# Unprecedented Chemistry of an Aryloxychlorodiazirine: Generation of a Dihalodiazirine and Diazirinone

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Diazirines are prime precursors of carbenes.[1] For example, archetypal electrophilic (CF_2),[2] ambiphilic (MeOCCl),[3] and nucleophilic (MeOCOMe)[4] can be generated from appropriate diazirines for spectroscopic and reactivity studies. Halodiazirines **1** are obtained from the hypohalite oxidation of amidines or isouronium salts (Graham oxidation).[5] Here, R can be alkyl, aryl, vinyl, or alkoxy (aryloxy), while X is Cl or Br.[5]

1   **2**   **3**
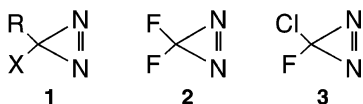
This extraordinary reaction can be coupled with subsequent nucleophilic exchange of X by, for example, fluoride[6] or alkoxide[7] to afford many additional diazirines,[1] including fluoromethoxy-diazirine[8] and dimethoxydiazirine.[4]

Given the centrality of dihalocarbenes in carbene chemistry,[9] dihalodiazirines are particularly desirable precursors. Difluoro-diazirine (**2**) is available by the reductive defluorination cyclization of perfluoroformamidine[2d] or bis(difluoroamino)difluoro-methane,[10a,b] and by the CsF-catalyzed, gas-phase isomerization of difluorocyanamide.[10c] Chlorofluorodiazirine (**3**) can also be obtained by reductive defluorination cyclization.[11] However, these preparations all require direct fluorination via intermediates that can be "shatteringly explosive".[12] Moreover, despite the utility of the two-step Graham oxidation−nucleophilic exchange sequence,[5−8] di-halodiazirines have not yet been prepared by this method. Here, we demonstrate how this can be done with a novel preparation of **3**, and we describe a remarkable accompanying reaction that, for the first time, generates diazirinone, the diaza analogue of cyclo-propenone.

To obtain a dihalodiazirine from **1**, "R" must be converted into a leaving group. Thus, phenoxychlorodiazirine (**4**)[13] was nitrated with nitronium tetrafluoroborate[14] (0 °C, $MeNO_2$) to give *p*-nitrophenoxychlorodiazirine (**5**) in 40% yield.[15] Diazirine **5** was characterized spectroscopically: IR, 1530 cm^{-1} (N=N); UV, λ_{max} 337, 353 nm (pentane), ^{1}H NMR (δ, $CDCl_3$), 7.47, 8.33 (A_2B_2 multiplets). Next, diazirine **5** in CD_3CN or $CDCl_3$ was reacted with "molten" tetrabutylammonium fluoride (TBAF)[6] at 0−25 °C for 10 h. The product mixture contained three principal components: *p*-nitrophenoxyfluorodiazirine (**6**), *p*-nitrophenol (**7**), and *p*-nitro-fluorobenzene (**8**) in the approximate ratio 28:17:55, respectively.
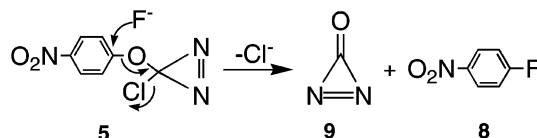

4, X=H
5, X=NO_2
6
7, Y=OH
8, Y=F
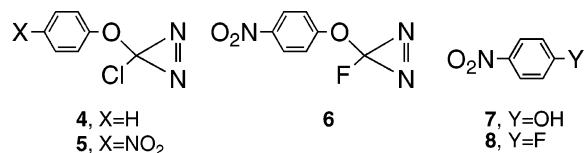
Products **7** and **8** were identified by NMR comparisons to authentic samples, as well as NMR spiking experiments. Fluoro-

Scheme 1
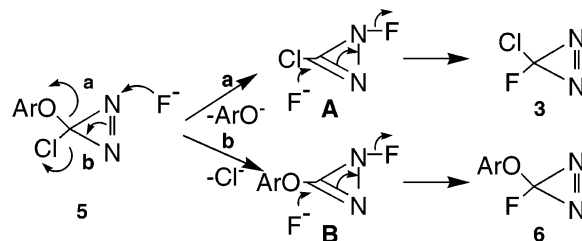
Scheme 2

diazirine **6**, the expected[6] halide exchange product of chlorodiazirine **5**, was purified by chromatography and characterized spectroscopically: IR, 1525 cm^{-1} (N=N), UV, λ_{max} 336, 352 nm (pentane); ^{19}F NMR (δ, $CFCl_3$, $CDCl_3$), −119.0; ^{1}H NMR (δ, $CDCl_3$), 7.38, 8.26 (A_2B_2 multiplets).[15]

Products **6**−**8** imply that reaction of diazirine **5** with F$^-$ follows three competitive pathways, where the first two channels involve alternative double S_N2' mechanisms for the diazirine halide exchange reaction;[5,16,17] cf., Scheme 1. S_N2' fluoride attack on **5** displaces either *p*-nitrophenoxide (later protonated to **7**, path a), affording isodiazirine intermediate **A**, or it displaces chloride (path b), yielding isodiazirine intermediate **B**. Subsequent S_N2' attacks of fluoride then convert **A** to chlorofluorodiazirine (**3**) and **B** to diazirine **6**.

