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.

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(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]

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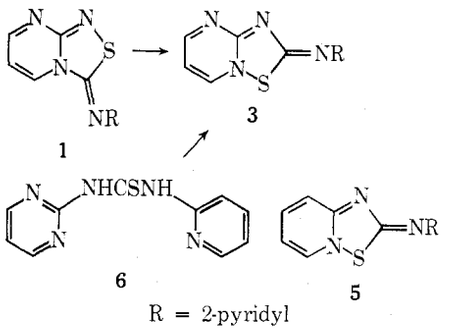
In a recent publication[2] the reaction of perchloromethyl mercaptan with 2- and 4-aminopyrimidines to give derivatives of the 3*H*-1,2,4-thiadiazolo[4,3-*a*]- and -[4,3-*c*]pyrimidine systems **1** (R = substituted-2-pyridyl or aryl) and **2** was described. Ring closure to the isomeric 2*H*-1,2,4-thiadiazolo[2,3-*a*]- 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).

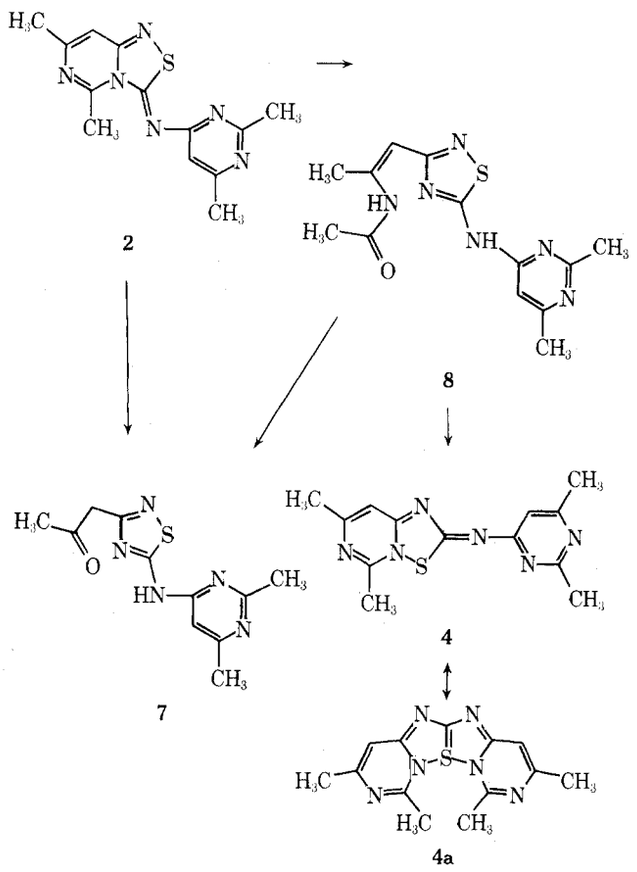


The structure of **3** is based on the close relationship of its spectral data[7] to that of **5** (R = 2-pyridyl) and on its alternative synthesis by the sulfuryl chloride oxidation of thiourea **6.**

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**

Scheme I



may best be represented as a resonance hybrid (4 ↔ 4a) reminiscent of the 1,6,6a-S^{IV}-trithiapentalenes.[10] Similar conclusions have been drawn[7] in order to explain the properties of **5** (R = 2-pyridyl).

Experimental Section[11]

2-(2-Pyridylimino)-2*H*-1,2,4-thiadiazolo[2,3-*a*]pyrimidine[12] (3, R = 2-pyridyl). 3-(2-Pyridylimino)-3*H*-1,2,4-thiadiazolo[4,3-*a*]pyrimidine (0.23 g) was suspended in a stirred solution of 10% HCl (10 ml) and ethanol (20 ml). The reaction mixture quickly achieved homogeneity and was stirred for 3 hr before being neutralized with $NaHCO_3$. The solvent was removed from the reaction mixture and the residue was extracted with a $CHCl_3$–H_2O mixture. Drying of the $CHCl_3$ layer over Na_2SO_4 and subsequent evaporation to dryness gave a yellow solid which, when treated with acetone (*ca.* 3 ml), gave pale yellow, irregular prisms: 0.20 g (87%); mp 254–255° dec; ir (KBr) 3000 (CH), 1620 (C=N) cm^{-1}; $\lambda_{max}^{CH_3OH}$ 344 nm (log ϵ 4.28), 293 (4.26), 247 (4.16), 235 (4.18), 215 (4.17); nmr (D_2O) δ 6.47–8.25 (m, 7, aromatic); mass spectrum *m/e* (rel intensity) $M^{\cdot+}$ 229 (100).

