57502-92-8; **7**, 79972-40-0; **8**, 79972-41-1; **9**, 50516-66-0; **10**, 57502-95-1; **11**, 57502-96-2; **12**, 14304-27-9; **13**, 79972-42-2; **14**, 57502-98-4; **15**, 115-19-5; **18**, 79972-43-3; **19**, 79972-44-4; **20**, 54857-48-6; **21**, 2028-63-9; **22**, 29334-61-0; **23**, 3249-33-0; **24**, 107-19-7; **25**, 59223-42-6; **26**, 539-88-8; **27**, 763-19-9; **28**, 79972-45-5; **29**, 5272-33-3; **30**, 79972-46-6; **31**, 2117-12-6; **32**, 79972-47-7; **33**, 5272-36-6; **34**, 79972-48-8; **35**, 78-27-3; **38**, 61065-26-7; **40**, 61065-23-4; **41**, 17356-19-3; **42**, 61065-27-8; **43**, 61065-24-5; **44**, 29171-20-8; **45**, 61096-15-9; **46**, 61096-16-0; **47**, 72-33-3; **48**, 61065-25-6; **49**, 79972-49-9; **50**, 61065-29-0; **51**, 697-37-0; **52**, 79972-50-2; **53**, 1719-19-3; **54**, 61065-28-9; **58**, 1123-27-9; **59**, 66617-41-2; **60**, 66617-42-3; **61**, 66617-44-5; **62**, 66617-43-4; **63**, 66617-39-8; **64**, 66617-45-6; **65**, 53735-49-2; **66**, 66617-46-7; **67**, 66617-47-8; **68**, 79972-51-3; **69**, 71127-55-4; **70**, 79972-52-4; **71**, 79972-53-5; DMA-DEA, 19429-85-7; DMF-DEA, 1188-33-6; DEF-DEA, 22630-13-3; pentyne, 627-19-0; methyl vinyl ketone, 78-94-4; acrolein, 107-02-8; *N,N*-dimethylbenzamide, 611-74-5; *N,N*-dimethylbenzamide diethyl acetal, 19429-87-9; *trans*-3-methoxy-19-norpregna-1,3,5(10),17(20)-tetraen-21-al, 16934-50-2.

Photolysis of Some Chlorinated Pyridazines[1]

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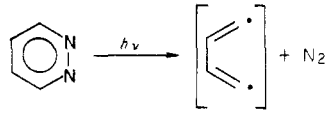
Photorearrangement of chlorinated pyridazines to chlorinated pyrazines proceeds with predictable regiocontrol if radical-stabilizing substituents are located at C_4 and C_5 of the pyridazine ring. Mechanistic studies imply that the chemistry originates from a reactive n,π^* singlet state. An activation barrier of ~4 kcal/mol is encountered as the excited state of tetrachloropyridazine rearranges to tetrachloropyrazine.

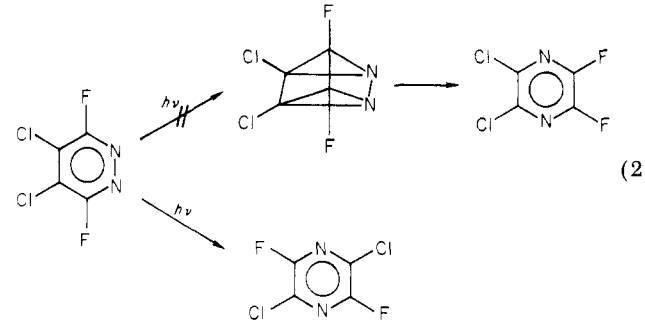
The photochemistry of chlorinated pyridazines is of interest for several reasons. Because they are isoelectronic with aryl chlorides, they may provide insight into the photoreactions of this important class of compounds. The two heteroatoms, however, provide access not only to the π,π^* excited states accessible to aryl halides but also to n,π^* excited states. It may be possible then to discover state-specific photoreactions in these molecules. For example, because of the low-lying n,π^* states, these molecules, in contrast to typical chlorinated benzenes,[2] may resist facile dechlorination; i.e., the lower lying singlet and triplet states are probably insufficiently energetic to induce dissociation of Ar–Cl.[3]

Since the ring system of pyridazines contains two adjacent nitrogen atoms, photoelimination of N_2, a common feature of the photochemical reactions of azines,[4] must be considered. Though correlation diagrams[5] indicate that the concerted loss of nitrogen from the planar lowest excited states of pyridazine (assumed to be planar) is orbital symmetry forbidden, gas-phase photolysis of pyridazine does generate nitrogen and, apparently, a C_4H_4 biradical,[6] (eq 1).



(1)

Lacking a convenient σ-dissociation pathway, chlorinated pyridazine excited states may undergo valence isomerization instead. Indeed, this process is well documented for the analogous fluorinated or perfluoroalkylated compounds.[7-13] The photorearrangement of tetrachloropyridazine to tetrachloropyrazine may well proceed through intermediate valence isomers. A double labeling experiment with 3,6-difluoro-4,5-dichloropyridazine had established, however, that a diazaprismane was not involved (eq 2).[13] In this paper we describe mechanistic



(2)

studies regarding the photorearrangement of chlorinated pyridazines and delineate the relationship between substitution pattern and the proclivity of a particular pyridazine to isomerize upon photoexcitation.

Results

Tetrachloropyridazine.[14] Because of its rearrangement efficiency, ready availability, and relatively low-lying

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(3) The bond dissociation energy of Ar–Cl is ~85–91 kcal/mol.[2a,b] From the absorption spectra, S_1 lies below 82 kcal/mol in tetrachloropyridazine.

