

Oxidation of Phenylhydrazine with Polyhalomethanes¹EARL S. HUYSER AND RICHARD H. S. WANG²

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Bromotrichloromethane and carbon tetrachloride undergo reaction with phenylhydrazine yielding nitrogen, chloroform, benzene, a halobenzene, and a hydrogen halide. Although these reactions are spontaneous in the dark, they are accelerated both by light and by peroxides. Evidence for a mechanism of these reactions involving formation of phenyldiimide as an intermediate produced in a free-radical chain reaction followed by reactions of phenyldiimide yielding benzene and a halobenzene is presented. Kinetic studies support a postulated bimolecular reaction of the reactants resulting in formation of free radicals to initiate the chain sequence in the dark reaction.

Phenylhydrazine has been reported to be oxidized to benzene and nitrogen, reactions presumably involving formation of phenyldiimide, by Fehling's solution,³ by mercuric oxide,⁴ by oxygen, metallic oxides, and permanganates and chromates in alkaline solution,⁵ by ferricyanide⁶ and by copper sulfate in acetic acid.⁷ Other oxidations of phenylhydrazine yielding nitrogen and phenol, reactions presumably involving the benzene diazonium cation as an intermediate oxidation product, have been accomplished using metallic oxides, permanganate, and chromate in acidic media⁵ and also by iodine and by potassium iodate in acidic solutions.⁸ The chemistry of phenyldiimide was investigated by Hardie and Thomson who generated this species from phenylhydrazine with metallic oxides in aromatic solvents.⁹ The formation of biphenyl as well as other mixed diaryls suggested the intermediacy of free phenyl radicals in the reactions of phenyldiimide. Cohen and Nicholson suggested that phenyldiimide, formed by reaction of N-phenyl-N'-benzoyldiimide (C₆H₅CON=NC₆H₅) with acid, base, or ferric ion, could decompose in homogeneous medium directly to benzene and nitrogen.¹⁰ Huang and Kosower,¹¹ who produced phenyldiimide by decarboxylation of phenylazofornic acid (C₆H₅N=NCO₂H) with dimethylamine hydrochloride or with lithium chloride, proposed a bimolecular decomposition of phenyldiimide to explain the formation of benzene and nitrogen.

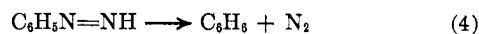
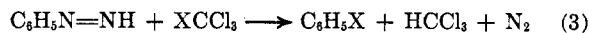
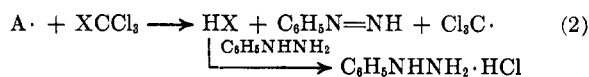
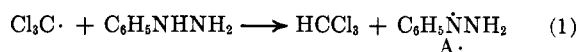
The present work is concerned with the reactions of phenylhydrazine with carbon tetrachloride and bromotrichloromethane. Our investigations of this reaction suggest the formation of phenyldiimide in a free-radical chain reaction involving the polyhalomethane and phenylhydrazine and subsequent reactions of phenyldiimide, either with itself or with the polyhalomethane yielding nitrogen, benzene, and a halobenzene.

Results and Discussion

Mixing phenylhydrazine and bromotrichloromethane results in immediate reaction as evidenced by evolution

of nitrogen gas and formation of insoluble phenylhydrazine hydrobromide. A similar, but somewhat slower, reaction is observed when phenylhydrazine and carbon tetrachloride are mixed in the dark. Table I lists the composition of the reaction products formed for reactions of both bromotrichloromethane and carbon tetrachloride with phenylhydrazine in dimethylformamide, a solvent which dissolves the phenylhydrazine hydrogen halide keeping the reaction mixtures homogeneous. Examination of products formed in these reactions shows that more bromobenzene than benzene is formed in the bromotrichloromethane reactions, whereas benzene is produced in larger quantities than chlorobenzene in the carbon tetrachloride reactions. Furthermore, the amount of chloroform produced in the bromotrichloromethane reactions relative to the other products is larger than that in the carbon tetrachloride reactions.

