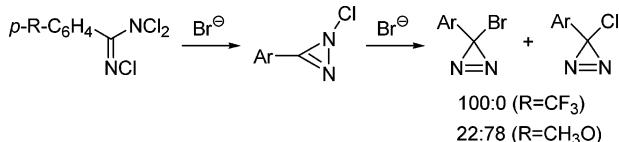# JOCNote

Reactivity of 1-Chloro-3-phenyldiazirines

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p-Substituted 1-chloro-3-phenyldiazirines (**5**), the putative intermediates of the reaction of *N,N,N'*-trichlorobenzamidines (**10**) with excess of bromide ions, react further to afford mixtures of 3-bromo- (**4**) and 3-chloro-3-phenyldiazirines (**6**). The **6**:**4** ratios inversely correlate with the Hammett σ_p and σ_p^+ constants of the *p*-substituents. The formation of **4**, proposed to proceed by *anti*-S_N2' mechanism, is predominant with electron-withdrawing *p*-substituents. Compounds **6**, the major products with electron-donating *p*-substituents, may arise from **5** by a [1,3]-sigmatropic shift of chlorine proceeding via polar transition structures **12**. The results of a gas-phase DFT (B3LYP/6-31+G*) study on the two mechanisms are consistent with experiment.

Two important reactions of 3-halodiazirines (**1**), that is, the formation of **1** by Graham's hypohalite oxidation of amidines[1] and the halogen-exchange reaction of **1**,[2] have been subject to scrutiny over the past two decades (Scheme 1).

The Graham reaction was proposed to proceed through 1-halodiazirines **3**,[1] which may be transformed to **1** via diazirinium-halide ion pairs **2-X** or by an S_N2' displacement. The former alternative was supported by the stability of diazirinium ions (**2**) deriving from their formal aromatic character; fragments with *m/z* corresponding to **2** were observed in the mass spectra of **1**. Calculated geometry and π-bond orders indicate that 3-unsubstituted diazirinium ion (**2a**) is aromatic.[3] However, the negative delocalization energy of **2a**, likely caused by significant positive charge located on each nitrogen atom, points at the nonaromaticity of **2a**.[4]

Ion pairs **2-X** were also commonly invoked in the diazirine halogen-exchange reactions. The kinetics and the leaving-group and salt effects of azide ion exchange with a series of *p*-substituted 3-bromo-3-phenyldiazirines (**4**) are consistent with

SCHEME 1. (a) Graham's Hypohalite Oxidation of Amidines (X = Cl or Br); (b) Diazirine Halogen-Exchange Reaction
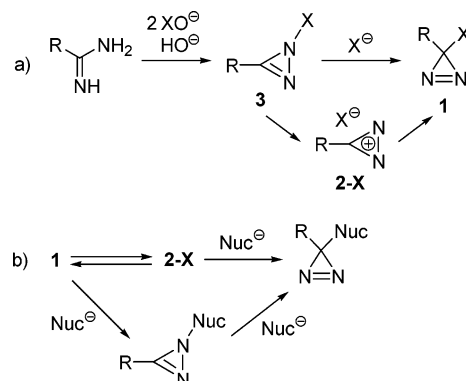
the intermediacy of **2-X** in this process.[5] However, the relative rates of halogen-exchange reactions of other 3-halodiazirines are not always in keeping with the general trend for cation-stabilizing substituents and could suggest intermediates other than **2-X**.[6] Additional observations, such as the reported failures in obtaining chemical or spectroscopic evidence for the ionization of **1** to **2-X** under a variety of conditions[7,8] or the facile halogen exchange occurring on the diazirine ring substituted with strongly cation-destabilizing trifluoromethyl group,[9] raised further questions about the accessibility of **2-X** in solution.

Dailey and Bainbridge[10] and Creary and Sky[11] presented experimental evidence that 3-bromo-3-phenyldiazirine (**4c**) reacts with terminally ^{15}N-labeled azide ion at the ring nitrogen, in accordance with the S_N2' mechanism. Indeed, additions of other nucleophiles (e.g., organometals[12] or phosphines[13]) to the ring nitrogen of diazirines are known. In light of these facts, the experimental data supporting the intermediacy of **2-X** were reinterpreted in the framework of S_N2' chemistry.