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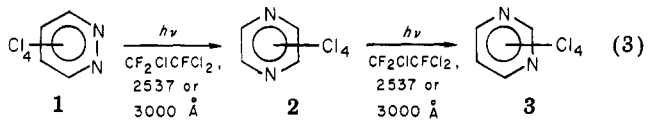
0022-3263/82/1947-0398$01.25/0

triplet state, tetrachloropyridazine (1) was chosen as a model compound for extended mechanistic studies of the photorearrangement.

Photoexcitation of 1 at 2537 or 3000 Å in Freon 113 ($CF_2ClCFCl_2$) led to smooth rearrangement to tetrachloropyrazine (2):[16] 15% ($\Phi = 0.015$) at 35 °C and 2537 Å; 80% at 35 °C and 3000 Å; 45% at 70 °C and 2537 Å. Upon prolonged irradiation, a slower conversion of 2 to tetrachloropyrimidine (3) occurred (eq 3).[15] Per-



1 2 3 (3)

halogenated solvents were required in order to achieve high yields of rearranged products, hydrocarbon solvents giving rise to polymeric products. These conversions could be conveniently followed by UV spectroscopy. For example, the absorption bands characteristic of 1 (λ = 320, 273 nm) diminish as the more intense band of 2 (λ = 309 nm) appears. Ultimately, the 1 and 2 bands disappear, leaving the residual absorption spectrum of 3 (λ = 275 nm). Similar absorption differences exist in trichloropyridazines and -pyrazines.

Sensitization (xanthone, acetone) and quenching (cyclopentene, norbornene) experiments were complicated by the interruption of the rearrangement by hydrocarbon solvents and by the high extinction coefficients of the pyridazine compared with those of the sensitizers (which required the use of high concentrations of the sensitizers).

However, when degassed solutions of 1 in Freon 113 were irradiated at 2537 Å in the presence and absence of 0.1 M benzene, a molecule known to function as either a triplet or singlet sensitizer, under conditions where benzene absorbs ~99% of the incident light, the rate is attenuated only by a factor of 2. Addition of varying concentrations (0, 0.01, 0.05 M) of *cis*-butene, a quencher of benzene triplets, to the benzene–tetrachloropyridazine–Freon 113 photolysis mixture caused no difference, within experimental error, in the rate of formation of tetrachloropyrazine. When a 0.1 M degassed chlorobenzene (a triplet sensitizer) solution in Freon 113 containing 1 (1×10^{-3} M) was irradiated at 35 °C with 2537-Å lamps, the rearrangement proceeded at least 50 times slower than did the photolysis in the absence of chlorobenzene. Addition of *cis*-butene at 0.01 M, a concentration sufficient to completely quench the chlorobenzene triplet, was without effect. Oxygen, the prototypical triplet quencher, was without effect on the rearrangement, 1 being observed to isomerize at identical rates in aerated and degassed solutions at 35 or 70 °C upon irradiation at 2537 Å.

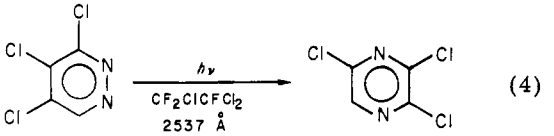
Irradiation of the long-wavelength (n,π^*) band of 1 resulted in isomerization more efficient than that observed when the shorter wavelength (π,π^*) transition was excited. Although no additional products were isolated upon irradiation of the π,π^* bond, the chemical yield of rearranged product was much lower.

When 1 was irradiated in a Fluorolube glass at 77 K, no rearrangement could be detected after 10 h of irradiation at 2537 Å. Temperature dependence of the relative rates of rearrangement in fluid solutions is summarized in Table I.

Table I. Relative Rates for 1 $\xrightarrow{h\nu}$ 2 in $CF_2ClCFCl_2$

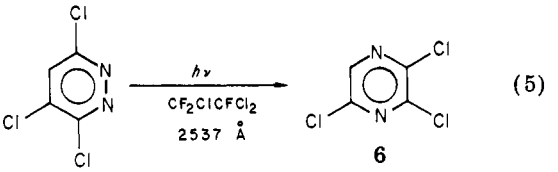
temp, °C	rel rate
10	1.0
35	3.0
65	15

Trichloropyridazines. Irradiation at 2537 Å of an aerated Freon 113 solution of 3,4,5-trichloropyridazine (4) revealed formation of trichloropyrazine (6; eq 4; $\Phi \approx 0.015$).



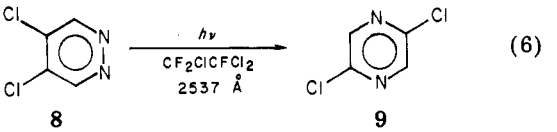
4 6 (4)

During this same period, no rearrangement could be detected from an aerated solution of 3,4,6-trichloropyridazine[17] (5). Prolonged irradiation resulted in only a slight shift of the long-wavelength band to shorter wavelength as 5 slowly disappeared. Analogous irradiation of a degassed solution of 5, however, did ultimately show isomerization to pyridazine (eq 5) although about 10 times slower than the 4 → 6 photoconversion ($\Phi \approx (1\text{–}2) \times 10^{-3}$).



