Pyrolysis of 3-Chloro-3-aryldiazirines, Kinetics and Mechanism

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The thermal decomposition of 3-chloro-3-aryldiazirines in various solvents has been investigated over the temperature range 60-100 °C. The intermediate carbenes have been isolated as norcaranes by the use of cyclohexene. Substituent effects on rates of reaction are small and a Hammett correlation was unsuccessful with either σ or σ^+ constants. Possible mechanisms for the decompositions are discussed.

La décomposition thermique des chloro-3 aryl-3 diazirines dans divers solvants, a été examinée dans un domaine de température de 60 à 100 °C. Les carbènes intermédiaires ont été isolés sous forme de norcaranes en présence de cyclohexène. Les effets des substituants sur les vitesses de réaction sont faibles et une corrélation de Hammett est appliquée sans succès que ce soit avec les constantes σ ou σ^+ . Les mécanismes possibles pour ces décompositions sont discutés. [Traduit par le journal]

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Introduction

The nature of the pathway of ring rupture in diazirine is not well understood. In the thermal decomposition of 3-chloro-3-alkyldiazirines (1, 2) Frey et al. proposed transition state I as the simplest representation for a diazirine decomposition, where the two carbon-nitrogen bonds are broken simultaneously. Schmitz (3) has postulated an ionic mechanism, II, as the most probable pathway on the grounds of the relative instability of a-ketopentamethylenediazirine as compared with pentamethylenediazirine. Mitsch and co-workers (4, 5) prefer a mechanism involving the transient existence of a diazomethane intermediate prior to the loss of nitrogen. It is likely that such a mechanism would require transition state III. Bottomly and

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Nyberg (6) have studied the thermal decomposition of 3,3-dimethyldiazirine at relatively low temperature and suggested that the transition state was non-cyclic and probably radical in nature.

In our recent work (7, 8), we observed that the rate of diazirine decomposition shows very little solvent effect and we concluded that the transition state of the rate determining step is likely to be more radical than ionic. The present work was undertaken to examine the effect of para-substituents on the rates and activation parameters in the thermal decompositions of a series of 3-chloro-3-aryldiazirines, in the hope that a further elucidation of the transition state would be provided.

Experimental

I.r. and n.m.r. spectra were obtained with Perkin–Elmer Model 257 and Varian Associates, T 60 instruments respectively. The chemical shifts are given in τ scale together with splitting patterns, assignments, and relative integrated areas. The u.v. spectra were measured with a Unicam sp. 800 spectrophotometer. V.p.c. analyses were carried out using a Perkin–Elmer model F 11 equipped with a hydrogen flame detector; the peak areas were integrated by a ball and disc integrator. Elemental analyses were by Franz Pascher, Bonn, Germany.

Solvents

Cyclohexene was passed through alumina column to remove impurities and was fractionally distilled. Diethyleneglycol monoethyl ether (DEGME) and dimethyl sulfoxide (DMSO) were stirred with calcium hydride for 1 day and fractionally distilled under anhydrous conditions.

3-Chloro-3-aryldiazirines

These compounds were prepared from the corresponding amidine hydrochlorides by oxidation with aqueous sodium hypochlorite in DMSO according to the method of Graham (9). The phenyl, p-tolyl and p-chlorophenyl compounds were purified by column chromatography (silica gel – pentane or pentane and dichloromethane). The p-methoxyphenyl and p-nitrophenyl compounds were recrystallized from pentane (Norite). Yields and physical properties are listed in Table 1.

Kinetics Procedure

(a) By Vapor Phase Chromatography

The rates of reaction were measured by following the disappearance of diazirine, as described previously (8).

