5.96–6.08 (m, 1, C-2 vinylic H), 6.42 (d, J = 10 Hz, 1, C-1 vinylic H), 6.84–7.04 (m, 3, aromatic H); ^{13}C NMR ($CDCl_3$) δ 27.0 (C-1), 23.3 (C-2), 127.8 (C-3 or 4), 128.4 (C-3 or 4), 126.1 (C-5), 142.2 (C-6), 127.3 (C-7 or 8), 127.8 (C-7 or 8), 132.6 (C-9), 133.9 (C-10), 15.7 (CH_2CH_3), 28.5 (CH_2CH_3); mass spectrum (70 eV), m/e (relative intensity) 158 (M^+, 32), 143 (25), 129 (62), 69 (100); exact mass spectrum calcd for $C_{12}H_{14}$ 158.1096, found 158.1103.

1,2-Dihydro-6-*n*-propylnaphthalene (30c): 99% from **29**; ^{1}H NMR ($CDCl_3$) δ 0.93 (t, J = 7 Hz, 3, $CH_2CH_2CH_3$), 1.52–1.72 (m, 2, $CH_2CH_2CH_3$), 2.22–2.32 (m, 2), 2.51 (t, J = 8 Hz, 2, $CH_2CH_2CH_3$), 2.73 (t, J = 8 Hz, 2, benzylic H), 5.96–6.08 (m, 1, C-2 vinylic H), 6.42 (d, J = 10 Hz, 1, C-1 vinylic H), 6.84–7.04 (m, 3, aromatic H); ^{13}C NMR ($CDCl_3$) δ 27.1 (C-1), 23.3 (C-2), 127.9 (C-3 or 4), 128.4 (C-3 or 4), 126.1 (C-5), 140.7 (C-6), 126.8 (C-7 or 8), 127.3 (C-7 or 8), 132.6 (C-9), 133.9 (C-10), 13.8 ($CH_3CH_2CH_3$), 24.6 ($CH_2CH_2CH_3$), 37.7 ($CH_2CH_2CH_3$); mass spectrum (70 eV), m/e (relative intensity) 172 (M^+, 57), 143 (100), 129 (70), 115 (14), 69 (94); exact mass spectrum calcd for $C_{13}H_{16}$ 172.1252, found 172.1249.

6-*n*-Butyl-1,2-dihydronaphthalene (30d): 98% from **29**; ^{1}H NMR ($CDCl_3$) δ 0.91 (t, J = 7 Hz, 3, $CH_2CH_2CH_2CH_3$), 1.24–1.44 (m, 2, $CH_2CH_2CH_2CH_3$), 1.48–1.64 (m, 2, $CH_2CH_2CH_2CH_3$), 2.22–2.32 (m, 2), 2.53 (t, J = 8 Hz, 2, $CH_2CH_2CH_2CH_3$), 2.73 (t, J = 8 Hz, 2, benzylic H), 5.96–6.08 (m, 1, C-2 vinylic H), 6.42 (d, J = 10 Hz, 1, C-1 vinylic H), 6.84–7.04 (m, 3, aromatic H); ^{13}C NMR ($CDCl_3$) δ 27.1 (C-1), 23.3 (C-2), 127.9 (C-3 or 4), 128.4 (C-3 or 4), 126.0 (C-5), 140.9 (C-6), 126.7 (C-7 or 8), 127.3 (C-7 or 8), 132.6 (C-9), 133.9 (C-10), 13.9 ($CH_2CH_2CH_2CH_3$), 22.4 ($CH_2CH_2CH_2CH_3$), 33.7 ($CH_2CH_2CH_2CH_3$), 35.3 ($CH_2CH_2CH_2CH_3$); mass spectrum (70 eV), m/e (relative intensity) 186 (M^+, 40), 143 (63), 129 (42), 69 (100); exact mass spectrum calcd for $C_{14}H_{18}$ 186.1318, found 186.1363.

Summary of Yields and Spectral Data for 6-Alkyltetralins 31. 6-Methyltetralin (31a): 99% from **30a**; ^{1}H NMR ref 50a; mass spectrum ref 54; exact mass spectrum calcd for $C_{11}H_{14}$ 146.1096, found 146.1107.

6-Ethyltetralin (31b): 97% from **30b**; ^{1}H NMR ($CDCl_3$) δ 1.20 (t, J = 7 Hz, 3, CH_2CH_3), 1.68–1.84 (m, 4), 2.55 (q, J = 7 Hz, 2, CH_2CH_3), 2.64–2.80 (m, 4, benzylic H), 6.84–7.0 (m, 3, aromatic H); mass spectrum (70 eV), m/e (relative intensity) 160 (M^+, 25), 145 (19), 131 (100), 115 (10); exact mass spectrum calcd for $C_{12}H_{16}$ 160.1252, found 160.1260.

6-*n*-Propyltetralin (31c). 98% from **30c**; ^{1}H NMR ($CDCl_3$) δ 0.94 (t, J = 7 Hz, 3, $CH_2CH_2CH_3$), 1.56–1.70 (m, 2, $CH_2CH_2CH_3$), 1.72–1.92 (m, 4), 2.50 (t, J = 8 Hz, 2, $CH_2CH_2CH_3$), 2.68–2.88 (m, 4, benzylic H), 6.84–7.0 (m, 3, aromatic H); mass spectrum (70 eV), m/e (relative intensity) 174 (M^+, 7), 145 (22), 131 (100); exact mass spectrum calcd for $C_{13}H_{18}$ 174.1408, found 174.1401.

6-*n*-Butyltetralin (31d). 98% from **30d**; ^{1}H NMR ref 55; mass spectrum ref 54.

Acknowledgment. We thank the Department of Energy (DE-AS20-82LC10821) for their financial support and Dr. Richard A. Heppner, David Proctor, and Michael Netzel for determining mass spectra.

Registry No. **2**, 83-33-0; **3a**, 767-60-2; **3b**, 2294-91-9; **3c**, 10408-76-1; **3d**, 2294-88-4; **4a**, 767-58-8; **4b**, 4830-99-3; **4c**, 60584-82-9; **4d**, 38857-75-9; **5a**, 17496-14-9; **5b**, 22351-56-0; **5c**, 92013-10-0; **6a**, 2177-47-1; **6b**, 17059-50-6; **6c**, 92013-11-1; **6d**, 92013-12-2; **7a**, 824-63-5; **7b**, 56147-63-8; **7c**, 64624-93-7; **7d**, 66324-75-2; **8**, 10485-09-3; **9**, 15115-60-3; **9** (alcohol), 16657-10-6; **10**, 16657-07-1; **11a**, 7372-92-1; **11b**, 92013-13-3; **11c**, 92013-14-4; **11d**, 92013-15-5; **12a**, 824-22-6; **12b**, 66256-38-0; **12c**, 92013-16-6; **12d**, 92013-17-7; **13**, 14548-39-1; **13** (alcohol), 75476-86-7; **14**, 75476-78-7; **15a**, 7480-80-0; **15b**, 66256-31-3; **15c**, 92013-19-9; **15d**, 92013-20-2; **16a**, 874-35-1; **16b**, 52689-24-4; **16c**, 92013-21-3; **16d**, 92013-22-4; **17**, 529-34-0; **17** (X = Br), 13672-07-6; **17** (alcohol, X = Br), 64245-04-1; **18a**, 4373-13-1; **18b**, 91720-19-3; **18c**, 92013-23-5; **18d**, 92013-24-6; **19a**, 1559-81-5; **19b**, 13556-58-6; **19c**, 66324-83-2; **19d**, 38857-76-0; **20a**, 1590-08-5; **20b**, 21568-62-7; **20c**, 50417-78-2; **20d**, 69627-18-5; **21a**, 2717-44-4; **21b**, 31861-78-6; **21c**, 92013-25-7; **21d**, 92013-26-8; **22a**, 3877-19-8; **22b**, 32367-54-7; **22c**, 66324-84-3; **22d**, 36230-28-1; **23**, 92013-27-9; **24**, 68449-30-9; **24** (alcohol), 92013-31-5; **25**, 87779-57-5; **26a**, 21564-78-3; **26b**, 92013-32-6; **26c**, 92013-33-7; **26d**, 92013-34-8; **27a**, 2809-64-5; **27b**, 42775-75-7; **27c**, 66324-85-4; **27d**, 66325-42-6; **28**, 32281-97-3; **28** (alcohol), 75693-15-1; **29**, 75693-17-3; **30a**, 2717-47-7; **30b**, 92013-35-9; **30c**, 92013-36-0; **30d**, 92013-37-1; **31a**, 1680-51-9; **31b**, 22531-20-0; **31c**, 42775-77-9; **31d**, 30654-45-6; diethyl malonate, 105-53-3; 2-bromobenzyl bromide, 3433-80-5; diethyl 2-(2-bromobenzyl)-malonate, 66192-11-8; 2-(2-bromobenzyl)malonic acid, 58380-12-4; 3-(2-bromophenyl)propionic acid, 15115-58-9; 3-(2-bromophenyl)propionyl chloride, 90725-40-9; 4-bromobenzyl bromide, 589-15-1; diethyl 2-(4-bromobenzyl)malonate, 70146-78-0; 2-(4-bromobenzyl)malonic acid, 92013-18-8; 3-(4-bromophenyl)-propionic acid, 1643-30-7; *o*-bromobenzyl cyanide, 19472-74-3; (*o*-bromophenyl)acetic acid, 18698-97-0; 2-(*o*-bromophenyl)ethanol, 4654-39-1; 2-(*o*-bromophenyl)ethyl bromide, 1746-28-7; diethyl 2-(2-(*o*-bromophenyl)ethyl)malonate, 92013-28-0; 2-(2-(*o*-bromophenyl)ethyl)malonic acid, 92013-29-1; 4-(*o*-bromophenyl)butyric acid, 90841-47-7; 4-(*o*-bromophenyl)butyryl chloride, 92013-30-4.

