temperature an additional 45 min and then allowed to warm slowly to ambient temperature. The reaction mixture was worked up as described above to furnish 1.5 g (8%) of **5**: bp 80–85 °C (10 mmHg); $^1$H NMR ($CDCl_3$) $\delta$ 5.9 (t, $J$ = 2.4 Hz, 1 H); 4.1 (q, $J$ = 2.8 Hz, 2 H); 2.6 (d, $J$ = 2.4 Hz, 1 H); 1.3–1.1 (M, 9 H).

**Reaction of Trifluoroethylene (6) with Ethyl Lithioisobutyrate: (*E* and *Z*)-Ethyl 3,4-Difluoro-2,2-dimethyl-3-butenoate (7 and 8) and Ethyl 2,2-Dimethyl-3,3,4-trifluorobutanoate (9).** A solution of 1 (129 mmol) was prepared in THF/HMPA as described above and kept at −60 °C. In a separate flask, 1,2-dibromo-1,1,2-trifluoroethane (34.4 g, 142 mmol) was added dropwise to a stirred slurry of powdered zinc (16.9 g, 258 mmol) in 75 mL of absolute ethanol. The resulting gaseous 1,1,2-trifluoroethylene was bubbled through the anionic solution at −60 °C. Upon completion of the addition, the mixture was allowed to warm slowly to −15 °C and was then worked up as described above to afford 18.7 g of an oil. Fractional distillation at 10 mmHg gave two fractions. The first (3 g, bp < 30 °C) consisted of THF, unreacted starting material, and a small amount of **7**. The second cut (10.8 g, bp 44–46 °C), consisted of **7**, **8**, and **9** in approximately a 76:16:8 ratio. The $^1$H NMR of **7** was identical to that reported previously.[10] The *Z* isomer **8** was identified by the vinylic $^1$H doublet of doublets centered at $\delta$ 6.4 ($J_{HF}$ = 17 and 76 Hz) vs $\delta$ 7.0 ($J_{HF}$ = 6 and 74 Hz) for the *E* isomer. The saturated ester **9** was identified by a doublet of triplets centered at $\delta$ 4.8 ($J$ = 13.5, 43 Hz). The ester mixture was further characterized by hydrolysis to the acids and subsequent formation and chromatographic separation of the corresponding *p*-chloroanilides. Additional spectroscopic data are included in the supplementary material.

**Reaction of TFE (10) with Ethyl α-Lithioisobutyrate. Ethyl 2,2-Dimethyl-3,4,4-trifluoro-3-propenoate (11) and 2,2-Dimethyl-3,3,4,4-tetrafluorocyclobutanone, Ethyl Hemiketal (12).** A solution of 1 (86 mmol) was prepared as described above and was stirred at −60 °C. In a separate flask, 1,2-dibromo-1,1,2,2-tetrafluoroethane (44.7 g, 172 mmol) was added dropwise to a stirred slurry of powdered zinc (16.9 g, 258 mmol) in 75 mL of absolute ethanol. The resulting gaseous TFE was bubbled through the cold, vigorously stirred anionic solution. Dry ice was added to the cooling bath as needed to maintain the reaction temperature at −60 °C. Upon completion of the addition, the solution was stirred at −60 °C for an additional 2 h and then was worked up as described above, and the solvents were removed at 0 °C. The residual oil was fractionally distilled to furnish 4.4 g of **11**, bp 30–32 °C (100 mmHg), and 3.0 g of **12**, bp 30–37 °C (10 mmHg). The remainder of the crude product was resinous pot residue. Compounds **11** and **12** were each further characterized as the derived acids (**13** and **14**) following hydrolysis with NaOH in EtOH.

For **11**: $^1$H NMR ($CDCl_3$) $\delta$ 4.2 (q, $J$ = 7 Hz, 2 H), 1.45 (br s, 6 H), 1.3 (t, $J$ = 7 Hz, 3 H); $^{19}$F NMR ($CDCl_3$) $\delta$ −102 (dd, $J$ = 36, 85 Hz, 1 F), −117 (dd, $J$ = 85, 110 Hz, 1 F), −175 (dd, $J$ = 36, 110 Hz, 1 F).

For **12**: $^1$H NMR ($CDCl_3$) $\delta$ 3.6–3.8 (m, 2 H), 3.1 (br s, −OH), 1.3 (t, $J$ = 7 Hz, 3 H), 1.2 (s, 6 H).

**3,4,4-Trifluoro-2,2-dimethyl-3-butenoic acid (13):** $^1$H NMR ($CDCl_3$) $\delta$ 8.5 (br s, 1 H), 1.5 (m, 6 H); $^{19}$F NMR ($CDCl_3$) $\delta$ −101 (dd, $J$ = 85, 35 Hz, 1 F), −117 (dd, $J$ = 85, 112 Hz, 1 F), −175 (dd, $J$ = 35, 112 Hz, 1 F).