(b) By Nitrogen Evolution Method

The reaction was carried out by mixing a specific amount

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Aryl	Yield* (%)	$I.r.^{\dagger}$ (N=N, cm ⁻¹)	U.v. λ max (ε)‡ (nm in cyclohexane)
<i>p</i> -Methoxy- phenyl	57	1565	412 (416), 391 (492), 372 (307), 354 (164), 337 (93)
<i>p</i> -Tolyl	58	1566	400 (314), 396 (305), 390 (285), 379 (346), 361 (220), 343 (130)
Phenyl	54	1570	395 (213), 389 (210), 384 (194), 374 (229), 370 (204), 355 (125), 339 (53)
p-Chlorophenyl	59	1570	396 (304), 391 (308), 386 (324), 375 (345), 357 (276), 340 (132)
p-Nitrophenyl	23	1579	385 (395), 380 (492), 366 (624), 348 (490), 330 (407)

TABLE 1. Yields and physical properties of 3-chloro-3-aryldiazirines

*Based on amidine hydrochlorides.

[†]Neat except *p*-nitrophenyl in carbon tetrachloride.

 $\pm \lambda_{\max}$ or shoulders of complicated characteristic absorption of diazirines.

TABLE 2. Observed wavelengths (nm) of 3-chloro-3-aryldiazirines

Solvent	<i>p</i> -Methoxy- phenyl	<i>p</i> -Tolyl	Phenyl	<i>p</i> -Chlorophenyl	<i>p</i> -Nitrophenyl
Cyclohexene	395	412	403	396	384
DMSO	394	410	400	392	_
DEGME	390	414	400	390	380

of diazirine with appropriate thermo-equilibrated solvent in the reaction vessel, which was immersed in the oil bath and connected to a gas burette. The first order rate coefficients were determined graphically from the plot of log $(V_{\infty} - V_i)$ against time where V_{∞} is the volume of nitrogen measured at infinite time and V_i is that at time *i*.

(c) By Ultraviolet Spectrophotometry

The detailed experimental procedure was as described in our earlier work (8). The first order rate coefficients were determined graphically from the plot of log $(D_t - D_{\infty})$ against time, where D_t is the optical density at the wavelength of observation and D_{∞} corresponds to that of the complete reaction. The wavelengths of observation are given in Table 2.

Product Analyses

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(a) Decompositions in Cyclohexene

(a-1) 7-Chloro-7-p-nitrophenylnorcarane

One gram of 3-chloro-3-*p*-nitrophenyldiazirine in 50 ml of cyclohexene was heated at 80° for 7 h. The solvent was removed under reduced pressure, leaving 1.3 g of yellow oil whose t.l.c. had one main spot with trace amount of other compounds. The n.m.r. of this material showed major peaks at $1.6 \sim 2.7$ (m, aromatic-H, 4) and at $7.8 \sim 8.8$ (m, cyclohexane ring-H, 10). Other minor absorptions showed two small sharp doublets of equal intensity at 5.27 and 5.40, and a small detectable multiplet at $4.1 \sim 4.8$; these absorp-

tions were probably due to the products (~15% estimated from peak area ratio in n.m.r. spectra) resulting from the insertion of carbene into the saturated C—H bonds of the cyclohexene ring. After leaving the oil at room temperature to air for several weeks, the major part crystallized. Repeated crystallization from petroleum ether (b.p. $30-80^{\circ}$) gave pale yellow crystals, m.p. 73.5-74.5: n.m.r. (in CDCl₃), 1.6-2.7 (m, aromatic H, 4); 7.7-9.0 (m, —CH₂— and

-ĊH—, 10).

Anal. Calcd. for C₁₃H₁₄ClNO₂: C, 62.03; H, 5.61; N, 5.56; Cl, 14.09. Found: C, 61.75; H, 5.43; N, 5.47; Cl, 14.04. (*a-2*) 7-Chloro-7-p-methoxyphenylnorcarane

The decomposition of 3-chloro-3-*p*-methoxyphenyl diazirine was carried out essentially as described in section a-1. A yellow oil (2.59 g) was obtained after removal of the solvent from a reaction mixture initially containing 2.0 g of diazirine. The n.m.r. spectrum (CCl₄) of the crude oil showed signals from aromatic protons at $2.5 \sim 3.5$, cyclohexane ring protons at $7.8 \sim 9.3$, two small sharp doublets at 5.4 and 5.5, and small multiplets at $4 \sim 5$; the methyl protons of the methoxy groups showed a triplet centered at 6.30. Unsuccessful attempts were made to separate the mixture was left to the atmosphere at room temperature for several weeks, crystals appeared which were extracted with petroleum ether yielding 0.65 g of crude

crystal. After two recrystallizations from methanol, 7-chloro-7-p-methoxyphenylnorcarane (0.4 g) was obtained, m.p. 45.0-45.5: n.m.r. (CCl₄) $2.5 \sim 3.3$ (m, aromatic H, 4);