A mechanism that accounts for these products and their distribution is shown in reactions 1-4. Reactions 1 and 2 comprise a free-radical chain sequence that accounts for formation of the hydrogen halide, part of the chloroform and phenyldiimide. Reactions 3 and 4 involve the phenyldiimide and result in formation of



nitrogen, benzene, the halobenzene, and part of the chloroform. If this mechanism is indeed operative, certain stoichiometric relationships between the reaction products can be expected. The amount of nitrogen should equal the sum of the amounts of the benzene and halobenzene in each case since nitrogen results only from the reactions of phenyldiimide producing

$$M_{\text{N}_2} = M_{\text{C}_6\text{H}_6} + M_{\text{C}_6\text{H}_5\text{X}}$$

these products. Chloroform, on the other hand, is formed both in the free-radical chain sequence producing phenyldiimide and in the reaction of this intermediate with the polyhalomethane yielding the halobenzene.

$$M_{\text{HCCl}_3} = M_{\text{C}_6\text{H}_6} + 2M_{\text{C}_6\text{H}_5\text{X}}$$

Consequently, the amount of chloroform produced should equal the sum of the amounts of benzene plus

(10) S. G. Cohen and J. Nicholson, *J. Amer. Chem. Soc.*, **86**, 3892 (1964); *J. Org. Chem.*, **30**, 1162 (1965); *J. Amer. Chem. Soc.*, **88**, 2247 (1966).

(11) P. K. C. Huang and E. M. Kosower, *ibid.*, **89**, 3910, 3911 (1967).

(1) This work was supported by a grant from the National Institutes of Health (AM-08517-02).

(2) Taken from the thesis submitted by R. H. S. W. in partial fulfillment of the requirements for the Ph.D. Degree from the University of Kansas, 1968.

(3) E. Fisher, *Ann.*, **190**, 101 (1878); H. Strache and M. Kitt, *Monatsh. Chem.*, **13**, 316 (1892).

(4) E. Fisher and W. Ehrhard, *Ann.*, **199**, 332 (1879).

(5) F. D. Chattaway, *J. Chem. Soc.*, 1323 (1907); 270 (1908).

(6) H. M. Kischner, *J. Russ. Phys. Chem. Ges.*, **31**, 1633 (1899).

(7) A. F. Rekasheva and B. E. Gruz, *Dokl. Akad. Nauk SSSR*, **92**, 337 (1952).

(8) C. O. Miller and N. H. Furman, *J. Amer. Chem. Soc.*, **59**, 161 (1937).

(9) R. L. Hardie and R. H. Thomson, *J. Chem. Soc.*, 2512 (1957).

TABLE I
 REACTIONS OF PHENYLHYDRAZINE WITH POLYHALOMETHANES IN DMF

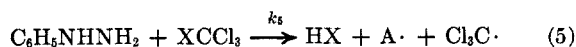
XCCl ₃ (mmol)	C ₆ H ₅ NHNH ₂ , mmol	Molar ratio of reactants	Time, hr (temp, °C)	Products, mmol			
				N ₂	C ₆ H ₆	C ₆ H ₅ X	HCCl ₃
BrCCl ₃ (36.0)	36.0	1:1	12 (110)	15.4	3.5	8.8	22.4
BrCCl ₂ (36.0)	36.0	1:1	22 (110)	17.5	5.4	10.8	25.1
BrCCl ₃ (180)	36.0	5:1	18 (110)	19.7	0.5	15.3	28.4
BrCCl ₃ (180)	36.0	5:1	18 (105)	<i>a</i>	0.5	13.5	27.1
Cl ₄ C (175)	35.0	5:1	21 (105)	11.6	9.6	1.3	10.3
Cl ₄ C (700)	35.0	20:1	4 (85)	10.9	6.3	1.5	8.8
Cl ₄ C (700)	35.0	20:1	6 (80)	11.3	6.9	2.1	9.9

^a Not determined.

two times the amount of halobenzene. Not only does the proposed mechanism explain the larger amounts of chloroform observed in the bromotrichloromethane reactions but, within the experimental certainty of the quantitative determinations, the predicted stoichiometric relationships of all the products were observed.