**3,3,4,4-Tetrafluoro-2,2-dimethylbutanoic acid (14):** $^1$H NMR ($CDCl_3$) $\delta$ 9.4 (br s, 1 H), 6.2 (tt, $J$ = 5.0, 53 Hz, 1 H), 1.5 (m, 6 H); $^{19}$F NMR ($CDCl_3$) $\delta$ −123 (br s, 2 F), −134 (br d, $J$ = 53 Hz, 2 F).

**Reaction of TFE (10) with Ethyl α-Lithiocyclohexanecarboxylate. 2,2,3,3-Tetrafluorospiro[5.3]nonan-1-one (16).** Reaction of 165 mmol of LDA, 150 mmol of ethyl cyclohexanecarboxylate, and 25 g (250 mmol) of TFE following conditions described above yielded 19.6 g (60%) of a colorless oil, bp 29–39 °C (8 mmHg). VPC analysis indicated **15** and **16** were present in a ratio of 5:95.

For **16**: mp 35 °C; bp 35–38 °C (8 mmHg); $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 1.75 (m, 4 H), 1.7–1.4 (m, 6 H); $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 199.9 (m), 119.39 (tt, $J$ = 309, 27 Hz), 117.62 (tt, $J$ = 22, 284 Hz), 26.3, 25.5, 23.3; $^{19}$F NMR ($CDCl_3$) $\delta$ −118 (br s, 2 F), −112.6 (br s, 2 F).

Dissolving **16** in ethanol at ambient temperature followed by low temperature (0 °C) evaporation of solvent regenerated the hemiketal **15**, which on attempted distillation was reconverted to the ketone **16**.

For **15**: $^1$H NMR $\delta$ 3.55–3.80 (m, 2 H), 3.2 (br s, 1 H), 1.4–1.85 (m, 10 H), 1.2 (t, $J$ = 8 Hz, 3 H).

Hydrolysis of **16** (or **15**) with 1 equiv of NaOH in ethanol generated the tetrafluoro acid **17**, mp 52 °C; $^1$H NMR $\delta$ 9.2 (br s, 1 H); 6.0 (tt, $J$ = 7, 52 Hz, 1 H); 2.3 (br d, $J$ = 12 Hz, 2 H); 1.2–1.8 (m, 8 H).

**Ethyl 2,2-Dimethyl-3,4,5,5,5-pentafluoro-3-pentenoate (19).** A solution of 1 (129 mmol) was prepared in THF/HMPA as described above. The anionic solution was stirred at −60 °C, and HFP (18; 58 g, 387 mmol) was bubbled through the cold solution, the temperature rising to −35 °C. The mixture was stirred at −60 °C for an additional 0.5 h and was then worked up under standard conditions. Solvent was removed at ambient pressure. Vacuum distillation of the crude oil yielded 16.5 g of **19** as a colorless oil: bp 38–41 °C (10 mmHg); $^1$H NMR ($CDCl_3$) $\delta$ 4.22 (q, $J$ = 7.1 Hz, 2 H), 1.50 (m, 6 H), 1.27 (t, $J$ = 7.1 Hz, 3 H); $^{19}$F NMR ($CDCl_3$) $\delta$ −68 (m, 3 F), −144 (dq, $J$ = 23, 134 Hz, 1 F), −171 (dd, $J$ = 12, 134 Hz, 1 F).

**(*Z* and *E*)-Ethyl 4-Chloro-3,4-difluoro-2,2-dimethyl-3-butenoate (21 and 22).** A solution of 1 (129 mmol) was prepared in THF/HMPA as described above. The anionic solution was stirred at −60 °C, and chlorotrifluoroethylene (26.1 g, 224 mmol) was bubbled through the cold solution, the temperature rising quickly to −20 °C. Addition of the gas was discontinued until the temperature again fell to −60 °C, and then the remainder of the gas was bubbled through without significant rise in temperature. Upon completion of the addition, the mixture was worked up as described above. Solvent was removed at ambient temperature. The crude product was distilled under vacuum to afford 12.7 g of *E*/*Z* isomers **21** and **22**, bp 42–55 °C (10 mmHg). An analytically pure sample was obtained by redistillation, bp 44–49 °C (10.5 g). By $^{19}$F NMR analysis the *Z*/*E* ratio is approximately 9:1: $^1$H NMR ($CDCl_3$) $\delta$ 4.17 (q, $J$ = 7.1 Hz, 2 H), 1.50 (m, 6 H), 1.28 (t, $J$ = 7.1 Hz, 3 H); $^{19}$F NMR ($CDCl_3$) *Z* isomer $\delta$ −121 (d, $J$ = 129 Hz, 1 F), −145 (d, $J$ = 129 Hz, 1 F); *E* isomer $\delta$ −105 (d, $J$ = 17 Hz, 1 F), −134 (d, $J$ = 17 Hz, 1 F).

