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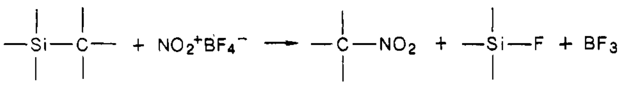
Desilylative Nitration of Alkyl- and Allylsilanes with Nitronium Salts[1]

Summary: Desilylative nitration of methyl- and ethylsilanes with nitronium tetrafluoroborate in sulfolane solution gives nitromethane and nitroethane, respectively. Higher alkylsilanes are also nitrated, but the reactions are followed by HNO_2 elimination. The method represents the first successful nitrodesilylations at saturated carbon. Allylsilanes react cleanly with NO_2BF_4 in methylene chloride solution to give nitropropenes in good to excellent yield. These reactions, however, involve initial attack by NO_2^+ on the allylic π-system followed by fluoride-induced trimethylsilyl elimination and not direct desilylative nitration at saturated carbon. 1-(Trimethylsilyl)but-2-ene gives exclusive secondary 3-nitrobut-1-ene and not the primary direct nitrodesilylation product 1-nitrobut-2-ene.

Sir: Nitration of hydrocarbons is one of the best studied and well-understood organic reaction.[2a] Generally, the nitration of aliphatic compounds takes place via a free radical mechanism,[2b] whereas aromatic compounds are preferentially nitrated by electrophilic reagents.

The isolation and characterization of stable nitronium salts has been an important development[3] in the study of nitration. Nitronium salts such as $NO_2^+BF_4^-$, PF_6^-, and SbF_6^- are extremely active for aromatic nitration and give high yields under mild conditions. Nitronium salts have also been found to nitrate aliphatic hydrocarbons. Olah and Lin[4] showed that even alkanes were nitrated by nitronium salts, but the reactions are generally complex and yields frequently low.

Due to the difference of electronegativity of carbon and silicon[5,6] and consequent higher nucleophilicity of Si–C bonds, we have considered the reaction of alkylsilanes with nitronium salts, as means of enhancing the reactivity of aliphatic compounds toward nitronium salts (eq 1). The reaction should also be favored due to the very high affinity of silicon for fluorine.



$$-\overset{|}{\underset{|}{Si}}-\overset{|}{\underset{|}{C}}- + NO_2^+BF_4^- \longrightarrow -\overset{|}{\underset{|}{C}}-NO_2 + -\overset{|}{\underset{|}{Si}}-F + BF_3 \quad (1)$$

Desilylative nitration of arylsilanes was observed by Benkeser, Speier, and Eaborn,[7-9] respectively, with intact ring nitration predominating and protodesilylation playing a significant role. Olah et al. reported[10] that nitronium salts in pyridine/$(HF)_x$ solution add to olefins, giving 1-fluoro-2-nitroalkanes, which then can be dehydrofluorinated to nitroolefins. Recently Schmitt and Bedford[11] reported that bis(trimethylsilyl)acetylene with NO_2BF_4 gives nitro(trimethylsilyl)acetylene. The reaction that is promoted by fluoride ion is in all probability proceeding through an addition–elimination path. To our knowledge no desilylative nitration at a saturated carbon was ever reported. We report now our initial findings of this reaction, which offers a new way to nitroalkanes and also ascertains for the first time true desilylative nitration at saturated carbon without the involvement of addition–elimination in desilylative nitration of π-systems.

The reaction of (trimethylsilyl)methane, i.e., tetramethylsilane with an equivalent of NO_2BF_4 was first studied. Due to its low boiling point (27 °C), the reaction was carried out in a pressure reactor. At temperatures between ambient and up to 80 °C, we observed that tetramethylsilane in sulfolane solutions is desilylatively nitrated by $NO_2^+BF_4^-$ to give nitromethane, trimethylfluorosilane, and boron trifluoride (eq 2).