Free-Radical Chain Sequence.—Hydrogen abstraction from the α -nitrogen by Cl₃C· yielding α -phenylhydrazyl radical A· should be at least as facile as the abstraction of hydrogen from hydrazine by Cl₃C·, a reaction suggested for oxidation of hydrazine to diimide by carbon tetrachloride.¹² Hydrogen atom transfer from A·, a radical analogous to α -aminoalkyl radicals which participate in hydrogen-atom transfer reactions to peroxides,¹³ to the polyhalomethane (reaction 2) is similar to that of α -hydroxyalkyl radicals to polyhalomethanes.¹⁴ Formation of phenyldiimide by this chain sequence is most likely the rate-determining factor in these reactions, and consequently the rate of nitrogen evolution becomes, in fact, the rate of formation of phenyldiimide. The observations that the reaction rate as measured by nitrogen evolution is markedly increased both by illumination and by the addition of a few mole per cent diacetyl peroxide support the suggestion that a free-radical chain reaction may be involved in these reactions. The acceleration by peroxide is observed only for the first 5–10% of reaction after which the rate is essentially the same as that of the reaction without peroxide. Induced decomposition of the peroxide by phenylhydrazine likely removes the peroxide and therefore decreases its effectiveness in starting new chains.

The dark reaction possibly is initiated in a bimolecular process in which two chain-carrying free radicals, namely Cl₃C· and A·, are formed along with hydrogen halide from the reactants (reaction 5). A bimolecular



initiation process such as this differs from either peroxide or light-induced reactions mainly in a kinetic sense, the latter two generally being unimolecular processes. The derived steady-state rate law for a bimolecularly initiated reaction for rate of formation of phenyldiimide, as measured by the rate of nitrogen evolution, would be over-all second order. The exact form of the rate law would depend on the particular chain-termination process operative in the reaction. If termination

were by coupling of two trichloromethyl radicals (reaction 6), the rate law would take the form shown in eq 7. If termination were by interaction of two α -



$$\text{rate} = \frac{k_5^{1/2}k_1}{k_6^{1/2}} [\text{XCCl}_3]^{1/2} [\text{C}_6\text{H}_5\text{NHNH}_2]^{1/2} \quad (7)$$

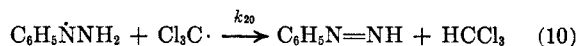
phenylhydrazyl radicals, quite possibly yielding phenylhydrazine and phenyldiimide in a disproportionation reaction as shown in eq 8, the rate law would have the



form given in eq 9. The rate law for a cross-termina-

$$\text{rate} = \frac{k_5^{1/2}k_2}{k_8^{1/2}} [\text{XCCl}_3]^{1/2} [\text{C}_6\text{H}_5\text{NHNH}_2]^{1/2} \quad (9)$$

tion process such as shown in eq 10 would be that shown in eq 11.



$$\text{rate} = \frac{k_5^{1/2}k_1^{1/2}k_2^{1/2}}{k_{10}^{1/2}} [\text{XCCl}_3] [\text{C}_6\text{H}_5\text{NHNH}_2] \quad (11)$$

Kinetic studies of the dark reaction of bromotrichloromethane and phenylhydrazine show that the reaction is second order over-all and follows the rate law given in eq 11. Table II lists the second-order reaction rate constants determined for the reactions performed in N,N-dimethylformamide.

