of Na_2CO_3 (0.3 g) in 25 ml of H_2O. Extraction of the resulting white suspension with CH_2Cl_2 followed by drying (K_2CO_3) and evaporation of the extracts afforded **3** (76 mg; 85% yield) as a pale yellow solid. Sublimation [50° (0.2 mm)] gave small crystals of **3**: mp 120–125°; nmr ($CDCl_3$) δ 2.66 (br s, 1), 3.77–4.22 (symmetrical m, 4), 6.16 (quintet, 1, J = 2 Hz), 7.27 (m, 5); ir (KBr) 3440, 1600, 1575, 1400, 1050, 750, 698 cm^{-1}; ir (CH_2Cl_2) 3360, 1603, 1578, 1500, 1410, 1070, 1040, 820 cm^{-1}; uv max (EtOH) 254 nm (ϵ 11,800). The results of three analyses (two of sublimed material) were erratic and not in good agreement with theory; the combined C, H, and N percentages in each case totaled less than 100% suggesting that some air oxidation of the samples had occurred before analysis.

(*Z*)-1-Amino-4-bromo-2-phenyl-2-butene Hydrobromide (5a). Gaseous HBr was rapidly passed through a solution of 2-phenyl-2-vinylaziridine (200 mg, 1.4 mmol) in 20 ml of ether. A pale purple precipitate (350 mg) formed. Recrystallization from aceto-

nitrile yielded 140 mg (34%) of **5a** as a white amorphous solid. An additional recrystallization afforded analytically pure **5a:** mp 148.5–150° (uncor.); nmr (DMSO-d_6) δ 4.10 (br s, 2), 4.46 (d, 2, J = 8.5 Hz), 6.35 (t, 1, J = 8.5 Hz), 7.47 (m, 5), 8.13 (broad peak, 3); nmr (D_2O) δ 4.34 (br s, 2), 4.40 (d, 2, J = 8.5 Hz), 6.43 (t, 1, J = 8.5 Hz), 7.56 (s, 5); ir (KBr) 3020–2600, 1595–1580, 1490, 1200, 1110, 760, 690 cm^{-1}; uv max (EtOH) 252 nm (ϵ 11,700). *Anal.* Calcd for $C_{10}H_{13}NBr_2$: C, 39.12; H, 4.27; N, 4.56. Found: C, 39.24; H, 4.26; N, 4.51.

(*Z*)-1-Amino-4-chloro-2-phenyl-2-butene Hydrochloride (5b). Gaseous HCl was rapidly passed through a solution of 2-phenyl-2-vinylaziridine (1) (200 mg, 1.4 mmol) in 20 ml of ether. A pale orange precipitate (200 mg) which was obtained afforded 120 mg (40%) of **5b** upon recrystallization from acetonitrile. One additional recrystallization gave analytically pure **5b:** mp 154–155° (uncor); nmr (DMSO-d_6) δ 4.03 (br s, 2), 4.56 (d, 2, J = 8 Hz), 6.24 (t, 1, J = 8 Hz), 7.46 (m, 5), 8.45 (broad peak, 3); nmr (D_2O) δ 4.18 (br s, 2), 4.35 (d, 2, J = 8 Hz), 6.18 (t, 1, J = 8 Hz), 7.43 (s, 5); ir (KBr) 3000–2610, 1590, 1210, 1110, 1000–990, 770, 696 cm^{-1}; uv max (EtOH) 245 nm (ϵ 11,600). *Anal.* Calcd for $C_{10}H_{13}NCl_2$: C, 55.06; H, 6.01; N, 6.42. Found: C, 54.56; H, 5.95; N, 6.40.

Neutralization of 5a. The hydrobromide **5a** (60 mg, 0.20 mmol) was dissolved in DMSO and treated with Na_2CO_3 as described below for **5b.** Following the usual workup procedure, the nmr spectrum of the crude product showed that **1** and **3** were present in a ratio of 1:1. Approximately 10% of other impurities were also present.