(54) Sikkar, R.; Martinson, P. *Acta. Chem. Scand., Ser. B* **1980**, *B34*, 551.

(55) Nakatsuji, Y.; Kubo, T.; Nomura, M.; Kikkawa, S. *Bull. Chem. Soc. Jpn.* **1978**, *51*, 618.

Lewis Acid Catalyzed Conversion of Alkenes and Alcohols to Azides[1]

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Received January 19, 1984

Hydrazoic acid, though unreactive to alkenes, adds readily to enol ethers. In the presence of Lewis acids, in particular $TiCl_4$, addition takes place readily to phenylethylenes or 1,1-disubstituted ethylenes to produce alkyl azides. Regiochemical, electronic, and steric influences were explored. $TiCl_4$ also served to catalyze conversion of benzyl or tertiary alcohols to azides. Monosubstituted alkenes or primary alcohols are not affected.

Organic azides are versatile substrates for organic synthesis. Such compounds not only interact with nucleophiles or electrophiles but also serve as nitrene precursors on thermal or photochemical excitation.[2] While aromatic azides can be obtained by a variety of methods, aliphatic azides are prepared chiefly by substitution of alkyl halides, diazo transfer to aliphatic amines, or additions to olefins.[3] Halogen azides have been employed extensively in addi-

(1) (a) Synthetic Methods 19. For paper 18, see: Hassner, A.; Munger, P.; Belinka, B. A., Jr. *Tetrahedron Lett.* **1982**, *23*, 699. (b) Address all correspondence to Prof. A. Hassner, Chemistry Department, Bar-Ilan University, Ramat-Gau, 52100, Israel.

(2) Biffin, M. E. C.; Miller, J.; Paul, D. B. "The Chemistry of the Azido Group"; Patais, S., Ed.; Wiley: London, 1971; Chapter 2.

(3) Smith, P. A. S. "Open-Chain Nitrogen Compounds"; Benjamin: New York, 1966; Vol. II, pp 211–256.

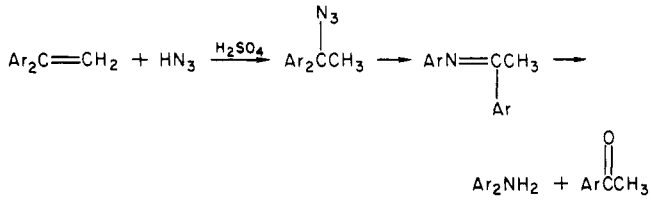
0022-3263/84/1949-4237$01.50/0

Table I. Catalyst Activity in Conversion of 4 to 5

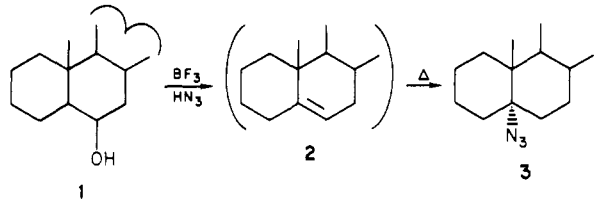
catalyst	yield, %	reaction time, h
$TiCl_4$	60	8
$AlCl_3$	56	30
BF_3OEt_2	48	18
$SnCl_4$	45	6
$SbCl_5$	decomposed azide	4
$PdCl_2$	0	18
HOAc	0	72
$AgClO_4$	0	10
$Ti(O\text{-}i\text{-}Pr)_4$	0	4

tions to olefins,[4] but reduction of the halide without affecting the azide function cannot be achieved effectively. Mercuric azide adds to certain olefins[5,6] while hydrazoic acid does not add readily except in the case of the strained cyclopropene[6] or in Michael additions to unsaturated carbonyl compounds.[7]

Attempts to add hydrazoic acid to diarylethylene in the presence of a strong acid,[7c], such as sulfuric acid, led to considerable decomposition due to the susceptability of the resulting azide to protonation and Schmidt rearrangement as shown in eq. 1.



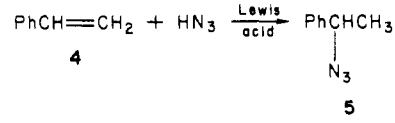
Recently, 6β-hydroxypregnane (1) was converted into the 5-azido compound **3** by means of BF_3 and hydrazoic acid.[8] Presumably, this reaction involves elimination of water to give a Δ^5-pregnene (**2**) which adds HN_3 in a Lewis acid catalyzed reaction.



We therefore felt it worthwhile to investigate Lewis acid induced additions of HN_3 to olefins and similar carbocation reactions that can lead to formation of alkyl azides.

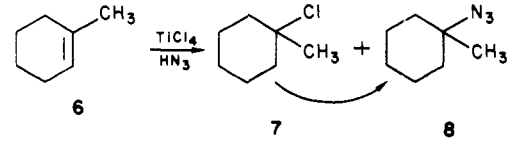
Results

Initially we chose styrene **4** as a substrate and studied the ability of various Lewis acids to facilitate hydrazoic acid addition. The progress of the reaction was followed

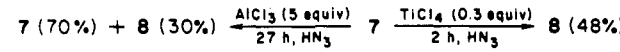


by ^1H NMR which allowed monitoring of the methyl doublet in **5**. Of the various acids tested, $TiCl_4$ and $AlCl_3$ gave the best yields of **5**, 60% in 8 h and 56% in 30 h, respectively (see Table I).

Both $TiCl_4$ and $AlCl_3$ catalyze HN_3 addition to styrenes, to 1,1-dialkylolefins, or to trisubstituted olefins, while monoalkyl or 1,2-disubstituted alkenes were practically unreactive (see Table II). Aluminum chloride offered an advantage over $TiCl_4$ in the case of some trisubstituted olefins, as was demonstrated in the case of 1-methylcyclohexene. The yield of azide **8** was 70% with $AlCl_3$ and 39% with $TiCl_4$.

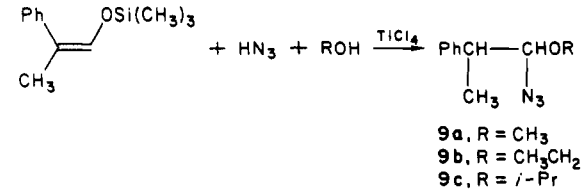


When the reaction of **6** with $TiCl_4$ was followed by NMR, it was apparent that two products (**7** and **8**) were formed initially, followed by conversion of chloride **7** into azide **8**. This conversion does not take place with hydrazoic acid alone but requires the presence of $AlCl_3$ or $TiCl_4$ and, hence, proceeds via solvolysis of **7** to a carbocation. Exchange of chloride for azide is much faster with $TiCl_4$ than with $AlCl_3$. Thus, exposure of **7** to HN_3 and $TiCl_4$ converted it into azide **8** in less than 2 h, while $AlCl_3$ required 27 h for 30% conversion. One disadvantage of $TiCl_4$ is that it causes polymerization.



