addition funnel, and nitrogen inlet were placed 38.7 g (0.29 mol) of aluminum chloride and 150 ml of methylene chloride. After the gas flow was established, monochloramine was added below the surface during 1 hr at 10–15°. After an additional 30 min, a 10-ml sample was removed. Uv analysis[24] indicated no chlorine and a trace of trichloramine present. The remaining mixture was hydrolyzed with 50 ml of hydrochloric acid and 50 ml of water for 5 min at 30°. Uv analysis of a 10-ml sample showed the presence of chlorine, but no trichloramine. Uv analysis of the first sample after 24 hr showed a larger amount of trichloramine.

Acknowledgment. We thank the Graduate School and the Center for Great Lakes Studies, University of Wisconsin—Milwaukee, for support of this work.

Reactions of Azirines. Carbene and Carbenoid Reactions[1]

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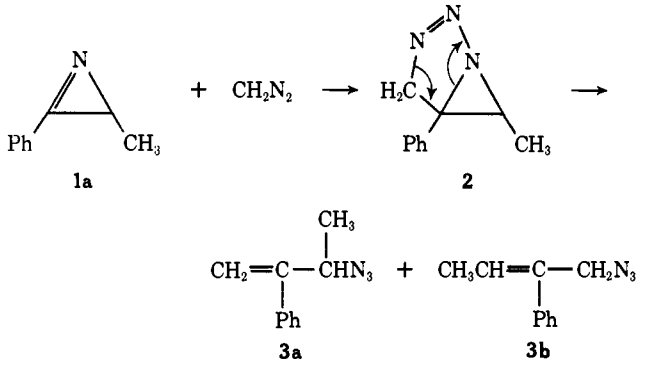
Abstract: The reaction of 1-azirines **1** with dichlorocarbene (generated from phenyl(trichloromethyl)mercury) led to formation of ring opened *N*-vinylimines **4**. Hydrolysis of **4a** produced propiophenone while treatment with azide ions gave a tetrazole. Attempts to prepare dichloroazabicyclobutanes **10**, by addition of trichloromethide ions to several azirines **1** followed by base-catalyzed ring closure of the intermediate aziridines **6**, led to azetines **9** except in the diphenyl substituted case **6c**, when **13**, a product of electrocyclic ring opening, resulted. The structure of azetines **9** was inferred from spectra including ^{13}C nmr spectra and chemical conversions. The formation of azetines **9** from **6** most likely involves an azabicyclobutane intermediate **10**. Chloroazetines **9** were further transformed to azetidinones **11** or methoxyazetine **12**.

The chemistry of azirines **1** has been of recent interest because of the high reactivity of this small ring system toward nucleophilic as well as electrophilic reagents.[2] It was also shown that this three-membered ring serves as a substrate in cycloadditions leading to pyrroles,[3] azepines,[4] pyridones,[5] and bicyclic dioxazines.[6] Experiments between azirines and carbene-like reagents have been somewhat limited. For instance, interaction of diazomethane with **1a** was shown to lead to allyl azides **3** presumably *via* cycloadduct **2**,[7] while



1a **2** **3a** **3b**

the addition of dimethylsulfonium methylide to **1b** represents the first successful synthesis of an azabicyclobutane.[8]

In connection with our continuing studies on the chemistry of azirines **1**, we would like to report on the interaction of **1** with carbenes leading to the formation of some unusual products.

Results

Generation of dichlorocarbene from phenyl(trichloromethyl)mercury[9] in refluxing benzene in the presence of 3-methyl-2-phenyl-1-azirine (**1a**) led to the open-chain product *N*-(dichlorovinylidene)-1-(1-phenylpropenyl)amine (**4a**). None of the azabicyclobutane expected from cycloaddition of $:CCl_2$ to the C=N of **1a** was detected. The structure of **4a** was apparent from its ir (C=N at 1640 cm^{-1}), nmr (methyl doublet at τ 8.24 and vinyl H at 4.8 (quartet)), and mass spectrum, as well as from its chemistry. Hydrolysis of **4a** in acid gave propiophenone and treatment with sodium azide gave the tetrazole **5**, behavior consistent with a dichloroimine structure. Altering the conditions to room temperature or 0° by generating $:CCl_2$ from phenyl(bromodichloromethyl)mercury[9] in the presence of sodium iodide still led to **4a** as the major product. Dichlorocarbene generated from potassium *tert*-butoxide and chloroform also produced **4a**. The reaction of 2,3-diethyl-1-azirine (**1d**) at room temperature gave the analogous **4d**.

Addition of trichloromethide ion to **1a** by means of trichloromethyllithium at −100° led to *cis*-3-methyl-2-phenyl-2-trichloromethylaziridine (**6a**). Further reaction with trimethyloxonium tetrafluoroborate yielded the aziridinium salt (**7**). When **6a** was allowed to stand over alumina, decomposition to dichloroacetophenone (**8**) took place. The stereochemical assign-

(1) (a) Chemistry of Small Rings. 20. For the previous paper in the series, see ref 5. (b) For a preliminary report, see A. Hassner, J. O. Currie, Jr., A. S. Steinfeld, and R. F. Atkinson, *Angew Chem., Int. Ed. Engl.*, 9, 731 (1970).

(2) See, for instance, (a) G. Smolinsky, *J. Org. Chem.*, 27, 3557 (1962); (b) S. Sato, H. Kato, and M. Ohta, *Bull. Chem. Soc. Jap.*, 40, 2936, 2938 (1967); (c) A. Hassner and F. W. Fowler, *J. Amer. Chem. Soc.*, 90, 2869, 2875 (1968); (d) N. J. Leonard and B. Zwanenburg, *ibid.*, 89, 4456 (1967).

(3) A. Padwa and J. Smolanoff, *ibid.*, 93, 549 (1971).

(4) (a) D. J. Anderson and A. Hassner, *ibid.*, 93, 4339 (1971); (b) V. Nair, *J. Org. Chem.*, 37, 802 (1972).

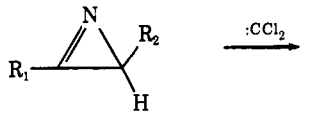
(5) A. Hassner and A. Kascheres, *ibid.*, 37, 2328 (1972).