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**Registry No.** **2**, 75-38-7; **3**, 131399-85-4; **4**, 75-35-4; **5**, 144193-96-4; **6**, 359-11-5; **7**, 85066-79-1; **8**, 131399-90-1; **9**, 144193-97-5; **10**, 116-14-3; **11**, 144193-98-6; **12**, 144193-99-7; **13**, 144194-00-3; **14**, 144194-01-4; **15**, 144194-02-5; **16**, 144194-03-6; **17**, 144194-04-7; **18**, 116-15-4; **19**, 144194-05-8; **20**, 79-38-9; **21**, 144194-06-9; **22**, 144194-07-0; ethyl isobutyrate, 97-62-1; ethyl cyclohexanecarboxylate, 3289-28-9; 1,2-dibromo-1,1-difluoroethane, 75-82-1; 1,2-dibromo-1,1,2-trifluoroethane, 354-04-1; 1,2-dibromo-1,1,2,2-tetrafluoroethane, 124-73-2.

**Supplementary Material Available:** Elemental analyses of all new compounds and preparation and characterization data of **7**, **8**, and **9** (2 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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## Surface-Mediated Reactions. 2. Addition of Hydrazoic Acid to Alkenes[1]

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Organic azides are versatile intermediates for organic synthesis.[2] Whereas aromatic azides can be readily ob-

(1) Part 1: Kropp, P. J.; Daus, K. A.; Crawford, S. D.; Tubergen, M. W.; Kepler, K. D.; Craig, S. L.; Wilson, V. P. *J. Am. Chem. Soc.* **1990**, *112*, 7433–7434.

0022-3263/92/1957-6646$03.00/0 

Table I. Addition of $HN_3$ to 2-Norbornene (1)[a]

| acid | equiv[c] | adsorbent | time, h | yield,[b] % 1[d] | 2 |
|---|---|---|---|---|---|
| $CF_3SO_3H$ | 0.25 | | 24 | 62 | 17 |
| $CF_3SO_3H$ | 0.25 | e | 0.5 | 79 | 7 |
| | | $SiO_2$[f] | 24 | 90 | 10 |
| $CF_3SO_3H$ | 0.25 | $SiO_2$ | 0.2 | 0 | 98 |
| | | | 0.5 | 0 | 68 |
| $CF_3SO_3H$ | 1.5 | $Al_2O_3$ | 0.2 | 15 | 85 |
| | | | 0.5 | 0 | 68 |
| 4-$CH_3C_6H_4SO_3H$[g] | 0.25 | $SiO_2$ | 4 | 81 | 7 |
| $H_2SO_4$ | 0.25 | $SiO_2$ | 1 | 58 | 14 |
| $CH_3SO_3H$ | 0.25 | $SiO_2$ | 24 | 27 | 42 |

[a] Conducted according to the standard procedure described in the Experimental Section, unless otherwise indicated. [b] Determined by gas chromatographic analysis relative to an internal hydrocarbon standard on aliquots removed from the reaction mixture. [c] [Acid]/[1]. [d] Contained small amounts of nortricyclene. [e] A solution containing 3 mmol of $(CH_3)_3SiN_3$ in 5 mL of $CH_2Cl_2$ was stirred with 2.5 g of silica gel for 20 min and filtered. To the filtrate was then added 1.0 mmol of 2-norbornene (1) followed by the acid catalyst. [f] The preceding experiment was repeated except that a new batch of $SiO_2$ was added to the filtrate instead of the acid catalyst. [g] Monohydrate.

tained by a variety of methods, aliphatic azides are more difficult to prepare.[3] Owing to its weak acidity, $HN_3$ does not undergo electrophilic addition to alkenes except for phenyl-substituted cyclopropenes[4] and electron-rich alkenes, such as vinyl ethers.[5,6] It has been found to undergo Lewis acid catalyzed addition to styrenes and to 1,1-dialkyl and trialkyl olefins.[5,7] Protic acid catalyzed additions of $HN_3$ to alkenes have also been reported,[8] but competing reaction of the newly formed azide with the acid catalyst frequently makes these low-yield processes.[9] Moreover, the necessity for generating and handling the highly toxic, and explosive, $HN_3$ limits the convenience of both of these methods. Azide ion has been employed in conjunction with mercury(II) salts for the synthesis of secondary and tertiary azides from terminal or strained alkenes.[4,10] However, the method fails for simple internal alkenes such as 1-methylcyclohexene (3), and the disposal of mercury(II) salts is required.