The mechanistic origins of the chemistry of **1** became still more complex after diazirine halogen-exchange reactions, proceeding via diazirinyl radicals ($S_{RN}1$)[2c,14] or, conceivably, via the formally antiaromatic diazirinyl anions,[15] had been reported.

If the majority of experimental observations, originally attributed to the intermediacy of **2-X**, can be explained in terms of S_N2' or $S_{RN}1$ chemistry, where do **2-X** fit in the overall

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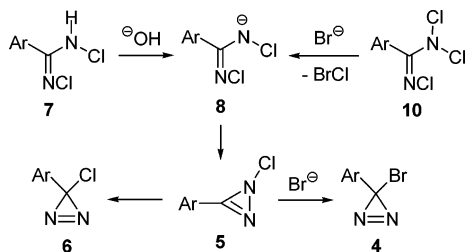(11) Creary, X.; Sky, A. F. *J. Am. Chem. Soc.* **1990**, *112*, 368.

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SCHEME 2. Base-Promoted vs Reductive Generation of **5** and Its Possible Further Reactions (Ar = *p*-R-C$_6$H$_4$)

SCHEME 3. Preparation of Trichloroamidines **10**[a]

	11	9	10
a: R=CF$_3$		68%	98%
b: R=Cl		51%	98%
c: R=H		35%	quant.
d: R=CH$_3$		13%	95%
e: R=CH$_3$O		93%	quant.

[a] Reaction conditions: (a) NaOCl/Et$_2$O,H$_2$O; (b) *t*-BuOCl/CH$_2$Cl$_2$. The decreasing yields of **9a−d** are due to increasing contamination of the used crude **11a−d** with ammonium chloride.[5] This problem did not occur with **9e**, as pure **11e**, prepared by a different method,[18] was used.

SCHEME 4. Reductive Dehalogenation of Trichloro-amidines **10**

	10	4	6
a: R=CF$_3$	92%	100 : 0	
b: R=Cl	93%	86 : 14	
c: R=H	86%	75 : 25	
d: R=CH$_3$	86%	43 : 57	
e: R=CH$_3$O	78%	22 : 78	

mechanistic scheme? It should be pointed out that **2-X** have been mostly suggested to originate by the ionization of the C−X bond in **1**, a process which may be thermodynamically unfavorable due to the relatively high energy of **2-X**. However, **2-X** could also be reached by the ionization of the N−X bond in **3**, a formally antiaromatic species higher in energy than **1**. For example, our calculations suggest that for X = Cl, the barrier to ionization of **3** is over 20 kcal/mol lower than that of **1** (vide infra).
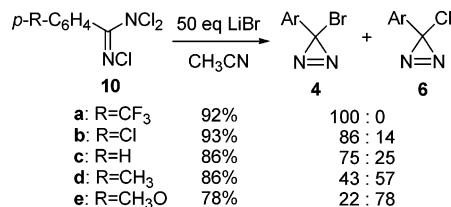
The possibility of the generation of **2-X** from **3** has rarely been addressed. Moss et al.[7] reported that some **3** (X = Cl; R = *i*-C$_3$H$_7$ or CH$_3$O), the putative intermediates of the base-promoted reaction of the corresponding *N,N'*-dichloroamidines, largely isomerize to **1** even in the presence of excess of another nucleophile (e.g., bromide or azide ions). The authors explained this observation by a competition between the foreign anion in solution and the chloride ion tightly associated with the diazirinium ion. Calculations by Krogh-Jespersen et al.[16] suggested that transition structures (TSs) connecting **3** and **1** (X = Cl; R = H or CH$_3$) resemble **2-X**. The degree of TS tightness, or "ion pair intimacy", is greater for R = H than for R = CH$_3$, as expected from the better cation-stabilizing ability of the latter substituent.