TABLE II

RATE DATA FOR REACTIONS OF BrCCl ₂ AND C ₆ H ₅ NHNH ₂ ^{a,b}		
[C ₆ H ₅ NHNH ₂]: [BrCCl ₂]	Temp, °C	<i>k'</i> × 10 ⁶ l. mol ⁻¹ sec ⁻¹ c
1:2 ^d	80	1.84 ± 0.02
2:1	80	1.74 ± 0.02
1:1	80	1.73 ± 0.03
1:1	70	1.02 ± 0.02
1:1	60	0.59 ± 0.02

^a $\Delta H^\ddagger = 11.9 + 0.02$, ^b $\Delta S^\ddagger = -46.9 \pm 0.3$. ^b Probable error. ^c $k' = (k_5^{1/2}k_1^{1/2}k_2^{1/2})/k_{10}^{1/2}$. ^d Initial molarities of reactants in DMF varied from 0.5 to 1.0 mol.

The activation parameters for the reaction given in Table II with their probable errors¹⁵ proved interesting and are in many regards suggestive of a bimolecular initiation process. Although the rate of the over-all process must take into consideration all of the steps outlined in the mechanism (initiation, chain propagation, and chain termination), the predominating fac-

(12) J. Wolinsky and T. Schultz, *J. Org. Chem.*, **30**, 3980 (1965).

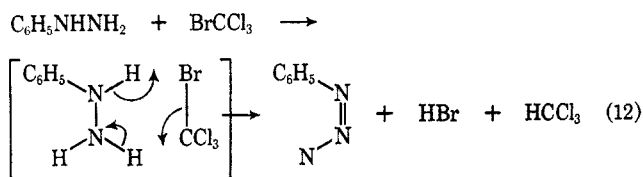
(13) E. S. Huysler, C. J. Bredeweg, and R. M. VanScoy, *J. Amer. Chem. Soc.*, **84**, 4148 (1964).

(14) See G. A. Rasuwajew in "Vistas in Free-Radical Chemistry," W. A. Waters, Ed., Pergamon Press, New York, N. Y., 1959, pp 224.

(15) Probable error is a measure of the reliability of the values for the activation parameters determined by a least-square's treatment of the reaction rate constants and their standard deviations. See E. L. Pearly, R. W. Taft, Jr., and C. A. DeFazio, *J. Amer. Chem. Soc.*, **77**, 837 (1955), and L. L. Selhalager and F. A. Long, *Advan. Phys. Org. Chem.*, **1**, 7 (1963).

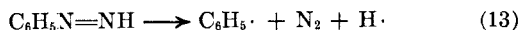
tor in determining the observed rate constants and hence the activation parameters will be the slowest reaction, in this case, the initiation reaction. The low entropy of activation suggests a highly ordered transition state for the bimolecular initiation process and is reminiscent of the low entropies of activation observed for thermal polymerizations, free-radical chain reactions that likely are initiated by bimolecular processes.¹⁶

The possibility certainly exists that the phenyldiimide, hydrogen halide, and chloroform proposed as products of the free-radical chain sequence 1 and 2 may be formed in a simple bimolecular reaction of phenylhydrazine and bromotrichloromethane. The observed products, the second-order kinetic rate law, and reaction rate parameters are all consistent for a four-centered reaction such as shown in eq 12. The accelera-

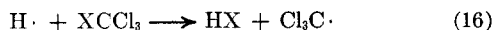
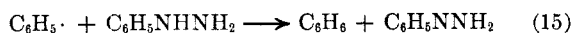
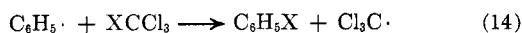


tion of the reaction rate by light and by diacetyl peroxide, however, is not tenable with such a process. Furthermore, the existence of free radicals as intermediates in the dark reactions finds support in the observation that an N,N-dimethylformamide solution with both bromotrichloromethane and phenylhydrazine reacts with galvinoxyl¹⁷ as evidenced by the disappearance of the characteristic purple color of this stable free radical in this solution within a short time after mixing the reagents. The color of the galvinoxyl disappears very slowly in solutions with only bromotrichloromethane in N,N-dimethylformamide and persists for many hours in solutions with only phenylhydrazine in N,N-dimethylformamide.

