matographed (silica gel, eluted with petroleum ether) and 2-quinolyldiphenylphosphine oxide was isolated and twice recrystallized from petroleum ether (40% yield): mp 139.5–140 °C; mass spectrum, *m/e* (relative intensity) 329 (13), 328 (17), 252 (52), 204 (47), 201 (23), 183 (17), 128 (63), 101 (43), 77 (100), 51 (53).

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Registry No. 1, 576-83-0; 2, 88-05-1; 3, 108-67-8; 2-ClQ, 612-62-4; NH_2^-, 17655-31-1; Ph_2P^-, 34676-89-6; Ph_2As^-, 14971-22-3; PhI, 591-50-4; (2,4,6-trimethylphenyl)diphenylphosphine oxide, 91239-43-9; 2-quinolyldiphenylphosphine oxide, 91239-45-1; 2-quinolyldiphenylarsine, 91239-44-0.

Perdeuteration and Selective Deuteration of Alkynols by Isomerization of Triple Bonds Using N-Deuterated Reagents

Suzanne R. Abrams

Plant Biotechnology Institute, National Research Council of Canada, Saskatoon, Saskatchewan, Canada S7N 0W9

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A novel method for introduction of deuterium into long-chain carbon compounds is described. The procedure is based upon isomerization of a triple bond of an $(n + 1)$-alkyn-n-ol to an ω-alkyn-n-ol using N-deuterated reagents and solvent. Isomerization of 2-alkyn-1-ols effects exchange of the protons from C-2 to the terminal carbon, resulting in perdeuteration of all methylene carbons of the chain except C-1. Reaction of $(n + 1)$-alkyn-n-ols $(n > 1)$ with deuterated isomerization reagents affords specific, selective deuteration of methylene carbons $> (n + 1)$. The reagents for these transformations are alkali metal amides of the solvent of the reaction, 1,3-diaminopropane-*N,N,N′,N′*-d_4. When the cation is sodium or potassium, isomerization of 2-decyn-1-ol affords 9-decyn-1-ol with 89% deuterium incorporation at C-2 to C-8 in isolated yields of 48–53%. An isomerization reagent prepared by addition of potassium *tert*-butoxide to the lithium salt of 1,3-diaminopropane-*N,N,N′,N′*-d_4 affords 93% deuterium incorporation and isolated yields of 52% or better. With this reagent 2-octadecyn-1-ol is rearranged to 17-octadecyn-1-ol with an overall deuterium incorporation of 93% over 31 exchangeable positions in 60% isolated yield.

Perdeuterated fatty acids and their derivatives are employed in studies of biological processes as probes for exploring biosynthetic and metabolic pathways[1] and in NMR and IR studies of the structure and function of micelles and membranes.[2] Current methods of synthesis of perdeuterated organic compounds are based upon catalytic exchange techniques in which protons are replaced by deuterons under extremely vigorous conditions (high pressures and temperatures and long reaction times).[3] Known methods are limited to preparation of compounds stable to the severe reaction conditions. Unsaturated compounds, for instance, are reduced in the course of deuteration.

Alkali metal amides in the diamine solvents such as 1,2-diaminoethane and 1,3-diaminopropane mediate isomerization of internal triple bonds to the terminal position of straight-chain hydrocarbons and alcohols.[4,5] Overall, during the course of such isomerization reactions, protons in the path of the migrating triple bond are stripped from the carbon skeleton and replaced by protons from the amide or from the solvent. We thought that such a remote functionalization reaction could be used to exchange protons of a methylene chain with deuterons if the solvent of the reaction was replaced by its N,N,N′,N′-tetradeuterated analogue. Such a procedure, if successful, would provide ready access to functionalized deuterated long-chain compounds and would have decided advantages over presently available methods. Reaction conditions would be more moderate; unsaturated perdeuterated compounds could be prepared from 2-alkyn-1-ols, and specfically partially deuterated chemicals would be accessible from disubstituted α-acetylenic alcohols. As well, deuterium labeling could be used to study the course of triple-bond migrations.