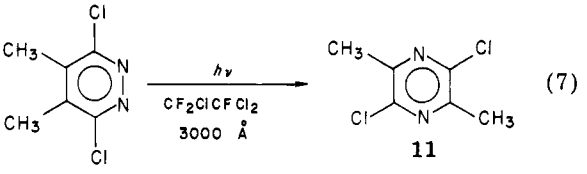
5 6 (5)

Dichloropyridazines. Two dichloropyridazines were examined: commercially available 3,6-dichloropyridazine[18] (7) and 4,5-dichloropyridazine (8).[19] Of these, 7 completely fails to rearrange under all tested conditions in perhalogenated solvents, but 8 rearranges smoothly at a rate comparable to that of 4 to 2,5-dichloropyrazine[20] (9; eq 6; $\Phi = 0.01$).



8 9 (6)

Similarly, 3,6-dichloro-4,5-dimethylpyridazine[21] (10) in degassed Freon 113 gave 2,5-dichloro-3,6-dimethylpyrazine (11)[22] upon irradiation with a Pyrex-filtered medium-pressure mercury arc (eq 7; $\Phi \approx 3 \times 10^{-3}$). This rearrangement was strongly diverted by oxygen: in an aerated solution 10 disappeared, forming 11 (in much lower yield)



10 11 (7)

(14) Chambers, R. D.; MacBride, J. A. H.; Musgrave, W. K. R. *J. Chem. Soc. C* **1968**, 2116.

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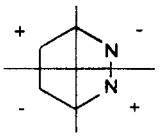


Figure 1. Nodal properties of the occupied π^* orbital in the pyridazine excited state.

Figure 2. Required bonding changes in the pyridazine–pyrazine photorearrangement.

and two additional unidentified oxygen-containing products.

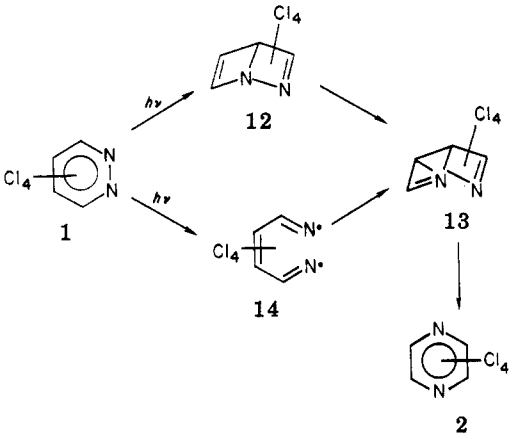
Other Pyridazines. The observation of oxygen, temperature, and solvent dependence in these rearrangements led us to reexamine several pyridazines which had been shown previously to decompose upon photoexcitation without rearrangement. For example, Lemal and coworkers[8] had noted that tetrakis(perfluoroethyl)-, 3,6-dichloro-, 3,6-dihydroxy-, and 3,6-difluoropyridazine as well as the unsubstituted compound fail to rearrange. Other authors had also failed to observe skeletal rearrangement of certain of these compounds while noting photochemical methylation, hydroxymethylation, hydrolysis, or polymerization in a wide variety of pyridazines and pyridazine *N*-oxides.[23] Maleic hydrazide (3,6-dihydroxypyridazine) has been observed to suffer ring cleavages on photolysis.[24] Indeed, we found that 3,6-dichloropyridazine and pyridazine failed to rearrange in degassed Freon 113 solutions irradiated at 2537 Å, as did maleic hydrazide in degassed water.

Discussion

Our results establish that appropriately substituted chlorinated pyridazines undergo photorearrangements parallel to those of the analogous fluorinated and perfluoroalkylated heteroaromatics. Labeling patterns for the rearranged chlorinated pyrazines are in complete agreement with the pattern of atom transpositions observed in 3,6-difluoro-4,5-dichloropyridazine.[8] The pyridazine 3- and 6-substitutents transform to pyrazine 2- and 5-substituents while substitutents at atoms 4 and 5 in the pyridazine appear at atoms 3 and 6 in the rearranged pyrazine. Specifically, then, **8** rearranges to **9**, and **10** rearranges to **11**. As noted previously,[8] this labeling pattern excludes the possible formation of a diazaprismane formed by sequential allowed [$_\pi 2_s + {}_\pi 2_s$] electrocyclizations. Rather, the bond-making and bond-breaking pattern can be summarized as in Figure 1, where dotted lines indicate developing bonds and curved lines indicate severing bonds.

We consider first the possibility that these bonding changes occur through a concerted pathway. That such a pathway must be considered follows from the observation that the nodal properties, i.e., the bonding and antibonding interactions in the occupied π^* level (Figure 1), neatly match the bond-making and bond-breaking processes required in Figure 2. This possibility is very doubtful, however, in light of Chambers' isolation of Dewar intermediates in the photorearrangements of a series of perfluorinated pyridazines.[10,11] Also a consideration of the transition-state geometry for the concerted transformation depicted in Figure 2 requires that the heteroaromatic become twisted so that the two halves of the skeleton lie in roughly perpendicular planes. Formation of such a species with the energy available from excitation of the n,π^* singlet band would indeed be remarkable. That the rearrangement does not occur from a vibrationally excited ground state is established by the observation that thermal isomerization of several perhalopyridazines leads almost exclusively to pyrimidines:[7,25,26] net 1,2- rather than 1,3-interchange of skeletal atoms.

Scheme I. Possible Intermediates in Pyridazine Photorearrangement



Alternate, more reasonable, stepwise mechanisms incorporating Chambers' Dewar isomers are shown in Scheme I. This scheme involves either a discrete Dewar species, **12**, formed before N–N cleavage or a diradical, **14**, formed from N–N cleavage which subsequently makes the required bonds for the rearranged Dewars **12** and/or **13**. The observation that perhalogenated solvents are required to achieve high yields of rearranged product suggests that the rearrangement might proceed through such a biradical which was intercepted by H-donor solvents. On the other hand, hydrogen abstraction by excited starting material is a plausible alternative interpretation of this fact.