Reactions of Phenyldiimide.—Two routes for reaction of the phenyldiimide were considered. Decomposition of this intermediate yielding phenyl radicals, nitrogen, and hydrogen atoms (reaction 13)

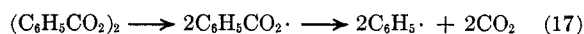


is not an acceptable path to the formation of the halobenzene by reaction of phenyl radicals with the polyhalomethane (reaction 14), benzene by reaction of phenyl radicals with phenylhydrazine (reaction 15), and hydrogen halide by reaction of hydrogen atoms with XCCl_3 (reaction 16) on two counts. First, such a



process would be a multiple chain reaction since each radical producing phenyldiimide in the free-radical chain sequence 1 and 2 would result in starting two new chains as the result of decomposition of the phenyldiimide. A marked acceleration of the reaction rate, even explosions, would be observed. Second, there is evidence that free phenyl radicals are not involved in the formation of the halobenzenes. Competition reactions involving formation of the halobenzenes from

mixtures of bromotrichloromethane and carbon tetrachloride were conducted using different sources of the phenyl moieties. The reactivity of BrCCl_3 relative to Cl_4C toward attack by phenyl radicals generated by decomposition of benzoyl peroxide (reaction 17) at



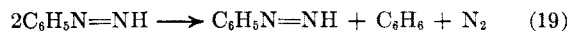
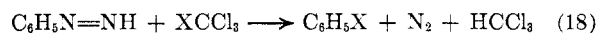
79.1° is different from that observed when the phenyl moiety is derived by reaction of phenylhydrazine with the polyhalomethanes, the phenylhydrazine-polyhalomethane system being less selective than benzoyl peroxide (Table III).

TABLE III
COMPETITION REACTIONS OF BrCCl_3 AND Cl_4C
TOWARD HALOBENZENE FORMATION (79.1°)^a

Phenyl moiety source	Initial mole ratio of Cl_4C to phenyl source	Ratio of [PhBr] to [PhCl] produced	Relative reactivity of BrCCl_3 to Cl_4C
Bz_2O_2	190	12.17	244
Bz_2O_2	190	10.86	217
$\text{C}_6\text{H}_5\text{NHNH}_2$	50	6.6	132
$\text{C}_6\text{H}_5\text{NHNH}_2$	50	6.15	123
$\text{C}_6\text{H}_5\text{NHNH}_2$	50	6.14	123

^a Initial ratio of $[\text{Cl}_4\text{C}]$ to $[\text{BrCCl}_3]$ is 20 in each case.

Examination of the product distribution data (Table I) indicates in both the BrCCl_3 and Cl_4C reactions that the ratio of halobenzene relative to benzene increases as the polyhalomethane concentration is increased. Such an observation is consistent with a mechanism in which the phenyldiimide reacts either with the polyhalomethane yielding the halobenzene, chloroform and nitrogen (reaction 18), or in a bimolecular reaction, possibly by the mechanism suggested by Huang and Kosower,¹¹ to form benzene and nitrogen (reaction 19).



Experimental Section

Materials.—Phenylhydrazine (Matheson Coleman and Bell) was distilled under vacuum (bp 138° at 20 mm) before using. Bromotrichloromethane (Dow Chemical Co.) was distilled under vacuum until it gave a single peak by gas chromatographic analysis (bp 50° at 80 mm). Carbon tetrachloride (Fisher Scientific Company) was distilled (bp 76°) and gave a single peak by glpc analysis. N,N-dimethylformamide (J. T. Baker Co., reagent grade) was distilled under vacuum (bp 60° at 40 mm) before using. Benzoyl peroxide and diacetyl peroxide (25% solution in dimethyl phthalate) were obtained from the Lucidol Division, Wallace and Tiernan, Inc., and were used without further purification. Galvinoxyl was prepared by the oxidation of 4,4'-dihydroxy-3,5,3',5'-tetra-*t*-butyldiphenylmethane with potassium ferricyanide.¹⁸ The glpc analyses were performed on a F & M Model 700 equipped with a Barber-Coleman recorder having a Disc integrator.