There have been reports of deuterium exchanges mediated by alkali metal amides. Brown[6] observed that the potassium salt of 1,3-diaminopropane was sufficiently basic to cause exchange of deuterons of benzene-d_6 by protons. Wotiz et al.[7] showed that the rate of rearrangement of 3- to 2-hexyne with the lithium salt of 1,2-diaminoethane-*N,N,N′,N′*-d_4 paralleled the rate of deuterium incorporation into the latter. Procedures for incorporation of deuterium into alkynes by base-mediated isomerization techniques have been reviewed.[8] Methods are limited to exchange at the terminal and propargylic positions.

We report our studies on the incorporation of deuterium into a variety of alkynols using an N,N,N′,N′-tetradeuterated diamine solvent and some derived alkali metal amide isomerization reagents.

Results and Discussion

In the cases discussed in this work, unless noted, rearrangement reactions proceeded to completion. That is, one isomer, that containing a terminal triple bond, was the exclusive product. Deuterium incorporations of products

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[1] Tulloch, A. P. *Chem. Phys. Lipid* **1979**, *24*, 391; *Progr. Lipid Res.* **1983**, *22*, 235.

[2] Cameron, D. G.; Martin, A.; Mantsch, H. H. *Science (Washington, D.C.)* **1983**, *219*, 180.

[3] Dinh-Nguyen, N.; A. Raal, *Prog. Chem. Fats Other Lipids* **1976**, *16*, 195. Atkinson, J. G.; Luke, M. O.; Stuart, R. S. *Can. J. Chem.* **1967**, *45*, 1511.

[4] Brown, C. A.; Yamashita, A. *J. Am. Chem. Soc.* **1975**, *97*, 891.

[5] Macaulay, S. R. *J. Org. Chem.* **1980**, *45*, 734.

[6] Brown, C. A. *J. Chem. Soc., Chem. Commun.* **1975**, 222.

[7] Wotiz, J. H.; Barelski, P. M.; Koster, D. F. *J. Org. Chem.* **1973**, *38*, 489.

[8] LaValley, J. C.; Saussey, J. In "The chemistry of the carbon-carbon triple bond"; Patai, S., Ed.; Wiley: Toronto, 1978; Chapter 20.

0022-3263/84/1949-3587$01.50/0

Table I. Deuterium Incorporations in ω-Alkynols from Isomerization Mediated by the Sodium Salt of 1,3-Diaminopropane-*N*,*N*,*N*′,*N*′-d_4

entry	starting material	product	yield, %	overall deuterium incorporation at exchangeable positions, %	
				by MS	by NMR
1	$HOCH_2C{\equiv}C(CH_2)_6CH_3$	$HOCH_2(CD_2)_7C{\equiv}CD$	48	89	87
2[a]	$HOCH_2C{\equiv}C(CH_2)_6CH_3$	$HOCH_2(CD_2)_7C{\equiv}CH$	35	89	86
3	$HO(CH_2)_4C{\equiv}C(CH_2)_3CH_3$	$HOCH_2(CD_2)_7C{\equiv}CD$	40	85	82
4[b]	$HOCH_2C{\equiv}C(CH_2)_{14}CH_3$	$HOCH_2(CD_2)_{15}C{\equiv}CH$	18	90	87
5	$H_3CCH_2CH(OH)C{\equiv}C(CH_2)_5CH_3$	$H_3CCH_2CH(OH)(CD_2)_6C{\equiv}CD$	35	87	88
6[c]	$H_3C(CH_2)_{12}CH(OH)C{\equiv}C(CH_2)_5CH_3$	$H_3C(CH_2)_{12}CH(OH)(CD_2)_6C{\equiv}CD$	14	90	
7[d]	$HOCH_2C{\equiv}C[C(H/D)_2]_{12}H$	$HOCH_2(CD_2)_{12}C{\equiv}CD$	31	89	90

[a] H_2O quench; isolated by TLC. [b] 12 equiv of reagent; 18 h reaction; H_2O quench. [c] The overall deuterium incorporation could not be estimated by ^{1}H NMR due to the large methylene envelope from the protonated portion of the molecule. [d] The 2-pentadecyn-1-ol was deuterated to the extent of 62%.