Anal. Calcd for $C_{10}H_7N_5S$: C, 52.38; H, 3.08; N, 30.55. Found: C, 52.15; H, 2.99; N, 30.32.

***N*-(2-Pyridyl)-*N'*-(2-pyrimidyl)thiourea (6).** *S*-Methyl *N*-(2-pyridyl)dithiocarbamate[13] (14.7 g), 2-aminopyrimidine (7.6 g), and toluene (200 ml) were refluxed for 18 hr. Filtration of the cooled reaction mixture gave a cream solid which crystallized from ethanol as colorless, matted needles: 9.1 g (49%), mp 203–204° dec; ir (KBr) 3200 (NH), 3000 (CH) cm^{-1}; $\lambda_{max}^{CH_3OH}$ 287 nm (log ϵ 4.44), 270 (4.38); nmr ($CDCl_3$) δ 7.20, 7.83, 8.85 (3 m, 7, aromatic), 8.50, 9.60 (2 broad s, 2, NH); mass spectrum *m/e* (rel intensity) $M^{\cdot+}$ 231 (100).

Anal. Calcd for $C_{10}H_9N_5S$: C, 51.93; H, 3.92; N, 30.28. Found: C, 51.70; H, 3.76; N, 30.47.

Alternative Synthesis of 3. Sulfuryl chloride (2.80 g) in dry $CHCl_3$ (10 ml) was added to a stirred solution of **6** (4.60 g) and dry $CHCl_3$ (100 ml). After refluxing for 15 min the reaction mixture was cooled and filtered. The precipitate was dissolved in H_2O and neutralized with $NaHCO_3$. The aqueous solution was extracted with $CHCl_3$ which was separated and dried over Na_2SO_4. Evaporation to dryness gave a yellow solid which, when treated with acetone, gave pale yellow, irregular prisms, identical in all respects with **3**: 1.0 g (22%), mp 254–255° dec, mmp 254–255° dec.

3-Acetonyl-5-(2,6-dimethyl-4-pyrimidylamino)-1,2,4-thiadiazole (7). The thiadiazolopyrimidine **2** (0.20 g) was stirred for 3 hr in 10% HCl (10 ml) and ethanol (10 ml). Neutralization with $NaHCO_3$ and filtration of the resulting precipitate gave a colorless solid which crystallized from aqueous ethanol as colorless, matted needles: 0.17 g (92%), mp 185–186°; ir (KBr) 3350 (NH), 3000 (CH), 1700 (CO), 1620 (C=N) cm^{-1}; $\lambda_{max}^{CH_3OH}$ 290 nm (log ϵ 4.29), 260 sh (3.82); nmr ($CDCl_3$) δ 2.22, 2.40, 2.58 (3 s, 9, CH_3), 3.40 (broad s, 1, NH), 3.95 (s, 2, CH_2), 6.78 (s, 1, aromatic); mass spectrum *m/e* (rel intensity) $M^{\cdot+}$ 263 (56).

Anal. Calcd for $C_{11}H_{13}N_5OS$: C, 50.17; H, 4.97; N, 26.60. Found: C, 50.34; H, 5.02; N, 26.58.

3-(2-Acetylamino-1-propen-1-yl)-5-(2,6-dimethyl-4-pyrimidylamino)-1,2,4-thiadiazole (8). The thiadiazolopyrimidine **2** (0.20 g) and 10% NaOH solution (10 ml) and ethanol (10 ml) were stirred for 2 hr at room temperature. Subsequent neutralization with 10% HCl and filtration gave a colorless solid which crystallized from $CHCl_3$ as colorless, irregular prisms:[14] 0.20 g (94%); mp ~270° dec; ir (KBr) 3250 (NH), 3000 (CH), 1680, 1670, 1610 (CO, NC=C, C=N) cm^{-1}; $\lambda_{max}^{CHCl_3}$ 287 nm (log ϵ 4.64); mass spectrum *m/e* (rel intensity) $M^{\cdot+}$ 304 (100).

Anal. Calcd for $C_{13}H_{16}N_6OS$: C, 51.29; H, 5.30; N, 27.61. Found: C, 51.14; H, 5.21; N, 27.41.