6.30 (s, OCH₃, 3); 7.7–9.0 (m, $-CH_2$ and $-CH_{-}$, 10). Anal. Calcd. for $C_{14}H_{17}CIO$: C, 71.03; H, 7.24; Cl, 14.98. Found: C, 70.81; H, 7.29; Cl. 14.88.

(a-3) Decomposition of 3-chloro-3-phenyl, 3-chloro-3-pchlorophenyl and 3-chloro-3-p-tolyldiazirine in cvclohexene

In the decomposition of the above diazirines, the same method was employed as described in the previous section, a-1. After the removal of solvent, the oils gave similar n.m.r. spectra as in sections a-1 and a-2, showing the aromatic and cyclohexane ring protons (and methyl protons in the case of p-tolyl) as the major, and two small sharp doublets at 5.1 \sim 5.5 together with a multiplet at $4 \sim 5$ as the minor. Distillation and column chromatography were ineffective in separating the mixture and no further attempts were made to isolate the products.

(b) Decomposition in DEGME

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(b-1) Isolation of p-nitrobenzaldehyde ethylene acetal

3-Chloro-3-p-nitrophenyldiazirine (1.8 g) in 80 ml of DEGME was heated at 80--90° for 7 h. On dilution with water, a precipitate was obtained which was dissolved in hot cyclohexane and refluxed with Norite for 5 min. After filtering the warm solution, the collected crystals were recrystallized from ethanol, yielding 0.6 g, m.p. 89.5-90.0°, lit. m.p. 90.59° (10); n.m.r. (CDCl₃), 1.6 ~ 2.5 (m, aromatic

-H, 4); 4.10 (s,
$$\begin{array}{c} H \\ C \\ Ph \end{array}$$
, 1); 5.90 (s, --CH₂-O--, 4)

From the extraction of the filtrate with chloroform, an additional 0.6 g of crude acetal was obtained. The acetal was decomposed in 2,4-dinitrophenylhydrazine-sulfuric acid-ethanol solution to give p-nitrobenzaldehyde-2,4dinitrophenylhydrazone; m.p. 317-319° (dec.), lit. m.p. 320° (dec.) (11).

(b-2) Decomposition of other diazirines in DEGME

The procedures are similar to those described in section b-1. In the case of the p-methoxyphenyl derivative, the crude reaction mixture contained $\sim 95\%$ anisaldehyde and a trace amount of impurity. The n.m.r. spectrum in CCl₄ showed

absorptions at 0.20 (s, CHO, 1); 2.1-2.8 (m, aromatic-H, 4) and 4.17 (s, O-CH₃, 3) and the i.r. compared well with the authentic sample. In the decompositions of 3-chloro-3-p-tolyl, 3-chloro-3-phenyl, 3-chloro-3-p-chlorophenyl diazirines, mixtures of aldehydes and acetals were obtained.

(c) Decomposition in DMSO

3-Chloro-3-phenyldiazirine (1 g) in 50 ml DMSO was heated at 80-85° for 3 h. The resulting mixture was diluted with water and extracted with ether. The extract was identified with authentic samples as a mixture of benzoic acid and benzaldehyde, which was left in air and oxidized to benzoic acid, 0.35 g. Similar results were obtained with other diazirines: 0.46 g of p-nitrobenzoic acid from 1 g of 3-chloro-3-p-nitro-phenyldiazirine and 0.42 g of p-toluic acid from 1 g of 3-chloro-3-p-tolyldiazirine.