(6) (a) F. P. Woerner, H. Reimlinger, and R. Merenyi, *Chem. Ber.*, 104, 2786 (1971); (b) A. Hassner, A. S. Miller, and M. J. Haddadin, *Tetrahedron Lett.*, 1972 (1972).

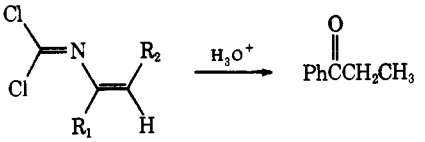
(7) A. L. Logothetis, *J. Org. Chem.*, 29, 3049 (1964); V. Nair, *ibid.*, 33, 2121 (1968).

(8) A. G. Hortman and D. A. Robertson, *J. Amer. Chem. Soc.*, 89 5974 (1967).

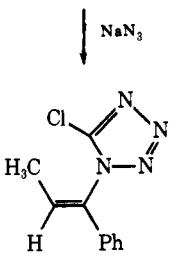
(9) D. Seyferth, J. M. Burlitich, R. J. Menasz, J. Y.-P. Mui, H. D. Simmons, Jr., A. J. H. Treiber, and S. R. Dowd, *ibid.*, 87, 4259 (1965).



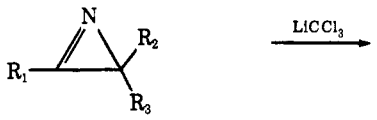
1a, R_1 = Ph; R_2 = Me
d, R_1 = R_2 = Et



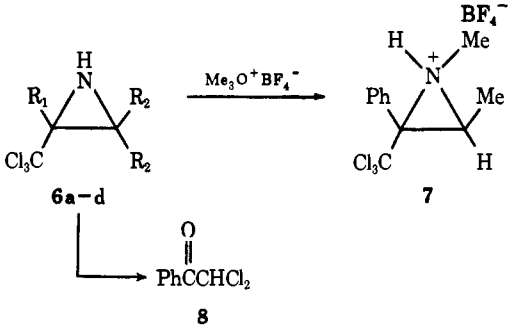
4a,d



5



1a, R_1 = Ph; R_2 = Me; R_3 = H
b, R_1 = Ph; R_2 = H; R_3 = H
c, R_1 = Ph; R_2 = Ph; R_3 = H
d, R_1 = Et; R_2 = Et; R_3 = H
e, R_1 = Ph; R_2 = Me; R_3 = Me



6a–d

7

8

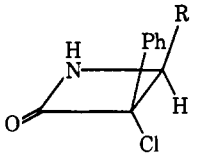
ment of cis phenyl:methyl substituents in aziridine **6a** is based on the chemical shift at τ 9.07 of the methyl substituent in **6a**. This is consistent with the observation that a methyl cis to a phenyl group tends to appear at higher field (τ 9.08–9.34) than a trans methyl group (τ 8.85–8.98).[10] Furthermore, in **6b** the hydrogen assumed to be trans to phenyl absorbs at τ 7.48 (compared with τ 7.1 in **6a**) while the cis hydrogen is found at τ 8.06. The cis stereochemistry in **6a** is also consistent with the approach of the reagent to the azirine from the least hindered side. For example, the reduction of **1a** with lithium aluminum hydride led to the stereospecific formation of *cis*-2-methyl-3-phenylaziridine.[11]

When both sides of the azirine ring are hindered as in the dimethyl substituted case **1e**, the starting material **1e** was completely recovered on exposure to trichloromethide anion.

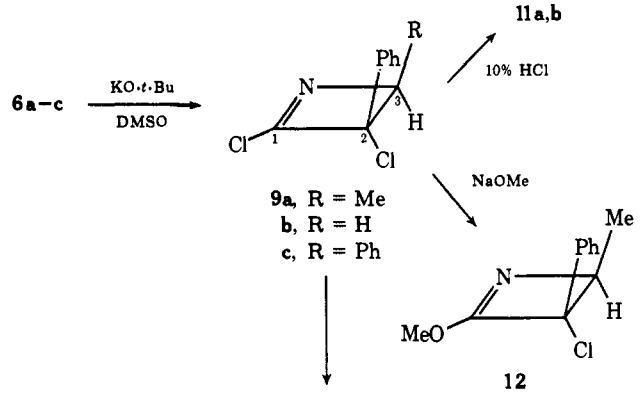
(10) (a) A. Laurent and A. Miller, *Tetrahedron Lett.*, 759 (1969); (b) A. Hassner and F. W. Fowler, unpublished results.

(11) A. Hassner and F. W. Fowler, *J. Amer. Chem. Soc.*, **90**, 2869 (1968).

Attempts to effect ring closure of **6a** to **10a** by means of tertiary amines or potassium *tert*-butoxide in THF led to recovery of starting material. On the other hand, treatment of a solution of the aziridine (**6a**) in DMSO with potassium *tert*-butoxide gave 2,3-dichloro-*cis*-4-methyl-3-phenyl-1-azetine (**9a**) in 55% yield. In analogy to the reaction of Schiff bases with dichlorocarbene or dichloromethyllithium, where the aziridine is formed,[12] the formation of the isomeric azabicyclobutane (**10a**) was expected. The ir absorption at 1580 cm^{-1} in **9a** does not permit a differentiation between the isomeric structures **9a** and **10a**.[13] That this is not the structure of the product has been clearly established. *exo*-4-Methyl-2-phenyl-1-azabicyclobutane (**10b**) was prepared by the method of Hortman[8] and compared with **9a**. The exo configuration in **10b** was assumed because of expected attack from the least hindered side, as well as from the presence of two protons at about τ 8.6, at a chemical shift where endo protons are expected. The methine proton in **9a** is found at τ 5.58 (much too low for structure **10a**),

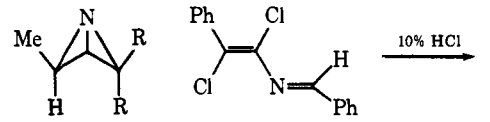


11a,b



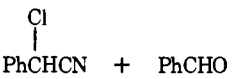
9a, R = Me
b, R = H
c, R = Ph

12



10a, R = Cl
b, R = H

13



and the ^{13}C–H coupling constant is 159 Hz (compared with 170 Hz in **10b**). When one considers the effect of the imino nitrogen in **9a** to cause the methine hydrogen to absorb at τ 5.58, one can predict a ^{13}C–H coupling of 146–167 Hz[14] (6–27 Hz greater than cyclobutene methylenes at 140 Hz[15]). The decisive proof

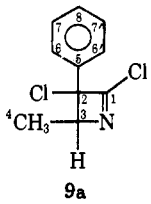
(12) O. C. Dermer and G. E. Ham, "Ethyleneimine and Other Aziridines," Academic Press, New York, N. Y., p 81.