A number of olefins, acyclic and cyclic, were converted to the azides in good yield by this method (see Table II). Solvents of choice are CH_2Cl_2 or $CHCl_3$ (ethanol free) rather than benzene, largely because of better solubility of the catalyst. Workup is very simple and involves passing the reaction mixture over a 2 × 4 cm column of alumina followed by evaporation of solvent. HN_3 addition proceeded regiospecifically in all cases. Primary and secondary alcohol and ester functions did not interfere with the HN_3 addition, although a larger amount of Lewis acid was necessary when these groups were present. Enol ethers and silyl enol ethers reacted with HN_3 without a catalyst to produce azido ethers in good yields.[9] Reaction of HN_3 with silyl enol ethers that possess α- or β-phenyl substituents produced aldehydes or ketones in addition to or instead of the HN_3 adducts (see Table II). The addition of $TiCl_4$ did not alter the ratio of azide to carbonyl compound.

During HN_3 addition to silyl enol ethers in the presence of alcohols, we observed that ether exchange took place in the presence of $TiCl_4$. This procedure was used to substitute methyl (**9a**), ethyl (**9b**), and isopropyl (**9c**) for the trimethylsilyl group in azido ethers and shows promise in synthesis of azido ethers. Phenol and *tert*-butyl alcohol did not substitute in these reactions.



Discussion

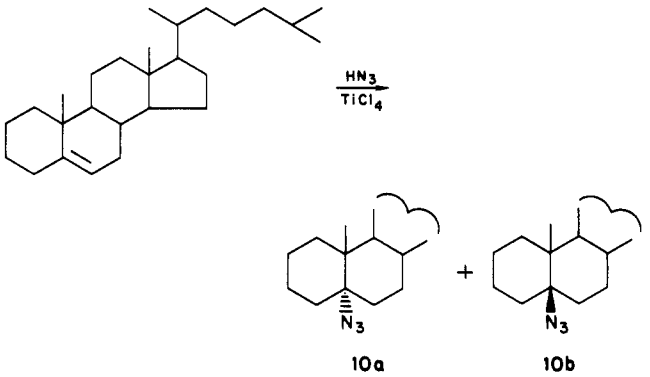
Data from Table II indicate that electron-rich alkenes such as enol ethers or silyl enol ethers can add HN_3 without the benefit of Lewis acid catalysts. Other olefins require

(4) Hassner, A. *Acc. Chem. Res.* **1971**, *9*, 1.
(5) Heathcock, C. H. *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 134.
(6) Hassner, A.; Galle, J. E. *J. Am. Chem. Soc.* **1972**, 94, 3930.
(7) (a) Boyer, J. H. *J. Am. Chem. Soc.* **1951**, *73*, 5248. (b) Awad, W. I.; Omran, S. M. A. R.; Nagier, F. *Tetrahedron* **1963**, *19*, 1591. (c) Ege, S. N.; Sherk, K. W. *J. Am. Chem. Soc.* **1953**, *75*, 354.
(8) (a) Khoung-Huu, Q.; Lukacs, G.; Pancrazi, A.; Goutard, R. *Tetrahedron Lett.* **1972**, 3579. (b) Khoung-Huu, Q.; Pancrazi, A. *Tetrahedron* **1974**, *30*, 2337.
(9) Trifluoroacetic acid catalyzed HN_3 addition was reported by Kyba, E. P.; Joh, A. M. *Tetrahedron Lett.* **1977**, *27*, 37.

the presence of a Lewis acid, preferably $TiCl_4$, but even then substituents that can stabilize a positive charge (phenyl or two geminal alkyl substituents) are required.[10a,b] The importance of stabilizing a positive charge in the transition state is further indicated by qualitative kinetic effects shown in Table III. *p*-Methoxy and methyl substituents increase the rate of reaction while electron-withdrawing Cl and NO_2 substitution slow down the reaction considerably.

The clean regiospecificity observed (see Table II) is also in consonance with development of a positive charge during the reaction.

From the stereochemical point of view, we determined that 5-cholestene produces a mixture of 5α- and 5β-azidocholestanes **10a** and **10b** which also speaks in favor of a carbocation intermediate.



Some steric effects were also observed inasmuch as tetramethylethylene adds HN_3 at least 25 times slower than the trisubstituted 1-methylcyclohexene.

These data are consistent with one of the following mechanistic pathways (Schemes I–III).

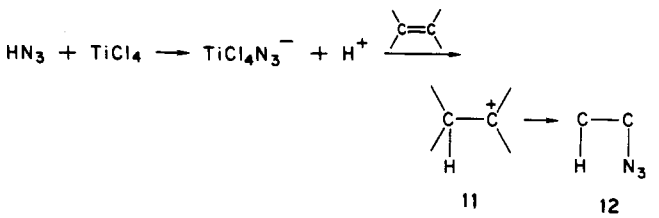
A mechanism similar to that shown in Scheme I has been proposed[10a] but also refuted[10b] for the addition of HCl to olefins. Against this mechanism speaks the fact that we observed no decrease in the rate of HN_3 addition to styrene upon addition of an equivalent of 2,6-di-*tert*-butylpyridine which is expected to readily neutralize a proton but not to complex with $TiCl_4$. By contrast, 2,6-di-*tert*-butylpyridine inhibits the $TiCl_4$-catalyzed addition of HCl to **7**.

The second pathway (Scheme II) involves formation of a $TiCl_4$–olefin π-complex **13** or possibly a σ-complex **14**, which then reacts with HN_3 via **15** or **11** to finally give the adduct.

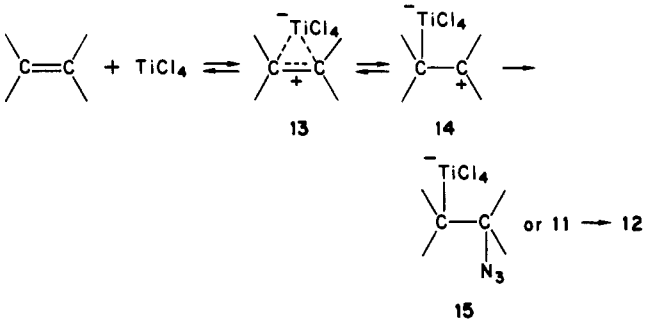
Furthermore, we cannot discount the possibility of ligand transfer to titanium before or after complexation[10c] with the olefin to produce **16**, a species analogous to **14** which can undergo internal transfer of a ligand to carbon (**15**) followed by metal proton exchange (Scheme III). Further work is needed to differentiate between the proposed schemes.

$TiCl_4$-Catalyzed Formation of Azides from Alcohols. The formation of azide **8** from the olefin **6** or from the chloride **7** in the presence of $TiCl_4$ as well as the known acid-catalyzed transformation of some alcohols to azides[11] led us to investigate if $TiCl_4$ would facilitate the conversion of alcohols to azides. It was already shown (Table II) that primary alcohols appear to be inert toward HN_3–$TiCl_4$. Yet, we found that benzylic, allylic, or tertiary alcohols react smoothly with an excess of HN_3 in the presence of

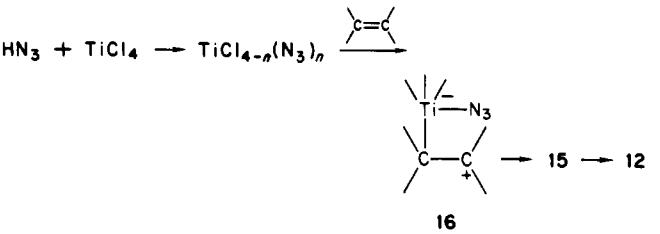
Scheme I



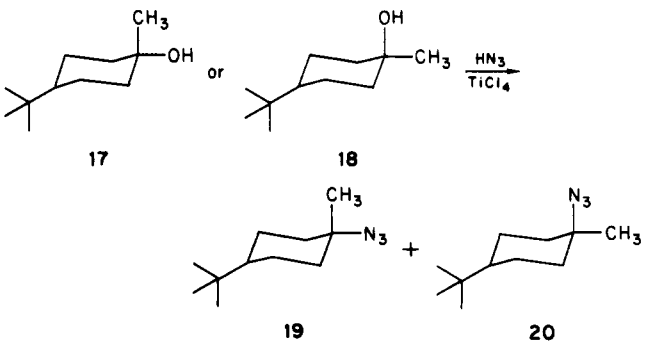
Scheme II



Scheme III



0.5 equiv of $TiCl_4$ to form azides in very good yield (see Table IV). The Lewis acid system represents a great improvement for allylic azide[12] as well as for benzylic azide synthesis.[7c] Stereochemistry is not maintained as indicated by the formation of the same mixture of azides (**19** and **20**) from either *cis*- or *trans*-4-*tert*-butyl-1-methylcyclohexanol (**17** or **18**). These data are consistent with the intermediacy of a carbocation derived from alcohols.