Results

All the compounds were unstable at room temperature; however, except for the p-methoxyphenyl derivative, they can be kept in Dry Ice for several weeks without significant decomposition. Owing to the instability of these diazirines, the elemental analyses were not possible. All the diazirines obtained gave the following characteristics: one clear spot on t.l.c. with various solvents, sharp i.r. spectra, complicated u.v. absorption between 420 and 320 nm (in cyclohexane), quantitative nitrogen evolution when heated in diethyleneglycol monoethyl ether (DEGME), crystallization at low temperature, and symmetrical v.p.c. peaks for *p*-tolyl, phenyl, and *p*-chlorophenyl derivatives. Three representative solvents were chosen for the decompositions: cyclohexene for non-polar; DMSO for polar aprotic, and DEGME for polar protic solvent. The concentrations of diazirine in various solvents were adjusted in such a way as to suppress the formation of azine (8). The reactions obeyed first order

3-Aryl				$10^4 k_1$	(s ⁻¹)		
	Method	60.0°	70.0°	75.0°	80.0°	90.0°	95.0°
<i>p</i> -Methoxy- phenyl	u.v.	1.10	3.2	6.2	10.6	29	
p-Tolyl	v.p.c.	0.45	1.51	2.91*	4.8	15.3*	24
Phenyl [†]	v.p.c.	_	1.06	1.95*	3.6	9.95*	
p-Chlorophenyl	v.p.c.	0.43	1.42	2.48*	5.0	13.2*	23
p-Nitrophenyl	u.v.	0.34	1.16	2.04	3.64†	10.9	18.7

TABLE 3. Rate constants for the thermal decomposition of 3-chloro-3-aryldiazirines in cyclohexene

*Average value of k_1 measured by v.p.c. and u.v. †Sample not degassed, $k_1 = 3.70 \times 10^{-4} \text{ s}^{-1}$. ‡10⁴ k_1 (s⁻¹), 28.9 at 100°; 79 at 110°.

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Solvent			$10^4 k_1^*$	(s ⁻¹)		
	<i>p</i> -Methoxy- phenyl	p-Tolyl	Phenyl	p-Chlorophenyl	<i>p</i> -Nitrophenyl	
Cyclohexene	6.2	2.91†	1.95†	2.48†	2.04	
DEGME	8.4	3.59	2.30	2.84	2.19‡	
DMSO	10.1	4.44	3.04	3.46	2.82	

Rate constants for the thermal decomposition of 3-chloro-3-aryldiazirines TABLE 4. in various solvents at 75°

*Measured by u.v. spectrophotometer. †Average value of k₁ measured by v.p.c. and u.v. ‡Measured by nitrogen evolution.



FIG. 1. Arrhenius plots for thermal decompositions of 3-chloro-3-aryldiazirines in cyclohexene:

X---C₆H

CI $\bigcirc, X = MeO; \quad \bullet, X = Me; \quad \Box, X = Cl; \quad \blacktriangle, X = NO_2;$ \triangle , X = H.

kinetics up to 90% completion (the first order rate constants were determined graphically from a minimum of eight runs). Rate constants for the thermal decompositions of the 3-chloro-3-aryldiazirines in cyclohexene are given in Table 3. The reproducibilities of the rate constants were $\pm 2-6\%$ by v.p.c. and $\pm 1-3\%$ by u.v. spectrophotometry. The Arrhenius plots of the rate data are shown in Fig. 1 and the least-squares treatment of the data gave the

following expressions with the errors quoted in standard deviation: k_1 (*p*-methoxyphenyl) = $10^{13.41\pm0.35}$ exp (-26,490 ± 560/*RT*) s⁻¹; k_1 (*p*-tolyl) = $10^{13.94\pm0.20}$ exp (-27,870 ± 310/*RT*) s⁻¹; k_1 (phenyl) = $10^{13.87\pm0.13}$ exp (-28,000 ± 215/RT) s⁻¹; k_1 (*p*-chlorophenyl) = $10^{13.81\pm0.24}$ exp $(-27,720 \pm 390/RT)$ s⁻¹; k_1 (*p*-nitro-phenyl) = $10^{13.80 \pm 0.07}$ exp $(-27,850 \pm 100/RT)$ s^{-1} . Table 4 gives the rate constants for the thermal decomposition of 3-chloro-3-aryldiazirines in various solvents at 75°.