We set out to extend the work of Moss et al.[7,16] by investigating the behavior of *p*-substituted 1-chloro-3-phenyl-diazirines (**5**) in the presence of an excess of bromide ions. The object of our study was to observe the effect of various *p*-substituents on the conversion of **5** to the corresponding 3-bromo- and 3-chlorodiazirines **4** and **6** (Scheme 2). We expected that **4** would be formed from **5** by the ionization-nucleophilic-capture pathway or by an S$_N$2' displacement. Alternatively, **6** would result from **5** by the ionization-recombination pathway or by a [1,3]-sigmatropic shift of chlorine. The choice of the *p*-substituted phenyl group enables the evaluation of electronic effects on the **6**:**4** product ratio while keeping steric effects virtually constant.

By analogy with the Moss et al. work,[7] 1-chlorodiazirines **5** should be generated upon deprotonation of *N,N'*-dichloroben-zamidines (**7**) and subsequent cyclization of the resulting anions **8**. However, Moss reported a failure in obtaining the *p*-unsubstituted dichloroamidine **7c** due to its disproportionation to chloro- and trichloroamidines **9c** and **10c**. Being aware of this problem, we chose to generate **5** from precursors other than **7** by a method that we had previously developed for the preparation of novel diazirines;[17] the requisite anions **8** can be generated by reductive dehalogenation of trichloroamidines **10** with bromide ions. Upon conversion of **8** to **5**, excess bromide

ions may react further with **5**, producing **4**. Trichloroamidines **10** can be readily prepared from amidine hydrochlorides **11** via chloroamidines **9** by sequential chlorination with sodium and *tert*-butyl hypochlorites (Scheme 3). Compounds **10** are yellow-orange solids with a chlorine-like odor, which are stable for long periods of time at 0 °C in the dark. They can be handled at room temperature without decomposition. Single-crystal X-ray analysis of the *p*-unsubstituted derivative **10c** revealed the *E* configuration of its amidine C=N bond.

Treatment of **10** with 50 equiv of lithium bromide in anhydrous acetonitrile afforded very good yields of crude **4**+**6** mixtures, nearly pure by ^{1}H and ^{13}C NMR (Scheme 4). The **6**:**4** ratio of each mixture was determined by comparing integral intensities of NMR signals of constitutionally corresponding ^{13}C atoms in **4** and **6**.[19] This method proved sufficiently accurate for our purposes if spectra with good signal-to-noise ratios were used; integral intensities of 2 to 4 peaks were compared in each case with consistent results. The observed **6**:**4** ratios varied greatly throughout the series of **10**. While the *p*-trifluoromethyl derivative **10a** afforded only **4a**, the **6**:**4** ratio nearly inversed on going to *p*-methoxy derivative **10e**, which yielded a 78:22 mixture of **6e** and **4e**. We have separately verified that the conversion of **4** to **6** and vice versa by the halogen-exchange reaction does not proceed on the time scale of our experiments (samples of **4e** or **6a** were recovered unchanged upon treatment with tetrabutylammonium chloride or lithium bromide, respectively, in acetonitrile). We thus believe that the observed **6**:**4** ratios reflect only the relative rates at which **4** and **6** are formed from **5**.

The observed **6**:**4** ratios fall on descending curves when plotted against the Hammett σ_p and σ_p^+ constants of the respective *p*-substituents (Figure 1). This substituent effect is consistent with the originally proposed competition between the unimolecular isomerization of **5** to **6** and the bimolecular

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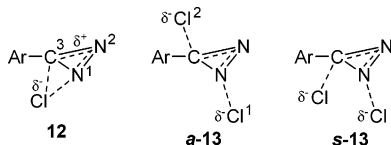
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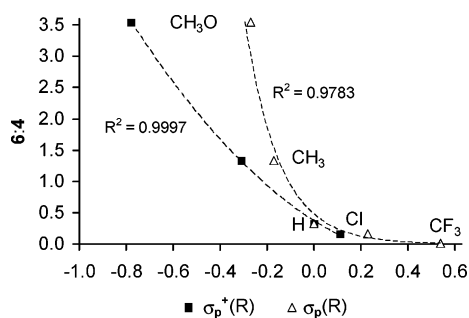
FIGURE 1. Plot of the observed **6:4** ratios vs the σ_p and σ_p^+ constants of the *p*-substituents R.

FIGURE 2. TSs studied by DFT calculations (Ar = *p*-R-C$_6$H$_4$).

