at −50 °C to yield 124 mg (41%) of **2** after flash chromatography; GC (5.3 min, 10%; 5.9 mim, 90%).

Method B was performed on 23.2 mg (0.163 mmol) of **5** with 0.17 mL (0.170 mmol) of catechol borane (1.0 M in THF) and 10.0 mL (0.016 M) of dichloromethane at −78 °C to yield 20.0 mg (85%) of **2** after flash chromatography; GC (5,3 min, 29%; 5.9 min, 71%).

***rel*-(2*S*,5*R*,α*S*)-α-Ethyl-5-methyltetrahydrofuranmethanol (4).** Method B was performed on 29.7 mg (0.209 mmol) of **6** with 0.21 mL (0.210 mmol) of Me_2S–BH_3 (1.0 M in dichloromethane) and 42 mL (0.005 M) of dichloromethane to yield 22.9 mg (67%) of crude **4**, and flash chromatography produced 10.5 mg (35%) of **4** as a clear colorless oil. **4**: ^{1}H NMR (250 MHz, $CDCl_3$) δ 4.07 (app hextet, J = 6.0 Hz, 1 H, H-5), 3.85 (app q, J = 7.0 Hz, 1 H, H-2), 3.32 (m, H-α), 2.03 (m, 2 H), 1.70–1.37 (m, 4 H), 1.23 (d, J = 6.0 Hz, 3 H, H-6), 1.00 (t, J = 7.4 Hz, 3 H, H-γ); IR 3600–3400, 2980, 2940, 2880, 1470, 1380, 990 cm^{-1}; TLC (2:2:1 hexane–CH_2Cl_2–ethyl acetate, R_f 0.32); GC (5.2 min, 6;% 5.7 min, 94%). The ^{13}C NMR data was the same as reported in ref 4.

Method B was performed on 33.2 mg (0.234 mmol) of **6** with 0.23 mL (0.230 mmol) of Me_2S–BH_3 (1.0 M in dichloromethane) and 13.0 mL (0.018 M) of dichloromethane at −50 °C to yield 26.7 mg (79%) of crude **4**; GC (5.2 min, 11%; 5.7 min, 89%).

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Registry No. 1, 89122-04-3; 2, 89194-24-1; 3, 89194-25-2; 4, 89194-26-3; 5, 112087-58-8; 5 (epoxy alcohol-isomer 1), 112087-59-9; 5 (epoxy alcohol-isomer 2), 112243-76-2; 6, 112087-60-2; 1-penten-3-ol, 616-25-1; 2-methoxypropene, 116-11-0; *trans*-5-octen-2-one, 19093-20-0; 1-butyne, 107-00-6; 2-methyl-2-(2-iodoethyl)-1,3-dioxolane, 53750-51-9; 2-(ethylenedioxy)-5-octynone, 104311-67-3; *cis*-5-octen-2-one, 22610-86-2.

Preparation and Crystal Structure of 3-(1-Naphthylmethyl)-3-chlorodiazirine

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Since the discovery of diazirines in 1960, extensive investigations have been conducted covering various aspects of this class of compounds. Advances in this field have been reviewed constantly to reflect the high level of activity in the chemistry of diazirines.[1-4]

Thus far, the C—N and N=N distances in diazirines have been obtained mostly by theoretical calculations based on observed rotational spectra.[3] The rotational spectra of diazirine and several methyl- and halogen-substituted diazirines have been recorded, and the structural parameters have been reported.[5-9] The structure of difluorodiazirine has been determined by electron-diffraction techniques.[10] The only X-ray analysis of a diazirine that has been reported is that of a heterodimetal complex of diazirine.[11,12] No X-ray studies of simple diazirines have been reported, and this is primarily because of the unsuccessful synthesis of a diazirine compound, which is crystalline and stable enough for X-ray analysis. Most diazirines are either gaseous or liquid at room temperature. The present study reports the first single-crystal X-ray diffraction analysis for a free diazirine, 3-(1-naphthylmethyl)-3-chlorodiazirine (1).