Nature of Products

In the thermal decompositions of diazirines in cyclohexene, the major products were 7-chloro-7-aryl norcaranes, addition products of arylchlorocarbene to the double bond of cyclohexene (see Scheme 1). As the melting points for the isolated norcaranes were sharp, it was assumed that the products consisted of only one of the two isomers whose conformation was not identified. The minor products are probably mixtures of isomers formed from the insertions of carbene to the saturated C-H bonds at the 3- and 4-positions in cyclohexene.

In the decomposition of 3-chloro-3-p-nitrophenyl diazirine in DEGME, the major product was benzaldehyde ethylene acetal. On the other hand, anisylaldehyde was isolated as the major product from the decomposition of 3-chloro-3*p*-methoxyphenyldiazirine. For the decomposition of the *p*-tolyl, phenyl, and *p*-chlorophenyl



SCHEME 1

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derivatives, mixtures of aldehyde and acetals were obtained. The above products were presumably formed via the mechanism shown in Scheme 2. The minor products are probably a mixture of isomers resulting from the insertion of arylchlorocarbene into the C-H bond neighbored to an oxygen atom (12, 13). From the n.m.r. peak area ratio of aldehyde (-CHO), aromatic protons, ethylene acetal (-CH2-O—), and the methyl proton of $-O-CH_2$ CH₃ group, the yields of O-H insertion products (aldehydes and acetals) were estimated to be 95, 71, 88, 86, and 80% for the decomposition of p-methoxyphenyl, p-tolyl, phenyl, p-chlorophenyl, and p-nitrophenyl derivatives respectively. Since the rates of hydrolysis of benzaldehyde ethylene acetals have a negative ρ value in the Hammett equation (14), the different ratios of acetal/aldehyde are reasonable.

From the thermolysis of 3-chloro-3-aryldiazirines in DMSO, mixtures of substituted benzaldehydes and benzoic acids were isolated. No further attempts were made to study the mechanism of these reactions.

Discussion

For the purpose of comparison, pertinent data from previous workers are summarized in Table 5. The present results confirm the conclusions of the earlier workers. The thermal decomposition of diazirines both in gas phase and in solution are typically unimolecular reactions with A factor equal to $10^{13.7\pm0.5}$. The minor solvent effects from Table 4 also agree with data reported in earlier studies. The decomposition of 3-chloro-3-aryldiazirines in each of the three solvents gave similar organic products and all the free energies of activation

Fable 5.	Activation	parameters f	or t	he t	hermal	decompositi	on of	diazirines
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R	$c \leq N_{N}$					
X	R	Condition	log A	E (kcal/mol)	ΔS^{+} (e.u.)	Reference
Fluoro	Fluoro	Vapor	13.40	32.5	0.5	4
Ethyl	Ethyl	,,	13.73	31.89	2.0	15
Chloro	Methyl	**	14.14	31.07	3.9	1
,,	Ethyl	,,	13.99	30.45	3.2	2
,,	n-Propyl	**	13.98	30.98	3.2	2
,,	i-Propyl	,,	14.01	30.59	3.3	2
,,	t-Butyl	**	13.36	29.50	0.3	2
••	Trichloromethyl	CCL	13.80	29.20	2.3	7
"	Phenyl	Cyclohexene	13.87	28.00	2.6	8
**	<i>p</i> -Methoxyphenyl	.,	13.41	26.49	0.5	This work
,,	n-Tolvl	"	13.94	27.87	2.9	,, ,,
,,	<i>p</i> -Chlorophenyl	· •,	13.81	27.72	2.3	** **
,,	<i>p</i> -Nitrophenyl	••	13 80	27.85	2.3	,, ,,
Bromo	Phenyl	• •	13.75	27.36	2.1	8

×. .