Experiments aimed at determining the excited state leading to rearranged product have demonstrated that π,π^* singlet excitation is not required, i.e., that excitation of the lower energy n,π^* singlet is sufficient for the rearrangement. Our observation that irradiation of the long-wavelength n,π^* or the shorter wavelength π,π^* band of **1** resulted in isomerization contrasts with the requirement for π,π^* excitation in the rearrangement of methyl-substituted pyrazines.[15] Since higher chemical yields for rearrangement are obtained upon n,π^* excitation (~3000-Å lamps) vis-à-vis π,π^* excitation (2537 Å lamps; 80% vs. 15%), it is clear that direct excitation to the n,π^* singlet is more effective in photorearranging tetrachloropyridazine than is excitation of the π,π^* transition. In the latter case, internal conversion to the lower energy n,π^* singlet probably competes with some destructive photoprocess.

Whether the n,π^* singlet or the π,π^* or n,π^* triplets which might be derived from it by intersystem crossing are responsible for the rearrangement is a more difficult problem. Triplet sensitization and quenching studies were undertaken to determine the multiplicity of the reactive

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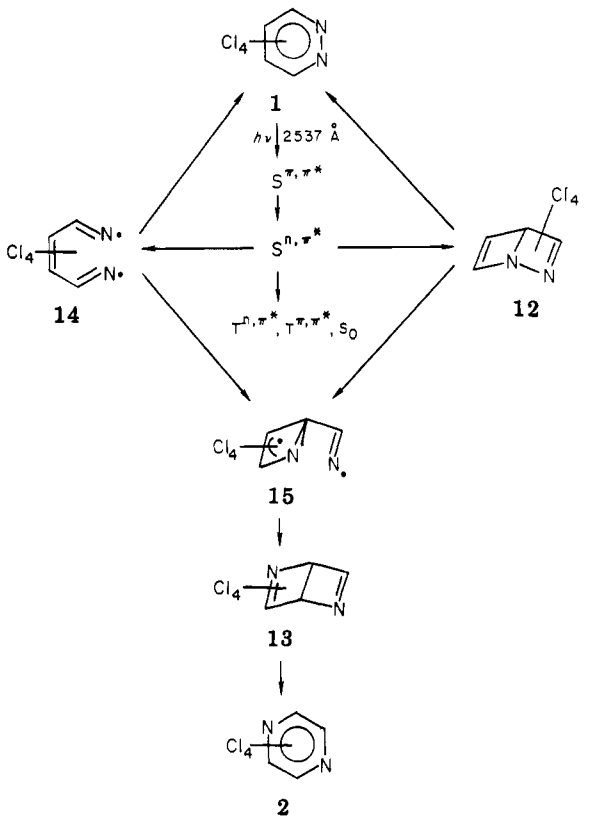
Scheme II. Proposed Mechanisms for the 1 → 2 Photorearrangement



excited state. The most easily interpretable sensitization experiments involved benzene and chlorobenzene. That the rearrangement proceeded at a comparable rate in the presence (where benzene absorbs ~99% of the incident light) and in the absence of benzene implies sensitization by benzene. The lack of an effect of *cis*-2-butene, a substance known to quench benzene triplets at a diffusion-controlled rate,[27] implies that the observed sensitization may be attributed to a benzene singlet. The lack of sensitization by chlorobenzene, a compound lacking a long-lived singlet but forming a long-lived triplet in perhalogenated solvents,[2a] reinforces this conclusion.[28] Similarly, the observation of identical initial isomerization rates in aerated and degassed solutions in the photolyses of **1**, **4**, and **8** is consistent with a reactive singlet. Nonetheless, oxygen does influence these photolyses. For example, at long reaction times (i.e., high conversion of starting material) a yellow color developed in degassed solutions of **1**, while aerated solutions remained colorless. Thus, oxygen may be functioning as a quencher of a triplet (nonrearrangement) process leading to destruction of tetrachloropyridazine. Alternately, oxygen may be acting as a radical scavenger, stopping a radical chain polymerization.

A pronounced temperature effect on the efficiency of the photorearrangement implies the existence of a thermal barrier en route. Since the isomerization is reasonably assumed to be a unimolecular process (and thus to have a rate independent of solvent viscosity), an apparent activation barrier of ~4 kcal can be calculated from the data in Table I. Since the starting material is completely unchanged at 77 K, this thermal barrier may be encountered early along the reaction coordinate either in the S_1 species itself or in the cyclization of biradical **14**. Thus, these mechanistic studies are consistent with Scheme II.

Since the allylic rearrangement of Dewar compound **12** to **13** is orbital topology forbidden in the geometrically favorable mode (suprafacial with retention), it is a reasonable surmise that biradical **15** is an intermediate in the pyridazine → pyrazine rearrangement whether the initial step be bond cleavage to biradical **14** or bond formation, yielding **12**. Either variation is consistent with the pattern of substituent effects observed in this study, for compounds such as **1**, **4**, **5**, **8**, and **10** which possess radical-stabilizing substituents at C_4 and/or C_5 (and thus can give relatively stable biradicals of the **15** type) do rearrange, while those which lack these substituents (e.g., **7**, maleic hydrazide, and the parent pyridazine) fail to rearrange. The sharply contrasting behavior of isomers **7** and **8** is particularly striking. There should be a statistical advantage to having radical-stabilizing substituents at both the 4- and 5-positions, which may explain in part the fact that **4** and **8** rearrange more efficiently than **5**. Chlorine is apparently more effective in stabilizing this developing radical center than is methyl, for **1** rearranges more readily than **10**. This order parallels the relative stabilizing effect of chlorine and methyl on incipient radicals formed, for example, via hydrogen abstraction by phenyl.[29] Return to the ground state of **1** is suggested in Scheme II for **12** and **14** because our mechanistic hypothesis requires an alternative fate for the immediate precursor of **15** should formation of the latter be unfavorable. That the photolysis of **5** and **10** is sensitive to oxygen implies that the biradical analogous to **14** or an excited state of the starting material (probably S(n,π*)) is chemically destroyed by oxygen when rearrangement to the analogue of **15** is relatively inefficient.