(13) Although azirines absorb in the ir at 1780 cm^{-1}, the C=N stretching in the much less strained azetines occurs at 1620 cm^{-1} as in 2-ethoxyazetines [G. Pifferi, P. Consonni, G. Pelizza, and E. Testa, *J. Heterocycl. Chem.*, **4**, 619 (1967)] or at 1580 cm^{-1} as in 2-phenylazetines [A. B. Levy and A. Hassner, *J. Amer. Chem. Soc.*, **93**, 2051 (1971)].

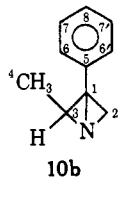
(14) B. I. Ionin and B. A. Ershov, "NMR Spectroscopy in Organic Chemistry," C. N. Turton and T. I. Turton, Translators, Plenum Press, New York, N. Y., 1970, p 144.

(15) S. Borcic and J. D. Roberts, *J. Amer. Chem. Soc.*, **87**, 1056 (1965).

is furnished by the ^{13}C spectrum of **9a** in which one of the carbons appears at a chemical shift of 25.9 ppm (relative to CS_2) corresponding to the imino carbon, while **10b** shows no absorption beyond those of the



9a

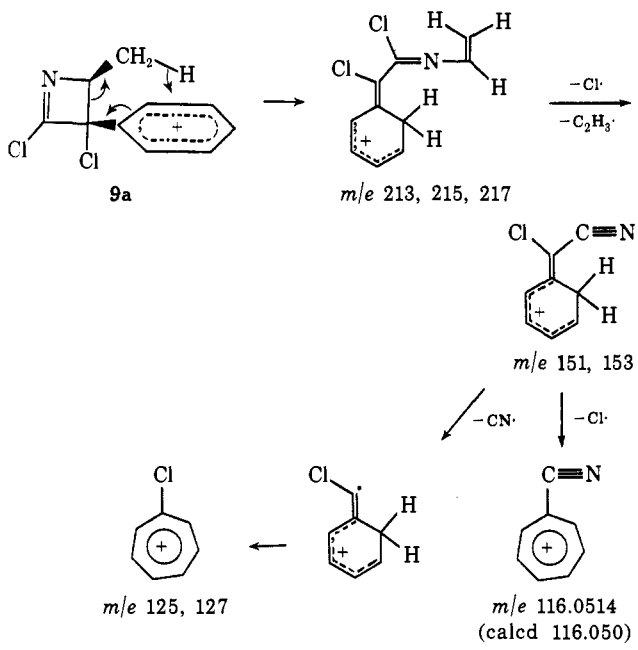


10b

^{13}C-nmr: (rel to TMS)			
	C-1	166.70	34.14
	C-2	75.88	53.28
	C-3	74.34	61.47
	C-4	15.59	12.90
	C-5	133.69	132.81
	C-6 or 7	128.33	127.66
	C-7 or 6	126.51	128.22
	C-8	126.90	127.17

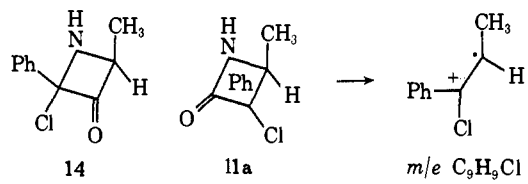
phenyl carbons at about 65 ppm. Isomeric azetines were eliminated as possibilities by considering the exact mass spectrum of **9a**. Scheme I, developed to explain

Scheme I



ions at *m/e* 125 ($C_7H_6{}^{35}Cl$, probably a chlorotropylium ion) and *m/e* 116, requires structure **9a** in cis configuration.

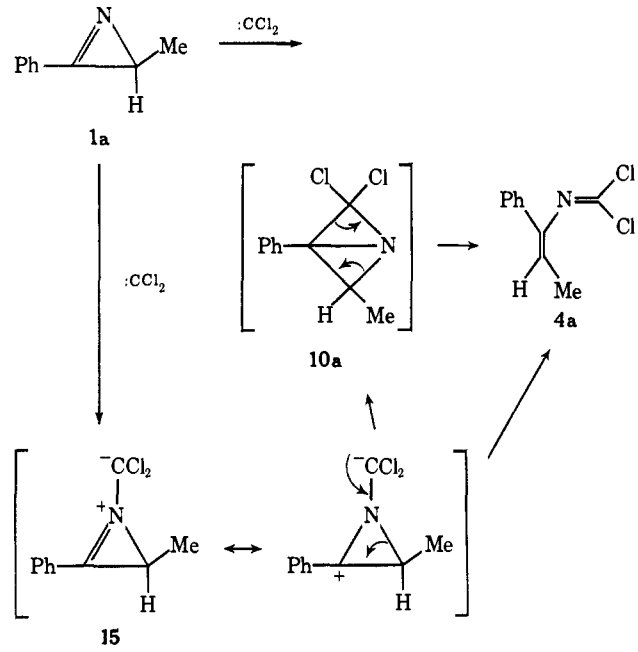
The chemical behavior of **9a** also supports its structure rather than that of **10a**. In contrast to the sensitivity of azabicyclobutanes toward acids, **9a** was recovered unchanged (80% yield) after stirring for 40 hr at 25° in anhydrous ether saturated with HCl. Aqueous HCl gave hydrolysis to *cis*-3-chloro-3-phenyl-4-methyl-2-azetidinone (**11a**). The isomeric 3-azetidinone structure **14** was eliminated by observing the ions