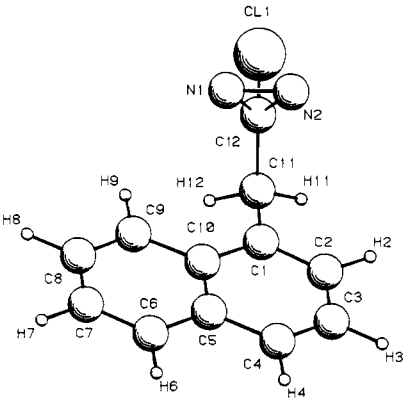

Figure 1. The molecular structure of 1.

Table I. Selected Bond Lengths (Å) and Bond Angles (deg) for 1 (Estimated Standard Deviations Are in Parentheses)

Distances			
Cl–C(12)	1.716 (8)	N(2)–C(12)	1.467 (11)
N(1)–N(2)	1.244 (10)	C(1)–C(11)	1.509 (11)
N(1)–C(12)	1.463 (10)	C(11)–C(12)	1.522 (12)
Angles			
N(2)–N(1)–C(12)	65.0 (6)	Cl–C(12)–N(2)	115.4 (6)
N(1)–N(2)–C(12)	64.7 (6)	Cl–C(12)–C(11)	115.4 (5)
C(2)–C(1)–C(11)	117.4 (6)	N(1)–C(12)–N(2)	50.3 (5)
C(10)–C(1)–C(11)	122.5 (6)	N(1)–C(12)–C(11)	123.0 (6)
C(1)–C(11)–C(12)	113.9 (7)	N(2)–C(12)–C(11)	121.8 (7)
Cl–C(12)–N(1)	115.5 (6)		

Results and Discussion

Although 1 is a new compound, it can be synthesized according to Graham's[13] method with minor modification. This method involves the conversion of 1-naphthylacetonitrile to the corresponding amidine hydrochloride, followed by oxidation by sodium hypochlorite to the diazirine. The title compound has been subjected to IR, UV, NMR, and MS analyses. Unlike other diazirines, the intensities of both the infrared N=N stretching frequency (1560 cm^{-1}) and the UV absorption band (356 nm) are very weak. In addition, 1 shows a moderately intense molecular ion peak in the mass spectrum, which is not at all a characteristic for diazirines. Most chlorodiazirines lose chlorine readily when subjected to mass spectral analysis and therefore produce no molecular ion peak.

Selected interatomic distances and interbond angles for 1 are listed in Table I. The aromatic rings exhibit no unusual features. Compound 1, shown in Figure 1, is essentially a substituted derivative of methylchlorodiazirine.[6] The structural parameters of the diazirine moiety of 1 are

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Table II. Comparison of Bond Lengths and Bond Angles for Diazirines (Estimated Standard Deviations Are in Parentheses)

	bond lengths, Å		bond angles, deg
compound	N=N	C—N	N—C—N
1[a]	1.244 (10)	1.465 (10)	50.3 (5)
$MeClCN_2$[b]	1.241 (5)	1.462	50.2 (5)
$MeBrCN_2$[c]	1.240 (5)	1.462	50.2
$(Me)_2CN_2$[d]	1.235 (5)	1.490 (10)	48.9
$MeHCN_2$[e]	1.235 (5)	1.481 (10)	49.3 (3)
H_2CN_2[f]	1.228 (3)	1.482 (3)	48.9
F_2CN_2[g]	1.293 (9)	1.426 (4)	53.9 (4)
2[h]	1.265	1.493	50.1

[a] 3-(1-Naphthylmethyl)-3-chlorodiazirine. [b] Reference 6. [c] Reference 7. [d] Reference 5. [e] Reference 8. [f] Reference 9. [g] Reference 10. [h] Reference 12; μ-(η^2-pentamethylenediazirine)-[pentacarbonylchromium(0)][pentacarbonylmolybdenum(0)].

in excellent agreement with those calculated for $MeClCN_2$, the only significant difference being that the C–Cl bond is slightly longer in $MeClCN_2$ (1.742 Å). This study therefore supports the theoretical calculations carried out for diazirines.