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FIG. 2. Plots of $\log_{10} k vs. \sigma$ for 3-chloro-3-aryldiazirine in various solvents; \bigcirc , cyclohexene; \blacktriangle , DEGME; \bigcirc , DMSO.

are in the range of 26.0 ± 0.3 kcal/mol. The differences in the activation energy between 3-chloro-3-aryldiazirines and 3-chloro-3-alkyl-diazirines are reasonably explained by resonance stabilization effects by the aryl group in terms of either mechanism I, II, or III.

The observed substituent effects on reaction rates are not explicable either by the charge separated transition state II or by the simultaneous bond breaking process as proposed by Frey et al. in I. If the reaction proceeds by mechanism II, the rate for the following substituents would be in the order of $p-NO_2 >$ p-Cl > H > p-CH₃ > p-CH₃O, which is almost opposite to the observed order: $p-CH_3O >$ p-CH₃ > p-Cl > $H \simeq p$ -NO₂. Thus, from the observed effects of substituents and the lack of solvent effects, the contribution of the ionic transition state II is not likely to be important in the thermal decomposition of diazirines. Schmitz (3) suggested that if mechanism I were to take place, the electron distribution on the carbon atom in the transition state must tend towards a sextet and such a transition cannot be stabilized by withdrawal of electrons. Taking the above into consideration, one would expect the rates to be p-CH₃O > p-CH₃ > H > p-Cl > p-NO₂, but these do not agree with the observed results.

Several examples of abnormal Hammett relation have been reported (16), but their explanations could not be applied to our present results. It is seen in Fig. 2 that plots of log k against σ (or σ^+) do not yield straight lines.



FIG. 3. Plots of $\log_{10} k vs. \sigma^+ - \sigma$ for 3-chloro-3aryldiazirine in various solvents; O, cyclohexene; \blacktriangle , DEGME; \bigcirc , DMSO.

However, a smooth curve (concave upward) may be drawn through all the points except that for the unsubstituted compound. Further, that the shape of the curves in each solvent is identical and increase in polarity of the solvent only displaces the curve upward. The curvature observed in each solvent is ascribed to varying resonance interactions in the transition state of the para-substituted compounds. Although the Hammett correlation was unsuccessful with our present results, a linear plot was obtained by plotting log k vs. $\sigma^+ - \sigma$ as shown in Fig. 3. The differences between σ^+ and σ are p-CH₃O, -0.510; *p*-CH₃, -0.141; *p*-Cl, -0.113; H, 0; $p-NO_2$, +0.012, and fall in the order of the kinetic data. These differences may be taken as a measure of the strength of conjugation of the substituents.

The possible structures of the transition state could be drawn as IIIa, b, and c. However, IIIc contributes little or nothing, as the nitrogen atom is more electronegative than the carbon atom. The free radical form IIIa may

be classified as an S radical in Walter's concept (17) in which the observed properties are shifted in the same direction with donor and acceptor substituents. On the other hand, the degree of contribution of different substituents to structure III*b* is likely to produce results such as these; p-CH₃O at best; p-CH₃ next in order; p-Cl very

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	<i>p</i> -Methoxy- phenyl	<i>p</i> -Tolyl	Phenyl	p-Chlorophenyl	p-Nitrophenyl
			$k_{\rm solvent}/k_{\rm cyc}$	clohexene	
Cyclohexene	1	1	1	1	
DEGME	1.35	1.23	1.18	1.15	1.07
DMSO	1.63	1.53	1.56	1.41	1.38
			$k_{\rm Ar}/k$	ph	
Cyclohexene	3.18	1.49	1	1.26	1.05
DEGME	3.65	1.56	1	1.23	0.95
DMSO	3.32	1.46	1	1.14	0.93