(purified by HPLC) were estimated by two independent techniques: ^{1}H NMR and GC/MS. In the NMR method, the integration of residual proton signals was compared to that of an intramolecular internal standard[9] so that extent of exchange at the methylene, propargylic, and terminal positions could be calculated. For the GC/MS determinations, trimethylsilyl ethers of alkynols were prepared. Mass discrimination was observed on elution of the trimethylsilyl ethers through the column, resulting in broadened peaks. The intensities of all the ions under the peaks were summed in the mass spectral analyses. The molecular ions were generally too weak to be useful, but the $(M - 15)^+$ ions commonly found in trimethylsilyl ethers were significant, and a cluster of peaks corresponding to deuterated $(M - 15)^+$ ions were observed. In each case corrections were made for $(M + 1)^+$ and $(M + 2)^+$ ions measured in the protonated analogue.

The two analytical techniques gave close agreement for deuterium incorporation. As trace impurities, such as proton-containing solvents, would lead to an overestimation of hydrogen content in the ^{1}H NMR, and as isotope effects in fragmentation in the mass spectrometer favor C–H over C–D bond cleavage, the deuterium incorporation estimates given in this work are thought to be minimum values.

Preparation of $D_2N(CH_2)_3ND_2$ and Its Sodium Salt. Initial studies were carried out with the N,N,N′,N′-d_4 analogue of the reagent we had developed earlier, the sodium salt of 1,3-diaminopropane.[5] 1,3-Diaminopropane-*N*,*N*,*N*′*N*′-d_4 was prepared from 1,3-diaminopropane by three exchanges with 100% deuterium oxide. The dry deuterated amine gave no N–H signal in the ^{1}H NMR spectrum (CCl_4) and had theoretical incorporation of deuterium bound to nitrogen of 98.8%. The sodium salt of the deuterated diamine ($Na^+DN^-(CH_2)_3ND_2$) was prepared by reaction of sodium hydride with excess solvent at 75 °C for 2.0 h to give a brown solution.

Isomerization of Alkynols with $Na^+DN^-(CH_2)_3ND_2$. A variety of alkynols (Table I) were isomerized by using 9.0 equiv of deuterated reagent for each of the acetylenic compound. The reactions were generally allowed to proceed for 1.5 h at 75 °C and then quenched with an excess of D_2O. Quenching with H_2O (entries 2 and 4) resulted in protonation at the terminal but not at the propargylic position. The theoretical deuterium incorporation at the exchangeable positions was 96–97%; the incorporations obtained were 86–90%. The yields quoted are of isolated purified material and are computed on the basis of the increased molecular weight observed; see paragraph at the end of paper about supplementary material.

In the case of the alkyn-1-ols (entries 1–4 and 7) it was anticipated that rearrangement with the deuterated reagent would produce ω-hydroxyalk-1-ynes in which the protons of the hydroxyl and those on C-2 to the terminal carbon would be exchanged. The protons on C-1 were expected to remain intact as the carbon would bear a negatively charged oxygen atom. This supposition was later confirmed (vide infra). Thus, the theoretical number of deuterons bound to carbon incorporated into 9-decyn-1-ol would be 15; the labile deuteron on the oxygen would be lost on workup.

It is interesting to note that the initial position of the triple bond in the chain is relatively unimportant with regard to the final deuterium incorporation in the 9-decyn-1-ol produced. The slight decrease (entry 3) demonstrates the random nature of the isomerization reaction. Deuteration at C-5 to C-10, and not at C-2 to C-4, would have resulted in nine deuterons being incorporated (67% of that for deuteration at C-2 to C-10).

2-Octadecyn-1-ol required longer reaction times and more reagent to produce the terminal isomer free of other intermediate species. The yield was poorer, but the deuterium incorporation was equally high.