Our rationalization of the substituent effects we have observed does not explain the facile rearrangement of perfluoropyridazine and various of its perfluoroalkyl-substituted derivatives. In general, neither α- nor β-substituted fluorine stabilizes a carbon radical center significantly.[30] Fluorine's pronounced preference for bonding to sp^3- rather than sp^2-hybridized carbon[31] (in highly fluorinated molecules) may be responsible, at least in part, for formation of the Dewar isomers which serve as precursors for pyrazines. The steric bulk of perfluoroalkyl substituents may assist in the valence isomerization process since folding of the molecular skeleton relieves nonbonded repulsion present in the pyridazines (another manifestation of the "perfluoroalkyl effect"[32]). Both of these effects help to explain why numerous perfluorinated Dewar isomers analogous to **13** and in certain cases even to **12** have been isolated, while no unfluorinated counterpart has been observed to date.

Experimental Section

Instrumentation. Ultraviolet spectra were measured on Unicam SP-800, Cary 14, or Cary 210 spectrophotometers. Analytical gas–liquid phase chromatography (GLC) was conducted on a Perkin-Elmer F-11 gas chromatograph (150-ft TCEP capillary column) or on an Antek 400 (10 ft × 1/8 in. 15% FFAP on 100/110-mesh Chromosorb P column or a 5 ft × 1/8 in., 10% OV-101 on 100/110-mesh Chromosorb G column). Preparative GLC was conducted on a Varian 920 (20 ft × 1/4 in., 20% Carbowax on 100/110-mesh Chromosorb P column). Mass spectra were measured on a Du Pont 21-471 spectrometer. Proton nuclear

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Table II. Photolysis of 1

irradn λ, nm	temp, °C	% yield of 2
253.7	35	0.15
253.7	70	0.45
~300	35	0.80

magnetic resonance (NMR) spectra were measured on a Perkin-Elmer R-24 or a Varian EM 390 spectrometer. Infrared (IR) spectra were obtained on a Beckmann Acculab-7 spectrometer. Melting points were obtained on a Fisher melting point block and were uncorrected.

General Procedure for Photolyses. Solutions (1×10^{-3} to 1×10^{-2} M) of the appropriate pyridazine in Freon 113 either were degassed by three freeze–pump–thaw cycles before being sealed into quartz ampules or were transferred to tightly capped quartz ampules after being shaken in air. These ampules were exposed to irradiation from 16 low-pressure mercury arcs in a circular array (Rayonet photochemical reactor) while suspended on a rotating support to assure nearly equal exposure of all samples being simultaneously irradiated. Either uncoated (2537 Å) or phosphor-coated (~3000 Å) lamps were used as light sources. Solutions were irradiated to about 25% destruction of pyridazine.

Quantum yields were determined at 2537 Å in a specially constructed apparatus in which eight sample ampules were simultaneously irradiated through double light baffles obtained by alignment of two sets of windows per ampule, one set having been machined parallel to the axis of the solid aluminum core containing the samples and the second set having been machined in an outer pot to assure exact alignment of the incident beam. This apparatus was covered with a lid to exclude incident light and was rotated in the cavity of the Rayonet photochemical reactor. Thus, samples of the appropriate pyridazine were exposed simultaneously with ethanolic potassium ferrioxalate solutions. Since the quantum yields for conversion of the pyridazines were much lower than those of the ferrioxalate actinometer,[33] fresh samples of potassium ferrioxalate were used at the beginning, middle, and end of the pyridazine irradiation period to ensure constant light flux. Quantum yields for pyridazine disappearance and pyrazine appearance were obtained relative to known quantum yields for Fe^{2+} appearance.[33] These conversions were determined quantitatively by GLC for tetrachloropyridazine and by UV spectroscopy of the *o*-phenanthroline complex for Fe^{2+}.[33] The quantum yields of the other pyridazines were obtained relative to that of tetrachloropyridazine in the same apparatus.

Temperature-dependent photolyses were conducted by irradiating degassed solutions (vide supra) of the appropriate pyridazine while mounted in quartz tubes through which temperature-controlled water was circulated. Irradiation was conducted in the cavity of a Rayonet photochemical reactor for a carefully timed period sufficient to produce identical decomposition mixtures as gauged by UV spectroscopy. Irradiations at 77 K were conducted by placing the appropriate degassed pyridazine solution (1×10^{-3} M in Fluorolube FS-5) into a quartz ESR tube which was inserted into a quartz Dewar flask containing liquid nitrogen. The Dewar flask and its contents were inserted into a modified cavity of the Cary 14 UV spectrometer for monitoring the photoconversion of the pyridazine. The frozen glass solution was irradiated at 2537 Å, with care being taken to maintain an ample level of liquid nitrogen to prevent cracking of the glass matrix. (Purified Fluorolube FS-5 is transparent at 2537 Å.)