In conclusion, a simple, direct, and regiospecific route to alkyl azides by $TiCl_4$ catalyzed addition of HN_3 to certain alkenes has been developed. Similarly, benzylic and tertiary alcohols can be converted to the corresponding azides on treatment with HN_3–$TiCl_4$, serving as a useful synthetic entry to such compounds.

Experimental Section

Melting points (taken on a Fisher-Johns block) are uncorrected. NMR spectra were recorded on a Varian EM-360 spectrometer using $(CH_3)_4Si$ as an internal standard. Infrared spectra were

(10) (a) "Friedel-Crafts and Related Reactions"; Olah, G., Ed.; Vol. I, pp 1574–1575. (b) Reference 10a, Vol. I, pp 210–211. (c) Such ligand displacement is known with $AlCl_3$ or $SbCl_5$.

(11) Edward, O.; Grieco, C. *Can. J. Chem.* **1974**, *53*, 3561. Arcus, C. L.; Lucken, E. A. *J. Chem. Soc.* **1955**, 1634.

(12) Foster, M. D.; Fierz, H. E. *J. Chem. Soc.* **1908**, *93*, 1174.

Table II. Addition of HN_3 to Olefins

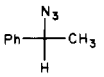
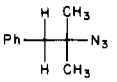
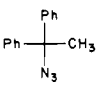
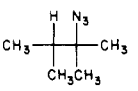
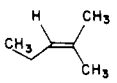
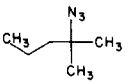
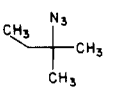
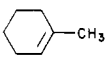
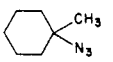
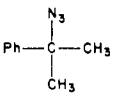
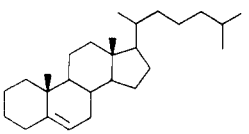
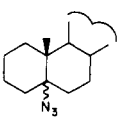
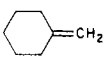
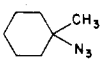
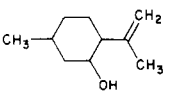
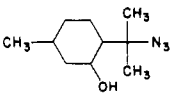
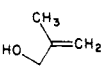
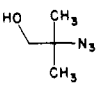
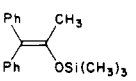
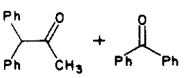
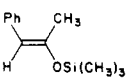
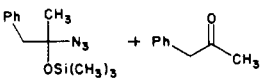
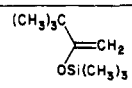
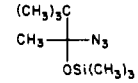
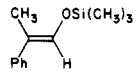
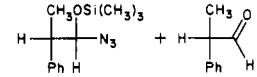
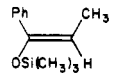
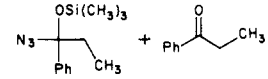
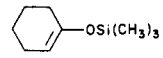
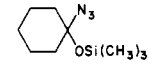
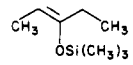
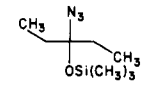
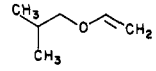
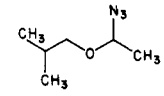
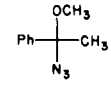
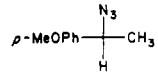
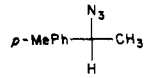
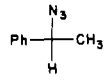
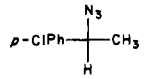
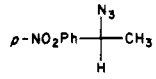
compd	product(s)	yield (%) of azide	catalyst
	 5	70	$TiCl_4$
	 21	65	$TiCl_4$
	 22	93	$TiCl_4$
	 23	73 89	$TiCl_4$ $AlCl_3$[a]
	 24	68 80	$TiCl_4$ $AlCl_4$[a]
	 25	52 90	$TiCl_4$ $AlCl_3$[a]
	 26	69	$TiCl_4$
	 27	52	$TiCl_4$
	 8	39 70	$TiCl_4$ $AlCl_3$[a]
	 45	75	$TiCl_4$
	 28	98	$TiCl_4$
	 8	70	$TiCl_4$
	 29	75	$TiCl_4$
	 30	38	$TiCl_4$
		>5	$TiCl_4$
	 31	34 69	$TiCl_4$ $AlCl_3$[a]

Table II (*Continued*)

compd	product(s)	yield (%) of azide	catalyst
	 **32**	91	$TiCl_4$ [b]
	 **33**	50	$TiCl_4$ [a,b]
	 **34**	46	$TiCl_4$ [a,b]
	 **36**	95	$TiCl_4$ [b]
	 **37**	93	$TiCl_4$ [b]
	 **38**	77	$TiCl_4$ [b]
	 **39**	98	$TiCl_4$ [b]

[a] Yield by NMR. [b] Similar results in the absence of $TiCl_4$.

Table III. Electronic Effects on $TiCl_4$-Catalyzed HN_3 Additions

product	reaction time	yield, %
 **40**	<5 min	54
 **41**	<5 min	86
 **5**	5 h	59
 **42**	60 h	59
 **43**	>100 h	0

recorded on a Perkin-Elmer Model PE-457 spectrometer. Mass spectra were taken on a Varian M.A.T. CH-5 instrument. Gas chromatographic analyses were carried out on a Varian Aerograph 200. Elemental analyses were performed by Atlantic Microlab, Inc., Atlanta, GA.

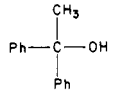
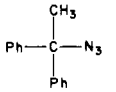
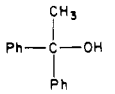
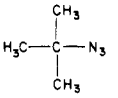
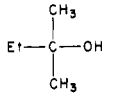
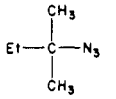
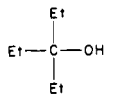
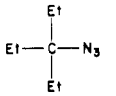
Commercially available reagents and solvents were usually reagent grade and distilled or recrystallized prior to use. Skellysolve F refers to a light petroleum fraction with bp 35–60 °C and Skellysolve B refers to a light petroleum fraction with bp 60–90 °C. The alumina used for all of the column chromatography was Fisher Scientific Company, Alumina Adsorption, type A-540. The azide products were identified by IR, NMR, and mass spectrometry. Because of their lability and explosive character, they were not distilled or submitted to elemental analysis. Their purity was indicated by NMR integration.

Preparation of Standard HN_3 Solutions. In a typical reaction a paste from dried phenolphthalein (65 g, 1.0 mol) and water (65 mol) was prepared in a three-necked flask fitted with an efficient stirrer, a dropping funnel, a thermometer, and a gas exit tube. Methylene chloride or chloroform (400 mL) was added, the mixture was cooled to 0 °C, and sulfuric acid (48 g, 0.5 mol) was added dropwise while the temperature was maintained between 0 and 5 °C. When the addition was complete, the organic layer was separated and dried (Na_2SO_4). When chloroform was the solvent, this dried solution was used directly. When methylene chloride was the solvent, the HN_3 solution was distilled from P_2O_5. Extreme caution is necessary when handling HN_3 because of its poisonous and explosive character. The concentration of the HN_3 solutions prepared by the above procedure (1.8 N) was determined by titration with a standard 0.1 N sodium hydroxide solution using phenolphthalein as the indicator. The solutions were stored in the cold (0 to 20 °C) and were stable for several months with only a slight decrease in HN_3 concentration.

Azide Conversion with $AlCl_3$. 1-Chloro-1-methylcyclohexane (**7**; 0.2 g, 1.5 mmol) and aluminum chloride (0.1 g, 0.75 mmol) were mixed in dry methylene chloride (10 mL), which was 2.5 N in hydrazoic acid (25 mmol), and stirred at room temperature. NMR integration indicated that after 27 h only 30% of the azide **8** had formed.

Azide Conversion with $TiCl_4$. The reaction as described above was carried out by using 3 mmol of **7**, 1 mmol of $TiCl_4$, and 6.7 mmol of HN_3. After 2 h the reaction mixture was passed down a 2 cm by 3 cm column of alumina, eluting with methylene

Table IV. $TiCl_4$-Catalyzed Formation of Azides from Alcohols

compd	product(s)	yield (%) of azide
$PhCH_2OH$	$PhCH_2N_3$ **44**	60
	 **45**	75
	 **35**	76
	 **46**	84
17	**19** + **20**	74
18	**19** + **20**	77
	 **47**	68
	 **48**	58
	 **49**	68
	 **50**	65
$PhCH{=}CHCH_2OH$	$PhCH{=}CHCH_2N_3$ **51**	84

chloride, and the solvent was removed to yield 0.2 g (48%) of azide **8**.