$C_9H_9{}^{35}Cl$ and $C_9H_9{}^{37}Cl$ ($M^+ - HNCO$) in the exact mass spectrum of **11a**. The reaction of **9a** with sodium methoxide gave *cis*-2-methoxy-3-chloro-3-phenyl-4-methyl-1-azetine (**12**). All attempts at reduction of **9a** or **11a** to the azetidine were unsuccessful. Azetine **9b**, being less substituted, is more labile and, if water is not excluded, is converted during work-up to the azetidinone **11b**. An attempt to convert *cis*-2,3-diphenyl-2-trichloromethylaziridine (**6c**) to azetine **9c** led instead to *N*-(benzylidene)-α,β-dichloro-α-styrylamine (**13**). In support of structure **13** rather than one analogous to **4** is its hydrolysis with 10% HCl to benzaldehyde and α-chloro-α-phenylacetonitrile in a 1:1 ratio.

Discussion

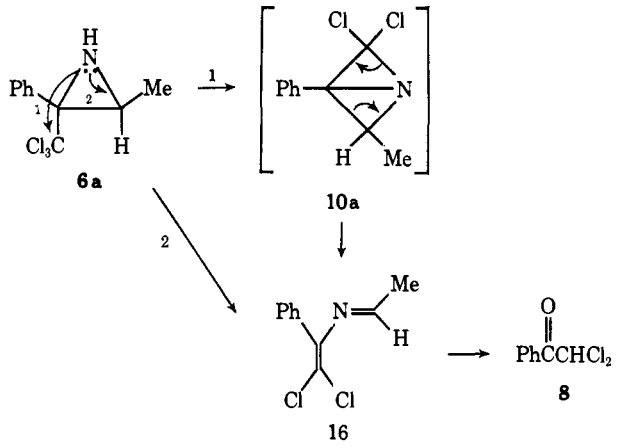
The reaction of 3-methyl-2-phenylazirine (**1a**) with dichlorocarbene to give **4a** appears to proceed *via* one of two possible pathways. One involves formation of the azabicyclobutane **10a** and subsequent rearrangement, in a manner analogous to the rearrangement of bicyclobutanes to butadienes. The alternative involves the formation of a dipolar species **15** with subsequent collapse to the product, either directly or *via* **10a**. We



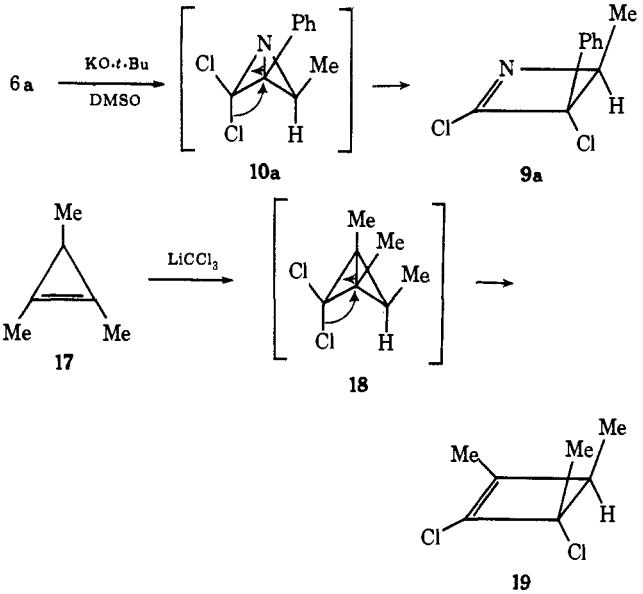
favor this second pathway for the reasons discussed below.

The trichloromethylaziridine (**6a**) reacted in the presence of alumina to lead ultimately to dichloroacetophenone (**8**). Although azabicyclobutane **10a** could have been involved here, it is certain that it cannot be an intermediate in the formation of **4**, **8**, and **9**. Only one of the two different directions of ring opening can be the lowest energy pathway. Since **10a** appears to be an intermediate in the conversion of **6a** to **9a**, we conclude that the intermediate **6** is probably involved in the hydrolysis of **16** on alumina leading to **8**. No attempts were made to establish that acetaldehyde was also formed in the hydrolysis.

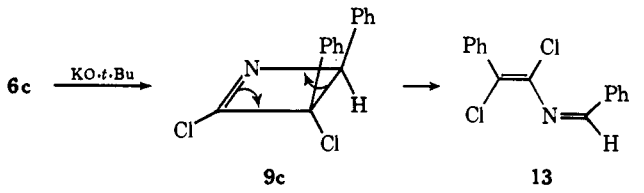
The intermediacy of **10a** in the reaction of **6a** with potassium *tert*-butoxide in DMSO seems more likely, since in fact no suitable alternative exists. The second step may proceed either with a chloride ion from the medium attacking the bridgehead carbon with sub-



sequent migration of the central bond and loss of one of the geminal chlorines or by concerted migration of the endo chlorine to the carbon bridgehead position (see below). To test the first possibility, the reactions were run in the presence of methoxide and cyanide ions. In neither case was the added ion incorporated into the 3 position of **9a**. The conclusion that endo chlorine migration takes place gains support from the recent observation that similar rearrangements take place in chlorazirines[16] as well as in carbocyclic system **18**.[17] As with the azirine, addition presumably took place exclusively on the least hindered side of the trimethylcyclopropene (**17**) to give *exo*-4,4-dichloro-1,2,3-trimethylbicyclobutane (**18**) followed by immediate rearrangement to the *cis*-cyclobutene **19**. If chlorine migration is so facile then azabicyclobutane **10** cannot be involved in either the formation of **4a** or **8**. The possibility that DMSO provides a necessary medium for migration in **10a** cannot be excluded, but in light of the rearrangement of **18** to **19** in dimethyl ether, this seems unlikely.



The different behavior of **6c**, which unlike **6a** or **6b** led to ring-opened product **13**, is attributable to the more facile electrocyclic ring opening of the diphenylazetine intermediate **9c**. Comparison with the analogous cyclobutene system[18] indicates that the presence of phenyl groups significantly lowers the transition state energy in the conrotatory ring opening to butadienes.