Materials. Unsymmetrical trichlorotrifluoroethane (Freon 113) was obtained from E. I. DuPont de Nemours Inc. and was vacuum distilled before use. Commercial samples (Aldrich) of 3,4,5-trichloropyridazine (**4**), 3,6-dichloropyridazine (**7**), and maleic hydrazide were purified by recrystallization and/or sublimation. Commercial samples (Aldrich) of spectral grade benzene, chlorobenzene, and pyridazine were distilled before use. *cis*-2-Butene (Matheson) was distilled from the lecture bottle directly into 10 mL of Freon 113. Tetrachloropyridazine (**1**),[14] tetrachloropyrazine (**2**),[16] 3,4,6-trichloropyridazine (**5**),[17] 2,3,6-trichloropyrazine (**6**),[34] 4,5-dichloropyridazine (**8**),[19] 3,6-dichloro-4,5-dimethylpyridazine (**10**),[21] and 2,5-dichloro-3,6-dimethylpyrazine (**11**)[22] were prepared by literature procedures and exhibited melting point ranges and IR and NMR spectra identical with those reported.

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Table III. Benzene Sensitization of the 1 → 2 Photorearrangement

[*cis*-2-butene], M	[benzene], M	rel fraction of rearrangement
0	0	1.00
0	0.1	0.45
0.01	0.1	0.42
0.05	0.1	0.51

Table IV. Attempted Chlorobenzene Sensitization of the 1 → 2 Photorearrangement

[*cis*-2-butene], M	[chlorobenzene], M	rel fraction of rearrangement
0	0	1.00
0	0.1	~0.015
0.01	0.1	~0.02

Photolysis of Tetrachloropyridazine (1).[14] By using the general photolysis procedure described above, a degassed 1×10^{-3} M solution of **1** [λ_{max} (F-113) 320, 273 nm] in Freon 113 was irradiated to 25% disappearance of starting material. The chemical yield of **2** (Table II) was determined by quantitative GLC (4 ft × $^1/_4$ in. QF-1 column, 120 °C). The product isolated was identical with an authentic sample of **2**[16] (λ_{max} (F-113) 309, 270, 230 nm). No other products have been identified. Polymerization and/or dehalogenation are possible alternate routes in these photolyses.

Benzene Photosensitization of Tetrachloropyridazine Rearrangement. Solutions of benzene (0.1 M) in Freon 113 were made 1×10^{-3} M in **1**. After varying concentrations of *cis*-2-butene had been added by condensing at 77 K appropriate pressures of the gas from the gas trap described in the chlorobenzene experiments, the solutions were rigorously degassed. A reference solution of **1** (1×10^{-3} M) in Freon 113 was similarly prepared and degassed. The solutions were irradiated simultaneously at 35 °C by rotating them in an unshielded support inside the circular array of 2537-Å lamps in the Rayonet photochemical reactor cavity. The progress of the reaction could be monitored crudely by UV spectroscopy. After about 15% destruction of **1**, the irradiation mixtures were carefully stripped of solvent and redissolved in 100 μL of Freon 113. The resulting mixtures were analyzed for the presence of tetrachloropyrazine by gas chromatography (4-ft QF-1 column, 120 °C; see Table III).

Attempted Chlorobenzene Sensitization of Tetrachloropyridazine Rearrangement. Solutions of chlorobenzene (0.1 M) in Freon 113 were made 1×10^{-3} M in **1**. One such sample was made 0.01 M in *cis*-butene by condensing an appropriate volume of gas at 77 K from a gas trap. A reference sample lacking chlorobenzene and *cis*-2-butene was similarly prepared. These degassed samples were irradiated simultaneously inside the Rayonet photochemical reactor equipped with 2537-Å lamps, and tetrachloropyrazine formation (Table IV) was monitored by gas chromatography (4-ft QF-1, 120 °C) as described in the benzene sensitization experiments.

Effect of Oxygen on Tetrachloropyridazine Rearrangement. Degassed and aerated solutions of **1** (2×10^{-3} M) in Freon 113 were sealed in quartz ampules. One pair of such ampules was irradiated at ambient temperature (~35 °C) at 2537 Å inside the Rayonet photochemical reactor. A second pair was mounted inside quartz tubes through which temperature-controlled water circulated (vide supra). The resulting apparatus, maintained at ~70 °C, was irradiated at 2537 Å, with the sample mounting being interchanged at half irradiation time. Progress of the reaction was monitored by UV spectroscopy. Both product development and starting material decomposition were found to occur at identical rates in the aerated and degassed solutions at each temperature. After the 35 °C irradiation had progressed for 5 h, a yellow color had developed in the degassed solution that was completely absent in the aerated solution.

Table V. Effect of Temperature on 1 Photorearrangement

temp, °C	irradn period, min	rel rates of rearrangement
65 ± 3	7.0	15.6
35 ± 1	31	3.5
10 ± 2	109	1.0
65 ± 3	6.5	15.1
35 ± 1	25	3.9
10 ± 2	98.5	1.0

Matrix Irradiation of Tetrachloropyridazine. The frozen glass solution of 1 (1×10^{-3} M) was irradiated at 2537 Å in the liquid nitrogen Dewar flask described in the general procedure. No evidence of rearrangement or destruction of starting material could be detected by UV spectroscopy after 1, 5, or 10 h of irradiation.

Effect of Temperature on Tetrachloropyridazine Rearrangement. Degassed solutions of 1 (2.5×10^{-3} M) in Freon 113 were mounted in quartz tubes through which temperature-controlled water was circulated. Irradiation at 2537 Å was undertaken in the cavity of the Rayonet photochemical reactor for a period sufficient to produce identical decomposition mixtures in the UV spectrum (Table V). Light flux was assumed to be constant.