The relevant structural parameters, which have been calculated for diazirine and a number of simply substituted diazirines, are listed in Table II. On the basis of the standard deviations for the N=N and C—N bond lengths of 1, these bonds are not considered to be significantly different from those derived for diazirine, methyldiazirine, and dimethyldiazirine. It should be noted, however, that a significant shortening of the C—N bonds and a lengthening of the N=N bond has been observed in the structure of difluorodiazirine.[10] It has been suggested that this is caused by the presence of the fluorine atoms, which compress the charge density around the carbon atom. Similarly, it is possible that the presence of the electronegative chlorine substituent in 1 could be the cause of slightly shorter C—N bonds and a marginally longer N=N bond than observed in diazirine and dimethyldiazirine.

The N–C–N plane forms an angle of 88.3° with the Cl–C(12)–C(11) plane. This is consistent with the angles between related planes in other diazirines, some of which have C_{2v} symmetry. The Cl–C(12)–C(11) bond angle is also similar to the Me–C–Me bond angle observed in dimethyldiazirine (119.7°) and the F–C–F bond angle in difluorodiazirine (111.8°).

The only other X-ray crystallographic study of a diazirine has been that of a heterodimetal complex of pentamethylenediazirine (2), where the N=N bond is bridging between a chromium atom and a molybdenum atom.[12] In this case, the N=N bond appears to be stretched when compared with other diazirines, while there has been no shortening of the C—N bond. This is possibly the result of π back-donation from the metals into the π^* (N=N) orbital.

The torsion angles associated with the atoms of the naphthylmethyl moiety of 1 clearly indicate no distortion of the planarity of the group. Another planar group is the Cl–C(12)–C(11)–C(1) moiety, which makes an angle of 79.5° with the naphthyl plane. The Cl—C(12) bond has a torsion angle of 176° with the C(11)—C(1) bond, and the N=N bond is almost parallel to the plane of the naphthyl rings. This is an arrangement that provides the least steric interaction of the nitrogen atoms and methylene hydrogen atoms with the hydrogen atoms of the naphthyl group. An alternative position for the chlorine atom and the N=N group, obtained by a 180° rotation of the C(11)—C(12) bond, would not be favorable because of the proximity of the chlorine atom to the naphthyl group.

Experimental Section

Synthesis of 3-(1-Naphthylmethyl)-3-chlorodiazirine. Anhydrous hydrogen chloride gas was bubbled through a solution of 1-naphthylacetonitrile (25 g, 0.15 mol) in dry ethanol (10 mL) and chloroform (30 mL) at 0 °C until the solution became saturated with HCl gas (6 g). The reaction flask was stoppered and kept in a freezer for 48 h. Anhydrous ether (150 mL) was added. The mixture became milky, and imido ether hydrochloride precipitated. The solvent was removed under reduced pressure, and the residue was dried in a desiccator over silica gel to yield a white solid. Anhydrous ammonia was bubbled into dry ethanol (300 mL) for 1.5 h at 0 °C, and imido ether hydrochloride, suspended in dry ethanol (80 mL), was slowly added to the stirred ammonia/ethanol solution at 0 °C. The mixture was allowed to stir at 0 °C overnight. The mixture was concentrated under reduced pressure until crystals of ammonium chloride precipitated. These were removed by filtration. Removal of the solvent from the filtrate under reduced pressure yielded 1-naphthylacetamidine hydrochloride (30 g, 0.14 mol; yield 90%).

1-Naphthylacetamidine hydrochloride (7.0 g, 0.032 mol), lithium chloride (20 g, 0.47 mol) in dimethyl sulfoxide (150 mL), and hexane (150 mL) were stirred at 0 °C. Sodium hypochlorite solution (7%, 300 mL) containing sodium chloride (60 g, 1.02 mol) was added to the mixture over 10 min followed by vigorous stirring for 1 h. The mixture was diluted with water (200 mL), the organic layer was separated, and the aqueous layer was extracted with hexane (2 × 100 mL). The combined extracts were washed with water (100 mL) and dried. The solvent was removed under reduced pressure, leaving an oily liquid. This crude product was purified by column chromatography on silica gel, eluting with hexane to give 3-(1-naphthylmethyl)-3-chlorodiazirine (1.6 g). The diazirine was crystallized from *n*-pentane to give a white crystalline solid, mp 41 °C. The spectral data of this product are as follows: IR ν_{max} 1560 cm^{-1} (weak); UV weak absorption at λ_{max} 356 nm; NMR ($CDCl_3$/TMS) δ 3.75 (CH_2, s, 2 H), 7.2–7.9 ($C_{10}H_7$, m, 7 H); mass spectrum (70 eV), *m/z* (relative intensity) 216 (M^+, 14), 218 (5), 188 ($[M - N_2]^+$, 9), 190 (3), 153 ($C_{12}H_9^+$, 100), 76.5 ($C_{12}H_9^{2+}$, 7).