Experimental Section[19]

N-(**Dichlorovinylidene**)-**1-(1-phenylpropenyl)amine** (**4a**). To 4.95 g (0.0125 mol) of phenyl(trichloromethyl)mercury dissolved in 25 ml of benzene (freshly distilled from P_2O_5) was added 1.63 g (0.0125 mol) of 3-methyl-2-phenyl-1-azirine (**1a**).[20] The mixture was heated to reflux under nitrogen for 45 hr, then cooled to room temperature, and the precipitate removed by filtration. The filtrate was concentrated to one-third volume, cooled, and filtered again. The concentration–filtration process was continued until no further precipitation occurred or until no mercury compounds were visible on tlc. The removal of all the solvent produced 2.5 g of an oil whose nmr spectrum indicated a 2:3 mixture of 3-methyl-2-phenyl-1-azirine and product, respectively.

The oil (2.5 g) was applied to layers of silica gel and the layers developed with hexane–benzene (47:3).

The major band (R_f *ca.* 0.21) yielded 1.1 g (41%) of an oil (**4a**): nmr (CCl_4) τ 2.72 (s, 5, aromatic), 4.8 (q, 1, J = 7.2 Hz, C=CH—), 8.24 (d, 3, J = 7.2 Hz, CH_3); ir (neat) 1640 (s) and 890 cm^{-1} (s); mass spectrum *m/e* (rel intensity) 213, 215, 217 (43, 30, 5, M^+), 178, 180 (24, 8), 117 (100, $M^+ - CCl_2N$), 115 (61.5). *Anal.* Calcd for $C_{10}H_9NCl_2$: C, 56.10; H, 4.21. Found: C, 56.25; H, 4.30.

The second band (R_f 0.35) yielded 10 mg of an oil: nmr ($CDCl_3$) τ 2.61 (s, 5, arom), 4.9 (q, 1, J = 7.2 Hz, C=CH), 8.22 (d, 3, J = 7.2 Hz, CH_3); ir (neat) 1640 (w, C=C), 835 cm^{-1} (s); mass spectrum *m/e* (rel intensity) 295, 297, 299, 301 (3.5, 3.45, 2.35, 0.43, $M^+ - C_{11}H_9NCl_4$), 260, 262, 264 (3.0, 2.66, 0.67, $M^+ - Cl$), 232, 234, 236 (3.3, 3.16, 1.1), 224, 226, 228 (3.3, 2.26, 0.67), 185, 187 (5.35, 3.65), 117 (100, $M^+ - C_2Cl_4N$).[21]

N-(**Dichlorovinylidene**)-**3-(3-hexenyl)amine** (**4d**). To 4.4 g (0.01 mol) of phenyl(bromodichloromethyl)mercury[22] dissolved in 45 ml of dry benzene was added 1.0 g (0.01 mol) of 2,3-diethyl-1-azirine (**1d**). To this mixture was added 1.5 g (0.01 mol) of NaI in 7 ml of dry dimethoxyethane. The reaction was stirred under N_2 for 19 hr at room temperature. The reaction mixture was treated as in the preparation of **4a** to give 0.5 g of a liquid product which the nmr spectrum indicated was a 4:5 mixture of the azirine and product, respectively. The excess azirine was removed by distillation *in vacuo* to give 265 mg of **4d**: nmr (CCl_4) τ 5.5–5.0 (m, containing apparent triplet, 1, J = *ca.* 7.4 Hz, C=C*H*–),

(16) J. Ciabattoni and M. Cabell, Jr., *J. Amer. Chem. Soc.*, 93, 1482 (1971).

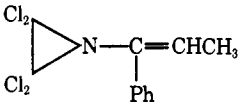
(17) B. M. Trost and R. C. Atkins, *Chem. Commun.*, 1274 (1971).

(18) The electrocyclic ring opening of *cis*-1,2,3,4-tetramethylcyclobutene proceeds with E_a = 35.8 kcal/mol [R. Criegee, *Angew. Chem., Int. Ed. Engl.*, 7, 559 (1968)], while for the tetraphenyl compound E_a = 25 kcal/mol [H. H. Freedman, G. A. Doorakian, and V. R. Sandel, *J. Amer. Chem. Soc.*, 87, 3019 (1965)].

(19) All melting and boiling points are uncorrected. Infrared spectra were recorded with a Perkin-Elmer IR-21 spectrometer and ^{1}H-nuclear magnetic resonance spectra were taken on a Varian A-60-A spectrometer. ^{13}C–H coupling constants were determined on a Varian HA-100 spectrometer with the aid of a time-averaging computer. Mass spectra were obtained on a Varian CH-5 instrument at 70 eV. Exact mass spectra were run by the Purdue University Mass Spectrometer Center. Microanalyses were performed by Galbraith Laboratories, Knoxville, Tenn.

(20) Prepared from 1-azido-1-phenyl-1-propene [A. Hassner and F. W. Fowler, *J. Org. Chem.*, 33, 2686 (1968)] by pyrolysis in refluxing benzene.

(21) The spectra of this minor product are consistent with the structure



formed from :CCl_2 addition to **4a**.

(22) D. Seyferth and J. M. Burlitch, *J. Organometal. Chem.*, 4, 127 (1965).

7.5–8.3 (m, 4, CH_2), 8.99 (two overlapping triplets, 6, CH_3); ir (neat) 1640 (vs) and 890 cm^{-1} (vs).

Hydrolysis of Enamine 4a. To 0.2 g of **4a** was added 3.0 ml of methanol and 10.0 ml of 20% aqueous HCl. After stirring 4 hr at 25°, the mixture was poured into 50 ml of water and extracted with 125 ml of ether in three portions. The combined ether layers were washed with water and dried over $MgSO_4$. Filtration and removal of solvent *in vacuo* gave a liquid which had nmr and ir spectra identical with those of an authentic sample of propiophenone. Similar results were obtained using concentrated H_2SO_4.