Neutralization of 5b. A solution of **5b** (60 mg, 0.28 mmol) in 0.6 ml of DMSO (or alternatively, 2 ml of H_2O) was rapidly added to a solution of 0.4 g of Na_2CO_3 in 20 ml of water with stirring. Stirring was continued for 10 min. The mixture was extracted with CH_2Cl_2. The extracts were combined, dried over K_2CO_3, and evaporated *in vacuo.* An nmr spectrum of the crude product showed the presence of only two compounds, **1** and **3.** The ratio of **1** to **3** was 6:5 by nmr assay.

Acknowledgments. We thank the Alfred P. Sloan Foundation, the National Science Foundation, and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for financial support.

Registry No.—**1,** 52906-57-7; **2,** 52906-58-8; **3,** 52906-59-9; **3** HBr, 52906-60-2; **5a,** 52951-32-3; **5b,** 52906-61-3; *exo*-2-methyl-3-phenyl-1-azabicyclobutane, 35903-66-3; 2,2-dimethyl-3-phenyl-1-azabicyclobutane, 35903-67-4; diisopropylamine, 108-18-9.

References and Notes

(1) (a) E. L. Stogryn and S. J. Brois, *J. Amer. Chem. Soc.,* **89,** 605 (1967); (b) A. Mishra, S. N. Rice, and W. Lwowski, *J. Org. Chem.,* **33,** 481 (1968); (c) L. Ferrero, M. Rouillard, M. Decouzon, and M. Azzaro, *Tetrahedron Lett.,* 131 (1974).

(2) (a) R. S. Atkinson and C. W. Rees, *Chem. Commun.,* 1230 (1967); (b) P. Scheiner, *J. Org. Chem.,* **32,** 2628 (1967); (c) see ref 1b.

(3) A. G. Hortmann and D. A. Robertson, *J. Amer. Chem. Soc.,* **94,** 2758 (1972).

(4) See *e.g.,* W. H. Saunders, Jr., and A. F. Cockerill, "Mechanisms of Elimination Reactions," Wiley-Interscience, New York, N.Y., 1973, pp 3, 4.

(5) Several N-substituted 2-vinylaziridines have been studied in this regard: see ref 1b above and also (a) R. S. Atkinson and C. W. Rees, *Chem. Commun.* 1232 (1967); 631 (1968); *J. Chem. Soc. C,* 778 (1969); (b) T. L. Gilchrist, C. W. Rees, and E. Stanton, *ibid.,* 3036 (1971). No simple N-unsubstituted 2-vinylaziridines have been observed to rearrange in this manner. Conversion to Δ^2-pyrrolines has also been observed: D. Borel, Y. Gelas-Mialhe, and R. Vessiere, *C. R. Acad. Sci., Ser. C,* **278,** 1393 (1974).

(6) (a) W. von E. Doering and J. B. Lambert, *Tetrahedron,* **19,** 1989 (1963); (b) C. S. Elliott and H. M. Frey, *J. Chem. Soc.,* 4289 (1965); (c) M. R. Willcott and V. H. Cargle, *J. Amer. Chem. Soc.,* **89,** 723 (1967); **91,** 4310 (1969); (d) J. W. Swenton and A. Wexler, *ibid.,* **93,** 3066 (1971), and references cited.

(7) It is noteworthy that the existence of the concerted "SN2′" mechanism is in dispute: see F. G. Bordwell, *Accounts Chem. Res.,* **3,** 281 (1970); F. G. Bordwell and T. G. Mecca, *J. Amer. Chem. Soc.,* **94,** 5829 (1972); P. B. D. de la Mare and C. Vernon, *J. Chem. Soc. B,* 1699 (1971); J. A. Hemmingson and B. D. England, *ibid.,* 1347 (1971).

(8) A number of reports concerned with formation of a *cyclopropyl* ring in homoallylic systems by an *inter*molecular SN2′-type mechanism have appeared: see M. Hanack and K. Görler, *Chem. Ber.,* **96,** 2121 (1963), and references cited; M. Hanack, *et al., Justus Liebigs Ann. Chem.,* **717,** 41 (1968). For examples of vinylcyclopropane and vinylbicyclobutane formation *via* intramolecular SN2′ reactions, see D. Schönleber, *Chem. Ber.,* **102,** 1789 (1969); H. K. Hall, Jr., and R. E. Yancy, III, *J. Org. Chem.,* **39,** 2862 (1974).