Previous studies in these laboratories have shown that silica gel and alumina greatly facilitate the addition of hydrogen halides to alkenes.[1] Moreover, the use of appropriate precursors that generate hydrogen halides in situ on hydrolysis over silica gel or alumina makes this a particularly convenient procedure for the preparation of alkyl halides.[1] More recent studies have shown that the effective acidities of a number of acids are substantially enhanced on adsorption to silica gel or alumina.[11] We wish now to report that silica gel and alumina mediate the addition of $HN_3$ to alkenes in the presence of an acid catalyst to give good-to-excellent yields of alkyl azides. Moreover, $HN_3$ can be conveniently prepared in situ by hydrolysis of $(CH_3)_3SiN_3$ over silica gel or alumina.

Table II. Addition of $HN_3$ to Other Alkenes[a]

| alkene | acid | equiv[c] | adsorbent | time, h | yield,[b] % alkene | azide |
|---|---|---|---|---|---|---|
| 3[d] | $CF_3SO_3H$ | 0.25 | $SiO_2$ | 0.5 | 1 | 88 |
| 5 | $CF_3SO_3H$ | 0.25 | e | 0.2 | 92 | 8 |
| 5 | $CF_3SO_3H$ | 0.25 | $SiO_2$ | 0.2 | 0 | 100[f] |
| 5 | $CF_3SO_3H$ | 1.5 | $Al_2O_3$ | 0.2 | 43 | 49[f] |
| | | | | 3 | 28 | 59[f] |
| 7[g] | $CF_3SO_3H$ | 0.25 | $SiO_2$ | 0.5 | 48 | 21 |
| | | | | 4 | 40 | 22 |
| 7[g] | $CH_3SO_3H$ | 1 | e | 8 | 100 | 0 |
| 7[g] | $CH_3SO_3H$ | 1 | $SiO_2$ | 5 | 25 | 45 |
| | | | | 8 | 14 | 40 |
| 7[g] | $CH_3SO_3H$ | 2 | $Al_2O_3$ | 24 | 97 | 0 |
| 9[g] | $CH_3SO_3H$ | 1.0 | e | 24 | 74 | 18 |
| 9[g] | $CH_3SO_3H$ | 1.0 | $SiO_2$ | 1 | 9 | 76 |
| 11 | $CF_3SO_3H$ | 0.25 | $SiO_2$ | 4 | 83 | 0 |
| 12 | $CF_3SO_3H$ | 0.25 | $SiO_2$ | 1 | 87[h] | 0 |
| | | | | 24 | 65[h] | 0 |

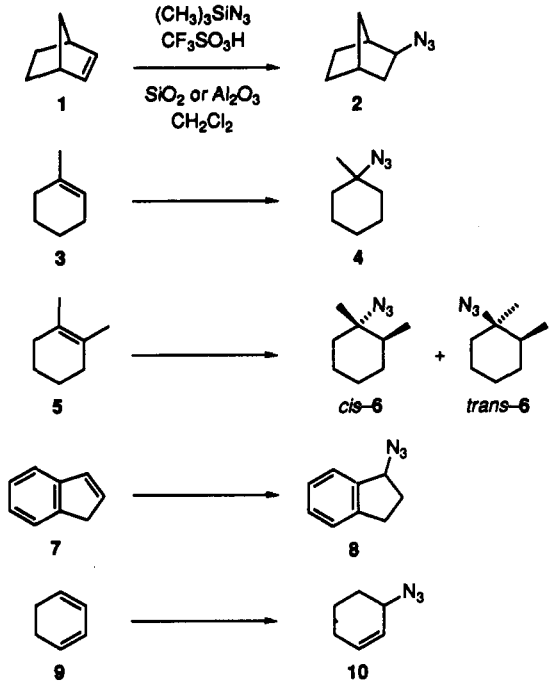
[a] Conducted according to the standard procedure described in the Experimental Section, unless otherwise indicated. [b] Determined by gas chromatographic analysis relative to an internal hydrocarbon standard on aliquots removed from the reaction mixture, unless otherwise indicated. [c] [Acid]/[alkene]. [d] Two mmol of $(CH_3)_3SiN_3$ used. [e] A solution containing 3 mmol of $(CH_3)_3SiN_3$ in 5 mL of $CH_2Cl_2$ was stirred with 2.5 g of silica gel for 20 min and filtered. To the filtrate was then added 1.0 mmol of alkene 5, 7, or 9 followed by the acid catalyst. [f] A 1:1 mixture of azides 6. [g] Solvent was $CDCl_3$. Yields determined by $^1H$ NMR analysis relative to an internal standard. [h] Mixture of 1-, 2-, 3-, and 4-octenes.