5-Chloro-1-(1-phenylpropenyl)tetrazole (5). To a solution of 0.31 g (4.7 mmol) of sodium azide dissolved in 2.5 ml of water was added 1.0 g (4.7 mmol) of **4a** dissolved in 9.0 ml of acetone. The mixture was stirred at 50° for 15 min and then heated at reflux for 50 min. The reaction mixture was cooled to room temperature and after 35 ml of CH_2Cl_2 was added it was extracted with 40 ml of water in two portions. The organic phase was then dried over $MgSO_4$ and filtered, and the solvent removed *in vacuo* to give 1.0 g of an oil. The product was separated from impurities on a preparative layer of silica gel that was developed with dichloromethane–hexane (1:1). Elution of the product from the silica gel with chloroform followed by removal of the solvent *in vacuo* gave an oil that crystallized on cooling. Recrystallization from CCl_4–pentane gave colorless crystals: mp 44.5–45.5°; nmr (CCl_4) τ 2.5–3.0 (m, 5, aromatic), 3.75 (q, 1, J = 7.2 Hz, C=CH—), 7.98 (d, 3, J = 7.2 Hz, CH_3).

Anal. Calcd for $C_{10}H_9N_4Cl$: C, 54.43; H, 4.11; N, 25.39. Found: C, 54.64; H, 4.12; N, 25.17.

***cis*-3-Methyl-2-phenyl-2-trichloromethylaziridine (6a).** A solution of 1.08 g (8.2 mmol) of 2-phenyl-3-methyl-1-azirine (**1a**) and 5.2 ml (65 mmol) of dry chloroform in 25 ml of dry tetrahydrofuran and 25 ml of anhydrous ether was cooled to −95° in an ether–liquid nitrogen slush bath. A solution of 1.12 g (10 mmol) of potassium *tert*-butoxide in 15 ml of tetrahydrofuran was added with stirring over 40 min keeping the reaction mixture below −90°. After stirring at −90° for 2 hr, 1 ml of water was added and the mixture was allowed to warm up to 0° before pouring into 100 ml of cold water. The resulting mixture was separated and the water layer extracted once with ether. The combined organic layers were dried over $MgSO_4$ and filtered, and the solvent removed *in vacuo*. Distillation in a bulb-to-bulb apparatus at 80° and 0.1 mm gave 1.54 g (75%) of **6a**: ir (neat) 3290 cm^{-1} (NH); nmr (CCl_4) τ 2.3–2.8 (m, 5, aromatic), 2.9 (q, 1, J = 5.7 Hz, CH), 8.1 (broad s, 1, NH), and 9.07 (t, 3, J = 5.7 Hz, CH_3); mass spectrum ($P^+ - Cl$) *m/e* 214, 216, 218 (rel intensity, 100, 64.4, 11.1).

An analytical sample was obtained by vpc using an SE-52 column at 150°.

Anal. Calcd for $C_{10}H_{10}NCl_3$: C, 47.93; H, 4.02. Found: C, 47.65; H, 3.92.

2-Phenyl-2-trichloromethylaziridine (6b). The same procedure described for the preparation of **6a** was used. Starting with 4.0 g of crude 2-phenyl-1-azirine (**1b**)[11] (containing 20% of vinyl azide) about 7 g of a brown oil was obtained. Chromatography over 200 g of alumina (activity I) with 50% chloroform–Skellysolve B removed the azide and further elution with 5% ethanol–chloroform gave 4.98 g (77%) of **6b** as a brown oil: ir (neat) 3260 cm^{-1} (NH); nmr (CCl_4) τ 2.2–2.9 (m, 5, aromatic), 7.48 (s, 1, CH trans to Ph), 8.06 (s, 1, CH cis to Ph), and 8.4 (s, 1, NH).

Anal. Calcd for $C_9H_8NCl_3$: C, 45.70; H, 3.41. Found: C, 45.53; H, 3.51.

***cis*-2,3-Diphenyl-2-trichloromethylaziridine (6c).** The procedure described for the preparation of **6a** was used starting with 19.3 g (0.1 mol) of 2,3-diphenylazirine (**1c**).[11] The ether solution of the product was decolorized with charcoal to give 31 g of the crude **6c** as a yellow solid. Recrystallization from methanol gave 22 g (70%) of white needles: mp 119.5–121°; ir (CCl_4) 3320 cm^{-1} (NH); nmr (CCl_4) τ 2.5–3.1 (m, 10, aromatic), 6.07 (broad s, 1, CH), and 7.6 (broad s, 1, NH). (D_2O causes loss of the τ 7.6 peak and sharpening of the 6.07 peak.)

Anal. Calcd for $C_{15}H_{12}Cl_3N$: C, 57.62; H, 3.87; Cl, 34.02; N, 4.48. Found: C, 57.71; H, 3.80; Cl, 33.97; N, 4.44.

***cis*-2,3-Diethyl-2-trichloromethylaziridine (6d).** The procedure used was the same as that for the preparation of **6a**, starting with 2,3-diethyl-1-azirine (**1d**).[11] The resulting brown oil was chromatographed over 100 g of silica gel eluting with 50% chloroform–petroleum ether. A 30% yield of **6d** was obtained as a yellow oil. The spectral data are as follows: ir (neat) 3330 cm^{-1} (NH); nmr (CCl_4) complex multiplets τ 7.5–9.1; mass spectrum *m/e* 180, 182, 184 (rel intensity 54, 37, 6, M^+).

1,2-Dimethyl-3-phenyl-3-trichloromethylaziridinium Tetrafluoroborate (7). To 0.15 g (0.6 mmol) of **6a** dissolved in 5 ml of dry dimethoxyethane was added 0.93 g (0.6 mmol) of trimethyloxonium tetrafluoroborate. The mixture was stirred under nitrogen for 1 hr and the solvent removed *in vacuo* to give a solid residue. This residue was dissolved in acetone–ether which upon cooling yielded 0.11 g (52%) of colorless crystals of **7**: nmr (acetone-d_6) τ 2.0–2.5 (m, 5, aromatic), 2.6–2.9 (broad singlet, 1, NH), 5.32 (q, 1, J = 6.5 Hz, CH), 6.91 (s, 3, NCH_3), 8.32 (d, 3, J = 6.5, CCH_3); ir (KBr) 3400 (NH) and 2210–2700 cm^{-1} (NH).