The α-acetylenic alcohols (entries 5 and 6) each contain 13 protons which should exchange as the triple bond migrates to the free end of the molecule. The proton on the carbon bearing the hydroxyl group would not be exchangeable and serves as the internal standard in the NMR integration. In the ^{1}H NMR spectrum of 1-docosyn-9-ol, the large methylene signal of the protonated portion of the molecule interfered with estimation of the total deuterium incorporation. However, mass spectra of the trimethylsilyl ethers of 10-undecyn-3-ol and 1-docosyn-9-ol show very clearly that deuterium was incorporated exclusively at the positions anticipated. The molecular ions suffered cleavage on either side of the carbon bearing the trimethylsilyloxy group. Thus α-cleavage on one side of the OTMS group gave ions of the same mass as the protonated analogue, and fragments from the other α-cleavage gave a cluster of peaks centered at *m*/*z* 223. The corresponding fragment in the protonated materials occurred at *m*/*z* 211.

These results demonstrate that alkyne isomerization using deuterated reagents can be used to introduce deuterium into the whole length or part of a methylene chain. Consistently, incorporations of 88–90% are obtained, while the theoretical value is 96–97%. A partially deuterated 2-alkyn-1-ol **3** was prepared as outlined in Scheme I. 7-Tetradecyne (**1**), was treated with 9 equiv of the deuterated reagent for 1.0 h at room temperature, affording

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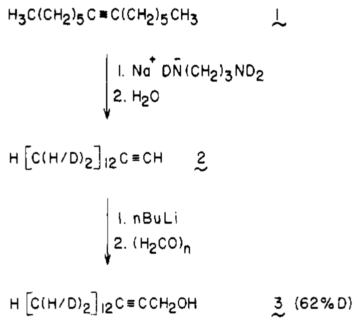
[9] Thomas, A. F. "Deuterium labelling in organic chemistry"; Meredith: New York, 1971; p 410.

Scheme I



a single product. The signals in the ^{1}H NMR spectrum were consistent with structure **2**, a partially deuterated alk-1-yne. Compound **2** was treated first with *n*-butyllithium and then with paraformaldehyde, affording 2-pentadecyn-1-ol (**3**). From the ^{1}H NMR and mass spectrum of **3**, the deuterium incorporation from the isomerization reaction was determined to be 62%. The yield, calculated upon the observed increase in molecular weight, was 80% over two steps. Thus, alkynes are partially deuterated by using this acetylene isomerization technique. This is to be expected as not every position along the chain is required to be traversed before the triple bond is trapped at the terminus of the chain. Rearrangement of the partially deuterated alkynol **3** (entry 7) with $Na^+DN^-(CH_2)_3ND_2$ under standard conditions gave similar levels of deuterium incorporation as those obtained from nondeuterated starting materials.

Improved Reagents for Higher Deuterium Incorporations. We reasoned that extraneous protons might be present in the solvent or might be generated on formation of the reagent. The latter was suspected as the reagent was a brown solution. Wotiz had reported that treatment of vicinal diamines with strong bases gave colored byproducts which were attributed to products of pyrazine radicals.[10] Such product formation by reaction of sodium hydride with 1,3-diaminopropane would involve C–H bond cleavage which could add protons to the medium. Other alkali metal deuterated reagents were sought that could be prepared free of byproducts and that were colorless.

In previous work,[11] we had prepared the lithium salt of 1,3-diaminopropane in 1,3-diaminopropane, a white solid suspended in a colorless liquid. This reagent was found to be inferior to its sodium analogue for the purpose of isomerizing triple bonds to the terminus of a chain as the rate of reaction was considerably slower. The deuterated analogue was prepared as before by reaction of lithium with the deuterated diamine and found to be colorless. A higher ratio of alkali metal amide to alkynol was employed to compensate for the slower rate. Deuterium incorporation in the 9-decyn-1-ol obtained on isomerization of 2-decyn-1-ol increased to 93% (Table II) at the exchangeable positions; however, the yield of isolated product was poor. Reaction of potassium hydride with the deuterated solvent produced the potassium reagent as a pale orange solution. An improved yield of 9-decyn-1-ol was obtained (53%), but the deuterium incorporation was similar to that of the sodium analogue. The *p*-nitrobenzoate of the 9-decyn-1-ol isolated from this last reaction was prepared. The ^{1}H NMR integration of the aromatic protons vs. the OCH_2 protons was 2:1, confirming that the protons on C-1 were not exchanged during the rearrangement reaction.