## Results

As shown in Table I, addition of a catalytic amount of $CF_3SO_3H$ to a stirred slurry of 2-norbornene (1), $(CH_3)_3SiN_3$, and silica gel in $CH_2Cl_2$ resulted in rapid addition of $HN_3$ to give the exo azide 2 in good yield. Under similar conditions except for the absence of silica gel, only a small amount of azide 2 was formed.[12] When $CF_3SO_3H$ and 2-norbornene (1) were added to a solution of $(CH_3)_3SiN_3$ that had been stirred with silica gel to effect hydrolysis to $HN_3$ and then filtered to remove the silica gel, much slower addition was observed than in the presence of silica gel.[13] Alumina was almost equally effective in mediating the addition of $HN_3$ provided that an additional amount of acid catalyst was employed to neutralize the adsorbent.[14] Longer reaction times over either silica gel or alumina resulted in lower yields of azide 2, apparently due to secondary decomposition of the azide by the acid catalyst. The sulfonic acids 4-$CH_3C_6H_4SO_3H$ and $CH_3SO_3H$, as well as $H_2SO_4$, were much less effective in catalyzing the addition.

More highly substituted alkenes were rapidly converted to tertiary azides through reaction with $(CH_3)_3SiN_3$ and a catalytic amount of $CF_3SO_3H$ over silica gel. Thus, 1-methylcyclohexene (3) afforded azide 4, and 1,2-dimethylcyclohexene (5) afforded the cis and trans isomers of azide 6 in a 1:1 ratio, which did not change with time

(2) See: Sheradsky, T. In *The Chemistry of the Azido Group*; Patai, S., Ed.; Wiley: London, 1971; Chapter 6.
(3) See: Biffin, M. E. C.; Miller, J.; Paul, D. B. In *The Chemistry of the Azido Group*; Patai, S., Ed.; Wiley: London, 1971; Chapter 2.
(4) Galle, J. E.; Hassner, A. *J. Am. Chem. Soc.* **1972**, *94*, 3930–3933.
(5) Hassner, A.; Fibiger, R.; Andisik, D. *J. Org. Chem.* **1984**, *49*, 4237–4244.
(6) $HN_3$ does undergo nucleophilic addition to unsaturated systems substituted with strongly electron-withdrawing substituents. See: Boyer, J. H. *J. Am. Chem. Soc.* **1951**, *73*, 5248–5252.
(7) Pancrazi, A.; Khuong-Huu, Q. *Tetrahedron* **1974**, *30*, 2337–2343.
(8) (a) Balderman, D.; Kalir, A. *Synthesis* **1978**, 24–26. (b) Ege, S. N.; Sherk, K. W. *J. Am. Chem. Soc.* **1953**, *75*, 354–357. (c) Schaad, R., E., U.S. Patent 2,557,924, 1951; *Chem. Abstr.* **1952**, *46*, 1028i.
(9) Arcus, C. L.; Marks, R. E.; Vetterlein, R. *Chem. Ind. (London)* **1960**, 1193. See also ref 8b.
(10) Heathcock, C. H. *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 134–135.
(11) Kropp, P. J.; Breton, G. W.; Craig, S. L.; Raleigh, J. S.; Crawford, S. D.; Jones, J. E., III. Manuscript in preparation.
(12) Apparently some hydrolysis of $(CH_3)_3SiN_3$ by adventitious water occurred to generate a small amount of $HN_3$ under these conditions.
(13) Similarly, only slow addition occurred when 2-norbornene (1) and a fresh batch of silica gel, but no acid catalyst, were added to a solution of $HN_3$ prepared by treating $(CH_3)SiN_3$ over silica gel and then filtering (Table I). Thus, both the adsorbent and the acid catalyst are required.
(14) The Fisher A540 alumina used in these studies neutralizes 0.4 mequiv of acid per gram: Kropp, P. J.; Daus, K. A.; Tubergen, M. W.; Kepler, K. D.; Craig, S. L.; Wilson, V. P.; Baillageron, M. M.; Breton, G. W. Manuscript in preparation.