Photolysis of 3,4,5-Trichloropyridazine (4) and 3,4,6-Trichloropyridazine (5).[17] Aerated solutions of 4 [λ_{max} (F-113) 318, 269 nm] and 5 [λ_{max} (F-113) 322, 277 nm] (5×10^{-4} M) in Freon 113 were irradiated at 35 °C with low-pressure mercury vapor lamps (2537 Å). After 1 h of irradiation, UV spectra of the photolysate mixture showed a decrease in the peaks at 318 and 269 nm corresponding to 4. A new peak appeared at 300 nm with a shoulder at 278 nm, consistent with formation of trichloropyrazine (6).[18] The presence of 6 was confirmed by GLC (4 ft × $^1/_4$ in. QF-1 column, 120 °C) which showed the presence of material identical with an authentic sample of 6 [λ_{max} (F-113) 300, 278 nm]. The ultraviolet spectrum of the photolysis mixture containing 5 was essentially unchanged by irradiation. Prolonged irradiation resulted in a slight shift of the n,π^* band as the 5 slowly disappeared.

An aerated solution of 5 (5×10^{-4} M) in Fluorolube FS-5 was placed in a UV cuvette on a heating plate for 1 h. No thermal decomposition could be detected by UV spectroscopy at 95 ± 10 °C. After 1 h of irradiation at this temperature with a Hanovia medium-pressure mercury vapor lamp, substantial yellowing had occurred. The shift of the n,π^* band from 322 to 305 nm was more pronounced than at the lower temperature.

A degassed solution of 5 (4×10^{-4} M) in Freon 113 was irradiated at 2537 Å at ~35 °C. After 5 h, a new peak appeared in the UV spectrum of the photolysis mixture at 300 nm with a shoulder at 278 nm. The original peaks at 318 and 269 nm had decreased in intensity with the growth of this new peak. Prolonged irradiation resulted in slow destruction of all peaks.

Photolysis of 3,6-Dichloropyridazine (7)[18] and 4,5-Dichloropyridazine (8).[19] Degassed solutions (1×10^{-3} M) of 7 [λ_{max} (F-113) 253, 274 nm] and 8 in Freon 113 were irradiated at 35 °C at 2537 Å. After 0.5 h, substantial decomposition of 8 had occurred, and a new band (yield ~60%) had appeared in the UV spectrum of the photolysate mixture. By mass spectroscopy, the product had the formula $C_4N_2H_2Cl_2$, and its UV spectrum [λ_{max} (F-113) 217, 280, 296 nm] was consistent only with a dichloropyrazine.[35] Coinjection showed the product to differ in relative retention volumes from authentic samples of 2,6-dichloropyrazine and 2,3-dichloropyrazine. Its structure is therefore assigned as 2,5-dichloropyrazine (9).[20,36] After 5 h, no new bands had appeared in the UV spectrum of the photolysate mixture obtained from 7, although some 7 had disappeared and a yellow color had developed.

Photolysis of 3,6-Dichloro-4,5-dimethylpyridazine (10). An aerated solution of 10 [λ_{max} (F-113) 272, 308 nm; 2×10^{-3} M] in Freon 113 was irradiated for 1 h at 2537 Å at ambient temperatures. No rearrangement could be detected by UV spectroscopy, but substantial decomposition of starting material had occurred.

An aerated solution of 10 (2×10^{-3} M) in Fluorolube FS-5 was placed in a UV cuvette on a heating plate for 1 h. No thermal decomposition could be detected by UV at 95 ± 10 °C. After 1 h of irradiation at this temperature with a Hanovia medium-pressure mercury vapor lamp, substantial yellowing had occurred. No evidence for rearrangement of 10 could be detected by UV spectroscopy.

An aerated solution of 10 (1×10^{-3} M) in glacial acetic acid was prepared. The position of the n,π^* bond had shifted from 308 to ~300 nm and decreased in intensity. Irradiation of this solution at 2537 Å resulted in rapid destruction of starting material. The products of this photoreaction absorbed light only at wavelengths shorter than 250 nm.

A solution of 10 (8×10^{-4} M) in Freon 113 was rigorously degassed. When the sample was irradiated by a Pyrex-filtered medium-pressure mercury arc, a new peak appeared in the UV spectrum of the photolysis mixture at 298 nm [λ_{max} (F-113) of 11 298 nm]. After careful removal of solvent by distillation at atmospheric pressure, a photoproduct with a retention time identical with that of an authentic sample of 11 was detected in 58% yield by gas chromatography (4-ft TCEP column, 70–170 °C temperature programmed at 30 °C/min).

A solution of 10 (0.025 M) in Freon 113 suitable for preparative gas chromatography was degassed by bubbling nitrogen through the photolysate. When the sample was irradiated as before, a thick brown polymer coated the walls of the irradiation vessel. Gas chromatography revealed two photoproducts in addition to fraction A. Collection of fraction A revealed a white crystalline substance whose IR and NMR spectra were identical with those of 11.