Table II. Rearrangement of 2- to 9-Decyn-1-ol with Various Deuterated Isomerization Reagents

reagent	isolated yield, %	9-decyn-1-ol overall deuterium incorporation, % by MS	by NMR
$Na^+D\bar{N}(CH_2)_3ND_2$	48	89	87
$Li^+D\bar{N}(CH_2)_3ND_2$	24	94	92
$K^+(D\bar{N}(CH_2)_3ND_2$	53	89	86
$K^+\bar{O}$-*t*-Bu/$Li^+D\bar{N}(CH_2)_3ND_2$	52	93	91

Addition of potassium *tert*-butoxide to preformed lithium salt of 1,3-diaminopropane-*N,N,N′,N′*-d_4 gave a pale yellow solution.[12] The isolated yield of deuterated 9-decyn-1-ol with this system was 52%; the overall deuterium incorporation was 92%. Thus it appears that addition of potassium *tert*-butoxide to $Li^+DN^-(CH_2)_3ND_2$ produces a reagent of similar character to $K^+DN^-(CH_2)_3ND_2$ in the rate of rearrangement and the isolated yield. The deuterium incorporation is nearly as high as that obtained with the lithium reagent alone. Rearrangement of 2-octadecyn-1-ol with $K^{+-}O$–*t*–Bu/$Li^+DN^-(CH_2)_3ND_2$ afforded 17–octadecyn–1–ol in 60% yield and 94% deuterium incorporation over the 31 exchangeable positions. Thus, this new reagent affords as high or higher yields of terminal isomers of long-chain compounds with extremely high deuterium incorporation.

Qualitatively, we observe that the rate of acetylene migration using the deuterated reagent and solvent appears to be somewhat slower than that for the protio analogue. The rate-determining step may be the transfer of a deuteron from the exceeding weakly acidic diamine solvent to the various carbanions. However, because of the large number and variety of proton/deuteron transfers and the random nature of the rearrangement, the rate-limiting factors would be difficult to establish.

The slight discrepancy between the theoretical deuterium incorporation and the highest obtained is probably due to several factors. First, contamination might result from proton containing starting materials or equipment; second, byproducts during formation of the reagent likely contribute a small amount of isotope dilution; and third, diffusion of the diamine from the reaction site may be sufficiently slow that protons from the carbon chain may be reattached at another site.

Conclusion

A novel method has been developed that allows efficient introduction of deuterium into long-chain compounds in good yield and high isotopic purity. All (from 2-alkyn-1-ols), or a specific portion of the carbon skeleton (from other *n*-alkyn-(*n* + 1)-ols), may be deuterated. The exclusive product of the rearrangement reaction is the terminal acetylene, a versatile functional group which can be manipulated by standard techniques to give a variety of useful compounds.

Experimental Section

Gas chromatographic separations were carried out with a Varian 3700 instrument equipped with a SP 2100 capillary column (J and W Scientific, 30 m) and a flame ionization detector. Alcohols were converted to their trimethylsilyl ethers before analysis with *N,O*-bis(trimethylsilyl)acetamide. ^{1}H NMR analysis of 1,3-diaminopropane-*N,N,N′,N′*-d_4 was carried out in carbon tetrachloride with internal $(CH_3)_4Si$ as reference. Analysis of all other products were carried out in deuteriochloroform with either $CHCl_3$

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(10) Wotiz, J. H.; Kleopfer, R. D.; Barelski, P. M.; Hinckley, C. C.; Koster, D. F. *J. Org. Chem.* **1972**, *37*, 1758.

(11) Abrams, S. R.; Nucciarone, D. N.; Steck, W. F. *Can. J. Chem.* **1983**, *61*, 1073.

(12) Abrams, S. R. *Can. J. Chem.* **1984**, *62*, 1333.

or $(CH_3)_4Si$ as reference. Reported integrations are those obtained after exchange with D_2O.

GC/MS were obtained by using a DB-5 column (60 m) in a Finnigan 4000 E instrument in the electron impact mode with an Incos 2300 data system. Mass spectra are reported in mass to charge units (m/z) with the relative intensities as percentages of the base peak given in parentheses.