TABLE 6. Relative rate for the thermal decomposition of 3-chloro-3-aryldiazirines at 75°

little; and a negative effect by the p-NO₂ substituent as compared with the unsubstituted compound. Hence, the fastest rate of decomposition is expected for 3-chloro-3-p-methoxyphenyl diazirine because its transition state is stabilized through both structures IIIa and b. The transition state of the 3-chloro-3-p-tolyldiazirine is also stabilized by both IIIa and bto a lesser extent owing to its smaller resonance ability. In the case of 3-chloro-3-p-chlorophenyldiazirine, the transition state is stabilized by structure IIIa, but the contribution resulting from IIIb may be little or nothing due to its inductive effect, which is opposite to that of the resonance effect. The contribution of p-NO₂ substituent to structure IIIa is likely to be of the same order as the p-CH₃O substituent; however, its strong electronegative nature does not favor the resonance structure IIIb and tends to cancel out the stabilization effect resulting from IIIa. Therefore, the observed rate appears to be similar to that of the unsubstituted compound.

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The fate of the diazirine after the achievement of the transition state is as interesting as the decomposition mechanism itself. Frey and Liu (2) have confirmed the formation of carbene in the thermal decomposition of 3-chloro-3-tbutyldiazirine by observing the formation of 1-chloro-2,2-dimethylcyclopropane. Evidence for carbene formation was also reported in the photolysis of 3-halo-3-phenyldiazirine (18). In our present work, the formation of 7-chloro-7arylnorcaranes from the reactions in cyclohexene is good evidence for the carbene intermediate. In addition, the formation of the insertion isomers (1:1) into the 3- and 4-positions of cyclohexene was detected. The carbene

generated from the thermal decomposition of 3-chloro-3-aryldiazirine is probably in its singlet state which is in agreement with the results from the selectivity studies of halophenyl carbenes (19, 20). Furthermore, if the carbene were singlet and collapsed to a sextet, there could be strong interaction between the empty orbital and an electron-donor species like the methoxy. Thus, the energy of the carbene might be lowered.



The relative rates for the thermal decomposition of 3-chloro-3-aryldiazirines at 75° are given in Table 6. For each of the compounds studied it is observed that the rate acceleration effect given by $k_{\text{solvent}}/k_{\text{cyclohexene}}$ shows an increase in going from a non-polar to a polar solvent. The relative magnitude of this effect is in the order of p-NO₂ < p-Cl < H < p-CH₃ < p-CH₃O. Although all compounds show an increase in rate constant with polar solvents, the comparison of substituted compounds with the unsubstituted compound shows that $k_{\rm Ar}/k_{\rm Ph}$ increases for p-CH₃O and p-CH₃ and decreases for p-Cl and p-NO₂ compounds as the polarity of the solvent is increased. The magnitude of the solvent effect is not large, with a factor of two being the largest increase in going from nonpolar to polar solvents. A much larger effect would be expected if the transition state polarization was a dominant factor in determining the rate of decomposition of diazirines. If a radical

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mechanism were operative, very little solvent effect would be expected. A rather small contribution from a mechanism involving the structure IIIb could account for the observed results. In the photolysis of diazirine, Amrich and Bell (21) have reported that 20% of the primary decomposition of diazirine is an isomerization to diazomethane. There is evidence that substituted diazirines can isomerize to diazo compounds (14, 22). However, most of the available data can also be interpreted by means of the homolytic process. As an example, the instability of α -ketodiazirine (3) could be attributed to the strong resonance effects of the α -carbonyl group. The decomposable nature of 3-chloro-3methoxydiazirine (9) and the isomerization of 3-methyl-3-vinyldiazirine to 3-methyl-pyrazole (23) could be explained in a similar manner.



In conclusion, we suggest a mechanism involving the breaking of one of the C--N bonds. This leads to a diradical (IIIa) and a diazomethane (IIIb) intermediate of which the latter contribution is probably small due to the lack of solvent effects. It is likely that the transition states have more radical character. Recently nonempirical self-consistent field and configuration-interaction studies of aziridine and oxazirane have been reported by Hayes and Siu (24). They have concluded that the electronic structure of open forms of these species is essentially a linear combination of the resonance system $B = A - C \leftrightarrow B - A = C$, and a diradical $\cdot B - A - C \cdot$ where A, B, and C are CH_2 NH, or O. These studies lend support to the possibility of homolytic and heterolytic dissociation.

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