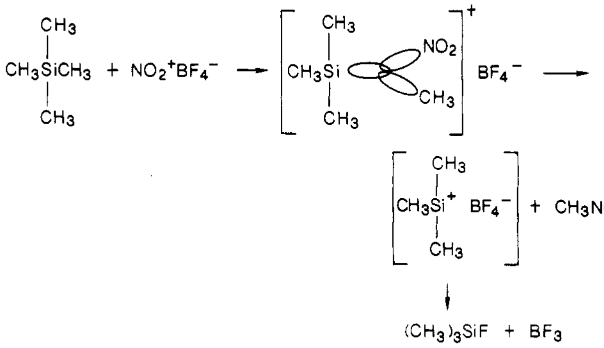
$$Me_4Si + NO_2^+BF_4^- \rightarrow MeNO_2 + Me_3SiF + BF_3 \quad (2)$$

The reaction is complete in 2 h to give ~80% (isolated, >90% GLC) yield of nitromethane (distilled isolated product) and the corresponding amount of trimethylfluorosilane and boron trifluoride (GC and MS analysis). If the reaction is continued for one more hour and the temperature is increased up to 140 °C, trimethylfluorosilane formed reacts further with $NO_2^+BF_4^-$ to give a second nitrolysis of a carbon/silicon bond (eq 3).

$$Me_3SiF + NO_2BF_4 \rightarrow MeNO_2 + Me_2SiF_2 + BF_3 \quad (3)$$

If the reaction of tetramethylsilane is carried out with 2 equiv of $NO_2^+BF_4^-$ for 3 h, 2 equiv of nitromethane are obtained. However, no further reaction is observed with excess of $NO_2^+BF_4^-$. Work with $NO_2^+BF_4^-$ is limited by its decomposition temperature of about 150 °C. More thermally stable salts, such as $NO_2^+SbF_6^-$ react similarly with tetramethylsilane, giving no further nitrolysis, in spite of applicable higher reaction temperatures up to 200 °C.

The desilylative nitration of tetramethylsilane is considered to involve typical σ-nitration of the C–Si bond via a five-coordinate two-electron three-center bonded siliconium–carbonium ion, which then cleaves giving nitromethane and fluorotrimethylsilane (eq 4). The reaction if greatly facilitated by the high affinity of fluoride for the developing trimethylsilyl cation.



(4)

We attempted to extend the desilylative nitration to homologous alkylsilanes to prepare higher nitroalkanes. The reaction of tetraethylsilane with NO_2BF_4 at 50 °C gives a 25% yield of nitroethane (as well as ethylene oligomers indicative of HNO_2 elimination from nitroethane, giving ethylene). No improved yield of nitroethane was observed if higher temperatures were used, only enhanced decomposition of the product. The reaction of tetra-

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(1) Considered: Synthetic Methods and Reactions. 129. For part 128, see: Hashimoto, T.; Prakash, G. R. S.; Shih, J. G.; Olah, G. A. *J. Org. Chem.*, in press.

(2) (a) Olah, G. A. Narang, S. C.; Olah, J. A.; Lammertsma, K. *Proc. Natl. Acad. Sci. U.S.A.* **1982**, *79*, 4487. (b) *Encyclopedia of Chemical Technology (Kirk-Othmer)*, 3rd ed.; Wiley-Interscience: New York, 1981; Vol. 15, pp 841, 969. "The Synthesis of Aliphatic and Alicyclic Nitro Compounds" *Organic Reactions*; Wiley-Interscience: New York, 1962; Vol. 12, p 101.

(3) Guk, Y. V.; Ilyushin, M. A.; Golod, E. L.; Gidaspov, B. V. *Russ. Chem. Rev. (Engl. Transl.)* **1983**, *52*, 285; Usp. Khim. **1983**, *52*, 499.

(4) Olah, G. A.; Lin, H. C. *J. Am. Chem. Soc.* **1971**, *93*, 1260.

(5) Colvin, E. *Silicon in Organic Synthesis*; Butterworths: London, 1980.

(6) Weber, W. P. *Silicon Reagents for Organic Synthesis*; Springer Verlag: New York, 1983.

(7) Benkeser, R. A.; Brumfield, P. E. *J. Am. Chem. Soc.* **1951**, *73*, 4770.

(8) Speier, J. L. *J. Am. Chem. Soc.* **1953**, *75*, 2930.