Isomerization reactions were carried out in glassware flame-dried under vacuum, under a slight positive pressure of dry nitrogen.

Preparation of 1,3-Diaminopropane-*N,N,N′,N′*-d_4. Under an atmosphere of nitrogen, to 1,3-diaminopropane (200 mL, 2.38 mol) cooled in an icebath was added D_2O (260 mL, 14.4 mol) and then benzene (dry, 550 mL). The mixture was heated to reflux and the water removed by means of a Dean-Stark trap. Most of the benzene was distilled, and then the solution was cooled in an ice bath and fresh additions of D_2O followed by benzene were introduced. After a total of three such exchanges, the 1,3-diaminopropane was distilled stored over activated 4-Å sieves, yielding approximately 130 mL of dry 1,3-diaminopropane-*N,N,N′,N′*-d_4 (bp 138-140 °C; density 0.85 g/mL); ^1H NMR δ 2.7 (t, $J = 6$ Hz, 4 H), 1.46 (q, $J = 6$ Hz, 2 H), and no NH absorption.

Isomerization of 2-Decyn-1-ol. To lithium wire (63 mg, 9.0 mmol) was added $D_2N(CH_2)_3ND_2$ (8.5 mL). The lithium partially dissolved to give a blue mixture which was heated in an oil bath at 70 °C for 1.5 h. To the resultant white suspension, cooled to 20 °C, was added potassium *tert*-butoxide (660 mg, 6.0 mmol). A pale lemon yellow solution was obtained in about 3 min. A solution of 2-decyn-1-ol (156 mg, 1.0 mmol) in $D_2N(CH_2)_3ND_2$ (2.0 mL) was added. The orange solution was stirred at 20 °C for 1.0 h and then cooled in an ice bath, and D_2O (20 mL) was added by syringe. The product was obtained by extraction of the reaction mixture with $CHCl_3$ 4 times. The combined organic phases were washed with water and saturated sodium chloride solution and then dried over sodium sulfate and filtered and the solvent was removed at reduced pressure. The crude product was purified by HPLC (Ultrasil-Si column, 10-μm silica, 10 × 25 cm, eluting with 2% isopropyl alcohol 98% hexane, at 5.0 mL/min, refractive index detector) affording-9-decyn-1-ol (80 mg, 48%): ^1H NMR δ 3.6 (s, 2.00 H), 2.2 (s, 0.67 H), 1.0 (s, 0.20 H), 1.2-1.6 (m, 0.87 H); mass spectrum of $(CH_3)_3Si$ ether, m/z (relative intensity) 226 (2.8), 225 (2.9), 224 (1.4), 223 (.5), 76 (100).

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Registry No. $HOCH_2C{\equiv}C(CH_2)_6CH_3$, 4117-14-0; $HO(CH_2)_4C{\equiv}C(CH_2)_3CH_3$, 68274-97-5; $HOCH_2C{\equiv}C(CH_2)_{14}CH_3$, 2833-97-8; $CH_3CH_2CH(OH)C{\equiv}C(CH_2)_5CH_3$, 91295-77-1; $CH_3(CH_2)_{12}CH(OH)C{\equiv}C(CH_2)_5CH_3$, 91295-78-2; $HOCH_2C{\equiv}C[C(H/D)_2]_{12}H$, 91311-04-5; $HOCH_2(CD_2)_7C{\equiv}CD$, 91295-79-3; $HOCH_2(CD_2)_7C{\equiv}CH$, 91295-80-6; $HOCH_2(CD_2)_{15}C{\equiv}CH$, 91295-81-7; $CH_3CH_2CH(OH)(CD_2)_6C{\equiv}CD$, 91295-82-8; $CH_3(CH_2)_{12}CH(OH)(CD_2)_6C{\equiv}CD$, 91295-83-9; $HOCH_2(CD_2)_{12}C{\equiv}CD$, 91295-84-0; $NaND(CH_2)_3ND_2$, 91295-85-1; $LiND(CH_2)_3ND_2$, 91295-86-2; $KND(CH_2)_3ND_2$, 91295-87-3; KO-*t*-Bu, 865-47-4; $NH_2(CH_2)_3NH_2$, 109-76-2; $D_2N(CH_2)_3ND_2$, 91295-88-4; $HO(CH_2)_8C{\equiv}CH$, 17643-36-6.