The other two photoproducts B and C were not collected. For determination of the source of these products, the photolysis was repeated on a GC scale. When a Freon 113 solution of 10 (0.025 M) was irradiated with 3000-Å lamps in the presence of oxygen, the yield of these products as determined by gas chromatography was ~2–3 times greater than that from an identical degassed solution. When an aerated solution of 11 was irradiated at 3000 Å, only the lower retention time product, B, could be detected. Irradiation of an identical degassed solution showed production of yet another photoproduct, but very little of B. It thus appears that the undesired products in the photolysis of 10 are formed

Table VI. Quantum Yields for 1 → 2 Photorearrangement

moles of 1 destroyed × 10^6	einsteins absorbed × 10^5	Φ_d
1.1	1.6	0.07
1.7	3.1	0.055
1.9	3.8	0.05
moles of 2 produced × 10^6	**einsteins absorbed × 10^5**	**Φ_r**
1.2	9.2	0.013
1.4	8.2	0.017
1.5	9.4	0.016

Table VII. Quantum Yields for the Photorearrangements of Chlorinated Pyridazines

pyridazine	moles of pyrazine formed × 10^6	rate of 2 formation/ rate of pyrazine formation	Φ_r(calcd)
1	18	1.00	0.015
4	17	1.06	0.014
	18	1.00	0.015
5	2.2	8.2	0.0018
	1.7	10.6	0.0014
8	12	1.5	0.010
	11	1.7	0.008
10	4.7	3.8	0.0036
	3.1	5.8	0.0026

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in the presence of oxygen from 10 and from its rearranged photoproduct 11.

Quantum Yields of Photorearrangement of Several Pyridazines. By use of merry-go-round quantum yield apparatus and the general procedures described above, quantum yields for decomposition of 1 (Φ_d) and photorearrangement of 1 to 2 (Φ_r) were obtained for 1 (Table VI). By use of the merry-go-round quantum yield apparatus and the general procedures described above, relative quantum yields determined for each of the remaining photorearranging pyridazines were compared with the now established quantum yield for rearrangement of 1 (Table VII).

Photolysis of Other Pyridazines. A degassed solution of pyridazine (1×10^{-3} M) in Freon 113 was prepared. A degassed solution of maleic hydrazide (1×10^{-3} M) was prepared in water since this compound was insoluble in Freon 113, perfluoromethylcyclohexane, and cyclohexane. These solutions were irradiated at 35 °C at 2537 Å. Progress of the photoreaction was followed by UV spectroscopy. The absorption of starting material in all three solutions quickly disappeared, with no hint of pyrazine formation being detectable by UV spectroscopy or by GLC.

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Reaction of Organotin Hydrides with Acetylenic Alcohols

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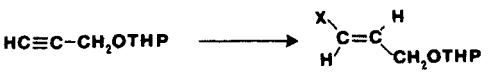
The reaction of di-*n*-butyltin dihydride and tri-*n*-butyltin hydride with mono- and disubstituted acetylenic alcohols has been studied. Di-*n*-butyltin dihydride reacts with certain monosubstituted acetylenic alcohols to give cyclic vinyltin ethers. With disubstituted acetylenic alcohols only divinylstannyl derivatives are obtained. Tri-*n*-butyltin hydride reacts with disubstituted acetylenic alcohols to give (*Z*)-2-(tri-*n*-butylstannyl)-2-alken-1-ols. Metalation and iodination of the resulting vinylstannanes are discussed.

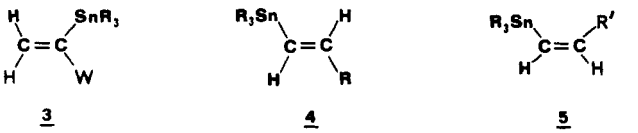
Vinyl organotin reagents have assumed an increasingly important role as intermediates for the synthesis of complex natural products. Corey and co-workers introduced the use of 1 as a convenient source of the protected



1, X = $SnBu_3$
2, X = Li

(*E*)-3-lithiopropenol 2 and its corresponding cuprate.[1] This report was soon followed by other examples of the synthetic utility of vinyltin compounds for the generation of vinylic nucleophiles.[2]

The most convenient method for the preparation of vinyltin compounds is by the addition of trialkyltin hydrides to the corresponding acetylenic compound. The reaction of tributyltin hydride with monosubstituted acetylenes bearing strongly electron-withdrawing substituents (CO_2R, C≡N, etc.) affords mainly, or even exclusively, the α-adduct 3.[3] Monosubstituted acetylenes bearing electron-releasing (alkyl, OR, etc.) or weakly electron-withdrawing substituents (CR_2OH, C_6H_5, etc.) afford mainly the β-*E* (4) and β-*Z* (5) adducts.[2b,d,e,4]



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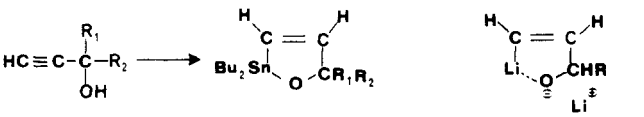
In 1973 Massol and co-workers reported the preparation of a series of cyclic vinyltin ethers (6) by the reaction of



6 a. $R_1 = R_2 = H$
b. $R_1 = H$, $R_2 = CH_3$
c. $R_1 = H$, $R_2 = C_3H_7$
d. $R_1 = R_2 = CH_3$
e. $R_1 = CH_3$, $R_2 = C_2H_5$

7 a. R = CH_3
b. R = C_5H_{11}

propargylic alcohols with dibutyltin dihydride.[5] These cyclic organotin compounds appeared to offer a convenient approach to useful derivatives of (*Z*)-3-lithiopropenols such as 7.[6] Herein we report the results of our study of the hydrostannylation of alkynols with dibutyltin dihydride and tributyltin hydride.

Results and Discussion

Reaction of Dibutyltin Dihydride with Monosubstituted Acetylenic Alcohols. The reaction of dibutyltin

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