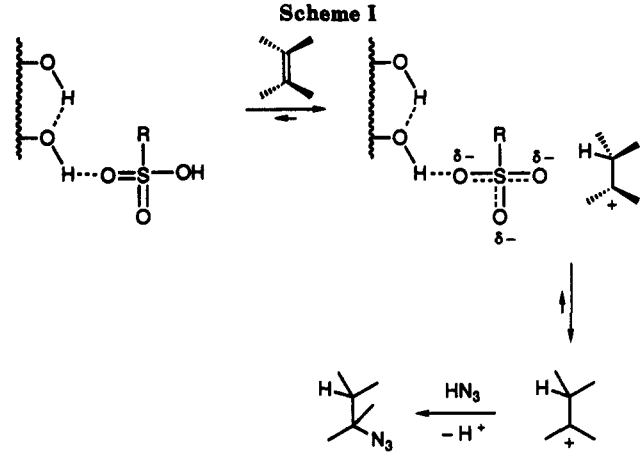



(Table II). Slower addition occurred over alumina. Once again, in a control run only a small amount of addition occurred when silica gel was used to hydrolyze the $(CH_3)_3SiN_3$ but was removed before alkene 5 and the acid catalyst were added to the reaction mixture. Treatment of indene (7) with $CF_3SO_3H$ and $(CH_3)_3SiN_3$ over silica gel resulted in an initial rapid addition that slowed down considerably after about half reaction, presumably because the catalyst had been consumed by secondary reaction with azide 8. Use of the weaker $CH_3SO_3H$ as catalyst resulted in slower, but more complete addition. No addition was observed over alumina in this case.[15] 1,3-Cyclohexadiene (9) underwent somewhat faster addition in the presence of $CH_3SO_3H$ over silica gel. Only very slow addition occurred in the absence of silica gel. The unstrained and less highly substituted cyclohexene (11) and 1-octene (12) afforded no detectable addition on treatment with $CF_3SO_3H$ and $(CH_3)SiN_3$ over silica gel. However, 1-octene (12) underwent isomerization to 2-, 3-, and 4-octene.

## Discussion

The preceding results show that silica gel and alumina facilitate the protonation of alkenes and that use can be made of this for the synthesis of tertiary, benzylic, and allylic azides. The procedure is made even more convenient by the use of $(CH_3)_3SiN_3$ with silica gel or alumina for the in situ generation of $HN_3$. A control study showed that $CH_3SO_3H$ is rapidly adsorbed from solution by silica gel and alumina, and similar behavior can be assumed for $CF_3SO_3H$. Since surface OH groups on silica gel and alumina normally serve as hydrogen bond donors,[16] the resulting interaction with the acid would be as shown in Scheme I, greatly enhancing the acidity of the acid and leading to protonation of the alkene from the surface. Unlike the surface-mediated addition of hydrogen halides, however, in which the resulting alkyl cation is rapidly

Scheme I




trapped by halide ion from the surface to give a syn addition product,[1] the cation in this case apparently diffuses from the surface and is trapped in solution by $HN_3$.[17] Since trapping in solution can occur with equal facility from either side, 1,2-dimethylcyclohexene (5) affords a 1:1 mixture of the syn and anti addition products *cis*- and *trans*-6, respectively. Although alkyl azides undergo competing acid-catalyzed decomposition,[9] the enhanced rate of addition under surface-mediated conditions permits their formation in high yield before secondary decay becomes extensive. The failure of cyclohexene (11) and 1-octene (12) to undergo addition is not due to lack of protonation since 1-octene (12) underwent extensive double bond isomerization. Apparently, the corresponding secondary cations have insufficient lifetimes to permit trapping by azide ion in competition with deprotonation. The slower rates of addition over alumina with $CF_3SO_3H$ and the lack of addition with $CH_3SO_3H$ are not due to lack of adsorption of the acids to the alumina surface since the control study showed that $CH_3SO_3H$ is rapidly adsorbed from solution by alumina. Apparently, acidities are more greatly enhanced on adsorption to silica gel than alumina. We continue to explore the rich potential of surface-mediated chemical reactivity.

## Experimental Section

All reagents were used as received except for indene (7), which was distilled prior to use. Column chromatography was carried out on Merck grade 60 (230–400 mesh) silica gel. Gas chromatographic analyses were performed with a 3-m × 3-mm stainless steel column packed with 20% SF-96 on 60-80 mesh Chromosorb P. Infrared spectra were obtained on neat samples. Nuclear magnetic resonance spectra were obtained at 250 MHz ($^1H$) or 63 MHz ($^{13}C$) in $CDCl_3$ solution.

**Standard Procedure.** A solution of 1.0 mmol of alkene and 0.1 mL of tetradecane as an internal standard in 5 mL of $CH_2Cl_2$ was added to 2.5 g of either Merck grade 40 chromatographic silica gel (35–70 mesh, 675 $m^2/g$) or Fisher A540 chromatographic alumina (pH 9, 210 $m^2/g$), which had been equilibrated with the atmosphere at 120 °C for at least 48 h and cooled to 25 °C in a dry, sealed flask. To this slurry was added 0.4 mL (3 mmol) of $(CH_3)_3SiN_3$ in one portion with stirring. After an additional 5 min, the acid catalyst was added (CAUTION: exothermic reaction). Periodically, 0.2-mL aliquots of the supernatant liquid were removed, diluted with 1 mL of $CH_2Cl_2$, neutralized by shaking with 1 mL of 5% $Na_2CO_3$ solution, dried over anhydrous $Na_2SO_4$, and analyzed by gas chromatography. For isolation of the azides, the reaction mixture was filtered under vacuum and the adsorbent rinsed well with $CH_2Cl_2$. The combined organic

(15) This is not due to lack of adsorption of the acid by alumina, since a control study showed that $CH_3SO_3H$ is rapidly adsorbed from $CH_2Cl_2$ solution by both silica gel and alumina.

(16) (a) Knözinger, H. In *The Hydrogen Bond. III. Dynamics, Thermodynamics and Special Systems*; Schuster, P., Zundel, G., Sandorfy, C., Eds.; North-Holland: Amsterdam, 1976; Chapter 27. (b) See also: Arnett, E. M.; Ahsan, T. *J. Am. Chem. Soc.* **1991**, *113*, 6861–6864.