Crystal data: $C_{12}H_9ClN_2$, M_r = 216.7, monoclinic, space group $C2/c$, (no. 15), a = 19.186 (9) Å, b = 8.750 (4) Å, c = 13.473 (6) Å, β = 109.60 (5)°, V = 2130.8 Å^3, Z = 8, D_{calcd} = 1.351 g cm^{-3}, $F(000)$ = 896 e, 22 °C, Cu Kα_1 (graphite-monochromated) radiation, λ = 1.540 51 Å, μ = 28.90 cm^{-1}.

Intensity Data Collection, Structure Determination, and Refinement. The crystal used for data collection was a flat plate of approximate dimensions 0.4 × 0.4 × 0.1 mm. A Picker FACS-1 four-circle diffractometer was used to measure the unit cell dimensions and to collect the data. The unit cell constants were obtained by least-squares analysis of the diffractometer setting angles of 12 well-centered reflections with 55° ≤ 2θ ≤ 80°. The intensities of 3062 reflections with 4° ≤ 2θ ≤ 110° were recorded with $\omega/2\theta$ scans. Of these, 1347 were unique and 758 had $I > 3\sigma(I)$. The intensities of three standard reflections were monitored and indicated a steady deterioration of the crystal to approximately 60% of its original scattering power. The intensities were reduced to a standard scale by routine procedures.[14] Corrections for Lorentz and polarization factors and for crystal deterioration were applied, but no corrections were made for absorption. Scattering factors for neutral atoms were those recorded in *International Tables for X-ray Crystallography*[15] and were corrected for the real part of anomalous dispersion.

The structure was solved by direct methods (MULTAN-80[16]) from which all the non-hydrogen atom positions were obtained. Refinement was carried out by using the SHELX-76[17] system. The structure was refined initially by a large block least-squares procedure with independent isotropic temperature factors on the heavy atoms. The hydrogen atom positions were determined from

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a difference-fourier synthesis, but the C–H distances were restrained to 1.08 Å. The final refinements were with anisotropic temperature factors on the non-hydrogen atoms and individual isotropic temperature factors on the hydrogen atoms. A two-block matrix least-squares method was employed, minimizing $\sum w\Delta F^2$ where $w^{-1} = \sigma^2|F_o| + 0.0002|F_o|^2$. The refinement converged at $R = 0.073$, $R_w = 0.074$, for 754 unique observed reflections ($I > 3\sigma(I)$) and 146 least-squares parameters. Four reflections were omitted because of suspected extinction. The final difference maps were flat, without recognizable residual features.

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Registry No. 1, 112399-65-2; 1-naphthylacetonitrile, 132-75-2; ethyl 1-naphthylacetimidate hydrochloride, 43002-67-1; 1-naphthylacetamidine hydrochloride, 16275-19-7.

Supplementary Material Available: Tables of atomic positional parameters, anisotropic temperature factors, interatomic distances, interbond angles, and torsion angles (6 pages). Ordering information is given on any current masthead page.

Carbon Leaving Group in Aromatic Nucleophilic Substitution. Quantitative Comparison with a Common Leaving Group

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Examples of carbon leaving groups in aromatic nucleophilic substitutions on activated substrates are scarce,[2,3] and as far as we know, no data are reported on the relative mobility of these groups with respect to the usual leaving groups, e.g., NO_2, F, Cl, Br. With the aim to fill this gap, we started a preliminary investigation, some time ago, on the reactivity of 4-(trichloromethyl)quinazoline (**1**) toward nucleophilic reagents.[4] Trihalomethyl groups are well known as leaving groups in the haloform reaction,[5] but they are seldom present as leaving groups in aromatic nucleophilic substitutions.[3]

In a previous paper, we reported that **1** reacts easily with methoxide ion in methanol to give the expected product of aromatic nucleophilic substitution at position 4, i.e., 4-methoxyquinazoline.[4] An accurate spectroscopic investigation of the reaction revealed that during the course of the reaction, at variance with the usual aromatic substitution mechanism, a covalent solvation adduct accumulates. Thus, this reaction seemed to us unfit for a quantitative assessment of the mobility of a trichloromethyl group in the aromatic nucleophilic substitution.