Supplementary Material Available: NMR and mass spectra of 9-decyn-1-ol, from isomerization of 2-decyn-1-ol with $NaHN(CH_2)_3NH_2$ and with $LiDN(CH_2)_3ND_3$, and full experimental details of reactions listed in Tables I and II (10 pages). Ordering information is given on any current masthead page.

Some Novel Reactions of *N*-Chlorodifluoromethanimine

Yuan Y. Zheng,[1] Charles W. Bauknight, Jr., and Darryl D. DesMarteau*

Department of Chemistry, Clemson University, Clemson, South Carolina 29631

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Some reactions of *N*-chlorodifluoromethanimine, $CF_2{=}NCl$, have been studied and are compared to related reactions of perfluoromethanimine, $CF_2{=}NF$. Fluoride promoted reactions of $CF_2{=}NCl$ result in evidence for the CF_3NCl^- anion, which is thermally less stable and less reactive than CF_3NF^-. Oxidation of CF_3NCl^-, formed in situ by reaction of $CF_2{=}NCl$ with KF or CsF, with Cl_2 forms CF_3NCl_2. With Br_2, CF_3NBrCl is formed along with CF_3NBr_2. The latter arises from a novel fluoride-catalyzed conversion of CF_3NBrCl to CF_3NBr_2 by Br_2, and the same products can be obtained starting with CF_3NCl_2, Br_2, and MF. Extension of this reaction to $C_2F_5NCl_2$ and $C_3F_7NCl_2$ is also discussed. Addition of $XOSO_2F$ (X = Cl, Br) to $CF_2{=}NCl$ forms the novel diazene $FSO_2OCF_2N{=}NCF_2OSO_2F$, presumably via the intermediate FSO_2OCF_2NClX addition products. Competitive reaction of $CF_2{=}NF$ and $CF_2{=}NCl$ with fluoride ion results in the preferential formation of CF_3NF^-. Nucleophilic attack of the latter on $CF_2{=}NCl$ forms the novel diaziridine $CF_3\overline{NCF_2N}Cl$, which can be reduced by Hg in trifluoroacetic acid to $CF_3\overline{NCF_2N}H$. The mechanism for the formation of the diaziridines is discussed.

Introduction

N-Chlorodifluoromethanimine, $CF_2{=}NCl$, was reported first in 1970.[2] However, there have been very few reports on the chemistry of this easily prepared imine.[3-5] Investigations of the chemistry of the related imine $CF_2{=}NF$[6,7] led us to undertake studies of the reaction chemistry of $CF_2{=}NCl$. As was found for $CF_2{=}NF$, $CF_2{=}NCl$ reacts readily with electrophilic halogen sources. Similarly, $CF_2{=}NCl$ reacts with fluoride ion from CsF and KF to form the anion CF_3NCl^-. However, the products of the reactions involving $CF_2{=}NCl$ are often different from those of $CF_2{=}NF$. These differences are easily explained by the photochemical and thermal instability of the

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[1] Visiting Scholar, Peoples Repulic of China.

[2] Young, D. E.; Anderson, L. R.; Fox, W. B. *J. Chem. Soc., Chem. Commun.* **1970**, 395.

[3] Young, D. E.; Anderson, L. R.; Fox, W. B. U.S. Patent 3689563; *Chem. Abstr.* **1972**, *78*, 29213.

[4] Swindell, R. F.; Zaborowski, L. M.; Shreeve, J. M. *Inorg. Chem.* **1971**, *10*, 1635.

[5] Zheng, Y. Y.; DesMarteau, D. D. *J. Org. Chem.* **1983**, *48*, 4844.

[6] Chang, S.-C.; DesMarteau, D. D. *J. Org. Chem.* **1983**, *48*, 771.

[7] Chang, S.-C.; DesMarteau, D. D. *Inorg. Chem.* **1983**, *22*, 805.

0022-3263/84/1949-3590$01.50/0