Anal. Calcd for $C_{11}H_{13}BCl_3F_4N$: C, 37.49; H, 3.72; N, 3.97; Cl, 30.18. Found: C, 37.68; H, 3.66; N, 3.80; Cl, 30.37.

Reaction of 6a on Alumina. Compound **6a** (0.057 g) was dissolved in pentane and placed on a column of neutral alumina (10.0 g) that had been prepared in pentane, and was allowed to remain on the column overnight. Subsequent elution with dichloromethane and removal of the solvent *in vacuo* gave 40 mg (72%) of dichloroacetophenone (**8**). The ir and nmr spectra were identical with those of an authentic sample.

***cis*-2,3-Dichloro-3-phenyl-4-methyl-1-azetine (9a).** A solution of 3.5 g (13.7 mmol) of **6a** in 65 ml of dry DMSO was stirred while 1.7 g (15.2 mmol) of potassium *tert*-butoxide in 30 ml of DMSO was added dropwise. The addition took 45 min and the resulting mixture was stirred 3 hr before being poured into 150 ml of cold saturated NaCl solution. After extraction with 300 ml of chloroform in three portions, the combined organic layers were washed with 500 ml of water in five portions and dried over $MgSO_4$. After evaporation of the solvent *in vacuo* the brown oil was placed on a column containing 100 g of silica gel. Elution with a 50:48:2 mixture of $CHCl_3$–Skellysolve B–ethanol gave a light yellow band followed by a dark brown band. The yellow band yielded 1.6 g (55%) of **9a** as a brown oil: ir (neat) 1580 cm^{-1} (C=N); nmr (CCl_4) τ 2.62 (s, 5, aromatic), 5.58 (q, 1, J = 6.7 Hz, CH), and 9.07 (d, 3, J = 6.7 Hz, CH_3); ^{13}C–H coupling constant for the methine proton, 159 Hz; mass spectrum *m/e* 213, 215, 217 (rel intensity 100, 71, 9, M^+).

Anal. Calcd for $C_{10}H_9NCl_2$: C, 56.10; H, 4.24. Found: C, 56.15; H, 4.47.

2,3-Dichloro-3-phenyl-1-azetine (9b). A solution of 2.0 g (8.5 mmol) of **6b** in 45 ml of DMSO was stirred under a N_2 atmosphere at 25° while 1.0 g (9.0 mmol) of potassium *tert*-butoxide in 35 ml of DMSO was added dropwise. After stirring for 2 hr, the mixture was extracted with 200 ml of hexane in ten portions. The combined extracts were filtered twice through paper and evaporated *in vacuo*. The resulting light brown oil was placed on a silica gel preparative tlc plate and eluted with chloroform. The strong band at R_f 0.60 gave 105 mg (6%) of **9b** as a yellow oil: ir (neat) 1580 cm^{-1} (C=N); nmr (CCl_4) τ 2.3–2.5 (m, 5, aromatic) and 5.58 (s, 2, CH_2); mass spectrum *m/e* (rel intensity) 199, 201, 203 (32, 22, 3.8, M^+), 198, 200, 202 (38, 27, 5.9, $M^+ - H$), 164, 166 (71, 26, $M^+ - Cl$), 138, 140 (40, 14, $M^+ - Cl - CN$), 103 (100, $M^+ - Cl_2 - CN$). The presence of azetidinone **11b** was also indicated. The latter was isolated if water was used in the work-up.

Anal. Calcd for $C_9H_7Cl_2N$: C, 54.03; H, 3.53; N, 7.00. Found: C, 54.07; H, 3.63; N, 7.11.

***cis*-3-Chloro-3-phenyl-4-methyl-2-azetidinone (11a).** A mixture of 0.6 g (2.8 mmol) of **9a** in 2 ml of acetone was added slowly to 25 ml of rapidly stirring 10% aqueous HCl. The resulting mixture was stirred 20 hr at room temperature. After neutralization with sodium carbonate the mixture was extracted with 40 ml of ether in two portions. The combined organic layers were dried over $MgSO_4$ and evaporated *in vacuo* giving 0.48 g (80%) of a brown oil. Four recrystallizations from benzene–petroleum ether gave **11a** as a yellow solid: mp 126–127.5°; ir (CCl_4) 3435, 3240 (NH) and 1798, 1778 cm^{-1} (C=O); nmr ($CDCl_3$) τ 2.6 (m, 6, NH and aromatic), 5.81 (q, 1, J = 6.4 Hz, CH), and 9.11 (d, 3, J = 6.4 Hz, CH_3); mass spectrum *m/e* (rel intensity) 152, 154 (92, 35, $M^+ - NHCO$), 117 (100, $M^+ - NHCO - Cl$).

Anal. Calcd for $C_{10}H_{10}ClNO$: C, 61.38; H, 5.15. Found: C, 61.66; H, 5.18.

3-Chloro-3-phenyl-2-azetidinone (11b). The same procedure used to hydrolyze **9a** was used except that the reaction time was only 5 hr. The product was purified on a silica gel preparative tlc plate. Elution with 50:45:5 chloroform:petroleum ether:ethanol gave a band at R_f 0.30 which yielded **11b** (29%) as a yellow oil. Recrystallization from benzene–petroleum ether gave fine white needles: mp 98–99°; ir (CCl_4) 3435, 3240 (NH) and 1797, 1778 cm^{-1} (C=O); nmr ($CDCl_3$) τ 2.3–2.7 (m, 5, aromatic), 3.0 (broad s, 1, NH), and 6.12 (s, 2, CH_2); mass spectrum *m/e* (rel intensity) 138, 140 (89, 29, $M^+ - NHCO$), 103 (100, $M^+ - NHCO - Cl$).

Anal. Calcd for C_9H_8ClNO: C, 59.51; H, 4.41. Found: C, 59.72; H, 4.20.