TABLE 1. Results of a B3LYP/6-31+G* (0 K, Gas Phase) Study of the 5-to-6 Isomerization via TS 12[a]

	$5 \rightarrow [12]^{\ddagger} \rightarrow 6$				
p-R-C$_6$H$_4$	ΔE	E_A	N^1−Cl (**12**)	C^3−Cl (**12**)	δ(Cl) (**12**)
a: R = CF$_3$	−27.4	13.6	2.448	2.506	−0.44
b: R = Cl	−26.0	12.8	2.466	2.519	−0.45
c: R = H	−25.6	12.7	2.469	2.520	−0.45
d: R = CH$_3$	−24.9	12.2	2.481	2.530	−0.48
e: R = CH$_3$O	−23.7	11.4	2.506	2.544	−0.50

[a] Corrected ZPEs are in kcal/mol, interatomic distances are in ångstroms, and the charges are of the Mulliken type.

TABLE 2. Results of a B3LYP/6-31+G* (0 K, Gas Phase) Study of the 5-to-6 Conversion via TSs a-13[a]

	$5+Cl^- \rightarrow [a\text{-}13]^{\ddagger} \rightarrow 6+Cl^-$		
p-R-C$_6$H$_4$	E_A	N^1−Cl^1 (**a-13**)	C^3−Cl^2 (**a-13**)
a: R = CF$_3$	4.0	2.039	3.541
b: R = Cl	4.9	2.062	3.575
c: R = H	7.1	2.072	3.624
d: R = CH$_3$	8.5	2.091	3.600
e: R = CH$_3$O	10.8	2.136	3.410

[a] Corrected ZPEs are in kcal/mol and interatomic distances are in ångstroms.

conversion of **5** to **4**.[20] The unimolecular mechanism, expected to comprise an accumulation of positive charge on the diazirine ring in the rate-determining step, is indeed predominant with **5** bearing electron-donating *p*-substituents. The smooth correlation of experimental data with the σ_p^+ constants especially supports this idea. The bimolecular process is preferred by **5** substituted with electron-withdrawing groups; this observation is consistent with nucleophilic attack on an electron-deficient diazirine ring.

We performed a gas-phase DFT (B3LYP/6-31+G*, 0 K) computational study[21] on two processes corresponding to the unimolecular and bimolecular pathways (Figure 2): (1) a [1,3]-sigmatropic shift of chlorine in **5**, proceeding through the C_1-symmetrical TSs **12** and (2) an S$_N$2′ attack of **5** by halide ion via TSs **13** (to facilitate the calculations, a *bromide* ion, used as the nucleophile in the experimental part, was replaced by a *chloride* ion). We have not explicitly studied any diazirinium−chloride ion pairs as a result of the difficulties associated with the computational treatment of ion-pair species.

The exothermicities (ΔEs) and the energy barriers (E_As) of the **5**-to-**6** isomerization decrease with increasing electron donation from the *p*-substituent (Table 1). This is consistent with the stabilization of the C=N bond in **5** and the partially
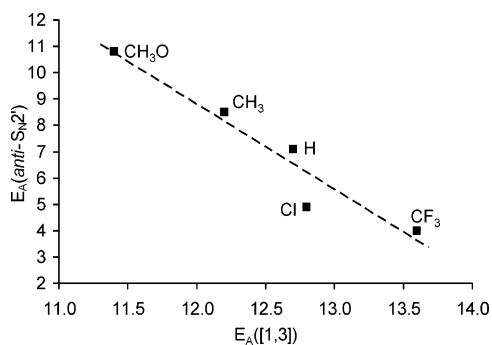
positively charged diazirine ring in **12** by electron-releasing groups. The tightness of **12** decreases (N^1−Cl/C^3−Cl distances and the partial charge on Cl increase) with increasing electron donation from the *p*-substituent.