We now report on the reaction of **1** with hydroxide ion in 1:1 MeCN/H_2O and on the quantitative comparison of the reactivity of **1** with that of 4-chloroquinazoline (**2**).

Results and Discussion

Compound **1** reacts rapidly, at room temperature, with tetrabutylammonium hydroxide ion in 1:1 MeCN/H_2O to give 4-hydroxyquinazoline (**3**) as the only product. No spectroscopic evidence was found for the accumulation of an intermediate during the reaction course.

Table I. Kinetic and Activation Data for the Reactions of 1 and 2 with OH^- in 1:1 MeCN/H_2O

compd	k_2 (25 °C), M^{-1} s^{-1}	$\Delta H^{\ddagger}$,[a] kcal mol^{-1}	$-\Delta S^{\ddagger}$,[a] cal deg^{-1} mol^{-1}
1[b]	3.18×10^{-2}	12.6 (0.5)	23.1 (1.6)
2[c]	8.34×10^{-3}	17.0 (0.7)	11.1 (2.2)

[a] Standard deviations in parentheses. [b] $k_2 \times 10^2$, M^{-1} s^{-1} (°C): 2.22 (20.6), 4.27 (28.3), 6.93 (36.2), 11.8 (43.6). [c] $k_2 \times 10^3$, M^{-1} s^{-1} (°C): 5.15 (20.4), 11.7 (28.1), 23.8 (36.1).

Since our aim was to compare the mobility of the trichloromethyl group with that of a more usual one, the chlorine atom was chosen as a reference group. Therefore, the reaction of **2** under the same conditions was studied. Also, in this case an aromatic nucleophilic substitution does occur, but, at variance with the reaction of **1**, 4-hydroxyquinazoline is not the only reaction product. A small amount of 4-(cyanomethyl)quinazoline (**4**) (6–12% yield, depending on the temperature), arising from the reaction of **2** with the conjugated base of MeCN, was in fact found. As for the reaction of **1**, no intermediate was observed in the reaction of **2** with hydroxide ion.

All kinetic measurements were carried out under pseudo-first-order conditions, with a large excess of the nucleophile. The rate constants for the reaction of **2** with OH^- were obtained from the observed rate constants and from the ratio of **3**/**4**, assuming a kinetic scheme of two first-order parallel reactions. Kinetic and activation data for the reactions of **1** and **2** with OH^- in 1:1 MeCN/H_2O are reported in Table I.

The rate constant values, at 25 °C, show that **1** is about 4 times more reactive than **2**; that is, the mobility of the trichloromethyl group in this reaction is slightly higher than that of the chlorine atom, which is generally considered a fairly good leaving group in aromatic nucleophilic substitutions.[6a]

On inspection of the activation parameters, an interesting feature emerges. The modest difference in the rate constants is the result of a compensation between the activation enthalpies and activation entropies of the two reactions. In fact, the reaction of **1** is characterized by an activation enthalpy 4.4 kcal mol^{-1} lower than the reaction of **2**, while **2** is favored by an activation entropy less negative by 12 eu. (3.6 kcal mol^{-1} at 25 °C).

Since aromatic nucleophilic substitution on activated substrates with anionic nucleophiles proceeds through an addition–elimination mechanism with the addition as the key step,[6b] the rate constants reported in Table I refer to the addition of the nucleophile to position 4 of the quinazoline ring. With this in mind, we can propose some tentative explanations for the differences in the activation parameters.

From the electronic point of view, the CCl_3 and Cl groups interact differently with the quinazoline ring. The chlorine atom is in fact conjugated with the π system of the ring, particularly with the two electron-withdrawing aza groups. This type of interaction (not possible for the trichloromethyl group) stabilizes the initial state whereas it is lost (at least partially) in the transition state owing to the hybridization change from sp^2 to sp^3 of the carbon atom at position 4. This different electron behavior can be partially responsible for the greater enthalpy of acti-

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