Hydrolysis of 8. The acetyl derivative **8** (0.10 g) was stirred for 2 hr in 10% HCl (5 ml) and ethanol (5 ml). Neutralization with $NaHCO_3$ and subsequent reduction in volume gave a colorless solid identical in all respects with **7**: 0.08 g (92%); mp 185–186°, mmp 185–186°.

5,7-Dimethyl-2-(2,6-dimethyl-4-pyrimidylimino)-2*H*-1,2,4-thiadiazolo[2,3-*c*]pyrimidine (4). The acetyl derivative **8** (0.20 g) and $POCl_3$ (20 ml) were refluxed for 1 hr. The reaction mixture was evaporated and the residue was triturated with methanol in order to decompose any residual $POCl_3$. After the methanol had been removed, the concentrate was dissolved in H_2O and neutralized with $NaHCO_3$. The aqueous solution was extracted with $CHCl_3$ and the $CHCl_3$ extract was separated and dried over Na_2SO_4. Evaporation to dryness gave a cream solid which crystallized from ethanol as colorless needles: 0.06 g (32%); mp ~370° dec; ir (KBr) 3050 (CH), 1620 (C=N) cm^{-1}; $\lambda_{max}^{CH_3OH}$ 344 nm (log ϵ 4.63), 255 sh (4.07), 237 (4.22); nmr ($CDCl_3$) δ 2.52, 2.83 (2 s, 6, CH_3), 7.08 (s, 1, aromatic); mass spectrum *m/e* (rel intensity) $M^{\cdot+}$ 286 (100).

Anal. Calcd for $C_{13}H_{14}N_6S$: C, 54.52; H, 4.93; N, 29.35. Found: C, 54.10; H, 4.93; N, 29.07.

Registry No.—**1** (R = 2-pyridyl), 40899-19-2; **2**, 40899-28-3; **3** (R = 2-pyridyl), 52856-33-4; **4**, 52906-78-2; **6**, 52827-10-8; **7**, 52827-11-9; **8**, 52827-12-0; *S*-methyl-*N*-(2-pyridyl)dithiocarbamate, 13037-46-2; 2-aminopyrimidine, 109-12-6.

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(1) (a) Support of this work by U.S. Public Health Service Research Grant CA 08495, National Cancer Institute, is gratefully acknowledged; (b) NDEA Trainee, 1970–1972; (c) abstracted from the Ph.D. Thesis of J.K. to be submitted Jan 1975.
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(12) The procedure for the alkaline rearrangement of **1** (R = 2-pyridyl) differed only in that neutralization was effected after ~10 min and gave a 73% yield of **3** (R = 2-pyridyl).
(13) E. B. Knott, *J. Chem. Soc.*, 1644 (1956).
(14) Compound **8** was too insoluble for nmr characterization.

A Mechanistic Study on Elimination Reactions over Solid Acid and Base Catalysts

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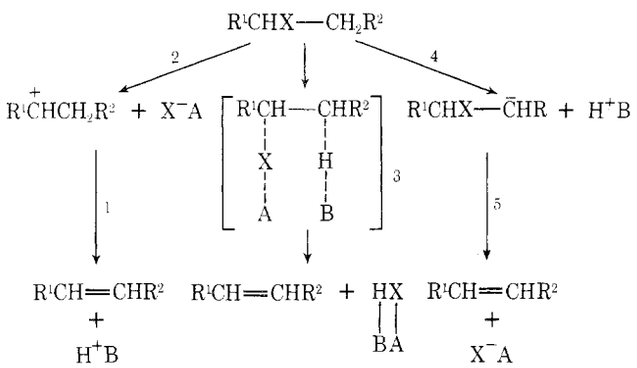
Possible mechanisms[2,3] of ionic HX elimination from haloalkanes over solid catalysts are summarized in Scheme I. By taking account of the rate-determining step, five

Scheme I



(A catalyst consists of acidic (A) and basic (B) sites.)