Addition of Hydrazoic Acid to Olefins. General Procedure. The olefin (10 mmol) was mixed with methylene chloride (40 mL), which was 1.7–2 N in hydrazoic acid (68–80 mmol), and cooled in an ice bath. To this cooled solution was added a solution of titanium tetrachloride (3 mmol) in methylene chloride (10 mL). After the addition was complete, the reaction mixture was allowed to stir at room temperature for 24 h and passed down a 3 cm by 3 cm column of alumina, eluting with methylene chloride. If necessary, the product was purified by flash chromatography. Removal of the solvent either by room-temperature distillation, if the reaction product was volatile, or on a rotary evaporator yielded the pure alkyl azide.

1-Azido-1-phenylethane (5) was prepared as a colorless liquid from styrene ($TiCl_4$, 70%, $AlCl_3$, 56%): IR (liquid film) 3070, 3040, 2980, 2110, 1495, 1455, 1380, 1310, 1250, 1075, 1040, 1000, 775, 715 cm^{-1}; NMR ($CDCl_3$) δ 7.36 (s, 5), 4.53 (d, J = 7 Hz, 1), 1.42 (d, J = 7 Hz, 3); MS, m/e (relative intensity) 147 (M^+, 6.19 (25), 118 (16), 105 (100), 104 (39), 77 (62), 51 (31), and 43 (18).

1-Azido-2-methyl-3-phenylpropane (21) was prepared as a colorless liquid from β,β-dimethylstyrene: IR (liquid film) 3080, 3050, 2995, 2950, 2115, 1492, 1460, 1395, 1378, 1270, 1235, 1135, 780, 760, 725 cm^{-1}; NMR ($CDCl_3$) δ 8.27 (s, 5), 2.73 (s, 2), 1.23 (s, 6); MS, m/e (relative intensity) 147 (M – N_2, 2.5), 146 (2.5), 133 (6), 132 (7.5), 117 (10), 106 (6), 105 (7.5), 91] (100), 85 (20), 83 (30), 65 (16), 56 (69).

1-Azido-1,1-diphenylethane (22) was prepared as a colorless liquid from 1,1-diphenylethene: IR (liquid film) 3070, 3040, 2990, 2110, 1595, 1490, 1450, 1382, 1250, 1080, 1055, 1040, 930, 860, 775, 758, 740, 715, 675, 610 cm^{-1}; NMR ($CDCl_3$) δ 6.32 (s, 10), 1.96 (s, 3); MS, m/e (relative intensity) 195 (M – N_2, 12), 181 (33), 180 179 (33), 178 (24), 165 (30), 154 (60), 153 (18), 152 (21), 85 (69), 83 (100), 77 (11), 48 (11).

1-Azido-1-phenylcyclohexane (23) was prepared as a colorless liquid from 1-phenylcyclohexene: IR (liquid film) 3090, 3060, 3030, 2940, 2860, 2110, 1495, 1450, 1260, 1140, 900, 767, 740, 707, 615, 565 cm^{-1}; NMR ($CDCl_3$) δ 7.2–7.6 (m, 5), 1,1–2.6 (m, 10); MS, m/e (relative intensity) 201 (M^+, 1.3), 173 (1.8), 172 (2.7), 160 (16.9), 159 (100), 130 (37.4), 117 (38), 104 (33.5), 91 (89), 77 (31), 51 (19.9), 41 (25.2).

1-Azido-1-phenylcyclopentane (24) was prepared as a colorless liquid from 1-phenylcyclopentene: IR (liquid film) 3090, 3060, 3030, 2960, 2880, 2105, 1495, 1450, 1337, 1250, 980, 765, 750, 710, 565 cm^{-1}; NMR ($CDCl_3$) δ 1.7–7 (m, 5), 1.6–2.5 (m, 8); MS m/e (relative intensity) 187 (M^+ 1.5), 169 (2.0), 158 (8.5), 154 (17), 146 (12),145 (100), 131 (12), 130 (50), 115 (14.6), 105 (11), 104 (27), 103 (60), 91 (60), 77 (42.7), 67 (10), 51 (27), 41 (24.4), 39 (19).

2-Azido-2,3-dimethylbutane (25) was prepared as a colorless liquid from 2,3-dimethyl-2-butene: IR (liquid film) 2950, 2105, 1460, 1385, 1260, 1160, 1115, 835, 7525 cm^{-1}; NMR ($CDCl_3$) δ 1.68 (m, 1), 1.22 (s, 6), 0.92 (d, J = 6 Hz, 6); MS, m/E (relative intensity) 127 (M^+, 0.96), 99 (1), 86 (2.9), 85 (40), 69 (9.2), 57 (16), 56 (75.2), 43 (100), 42 (35), 41 (45.7).

2-Azido-2-methylpentane (26) was prepared as a colorless liquid from 2-methyl-2-pentene: IR (liquid film) 2960, 2888, 2110, 1465, 1395, 1380, 1270, 1195, 1180, 1160, 922, 860 cm^{-1}; NMR ($CDCl_3$) δ 0.8–1.7 (m, 7), 1.25 (s, 6); MS, m/e (relative intensity) 127 (M^+, 0.25), 85 (4.5), 71 (7.5), 70 (7.5), 69 (12.5), 57 (15), 56 (75), 55 (12.5)[, 43 (100), 42 (42.5), 41 (47.5), 39 (22.5).

2-Azido-2-methylbutane (27) was prepared as a colorless liquid from 2-methyl-2-butene: IR (liquid film) 2975, 2940, 2890, 2110, 1465, 1390, 1385, 1270, 1205, 1180, 1160, 1070, 1020, 935, 860, 760 cm^{-1}; NMR ($CDCl_3$) δ 0.95–1.55 (A_2B_3, 5), 1.28 (s, 6); MS, m/e (relative intensity) 113 (M^+, 7.5), 86 (6), 85 (18), 84 (10.5), 71 (55), 70 (31.4), 56 (100), 55 (30), 43 (100), 42 (82), 41 (39), 31 (29.4).

1-Azido-1-methylcyclohexane (8) was prepared as a colorless liquid from 1-methylcyclohexene ($TiCl_4$, 39%, $AlCl_3$, 70% by NMR): IR (liquid film) 2980, 2900, 2110, 1455, 1390, 1270, 1172, 978, 943, 870, 832, 817, 760 cm^{-1}; NMR ($CDCl_3$) δ 1.5 (br s, 10), 1.3 (s, 3); MS, m/e (relative intensity) 139 (M^+, 4), 112 (2.4), 111 (13), 110 (3.6), 98 (5.5), 97 (62), 96 (13), 83 (14), 82 (9), 81 (20.6), 69 (3), 68 (46), 55 (100), 42 (87), 41 (45), 39 (30). **8** was also obtained in 70% yield from methylenecyclohexane.

5-Azidocholestane (28) was prepared as a colorless liquid from Δ^5-cholestane: IR (liquid film) 2940, 2870, 2110, 1470, 1454, 1385, 1270, 1220, 1170, 944, 770 cm^{-1}; NMR ($CDCl_3$) δ 0.9–2 (m, 31), 0.93 (s, 3), 0.83 (s, 3), 0.67 (s, 3).

2-(2-Azidoisopropyl)-5-methylcyclohexan-1-ol (29) was prepared as a colorless liquid from 2-isopropenyl-5-methylcyclohexan-1-ol: IR (liquid film) 3430 (br), 2920, 2110, 1450, 1390, 1374, 1260, 1152, 1060, 1035, 1020, 860 cm^{-1}; NMR ($CDCl_3$) δ 3.61 (2.1), 0.8–2.1 (m, 11), 1.35 (s, 6); MS m/e (relative intensity) 154 (M – HN_3, 3.3), 112 (31), 95 (37), 83 (33), 81 (29), 69 (34), 56 (100), 55 (63), 41 (33).

2-Azido-2-methylpropan-1-ol (30) was prepared as a colorless liquid from 2-methyl-2-propen-1-ol: IR (liquid film) 3360 (br), 2970, 2920, 2880, 2110, 1465, 1390, 1382, 1240, 1190, 1125, 1065, 990, 840 cm^{-1}; NMR ($CDCl_3$) δ 3.63 (s, 2), 3.3 (s, 1), 1.58 (s, 6); MS m/e (relative intensity) 73 (M – N_3, 22), 72 (35), 57 (22), 56 (13), 55 (30.4), 43 (70), 41 (100), 39 (43.5).