On the S$_N$2′ pathway, there are two possible geometries of TSs **13**, given by the anti or syn relationship of the incoming and leaving chloride ions (Figure 2). Our MP2/6-311+G** calculations indicate that the simplest, 3-unsubstituted (non-phenyl) *anti*-TS is 5.4 kcal/mol lower in energy than the corresponding *syn*-TS. This result is in keeping with that for the analogous 3-chlorocyclopropene system, where the syn−anti energy difference of 6.1 kcal/mol was explained by stereoelectronic and Coulombic effects.[22] We thus assumed that the TSs *a*-**13** are lower in energy than *s*-**13** and, therefore, considered only the former species for further DFT calculations. As expected for a nucleophilic attack on an electron-deficient center, the energy barriers to the S$_N$2′ reaction decrease with increasing electron withdrawal from the *p*-substituent (Table 2). The calculated short N^1−Cl^1 and long C^3−Cl^2 distances indicate that *a*-**13** are early TSs. While the N^1−Cl^1 lengths inversely correlate with electron-withdrawing ability of the *p*-substituent, the same trend is not observed for the C^3−Cl^2 distances, probably due to the inaccuracy of their calculation caused by flat potentials of *a*-**13**.

In agreement with the experimentally observed dependence of the **6:4** ratio on the electronic properties of the *p*-substituents, there is an inverse relationship between the calculated E_As of the unimolecular isomerization and bimolecular conversion of **5** to **6** (Figure 3). The former E_As are generally higher than the latter E_As (11.4−13.6 kcal/mol vs 4.0−10.8 kcal/mol). However, the calculated energy barriers for the two processes can be compared only qualitatively, as their influences on the actual reaction rates are not identical due to different kinetic orders of both reactions.

In summary, 1-chlorodiazirines **5** are likely generated by the reaction of trichloroamidines **10** with bromide ions. 3-Bromo-

(20) A reviewer suggested an alternative reaction mechanism that might be of importance for R = CF$_3$. The BrCl formed upon reductive dechlorination of **10a** (Scheme 2) may react with excess bromide ion to generate Br$_2$, which is then nucleophilically attacked by a *p*-CF$_3$-stabilized diazirinyl anion to form **4a**. The anion would result from a single-electron transfer (SET) to **5a**, followed by the loss of chloride ion and another SET.

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FIGURE 3. Plot of E_As of the [1,3]-sigmatropic shift of chlorine in **5** vs. E_As of the *anti*-S_N2' reaction of **5** with chloride ion (B3LYP/6-31+G*, 0 K, gas phase). Corrected ZPEs are in kcal/mol.

diazirines **4** may be formed by further *anti*-S_N2' reaction of **5** with bromide ion. As expected for a nucleophilic attack on an electron-deficient diazirine ring, the formation of **4** is facilitated by electron-withdrawing *p*-substituents. 3-Chlorodiazirines **6** may arise from **5** by a [1,3]-sigmatropic shift of chlorine. In agreement with theory, this reaction, proceeding via polar TSs **12** with an accumulation of positive charge on the diazirine ring, is predominant with **5** bearing electron-donating *p*-substituents. The results of a DFT study of the two mechanisms are consistent with experiment. There is an inverse relationship between the calculated E_As of the [1,3]-sigmatropic shift of chlorine in **5** and the S_N2' reaction of **5** with chloride ion.

Experimental Section

Caution! Neat diazirines are potentially shock sensitive and may violently decompose without warning. All operations with neat diazirines should be carried out behind a safety shield. However, we have never experienced any violent decomposition of diazirines **4** *and* **6**.

N-**Chloro-*p*-R-benzamidines (9).** In a magnetically stirred two-necked 500-mL round-bottomed flask equipped with an addition funnel and thermometer was placed 50.0 mmol of the corresponding benzamidine hydrochloride **11** (**a−d**,[5] **e**[18]) in 25 mL of H_2O and 250 mL of Et_2O. The reaction mixture was cooled below 5 °C. Then 78.0 g of 5.25% commercial bleach (55.0 mmol of NaOCl) was added dropwise with vigorous stirring while maintaining the temperature below 7 °C. When the addition was completed, the reaction mixture was stirred for another 5 min. Two layers were separated, and the aqueous phase was extracted with 3 × 250 mL of Et_2O. The combined organic phases were dried over $MgSO_4$ for 1 h at rt and concentrated under reduced pressure at rt. The crude products, obtained as white or pale yellow solids, were used without further purification for the preparation of trichloroamidines **10**. (Characterization data for **9** are given in the Supporting Information.)