Type of Elimination Mechanism

Rate-determining step	Intermediate	Abbreviation of mechanisms
1	Carbonium ion	E1
2	Carbonium ion	$E2_{Ca}$
3	Simultaneous cleavage of C–H and C–X bonds	E2 concerted
4	Carbanion	$E2_{Cb}$
5	Carbanion	$E1_{Cb}$

kinds of mechanisms are conceivable. The abbreviations are defined based on the following concept. Suffixes Ca and Cb in the abbreviation of the mechanism mean that carbonium ions and carbanions, respectively, are involved in the elimination process as intermediates. The rate-determining step distinguishes E1 and E2. That is, the step of intermediate formation is rate determining in E2 (except for E2 concerted, which is a one-step reaction), whereas the following step is in E1. E1, E2 concerted, and $E1_{Cb}$ need no comment, although conjugated acid or base of the catalyst might play some roles in $E1_{Cb}$ or E1 over the solid catalyst. $E2_{Ca}$ and $E2_{Cb}$ seem to be possible mechanisms over solid catalysts at elevated temperatures. The differences in these mechanisms can be considered to be present in the degree of C–H or C–X bond fission of the intermediate,[4] so that these mechanisms should change continuously according to the strength of interaction between a substrate and a catalyst. For elimination reactions of a certain reactant over a series of solid catalysts, the reaction may proceed *via* an $E2_{Ca}$ mechanism on a catalyst of moderate acidity, whereas with a basic catalyst it may occur *via* an $E2_{Cb}$ process. The

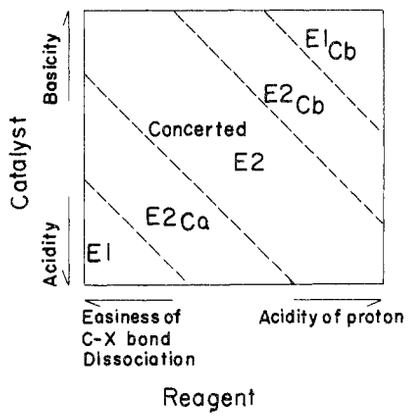


Figure 1. Schematic diagram of mechanism transitions according to the acid–base properties of catalysts and substrates. Abbreviations of mechanisms refer to the text.

E2 concerted mechanism may be possible on a catalyst which is neutral or consists of binary sites of acidity and basicity like alumina.[5] On a catalyst of which acidity or basicity is strong enough, the E1 or $E1_{Cb}$ mechanism may be realized. As for reactants, the same situation should occur. That is, a highly acidic reactant prefers a carbanion-type intermediate and a reactant in which halide is easily eliminated favors a carbonium ion-type intermediate. Continuous changes in acidity or basicity of catalysts and/or substrate structure[2c] may bring about continuous transitions of elimination mechanisms, as schematically described in Figure 1.

In an attempt to study the transitions of elimination mechanisms, the kinetic isotope effects in dehydrohalogenation of 1,2-dibromoethane and 1,1,2,2,-tetrachloroethane and product distributions from 1,1,2-trichloroethane and 1,2-dihalopropanes over some solid catalysts have been investigated. The product distributions from 1,1,2-trichloroethane and reactivity orders of some chloroalkanes over solid catalysts have been explained in terms of $E2_{Ca}$ on solid acids, $E2_{Cb}$ on solid bases, and E2 concerted on alumina in previous papers.[6] Product distributions were found to change continuously according to the acidity of the catalysts.[6] An object of the present study is to understand such a continuous change from a mechanistic aspect.

Experimental Section

Reagents. Haloethanes used were obtained from Tokyo Kasei Co. Deuterated 1,2-dibromoethane ($C_2D_4Br_2$) and 1,1,2,2-tetrachloroethane ($C_2D_4Cl_4$) (Merck) were used without further purification.

Catalysts. Silica–alumina (13% Al_2O_3), alumina, and KOH–SiO_2 were described in previous papers.

Apparatus and Procedures. Elimination reactions were observed by means of microcatalytic gas chromatography with a column of TCP (4m) at 60°. All reactions were carried out at 300° under a helium gas flow of atmospheric pressure. No occurrence of elimination was observable over the glass-wool packing, implying small contribution of simple pyrolysis. The elimination reaction was of first order under the experimental conditions, and the conversion was verified to be a linear function of the reciprocal space velocity (RSV) at low conversions. Thus, the slope of conversion/RSV gives the apparent rate constant, k (ml/g min). Experimental details have been described in previous papers.[8]

Results and Discussion

Product Distributions in Eliminations of Haloalkanes over Solid Catalysts. 1,2-Dihalopropane may give *trans*- and *cis*-1-halopropene (I), allyl halide (II), and 2-halopropene (III) through HX elimination over solid acids and bases. The reaction paths depicted in Schemes II–IV may explain formation of these products by various mecha-