(9) Deans, F. B.; Eaborn, C. *J. Chem. Soc.* **1957**, 498.

(10) Olah, G. A.; Welch, J. T.; Vankar, Y. D.; Nojima, M.; Kerekes, I.; Olah, J. A. *J. Org. Chem.* **1979**, *44*, 3872.

(11) Schmitt, R. J.; Bedford, C. D. *Synthesis* **1986**, 132.

0022-3263/87/1952-0701$01.50/0

propylsilane did not give isolable nitropropane but only propene indicative of ready HNO_2 elimination. When trimethylpropylsilane was reacted similar results were obtained together with 10% of nitromethane, indicating competing nitrodesilylation at the methyl carbon.

Subsequently the desilylative nitration of expected more reactive allylsilanes was studied with NO_2BF_4. In fact, allylsilanes are known to be very reactive toward electrophiles but give the corresponding products of allylic rearrangements.[5,6,12]

The reaction of allylsilane with NO_2BF_4 in dichloromethane solution was found to give 80% yield of the corresponding 3-nitroprop-1-ene (eq 5).

$$CH_2{=}CHCH_2SiMe_3 + NO_2^+BF_4^- \xrightarrow{CH_2Cl_2} CH_2{=}CHCH_2NO_2 + Me_3SiF + BF_3 \quad (5)$$

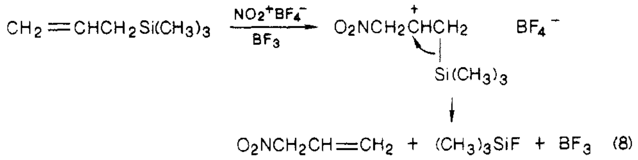
Representative is the reaction of allyltrimethylsilane with $NO_2^+BF_4^-$. In a 50-mL three-necked flask was added 0.001 mol of allyltrimethylsilane to 10 mL of dry dichloromethane. The system was cooled to −78 °C. $NO_2^+BF_4^-$ (0.001 mol, 1.33 g) was slowly added during a period of 20 min. A slow stream of dry nitrogen was passed through the system to purge trimethylfluorosilane and boron trifluoride formed in the reaction. After 30 min all the nitronium salt had disappeared. The mixture was then allowed to warm to room temperature, dichloromethane distilled off at atmospheric pressure, and the product distilled under vacuum: bp 62 °C/(25 mm); yield, 80%; ^{13}C NMR δ 77.75 (C_3), 123.86 (C_2), 126.62 (C_3); ^1H NMR δ 4.95 (CH_2NO_2, 2 H, d), 5.40 (CH, 1 H, m), 5.75–6.00 ($CH_2{=}$, 2 H, m).

Other allylsilanes such as 2-methyl-3-(trimethylsilyl)propene and 1-(trimethylsilyl)but-2-ene were also reacted under similar conditions and gave the corresponding 2-methyl-3-nitropropene and 3-nitro-but-1-ene in 65% and 75% yields, respectively (eq 6 and 7).

$$CH_2{=}C(CH_3)CH_2Si(CH_3)_3 + NO_2^+BF_4^- \rightarrow CH_2{=}C(CH_3)CH_2NO_2 + (CH_3)_3SiF + BF_3 \quad (6)$$

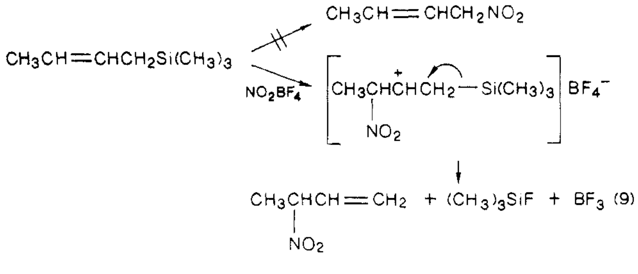
$$CH_3CH{=}CHCH_2Si(CH_3)_3 + NO_2^+BF_4^- \rightarrow CH_3CH(NO_2)CH{=}CH_2 + (CH_3)_3SiF + BF_3 \quad (7)$$

The desilylative nitration of allylsilanes is considered to proceed through initial electrophilic attack of NO_2^+ on the allyl system followed by desilylative elimination (eq 8).