When the reaction of **5** and TBAF was continuously swept with a nitrogen stream, diazirine **3** could be trapped in 0.5 mL of $CDCl_3$ at 77 K[15] and characterized spectroscopically: ^{19}F NMR (δ, $CFCl_3$, $CDCl_3$), −105.6; IR, 1562 cm^{-1} (N=N) [lit.,[11] 6.50 μ, 1538 cm^{-1}]; UV, λ_{max} 324, 340, 356 nm ($CDCl_3$) [lit.,[11] 310−360 nm, gas phase). Photolyis of **3** in $CDCl_3$ and isobutene (350 nm, sealed tube) gave 1-chloro-1-fluoro-2,2-dimethylcyclopropane[15,18] (the adduct of ClCF), identified spectroscopically and by comparison to an authentic sample.[15,19]

The third (and dominant) channel from the reaction of **5** and TBAF is the most unusual; cf., Scheme 2. Reaction of ~0.2 g of molten TBAF with 50 mg of **5** in 0.2 mL of $CDCl_3$ or 1,2-dichloroethane (DCE) in an IR cell at −10 to −15 °C afforded CO (2117 and 2168 cm^{-1}).[20] Immediately after reagent mixing, a strong absorption appeared at 2150 cm^{-1} and gradually decayed over 3−5 min as the reaction temperature rose toward ambient; simulta-neously, CO appeared at 2115 and 2173 cm^{-1}; cf., Figure 1. We attribute the transient IR feature at 2150 cm^{-1} to diazirinone (diazacyclopropenone), **9**, which subsequently fragments to CO (and N_2).[21]
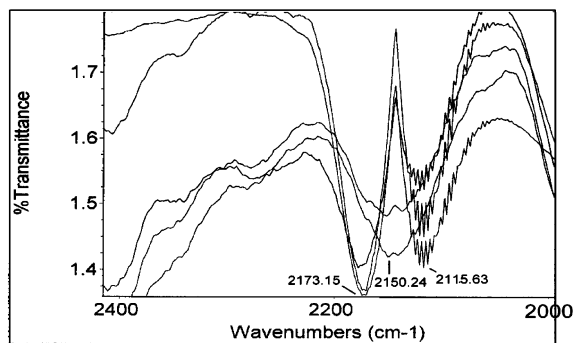
Figure 1. Infrared spectra following reaction of diazirine **5** with TBAF. Diazirinone (**9**) at 2150 cm^{-1} decreases as CO at 2115 and 2173 cm^{-1} increases. Including ∼2 min of preparation time, the lifetime of **9** in this experiment is ∼5 min.

Formation of *p*-nitrofluorobenzene **8** from diazirine **5** and TBAF (see above) requires that Cl$^-$ and a N$_2$CO fragment be liberated. Computational studies in which we attempted to optimize a Meisenheimer complex formed by fluoride addition at the ipso carbon of **5** (see Scheme 2) led to Cl$^-$, **8**, and diazirinone **9** (i.e., N$_2$CO).[15] The computations of Korkin et al. find **9** to be the most stable of various N$_2$CO isomers; for example, it is about 11 kcal/mol more stable than its known linear isomer nitrosyl cyanide (O=N−CN).[22] The decomposition of **9** to CO + N$_2$ is exothermic by >90 kcal/mol,[22,23] but requires an activation energy of 24[24]−27[22,23] kcal/mol, so that **9** should be observable, if metastable.

The (unscaled) computed[22] IR C=O frequency for **9** is 2064 cm^{-1} (B3LYP) or 2079 cm^{-1} (MP 2), reasonable fits to our observed 2150 cm^{-1}. A better fit is O=N−CN, with a reported CN absorption at 2170 cm^{-1} (gas phase),[25] although it is difficult to envision its direct generation from diazirine **5** and F$^-$. We prepared O=N−CN from nitrosyl chloride[26] and AgCN.[27] Reaction of cold (−20 °C) O=N−CN in DCE with TBAF in the IR cell led to *immediate* disappearance of O=N−CN at 2164 cm^{-1}, coupled with the appearance of CO (2116 and 2169 cm^{-1}). O=N−CN is known[28] to (gradually) afford CO and N$_2$ (presumably via prior dissociation to NO and CN radicals),[28] but how fluoride catalyzes this conversion is unclear.

Importantly, the reaction of O=N−CN with TBAF (immediate decomposition) differs from that of the product from **5** and TBAF (decomposition over 5−9 min). We conclude that the carrier of the 2150 cm^{-1} IR band from the reaction of **5** and TBAF is diazirinone **9**, which decays to CO and N$_2$ with a lifetime of 5−9 min at −20 to 25 °C (in the presence of TBAF). The formation of **9** in this reaction, and its properties, are in reasonable accord with computational studies.[15,22−24]

In summary, the reaction of *p*-nitrophenoxychlorodiazirine **5** with TBAF follows three channels: (1) ∼17% of *p*-nitrophenoxide/F$^-$ exchange to chlorofluorodiazirine **3** and *p*-nitrophenol **7**, (2) ∼28% of Cl/F exchange to *p*-nitrophenoxyfluorodiazirine **6**, and (3) ∼55% of ipso fluoride attack, affording *p*-nitrofluorobenzene **8** and the previously unknown diazirinone **9**.[29]

Supporting Information Available: Experimental procedures and computational studies for Scheme 2. This material is available free of charge via the Internet at http://pubs.acs.org.

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