(9) All melting points and boiling points are uncorrected. The following spectrometers were used: nmr, Varian A-60A; ir, Perkin-Elmer 457; uv, Cary 14. Microanalyses were performed by Galbraith Laboratories, Knoxville, Tenn.

Bridgehead Nitrogen Heterocycles. VIII. Dimroth Rearrangement of 3*H*-1,2,4-Thiadiazolopyrimidines[1]

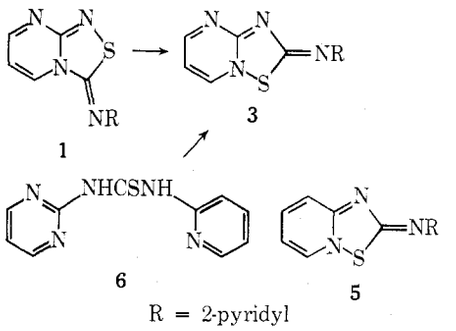
K. T. Potts* and J. Kane

Department of Chemistry, Rensselaer Polytechnic Institute, Troy, New York 12181

Received July 22, 1974

In a recent publication[2] the reaction of perchloromethyl mercaptan with 2- and 4-aminopyrimidines to give derivatives of the 3*H*-1,2,4-thiadiazolo[4,3-*a*]- and -[4,3-*c*]pyrimidine systems **1** (R = substituted-2-pyridyl or aryl) and **2** was described. Ring closure to the isomeric 2*H*-1,2,4-thiadiazolo[2,3-*a*]- and -[2,3-*c*]pyrimidine systems **3** (R = substituted-2-pyridyl or aryl) and **4** was excluded on the basis of the similar spectral characteristics of **1** and **2** and the 3*H*-1,2,4-thiadiazolo[4,3-*a*]pyridine[3] system. Confirmation of the initial structural assignments has now been obtained by the isolation and characterization of systems **3** and **4** by Dimroth-type rearrangement[4a] of **1** and **2** and by the independent synthesis of **3.**

Dimroth-type rearrangements have been reported[4b] in a variety of ring-fused pyrimidine systems and the *s*-triazolo[4,3-*a*]- and -[4,3-*c*]pyrimidine systems have been found to undergo facile rearrangement in either acid or alkaline medium.[5,6] It was therefore anticipated that systems **3** and **4** could be prepared by the Dimroth-type rearrangements of **1** and **2** and, indeed, treatment of 3-(2-pyridylimino)-3*H*-1,2,4-thiadiazolo[4,3-*a*]pyrimidine (**1,** R = 2-pyridyl) with either 10% ethanolic HCl or 10% ethanolic NaOH resulted in the formation of 2-(2-pyridylimino)-2*H*-1,2,4-thiadiazolo[2,3-*a*]pyrimidine (**3,** R = 2-pyridyl).



The structure of **3** is based on the close relationship of its spectral data[7] to that of **5** (R = 2-pyridyl) and on its alternative synthesis by the sulfuryl chloride oxidation of thiourea **6.**

Under similar conditions 5,7-dimethyl-3-(2,6-dimethyl-4-pyrimidylimino)-3*H*-1,2,4-thiadiazolo[4,3-*c*]pyrimidine (**2**) gave no rearranged products; with 10% ethanolic HCl a product for which structure **7** is best in accord with the spectral and analytical data was obtained. Similar results have been obtained[6,8] in the Dimroth rearrangement of the *s*-triazolo[2,3-*c*]- and -[4,3-*c*]pyrimidine systems. Attempted rearrangement in 10% ethanolic NaOH gave a product which corresponded to the addition of water to the starting material. All available data are in agreement with its formulation as Dimroth intermediate **8** and the isolation of such intermediates, although rare, is not without precedent.[9] Hydrolysis of **8** in 10% ethanolic HCl again resulted in the formation of ketone **7** (Scheme I).

Refluxing **8** in $POCl_3$ for 1 hr resulted in the formation of 5,7-dimethyl-2-(2,6-dimethyl-4-pyrimidylimino)-2*H*-1,2,4-thiadiazolo[2,3-*c*]pyrimidine (**4**). It is particularly interesting to note that the nmr spectrum of **4** showed only two signals for the four methyl groups and a single signal for the two aromatic protons suggesting that structure **4**