N,N,N'-**Trichloro-*p*-R-benzamidines (10).** In a magnetically stirred 500-mL round-bottomed flask was placed 50.0 mmol of the corresponding *N*-chlorobenzamidine **9** in 100 mL of CH_2Cl_2. The reaction mixture was cooled with an ice−water bath. Then 54.3 g (0.50 mol) of *tert*-BuOCl in 100 mL of CH_2Cl_2 was added dropwise in the dark. When the addition was completed, the reaction flask was kept at 0 °C for 24 h. Upon concentration under reduced pressure at rt, the products were obtained as yellow-orange solids with a strong chlorine-like odor. (Characterization data for **10** are given in the Supporting Information.)

Reductive Dehalogenation of 10 to Mixtures of 3-Bromo- and 3-Chloro-3-(*p*-R-phenyl)diazirines (4 and 6). In a magnetically stirred 1-L round-bottomed flask, 20.0 g (0.23 mol) of dry LiBr was dissolved in 340 mL of CH_3CN. Then 4.60 mmol of the corresponding trichlorobenzamidine **10** in 25 mL of CH_3CN was added dropwise over 5 min at rt in the dark with vigorous stirring. When the addition was completed, the reaction mixture was stirred for another 10 min. Then 250 mL of pentane and 100 mL of 10% aqueous $NaHCO_3$ were added. The pentane layer was separated, and the aqueous phase was extracted with 4 × 250 mL of pentane. Combined pentane layers were dried over $MgSO_4$ for 2 h at 0 °C. Upon concentration under reduced pressure at rt, the **4**+**6** mixtures were obtained nearly pure by ^{1}H and ^{13}C NMR as pale yellow or yellow liquids with a characteristic odor. The approximate **6**:**4** ratios were determined from integral intensities of NMR signals of constitutionally corresponding ^{13}C atoms in **4** and **6** (denoted below by the corresponding letters);[19] spectra with good signal-to-noise ratios were used for this purpose. **R = CF$_3$ (4a):** 92% yield (no **6a** was observed); ^{13}C NMR (CDCl$_3$) δ 140.4, 131.6 (q, J_{C-F} = 33 Hz), 127.2, 125.5 (q, J_{C-F} = 4 Hz), 123.6 (q, J_{C-F} = 273 Hz), 36.5. **R = Cl (4b+6b):** 93% total yield. **4b:** 86%; ^{13}C NMR (CDCl$_3$) δ 135.7, 135.2 (A), 128.6, 127.9 (B), 36.9. **6b:** 14%; ^{13}C NMR (CDCl$_3$) δ 135.6, 134.2 (A), 128.7, 127.2 (B), 46.4. **R = H (4c+6c):** 86% total yield. **4c:** 75%; ^{13}C NMR (CDCl$_3$) δ 136.7 (A), 129.4, 128.48, 126.7 (B), 38.0. **6c:** 25%; ^{13}C NMR (CDCl$_3$) δ 135.7 (A), 129.8, 128.51, 126.0 (B), 47.1. **R = CH$_3$ (4d+6d):** 86% total yield. **4d:** 43%; ^{13}C NMR (CDCl$_3$) δ 139.5 (A), 133.9 (B), 129.1, 126.5 (C), 38.2, 21.05. **6d:** 57%; ^{13}C NMR (CDCl$_3$) δ 139.4 (A), 132.8 (B), 129.2, 125.8 (C), 47.2, 21.07. **R = CH$_3$O (4e+6e):** 78% total yield. **4e:** 22%; ^{13}C NMR (CDCl$_3$) δ 160.52 (A), 128.8 (B), 127.9 (C), 113.8 (D), 55.4, 38.1. **6e:** 78%; ^{13}C NMR (CDCl$_3$) δ 160.48 (A), 127.8 (B), 127.3 (C), 113.9 (D), 55.4, 47.1.

Supporting Information Available: Characterization data for **9** and **10**; X-ray structure of **10c**; structures and energies of **5**, **6**, **12**, **5**+Cl⁻, and *a*-**13** optimized at the B3LYP/6-31+G* level. This material is available free of charge via the Internet at http://pubs.acs.org.

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