(8)

This is clearly borne out in the reaction of 1-(trimethylsilyl)but-2-ene, where the product is not 1-nitrobut-2-ene (the direct desilylative nitration product) but only secondary 3-nitrobut-1-ene (eq 9).



(9)

The desilylative nitration of alkylsilanes such as tetramethylsilane with nitronium tetrafluoroborate proceeds readily. This is the first example of desilylative nitration at saturated carbon and extends the scope and knowledge of electrophilic reactions at saturated Si–C bonds. As boron trifluoride is also formed as byproduct in the reactions it can facilitate in case of secondary and tertiary systems HNO_2 elimination and formation of olefins. 2-Nitropropane and 2-methyl-2-nitropropane when treated with BF_3 indeed were found readily eliminate HNO_2 to the corresponding olefins with subsequent polymerization. Allylsilanes in contrast give generally high yields of nitroalkenes. Their reactions, however, proceed via initial NO_2^+ attack on the π-system followed by desilylative elimination. Our work is continuing to overcome limitations and to make the desilylative nitration of aliphatic silanes a general method for the preparation of nitroaliphatics.

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Asymmetric Reduction of Phosphinyl Imines with Hydride Reagents. Enantioselective Synthesis of Chiral Primary Amines

Summary: Prochiral diphenylphosphinyl imines are asymmetrically reduced by chiral hydride reagents to chiral diphenylphosphinylamines. For dialkyl examples, the enantioselectivities obtained are the highest thus far for hydride reductions of imine derivatives.

Sir: In contrast to the considerable successful attention devoted to the asymmetric reduction of prochiral ketones to chiral alcohols[1] with hydride reagents, corresponding studies and identification of useful enantioselective conversions of imine derivatives to amines have been sparse, and only very limited success has been obtained.[2]

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(12) Calas, R. *J. Organomet. Chem.* **1980**, *200*, 11.

(1) For reviews, see: (a) Midland, M. M. *Asymmetric Synthesis*; Morrison, J. D., Academic: New York, 1983; Vol. 2, Chapter 2. (b) Grandbois, E. R.; Howard, S. I.; Morrison, J. D. *Asymmetric Synthesis*; Morrison, J. D., Ed.; Academic: New York, 1983; Vol. 2, Chapter 3. (c) Haubenstock, H. *Top. Stereochem.* **1983**, *14*, 231. Recent additional studies include the following. (d) *B*-(3-pinanyl)-9-borabicyclo[3.3.1]nonane: Brown, H. C.; Pai, G. G. *J. Org. Chem.* **1985**, *50*, 1384 and cited references. (e) Diisopinocampheylchloroborane: Chandrasekharan, J.; Ramachandran, P. V.; Brown, H. C. *J. Org. Chem.* **1985**, *50*, 5446; Brown, H. C.; Chandrasekharan, J.; Ramachandran, P. V. *J. Org. Chem.* **1986**, *51*, 3394. (f) K 9-*O*-DIPGF-9-BBNH: Brown, H. C.; Park, W. S.; Cho, B. T. *J. Org. Chem.* **1986**, *51*, 1984; Brown, H. C.; Cho, B. T.; Park, W. S. *J. Org. Chem.* **1986**, *51*, 3396. Other dialkylmonoalkoxyborohydrides, Brown, H. C.; Park, W. S.; Cho, B. T. *J. Org. Chem.* **1986**, *51*, 3278. (g) Chiral sulfamides/$LiAlH_4$: Hawkins, J. M.; Sharpless, K. B. *J. Org. Chem.* **1984**, *49*, 3861. (h) β-Amino alcohols/BH_3: Itsumo, S.; Ito, K.; Hirao, A.; Nakahama, S. *J. Org. Chem.* **1984**, *49*, 1984 and cited references. (i) Polymeric (*S*)-prolinol/BH_3: Itsumo, S.; Ito, K.; Hirao, A.; Nakahama, S. *J. Chem. Soc., Perkin Trans. 1* **1984**, 2887.

0022-3263/87/1952-0702$01.50/0