***cis*-2-Methoxy-3-chloro-3-phenyl-4-methyl-1-azetine (12).** A mixture of 0.110 g (0.51 mmol) of **9a** and 0.050 g (0.95 mmol) of sodium methoxide in 7 ml of methanol was stirred at 25°. After 22 hr, tlc showed no more starting material. The mixture was evaporated to 1 ml of liquid and placed on a silica gel preparative tlc plate. Elution with 10:85:5 chloroform–Skellysolve B–ethanol gave a band at R_f 0.60 which yielded 30 mg (28%) of **12** as a light yellow oil: ir (neat) 1633 cm^{-1} (C=N); nmr (CCl_4) τ 2.7 (s, 5, aromatic), 5.99 (s, OCH_3), 6.02 (q, J = 6.7 Hz, CH, total area of 5.99 and 6.02 peaks is 4), and 9.12 (d, 3, J = 6.7 Hz, CH_3); mass spectrum *m/e* (rel intensity) 209, 211 (78, 46, M^+), 208, 210 (41, 29, $M^+ - 1$), 194, 196 (64, 22, $M^+ - Me$), 174 (100, $M^+ - Cl$), and 159 (43, $M^+ - Me - Cl$).

Anal. Calcd for $C_{11}H_{12}ClNO$: C, 63.01; H, 5.77; Cl, 16.91. Found: C, 63.05; H, 5.93; Cl, 16.84.

***N*-(Benzylidene)-α,β-dichloro-α-styrylamine (13).** A solution of 2.0 g (6.4 mmol) of **6c** was stirred in 40 ml of DMSO under a N_2 atmosphere while 0.84 g (7.5 mmol) of potassium *tert*-butoxide in 25 ml of DMSO was added dropwise. Addition took 45 min and stirring was continued for 6 hr. The resulting mixture was poured into 100 ml of salt solution and extracted with 120 ml of chloroform in two portions. The combined organic layers were dried over $MgSO_4$, decolorized with charcoal, and filtered, and the solvent removed *in vacuo*. The resulting yellow solid was placed on a column of 30 g of silica gel and eluted with 10% chloroform–petroleum ether. A light yellow band separated and was collected. Removal of solvent gave **13** as a yellow oil which crystallized at −20° and was very hygroscopic: ir (neat) 1605 cm^{-1} (C=N); nmr (CCl_4) τ 2.2–2.9 (m, aromatic) and 1.62 (s, CH).

Anal. Calcd for $C_{15}H_{11}Cl_2N$: C, 65.23; H, 4.02; N, 5.07; Cl, 25.68. Found: C, 65.00; H, 4.22; N, 5.21; Cl, 25.41.

Hydrolysis of 13. Using the same procedure as in the hydrolysis of **6a** to **11a**, **13** was hydrolyzed in 20 hr to a 1:1 ratio of benzaldehyde and α-chlorophenylacetonitrile. The yield of the mixture was 20% with 50% of **13** remaining unchanged. Hydrolysis for 45 hr at 25° gave a 52% yield of benzaldehyde but only a 10% yield of the nitrile. These components were separated on preparative silica gel plates. Elution with 60% chloroform–petroleum ether gave the benzaldehyde at R_f 0.45, and the nitrile at R_f 0.55. Benzaldehyde was identified by comparing the ir with an authentic sample as well as vpc comparison using a 3% XE-60 column at 75°. In addition, the mass spectrum showed a parent peak at *m/e* of 106. α-Chlorophenylacetonitrile was identified by its mass spectrum, *m/e* (rel intensity) 151, 153 (19, 6.5, M^+), 116 (100, $M^+ - Cl$), 89 (19, $M - Cl - HCN$); a metastable peak at *m/e* 68 indicates that the *m/e* 89 peak is derived from the 116 peak by loss of 27 (HCN). In addition the nmr spectrum (CCl_4) shows τ 2.53 (m, 5, aromatic) and 4.5 (s, 1, CH).

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Mechanism of the Ferric Ion Catalyzed Decomposition of Hydrogen Peroxide. Effect of Organic Substrates[1]

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Abstract: The retardation of the Fe^{3+} catalyzed decomposition of H_2O_2 in $HClO_4$ solution by a number of organic substrates has been examined. Results with acetone, acetic acid, and *tert*-butyl alcohol are consistent with the redox chain mechanism of Barb, Baxendale, George, and Hargrave on the assumption that the substrates trap hydroxyl radicals which otherwise react with H_2O_2. Data show the predicted form and yield ratios of rate constants in fair agreement with those derived from radiation chemistry and Fe^{2+}–H_2O_2 experiments. The treatment also predicts the observed dependence on $[H^+]$, effect of Cu^{2+}, and primary isotope effect with CD_3COCD_3, and indicates kinetic chains of 30, much shorter than those estimated by Barb, *et al.*

Although the ferric ion catalyzed decomposition of hydrogen peroxide in acid solution has long been of interest and has received extensive study, two completely conflicting interpretations exist for its mechanism. The older scheme, elaborated by Barb, Baxendale, George, and Hargrave,[3] involves a redox radical chain

$$Fe^{3+} + H_2O_2 \xrightarrow{k_1} Fe^{2+} + HO_2\cdot + H^+ \quad (1)$$

$$Fe^{2+} + H_2O_2 \xrightarrow{k_2} Fe^{3+} + HO^- + HO\cdot \quad (2)$$

$$HO\cdot + H_2O_2 \xrightarrow{k_3} H_2O + HO_2\cdot \quad (3)$$

$$HO_2\cdot + Fe^{3+} \xrightarrow{k_4} H^+ + Fe^{2+} + O_2 \quad (4)$$

$$HO_2\cdot + Fe^{2+} \xrightarrow{k_5} HO_2^- + Fe^{3+} \quad (5)$$

leading to an overall rate expression at high H_2O_2/Fe^{3+} ratios.

$$-d[H_2O_2]/dt = 2(k_1k_2k_4/k_5)^{1/2}[H_2O_2][Fe^{3+}] \quad (6)$$

More recently, Kremer and Stein[4] have proposed an alternative path not involving $HO\cdot$ or Fe^{2+}, but a series of intermediate complexes.

$$H_2O_2 + Fe^{3+} \rightleftharpoons H^+ + FeOOH^{2+} \longrightarrow HO^- + FeO^{3+} \xrightarrow{H_2O_2} O_2 + H_2O + Fe^{3+} \quad (7)$$

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