(17) Consistent with this is the observation that $^1H$ NMR analysis of aliquots of the supernatant liquid from reaction mixtures showed a broad signal at δ 4.5 attributable to $HN_3$. Thus, in contrast with $CH_3SO_3H$ and $CF_3SO_3H$, most, if not all, of the weaker $HN_3$ remains in solution.

fractions (~60 mL) were washed with 2 × 30 mL of 5% $Na_2CO_3$ solution, dried over $MgSO_4$, filtered, and concentrated by rotary evaporation. Purification by column chromatography afforded the azides on elution with hexanes.

***exo*-2-Azidobicyclo[2.2.1]heptane (2).** Treatment of 2-bicyclo[2.2.1]heptene (1) as outlined in Table I afforded azide 2 as a colorless liquid: IR 2960, 2090 ($-N_3$), 1450, 1245 $cm^{-1}$; $^1H$ NMR $\delta$ 3.45 (ddd, $J$ = 7.6, 2.6, and 1.3 Hz, 1 H, CH-2n), 2.28 (m, 2 H, CH-1 and -4), 1.5 (m, 5 H), 1.1 (m, 3 H); $^{13}C$ NMR $\delta$ 64.0, 41.6, 37.8, 35.5, 34.9, 28.1, 25.5 (lit.[18] IR 2100 $cm^{-1}$; $^1H$ NMR ($CCl_4$) $\delta$ 3.55–3.25 (m, 1 H), 2.4–2.2 (m, 2 H), 1.7–0.95 (m, 8 H)).

**1-Azido-1-methylcyclohexane (4).** Treatment of 1-methylcyclohexene (3) as outlined in Table II afforded azide 4 as a colorless liquid: IR 2935, 2090 ($-N_3$), 1445, 1253, 1155 $cm^{-1}$; $^1H$ NMR (400 MHz) $\delta$ 1.68 (m, 2 H), 1.5 (m, 5 H), 1.40 (m, 2 H), 1.29 (s, 3 H), 1.25 (m, 1 H) (lit.[4] IR 2980, 2100, 1455, 1172 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 1.5 (br s, 10 H), 1.3 (s, 3 H)).

***cis*- and *trans*-1-Azido-1,2-dimethylcyclohexane (*cis*- and *trans*-6).** Treatment of 1,2-dimethylcyclohexene (5) as outlined in Table II afforded a 1:1 mixture of azides *cis*- and *trans*-6. Anal. Calcd for $C_8H_{15}N_3$: C, 62.71; H, 9.87; N, 27.42. Found: C, 62.90; H, 9.80; N, 27.30.

Further purification by preparative HPLC on a silica column afforded, on elution with hexane, azide *cis*-6 as a colorless oil: IR 2920, 2085 ($-N_3$), 1465, 1255 $cm^{-1}$; $^1H$ NMR $\delta$ 1.60 (m, 9 H), 1.14 (s, 3 H, $CH_3$-1), 0.90 (d, $J$ = 6.7 Hz, 3 H, $CH_3$-2); $^{13}C$ NMR $\delta$ 64.8, 39.2, 37.0, 31.0, 24.6, 22.9, 17.7, 15.9.[19]

Azide *trans*-6 was obtained as a colorless oil: IR 2940, 2090 ($-N_3$), 1455, 1255 $cm^{-1}$; $^1H$ NMR $\delta$ 1.87 (m, 1 H), 1.68 (m, 1 H), 1.53 (m, 2 H), 1.32 (m, 5 H), 1.31 (s, 3 H, $CH_3$-1), 0.89 (m, 3 H, $CH_3$-2); $^{13}C$ NMR $\delta$ 64.2, 40.9, 37.4, 30.7, 25.8, 24.7, 22.2, 15.8.[19]

**1-Azido-2,3-dihydro-1*H*-indene (8).** Treatment of indene (7) as outlined in Table II afforded azide 8 as a colorless liquid, which slowly decomposed at room temperature: IR 3070, 3020, 2940, 2090 ($-N_3$), 1475, 1455, 1230 $cm^{-1}$; $^1H$ NMR $\delta$ 7.4 (m, 1 H), 7.25 (m, 3 H), 4.85 (dd, $J$ = 7.2 and 4.8 Hz, 1 H, CH-1$\alpha$), 3.06 (ddd, $J$ = 16.0, 8.2, and 6.6 Hz, 1 H, CH-3$\beta$), 2.85 (ddd, $J$ = 16.0, 8.1, and 5.4 Hz, 1 H, CH-3$\alpha$), 2.43 (dddd, $J$ = 14.0, 8.1, 7.2, and 6.6 Hz, 1 H, CH-2$\alpha$), 2.10 (dddd, $J$ = 14.0, 8.2, 5.4, and 4.8 Hz, 1 H, CH-2$\beta$); $^{13}C$ NMR $\delta$ 143.3, 140.4, 128.5, 126.5, 124.7, 124.2, 65.6, 32.2, 30.1.