Oxidations of Phenylhydrazine with Polyhalomethanes.—Reaction mixtures consisting of phenylhydrazine and the polyhalomethanes in the amounts shown in Table I were heated in a 20 molar excess of N,N-dimethylformamide at the indicated temperatures. The volume of nitrogen produced was measured with a gas buret, and the quantity was determined by correcting the volume to standard conditions.¹⁹ The amounts of benzene and chloroform produced were determined by weighing out a portion of the reaction mixture with *n*-hexane which served as an internal standard for the glpc analysis which was performed on a 15 ft by 1/4 in. column packed with 20% Dow E-600 on acid washed

(18) M. S. Kharasch and B. S. Joshi, *J. Org. Chem.*, **22**, 1435 (1957).

(19) Some error in the volume of nitrogen likely results from the vapor pressure exerted by chloroform produced in the reaction mixture.

(16) C. Walling and E. R. Briggs, *J. Amer. Chem. Soc.*, **68**, 1141 (1946).

(17) P. D. Bartlett and T. Funahashi, *ibid.*, **84**, 2596 (1962).

Chromosorb W. The amounts of bromobenzene produced in the reactions with bromotrichloromethane were determined gas chromatographically with another portion of the reaction mixture weighed out with *t*-butylbenzene as the internal standard using a 12 ft by 1/4 in. column packed with 15% Ucon polar on acid washed Chromosorb W. In the carbon tetrachloride reactions, the amount of chlorobenzene produced was determined in a similar manner using *m*-chlorotoluene as the internal standard.

A 10^{-3} to 10^{-4} M solution of galvinoxyl in N,N-dimethylformamide was prepared. To ~5 ml of this solution in a test tube was added 3 drops of bromotrichloromethane and 3 drops of phenylhydrazine, and the tube immediately stoppered and placed in a dark cabinet. Within 3 min the color of the galvinoxyl had disappeared. Similar treatment of 5 ml of the galvinoxyl solution with 5 drops of bromotrichloromethane yielded a solution in which the characteristic color of galvinoxyl was present after 30 min but had disappeared when allowed to stand overnight. Treatment of 5 ml of the galvinoxyl solution with 5 drops of phenylhydrazine gave a solution in which the purple color of galvinoxyl persisted after being allowed to stand overnight.

Rate Determinations.—Solutions of bromotrichloromethane in N,N-dimethylformamide were placed in a three necked, round bottomed flask. The reaction flask was connected through a condenser and to a gas buret. After thoroughly flushing the system with nitrogen for 20 min, a solution of phenylhydrazine in N,N-dimethylformamide was added to the bromotrichloromethane solution. The flask was immediately immersed in a constant temperature oil bath. After a 5 min induction period the reading on the gas buret was taken as the initial reading of the gas in the system. The volume of nitrogen produced was read periodically from the gas buret, and the extent of reaction was calculated from the amount of nitrogen produced. In the case of the light-induced reaction, a 270-W G. E. sun lamp was employed as the

source of the radiation, and the flask was thermostated in a water bath.

Determination of Relative Reactivities of Bromotrichloromethane and Carbon Tetrachloride toward Benzoyl Peroxide.—A mixture consisting of benzoyl peroxide (0.1634 g, 0.7 mmol), bromotrichloromethane (1.3220 g, 6.7 mmol), and carbon tetrachloride (20.52 g, 133.40 mmol) was evenly divided and placed in two Pyrex tubes. The tubes were then sealed and immersed in a constant temperature oil bath at 79.5° for 21 hr. The reaction mixtures were analyzed by glpc using an 8 ft × 1/4 in. column packed with 12% diethylene glycol succinate on Chromosorb P using *m*-chlorotoluene as the internal standard for the glpc determinations of the amounts of bromobenzene and chlorobenzene formed in the reaction. Two runs were carried out, and the ratios of bromobenzene to chlorobenzene found were 12.17 and 10.86 indicating reactivity ratios of BrCCl₃ with respect to CCl₄ toward phenyl radicals of 244 and 217, respectively.