Addition of HN_3 to 1,1-Diphenyl-2-(trimethylsiloxy)-1-propene. The silyl ether (1 g, 3.35 mmol) and methanol (1.5 g, 47 mmol) were mixed in chloroform (40 mL), which was 1.7 N in hydrazoic acid (68 mmol), and titanium tetrachloride (0.2 g, 1.01 mmol) was added dropwise to the chloroform solution. The reaction mixture was stirred for 48 h and then passed down a 3 cm by 3 cm column of alumina, eluting with chloroform. The solvent was removed to yield a yellow oil (0.89 g). NMR and IR showed this oil to contain two major products, 1,1-≤diphenylacetone and benzophenone, in about equal proportions. Less than 5% of the azide product was present.

HN_3 Additions to Enol Ethers. General Procedure. The enol ether (0.2 mmol) was mixed with methylene chloride (20 mL), which was 1.7 N in hydrazoic acid (34 mmol), and stirred at room temperature. After from 1–48 h the solvent was removed on a rotatory evaporator to give the azide. Any carbonyl products were removed by passing the crude product down a 2 cm by 3 cm column of alumina, eluting with Skellysolve F. Removal of the solvent usually gave pure azide.

2-Azido-1-phenyl-2-(trimethylsiloxy)propane (31, 17 h). The crude NMR spectrum showed a 69 to 31 ratio of the azide adduct **31** and 1-phenylacetone. The isolated yield of the azide was 34%: IR (liquid film) 3070, 3030, 2960, 2110, 1600, 1500, 1455, 1380, 1260, 1130, 1100, 1020, 900, 860, 770, 715 cm^{-1}; NMR ($CDCl_3$) δ 7.31 (s, 5), 2.7 (s, 2), 1.5 (s, 3), 0.17 (s, 9); MS *m/e* (relative intensity) 221 (M–N_2, 28), 207 (10), 206 (43), 191 (18), 134 (15), 130 (30), 117 (12), 45 (28), 43 (65).

2-Azido-3,3-dimethyl-2-(trimethylsiloxy)butane (32) was prepared as a colorless liquid from 3,3-dimethyl-2-(trimethylsiloxy)-1-butene (16 h, 91%): IR (liquid film) 2950, 2870, 2110, 1585, 1400, 1380, 1370, 1260, 1160, 1100, 1040, 990, 830, 823, 770, 700, 632 cm^{-1}; NMR ($CDCl_3$) δ 1.45 (s, 3), 0.95 (s, 9), 0.2 (s, 9); MS, *m/e* (relative intensity) 174 (3.9), 173 (M – N_3, 23.9), 159 (6.1), 158 (9), 157 (5), 106 (6.7), 75 (20), 74 (10.9), 73 (100), 57 (25.5), 45 (10.6), 41 (16.4).

Addition of HN_3 to 2-Phenyl-1-(trimethylsiloxy)-1-propene. Formation of 33. The crude NMR and IR spectra showed the product to be a mixture of 2-phenylpropanal (40%) and azide **33** (50%, 48 h): IR (liquid film) 2110 and 1260 (N_3), 775 and 715 cm^{-1} (Ph); NMR ($CDCl_3$) δ 7.33 (s, 5), 4.84 (d, J = 7 Hz, 1), 3.05 (q, J = 7 Hz, 1), 1.36 (d, J = 7 Hz, 3), 0.1 (s, 9).

Addition of HN_3 to 1-Phenyl-1-(trimethylsiloxy)-1-propene. Formation of 34. The crude NMR and IR spectra showed the product mixture to contain 13% starting material, 40% propiophenone, and 46% azide **34** (17 h): IR (liquid film) 2120 and 1260 (N_3), 770 and 710 cm^{-1} (Ph); NMR ($CDCl_3$) δ 7.1–7.6 (m, 9), 2.03 (q, J = 7 Hz, 2), 0.75 (t, J = 7 Hz, 3), 0.15 (s, 9). If the reaction was run for 35 h, only propiophenone was isolated.

1-Azido-1-(trimethylsiloxy)cyclohexane (36) was prepared as a colorless liquid from 1-(trimethylsiloxy)cyclohexene (16 h, 95%): IR (liquid film) 2940, 2860, 2110, 1450, 1365, 1255, 1160, 1120, 1090, 1970, 1015, 1000, 915, 895, 850, 765 cm^{-1}; NMR ($CDCl_3$, no internal standard) δ 1.0–1.6 (m, 10), 0.0 (s, 9); MS *m/e* (relative intensity) 213 (M^+, 2.1), 184 (2), 171 (61.7), 155 (9.4), 115 (6.2), 100 (6.4), 75 (24.7), 73 (100), 45 (14.7), 41 (13.7).

3-Azido-3-(trimethylsiloxy)pentane (37) was prepared as a colorless liquid from 3-(trimethylsiloxy)-2-pentene (26 h, 93%): IR (liquid film) 2960, 2870, 2110, 1460, 1260, 1170, 1125, 1085, 1020, 1005, 890, 853, 770, 700, 645 cm^{-1}; NMR ($CDCl_3$) δ 1.72 (q, J = 7.5 Hz, 4), 1.9 (t, J = 7.5 Hz, 6), 0.17 (s, 9); MS, 174 (M – N_2, 9), 173 (41), 172 (12), 159 (9), 158 (53), 147 (18), 143 (21), 115 (21), 101 (29), 100 (74), 86 (18), 84 (38), 75 (41), 73 (100), 57 (71), 45 (32), 44 (24), 43 (26).

1-Azidoethyl isobutyl ether (38) was prepared as a colorless liquid from isobutyl vinyl ether (5 H, 77%: IR (liquid film) 2880–2970, 2110, 1460, 1385, 1340, 1230, 1115, 1075, 905, 840, 820, 730 cm^{-1}; NMR ($CDCl_3$) δ 4.5 (br q, J = 6 Hz, 1), 3.37 (ddd, J = 11, 9, 7 Hz, 2), 1.72 (dsept, J = 7.7 Hz, 1), 1.45 (d, J = 6 Hz, 3), 0.95 (d, J = 7 Hz, 6); MS, *m/e* (relative intensity) 101 (M – N_3, 2), 100 (18), 86 (12), 85 (5), 84 (19), 83 (6), 74 (4), 73 (7), 72 (7), 60 (100), 56 (45), 43 (75), 42 (97), 41 (82).

1-Azido-1-phenylethyl methyl ether (39) was prepared as a colorless liquid from methyl 1-phenylvinyl ether (1 h, 98%): IR (liquid film) 3060, 3010, 2970, 2920, 2110, 1490, 1450, 1380, 1270, 1250, 1200, 1140, 1080, 1050, 870, 860, 780, 815, 680, 620 cm^{-1}; NMR ($CDCl_3$) δ 7.43 (m, 5), 4.9 (s, 3), 1.73 (s, 3); MS, *m/e* (relative intensity) 149 (M – N_2, 45), 148 (64), 135 (70), 134 (48), 118 (58), 104 (64), 103 (39), 91 (42), 77 (100), 51 (51.5), 43 (58).

Addition of HN_3 to Trimethylsilyl Enol Ethers with Exchange of the Trimethylsilyl Group. General Procedure. The enol ether (10 mmol) and the alcohol (25 mmol) were mixed with methylene chloride (40 mL), which was 1.7 N in hydrazoic acid (68 mmol), followed by the addition of titanium tetrachloride (0.5 mmol), and stirred at room temperature. After 2 h the reaction mixture was passed down a 3 cm by 3 cm column of alumina and the solvent removed to yield the new azido ethers **9a–c**, contaminated with about 5% of the aldehyde The aldehyde was removed by passing the crude product down a 1 cm by 3 cm column of alumina, eluting with Skellysolve F.

1-Azido-2-phenylpropyl methyl ether (9a) was prepared as a colorless liquid from 2-phenylpropenyl trimethylsilyl ether (2 h, 75%): IR (liquid film) 3080, 3060, 3020, 2970, 2920, 2110, 1490, 1380, 1330, 1220, 1190, 1135, 1090, 1020, 975, 930, 860, 777, 706, 585 cm^{-1}; NMR ($CDCl_3$) δ 7.23 (s, 5), 4.35 (d, J = 6 Hz, 1), 3.42 and 3.35 (s and s, 3), 3.02 (dq, J = 7 Hz, 1), 1.32 (d, J = 7 Hz, 3); MS, *m/e* (relative intensity) 149 (M – N_3, 7.2), 148 (5.1), 117 (7.8), 116 (13.5), 106 (12.4), 105 (100), 104 (11), 103 (15), 91 (15.4), 83 (14.60), 79 (22.8), 77 (33), 51 (13.3), 41 (11.7), 39 (13.4).