**3-Azidocyclohexene (10).** Treatment of 1,3-cyclohexadiene (9) as outlined in Table II afforded azide 10 as a colorless liquid, which slowly decomposed at room temperature: IR 3030, 2942, 2095 ($N_3$), 1651, 1451, 1256, 910, 735 $cm^{-1}$; $^1H$ NMR $\delta$ 5.97 (ddt, $J$ = 1.5, 3.7, and 10.0 Hz, 1 H, CH-1), 5.67 (ddt, $J$ = 2.2, 3.9, and 10.0 Hz, 1 H, CH-2), 3.82 (br m, 1 H, CH-3), 2.1 (m, 2 H), 1.72 (m, 4 H); $^{13}C$ NMR $\delta$ 132.7, 124.8, 55.9, 28.6, 24.7, 19.1 (lit.[20] $^1H$ NMR ($CCl_4$) $\delta$ 5.83 (m, 4 H), 4.0–3.6 (m, 1 H), 2.2–1.4 (m, 6 H)).

**Studies on the Adsorption of $CH_3SO_3H$ to Silica Gel and Alumina.** To a solution of 65 $\mu$L (1.0 mmol) of $CH_3SO_3H$ in 5 mL of $CDCl_3$ was added 2.5 g of $SiO_2$ that had been prepared as described above. Analysis by $^1H$ NMR of an aliquot removed after 5 min of stirring showed no detectable signal at $\delta$ 3.16 attributable to $CH_3SO_3H$. A similar experiment with $Al_2O_3$ using 2.0 mmol of $CH_3SO_3H$ gave the same result.

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**Registry No.** 1, 498-66-8; 2, 22526-51-8; 3, 591-49-1; 4, 22530-83-2; 5, 1674-10-8; *cis*-6, 144192-65-4; *trans*-6, 144192-66-5; 7, 95-13-6; 8, 144192-67-6; 9, 592-57-4; 10, 16717-84-3; 11, 110-83-8; 12, 111-66-0; $Al_2O_3$, 1344-28-1; $CF_3SO_3H$, 1493-13-6; 4-$CH_3C_6H_4SO_3H$, 104-15-4; $H_2SO_4$, 7664-93-9; $CH_3SO_3H$, 75-75-2; $(CH_3)_3SiN_3$, 4648-54-8; HN, 7782-79-8.

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# A Convenient Synthesis of Benzohydroximoyl Chlorides as Nitrile Oxide Precursors by HCl/*N*,*N*-Dimethylformamide/Oxone System

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Nitrile oxides are important intermediates in organic synthesis, particularly in [3 + 2] cycloaddition reactions to form isoxazolines or isoxazoles.[1] Among several methods developed for the in situ generation of nitrile oxides, two have been extensively used: (a) the dehydration of primary nitro derivatives (Mukaiyama procedure for aliphatic nitrile oxides)[2] and (b) the base-induced dehydrohalogenation of hydroximoyl chlorides (Huisgen's methodology for aromatic nitrile oxides).[3] Thus, convenient methods for the synthesis of substituted benzohydroximoyl chlorides (aromatic nitrile oxide precursors) have received much attention.[4] Previously reported preparations of benzohydroximoyl chlorides by chlorination of the corresponding aldoximes have required either the use of chlorine,[4a] nitrosyl chloride,[4b] and *tert*-butyl hypochlorite[4c] or a complex experimental procedure utilizing *N*-chlorosuccinimide (NCS) in *N*,*N*-dimethylformamide (DMF).[4d] While the NCS/DMF method provided satisfactory yields of products for several types of aromatic aldoximes, ring chlorination could not be controlled with the strongly activated aromatic aldoximes by electron-donating substituents. An alternative method for the chlorination of benzaldoximes having electron-donating substituents with *tert*-butyl hypochlorite in carbon tetrachloride suffered from low yields.

During our investigations on nitrile oxides,[5] we have found that anhydrous hydrogen chloride in DMF/Oxone (potassium peroxymonosulfate, Aldrich) system provides a particularly selective and by far the most convenient method of preparation of benzohydroximoyl chlorides 2 from the corresponding aldoximes 1 (Scheme I).

Isolated yields of products are excellent, and this method can be applied to benzaldoximes regardless the electronic nature of the substituents. Either *m*-CPBA or Oxone might be used[6] in the chlorination of benzaldoximes for the generation of $Cl^+$. However, the use of *m*-CPBA as an oxidant requires a tedious removal of *m*-chlorobenzoic acid from the product.

The reaction conditions and workup procedures for the preparation of benzohydroximoyl chlorides are very simple

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