Determination of Relative Reactivities of Bromotrichloromethane and Carbon Tetrachloride toward Phenylhydrazine.—A mixture consisting of phenylhydrazine (0.4365 g, 4.00 mmol), bromotrichloromethane (1.9830 g, 10.00 mmol), and carbon tetrachloride (30.77 g, 200.00 mmol) was evenly divided and placed in three Pyrex tubes. The same procedure and method of analysis as described above were followed. The relative reactivity ratios of BrCCl₃ with regard to CCl₄ toward attack by phenyldiimide, as determined from the relative amounts of the halobenzenes, were 132, 123, and 123 for the three separate runs.

Registry No.—Phenylhydrazine, 100-63-0; bromotrichloromethane, 75-62-7; carbon tetrachloride, 56-23-5; benzoyl peroxide, 94-36-0; bromobenzene, 108-86-1; chlorobenzene, 108-90-7.

Effects of Hydrogen-Bond Formation by Phenols on the Conformational Equilibrium of *trans*-1,2-Dimethyl-3-isopropylaziridine^{1,2}

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The conformational equilibrium for inversion about nitrogen of *trans*-1,2-dimethyl-3-isopropylaziridine in cyclopentane was studied as a function of temperature in the presence and absence of equimolar substituted phenols. Hydrogen-bond formation is shown to occur between the amine and the phenols. The inversional equilibrium is shifted by the presence of phenols, and these shifts are particularly pronounced at low temperature or in the presence of a highly bulky phenol. The shifts are attributed to stereoselective hydrogen-bond formation between the phenol and the less stable invertomer.

Solvent effects on conformational equilibria are a matter of considerable interest when attempting to compare physical and chemical properties obtained under different conditions. Extensive work by Eliel and his colleagues clearly established that the conformational energy of amino and of hydroxyl groups differs in protic and aprotic solvents.^{4,5} This seemed to us to be a most significant result because of the implication that a hydrogen-bond interaction could markedly change the conformational equilibrium of a molecular system. We have been interested in examining cases based on relatively simple molecular systems in which conformational equilibria are significantly shifted as the result of complexation phenomena. Such a system

would thus constitute a model for the introduction of conformational strain energy in a substrate such as might occur in an enzyme-substrate complex.

It appeared that the conformational equilibrium of *trans*-1,2-dimethyl-3-isopropylaziridine⁶ (1), shown in Scheme I, might be affected by the presence of hydrogen-bond donors such as alcohols or phenols. This follows from the fact that in conformer **1a** the potential donor would experience greater steric repulsion (as shown in **2a**) than would a hydrogen-bonding reagent interacting with conformer **1b** (as shown in **2b**). The result of such a preferential hydrogen-bonding interaction would be to lead to a net stabilization of conformer **1b** and consequently a shift in K_{eq} . The hydrogen-bonded conformers shown in **2a** and **2b** represent only one form present in an effectively infinite distribution of hydrogen-bonded species, and our hypothesis requires that such forms constitute an experimentally observable proportion of the average

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(2) Presented in part at the 155th National Meeting of the American Chemical Society, San Francisco, Calif., March 31–April 5, 1968.

(3) National Science Foundation Undergraduate Research Participant, 1967.

(4) E. L. Eliel, *Angew. Chem. Intern. Ed. Engl.*, **4**, 761 (1965).

(5) E. L. Eliel, E. W. Della, and T. H. Williams, *Tetrahedron Lett.*, 831 (1963); E. L. Eliel and S. H. Schroeter, *J. Amer. Chem. Soc.*, **87**, 5031 (1965).

(6) A. T. Bottini, R. L. VanEtten, and A. J. Davidson, *ibid.*, **87**, 755 (1965).