The ethyl ether 9b was isolated as a colorless liquid (2 h, 92%): IR (liquid film) 3090, 3070, 2980, 2930, 2110, 1495, 1455, 1380, 1260, 1230, 1100, 940, 860, 770, 710 cm^{-1}; NMR ($CDCl_3$) δ 7.23 (s, 5), 4.43 (d, J = 7 Hz, 1), 3.63 (dq, J = 7 Hz, 1), 1.35 (d, J = 7 Hz, 3), 1.22 (t, J = 7 Hz, 3); MS, *m/e* (relative intensity) 163 (M – N_3, 4.2), 162 (1.3), 144 (3), 135 (7), 106 (10), 105 (100), 104 (6.4), 100 (12), 91 (6.6), 79 (12.5), 78 (6.5), 77 (17.5), 73 (21.6), 57 (6.8), 51 (6.5), 43 (9.6).

The isopropyl ether (9c) was isolated as a colorless liquid (2 h, 85%): IR (liquid film) 3090, 3070, 3020, 2980, 2940, 2120, 1603, 1500, 1460, 1390, 1335, 1230, 1135, 1090, 940, 935, 865, 775, 715 cm^{-1}; NMR ($CDCl_3$) δ 7.32 (s, 5), 4.47 (dd, J = 6, 6, 1.6 Hz, 1), 3.81 (dsept, J = 6, 6 Hz, 1), 3.03 (dd, J = 7, 7 Hz, 1), 1.35 (m, 3), 1.22 (m, 3), 1.02 (m, 3); MS, *m/e* (relative intensity) 177 (M – N_3, 11), 176 (3), 149 (8), 148 (4.5), 135 (53), 114 (62.5), 106 (37.5), 105 (66), 104 (20), 103, 91 (22) 79 (34), 78 (16), 77 (44), 72 (95), 43 (100).

Reaction of HN_3 with Substituted Styrenes. The corresponding styrene (7.5 mmol) was mixed with methylene chloride (25 mL), which was 1.9 N in hydrazoic acid (43 mmol), and titanium tetrachloride (2.5 mmol) was added dropwise. The solution was stirred at room temperature and was followed by NMR until all of the starting material had disappeared. The reaction times are recorded in Table III. Then an excess of water was added and the solution stirred for 10 min, after which time the reaction mixture was dried over sodium sulfate and filtered, and the solvent was removed to yield the azide as a water white liquid.

1-Azido-1-(*p*-methoxyphenyl)ethane (40) was prepared as a colorless liquid from *p*-methoxystyrene (5 min, 54%): IR (liquid film) 2960, 2925, 2830, 2110, 1600, 1578, 1505, 1450, 1375, 1300, 1245, 1180, 1035, 840, 750, 580 cm^{-1}; NMR ($CDCl_3$) δ 7.07 (AA'BB', 5), 4.52 (q, J = 7 Hz, 1), 3.75 (s, 3), 1.61 (d, J = 7 Hz, 3); MS, *m/e* (relative intensity) 178 (1.75), 177 (M^+, 16), 149 (10.5), 136 (14), 135 (100), 134 (26), 121 (10.5), 119 (9), 105 (12), 91 (20), 85 (14), 83 (20), 77 (17.5).

1-Azido-1-(*p*-methylphenyl)ethane (41) was prepared as a colorless liquid from *p*-methylstyrene (5 min, 86%): IR (liquid film) 3010, 2970, 2920, 2110, 1510, 1445, 1375, 1302, 1242, 1060, 1022, 996, 822, 740, 560 cm^{-1}; NMR ($CDCl_3$) δ 7.23 (s, 5), 4.53 (q, J = 7 Hz, 1), 2.32 (s, 3), 1.47 (d, J = 7 Hz, 3); MS, *m/e* (relative intensity) 162 (1.6), 161 (M^+, 11.5), 133 (7.4), 132 (6.5), 120 (10.6), 119 (100), 118 (26), 117 (15), 91 (48), 77 (7.4), 65 (19.7), 63 (8), 51 (8), 42 (7.4), 41 (7.4), 39 (14).

1-Azido-1-(*p*-chlorophenyl)ethane (42) was prepared as a colorless liquid from *p*-chlorostyrene (60 h, 59%): IR (liquid film) 2970, 2920, 2110, 1487, 1445, 1405, 1372, 1327, 1292, 1240, 1095, 995, 833, 565 cm^{-1}; NMR ($CDCl_3$) δ 7.3 (m, 5), 4.53 (q, J = 7 Hz, 1), 1.45 (d, J = 7 Hz, 3); MS (*m/e* (relative intensity) 183 (M^+ 4.7), 181 (M^+, 15), 155 (3.8), 154 (6), 153 (15), 152 (15), 141 (32.4), 140 (21), 139 (100), 138 (35), 113 (15), 111 (38), 103 (44), 77 (23.5), 75 (29.4), 51 (23.5), 50 (20.6), 42 (17.7).

1-Azido-1-(*p*-nitrophenyl)ethane (43) was detected by NMR after 100 h in less than 5% yield.

Addition of HN_3 to Styrene (4) in the Presence of 2,6-Di-*tert*-butylpyridine. Styrene (1 g, 10 mmol) and 2,6-di-*tert*-butylpyridine (0.4 g, 2.1 mmol) were mixed in chloroform (40 mL), which was 1.7 N in hydrazoic acid (68 mmol). To this solution was added, dropwise with stirring, titanium tetrachloride (0.25 g, 1.3 mmol). Stirring was continued at room temperature for 6 h followed by the addition of excess water. After 15 min of stirring, the wet reaction mixture was dried over sodium sulfate and filtered, and the solvent was removed to yield 1.5 g of an orange oil. NMR showed this oil to contain only azide **5** and 2,6-di-*tert*-butylpyridine. The yield, calculated by subtracting

the 0.4 g of pyridine initially introduced, was 1.1 g (71%).

Conversion of Benzylic Alcohols into Azides. General Procedure. The alcohol (10 mmol) was mixed with ethanol-free chloroform (35 mL), which was 1.7 N in hydrazoic acid (60 mmol), followed by the dropwise addition of titanium tetrachloride (5 mmol). The solution was stirred at room temperature for 2 h. Chromatography through a 4 cm by 3 cm column of alumina and removal of the solvent yielded the pure azide as a water white oil.

Benzyl azide (44) was prepared as a colorless liquid from benzyl alcohol (60%): IR (liquid film) 3090, 3065, 3030, 2960, 2870, 2110, 1495, 1455, 1270, 1215, 1090, 823, 775, 707, 690, 595 cm^{-1}; NMR ($CDCl_3$) δ 7.24 (s, 5), 4.4 (s, 2); MS, *m/e* (relative intensity) 133 (M^+, 1.8), 126 (19), 91 (100), 65 (11.3), 63 (10.6), 39 (10.8).

1-Azido-1-phenylethane (45) was prepared as a colorless liquid from 1-phenylethanol (75%; identical with **45** prepared by addition of HN_3 to 2-methylstyrene).

2-Azido-2-phenylpropane (35) was prepared as a colorless liquid from 2-phenylpropan-2-ol (76%): IR (liquid film) 3090, 3060, 3030, 2980, 2930, 2870, 2110, 1600, 1495, 1450, 1390, 1370, 1260, 1190, 1150, 1107, 1080, 1036, 773, 710, 640, 585 cm^{-1}; NMR ($CDCl_3$) δ 7.32 (m, 5), 1.53 (s, 6); MS, *m/e* (relative intensity) 161 (M^+, 5.2), 120 (9.8), 119 (100), 118 (19.3), 103 (11.4), 91 (45.3), 77 (52.4), 56 (10.5), 51 (27.2), 41 (15.5), 39 (11.1).

Azidodiphenylmethane (46) was prepared as a colorless oil from diphenylmethanol (84%): IR (liquid film) 3065, 3035, 2880, 2115, 1600, 1585, 1492, 1450, 1245, 1085, 1035, 877, 767, 752, 710, 650 cm^{-1}; NMR ($CDCl_3$) δ 7.24 (s, 10), 5.62 (s, 1); MS, *m/e* (relative intensity) 209 (M^+, 2), 181 (100), 180 (90), 104 (23), 103 (67), 85 (27), 83 (50), 78 (20), 77 (70), 76 (27), 51 (33). Identical with **45** prepared by addition of HN_3 to α-methylstyrene (75%).

1-Azido-4-*tert*-butyl-1-methylcyclohexane (19 and 20). Either the equatorial (**17**) or the axial (**18**) alcohol (1 g, 5.9 mmol) was placed in chloroform (40 mL), which was 1.7 N in hydrazoic acid (68 mmol), followed by the dropwise addition, with stirring, of titanium tetrachloride (1.1 g, 5.9 mmol). After 12 h the reaction mixture was passed down a 3 cm by 3 cm column of alumina, eluting with chloroform. The solvent was removed to yield the azide mixture as a clear oil (0.85 g, 77%, from **17** and 0.81 g, 74%, from **18**). The NMR, IR, and MS for both products are identical. Therefore, they are either the same isomer or the same mixture of isomers: IR (liquid film) 2950, 2880, 2110, 1450, 1320, 1270, 1201, 1133, 993, 942, 921, 883, 830 cm^{-1}; NMR ($CDCl_3$) δ 1.27 (s, 3), 0.9-2.1 (m, 9), 0.87 (s, 9); MS, *m/e* (relative intensity) 153 (M - N_2, 30), 152 (5.1), 124 (8.1), 110 (7.9), 97 (33), 96 (18), 95 (16), 83 (24.8), 82 (10.2), 81 (23.8), 69 (20.6), 68 (30.5), 67 (14), 57 (100), 56 (17.5), 55 (37.7), 41 (40.7).

1-Azido-1,1-diphenylethane (47) was prepared as a colorless liquid from 1,1-diphenylethanol (68%): IR (liquid film) 3070, 3040, 2930, 2110, 1610, 1495, 1450, 1375, 1250 cm^{-1}; NMR ($CDCl_3$) δ 7.17 (s, 10), 1.9 (s, 3).

***tert*-Butyl azide (48)** was prepared as a colorless liquid from *tert*-butyl alcohol (58%): IR (liquid film) 2980, 2940, 2110, 1455, 1375, 1255 cm^{-1}; NMR ($CDCl_3$) δ 1.23 (s, 9).

2-Azido-2-methylbutane (49) was prepared as a colorless liquid from 2-methyl-2-butanol (68%): IR (liquid film) 2970, 2930, 2110, 1460, 1380, 1260 cm^{-1}; NMR ($CDCl_3$) δ 1.53 (q, 2), 1.30 (s, 6), 0.95 (t, 3).

3-Azido-3-ethylpentane (50) was prepared as a colorless liquid from 3-ethyl-3-pentanol (65%): IR (liquid film) 2985, 2950, 2110, 1460, 1380, 1260 cm^{-1}; NMR ($CDCl_3$) δ 1.57 (q, 6), 0.95 (t, 9).

Cinnamyl azide (51) was prepared as a colorless liquid from cinnamyl alcohol (84%): IR (liquid film) 3060, 3030, 2920, 2110, 1950, 1880, 1800, 1665, 1450, 1250 cm^{-1}; NMR ($CDCl_3$) δ 7.22 (x, 5), 6.20 (m, 2), 3.80 (d, 2).

Acknowledgment. This research was supported by DHEW Grant CA-19203 from the National Cancer Institute, NIH.

Registry No. **4**, 100-42-5; **5**, 32366-25-9; **6**, 591-49-1; **8**, 22530-83-2; **9a**, 91633-37-3; **9b**, 91633-38-4; **9c**, 91633-39-5; **10a**, 91633-22-6; **10b**, 91633-40-8; **17**, 16980-56-6; **18**, 16980-55-5; **19**, 91633-34-0; **20**, 91633-35-1; **21**, 83386-09-8; **22**, 22293-23-8; **23**, 66021-71-4; **24**, 66021-70-3; **25**, 91633-20-4; **26**, 91633-21-5; **27**, 32872-42-7; **29**, 91633-23-7; **30**, 71879-79-3; **31**, 91633-25-9; **32**, 91633-26-0; **33a**, 65501-08-8; **34**, 91633-27-1; **35**, 32366-26-0; **36**, 69664-68-2; **37**, 91633-28-2; **38**, 91633-29-3; **39**, 65501-11-3; **40**, 91633-30-6; **41**, 91633-31-7; **42**, 91633-32-8; **43**, 91633-33-9; **44**, 622-79-7; **46**, 6926-47-2; **48**, 13686-33-4; **50**, 91633-36-2; **51**, 57294-86-7; $TiCl_4$, 7550-45-0; $AlCl_3$, 7446-70-0; BF_3-OEt_2, 109-63-7; $SnCl_4$, 7646-78-8; $SbCl_5$, 7647-18-9; $PdCl_2$, 7647-10-1; HOAc, 64-19-7; $AgClO_4$, 7783-93-9; $Ti(O\text{-}i\text{-}Pr)_4$, 546-68-9; $PhCH{=}C(CH_3)_2$, 768-49-0; $Ph_2C{=}CH_2$, 530-48-3; $(CH_3)_2C{=}C(CH_3)_2$, 563-79-1; $CH_3CH_2CH{=}C(CH_3)_2$, 625-27-4; $CH_3CH{=}C(CH_3)_2$, 513-35-9; $PhC(CH_3){=}CH_2$, 98-83-9; $HOCH_2C(CH_3){=}CH_2$, 513-42-8; $Ph_2C{=}C(CH_3)OSi(CH_3)_3$, 51425-63-9; $PhCH{=}C(CH_3)OSi(CH_3)_3$, 43108-63-0; $CH_2{=}C(OSi(CH_3)_3)C(CH_3)_3$, 17510-46-2; $PhC(CH_3){=}CHOSi(CH_3)_3$, 51075-23-1; $CH_3CH{=}C(Ph)OSi(CH_3)_3$, 37471-46-8; $CH_3CH{=}C(CH_2CH_3)OSi(CH_3)_3$, 17510-47-3; $(CH_3)_2CHCH_2OCH{=}CH_2$, 109-53-5; $PhC(OCH_3){=}CH_2$, 4747-13-1; $PhCH_2OH$, 100-51-6; $PhCH(CH_3)OH$, 98-85-1; $PhC(CH_3)_2OH$, 617-94-7; Ph_2CHOH, 91-01-0; $Ph_2C(CH_3)OH$, 599-67-7; $(CH_3)_3COH$, 75-65-0; $EtC(CH_3)_2OH$, 75-85-4; Et_3COH, 597-49-9; $PhCH{=}CHCH_2OH$, 104-54-1; $p\text{-}CH_3OC_6H_4CH{=}CH_2$, 637-69-4; $p\text{-}CH_3C_6H_4CH{=}CH_2$, 622-97-9; $p\text{-}ClC_6H_4CH{=}CH_2$, 1073-67-2; $p\text{-}NO_2C_6H_4CH{=}CH_2$, 100-13-0; HN_3, 7782-79-8; $Ph_2CHCOCH_3$, 781-35-1; Ph_2CO, 119-61-9; $Ph_2CHC(CH_3)(N_3)OSi(CH_3)_3$, 91633-24-8; $PhCH_2COCH_3$, 103-79-7; $PhCH(CH_3)CHO$, 93-53-8; $PhCOCH_2CH_3$, 93-55-0; 1-phenylcyclohexene, 771-98-2; 1-phenylcyclopentene, 825-54-7; 5-cholestene, 570-74-1; methylenecyclohexane, 1192-37-6; 2-isopropenyl-5-methylcyclohexanol, 7786-67-6; 1-[(trimethylsilyl)oxy]cyclohexene, 6651-36-1; 1-chloro-1-methylcyclohexane, 931-78-2.

Cyclizations of ω-Alkynyl Halides by Cr(II) Reduction[1]

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Received May 16, 1984

Reduction of halides of the types $RC{\equiv}C(CH_2)_nX$ with Cr(II) in aqueous DMF containing ethylenediamine proceeds by way of the intermediate radicals which cyclize regioselectively in the $n = 4$ and $n = 5$ cases to give substituted methylenecycloalkanes. Experimental conditions which favor longer lifetimes for the intermediate radicals (low concentrations, slow addition times, and an inverse-addition mode) result in increased cyclization. The iodides curiously give more cyclic product than the corresponding bromides. These results are discussed.

Cyclizations of free radicals possessing remote unsaturation have been studied in some detail, particularly in the olefinic series where a good understanding of the potential and limitations of these reactions has been achieved, in-

0022-3263/84/1949-4244$01.50/0