lected were dried ($MgSO_4$) and concentrated. The solid residue **15** was recrystallized from ether: mp 230 °C dec; yield, 40%; mass spectrum, $M^+$ $m/e$ 333; IR (KBr) $\nu$(C═C) 1650 $cm^{-1}$ (weak); Anal. found: C, 74.37; H, 12.45; N, 12.45; $H_2O$, 1.7. $C_{21}H_{39}N_3$ + 1.7% $H_2O$ requires: C, 74.3; H, 12.0; N, 12.4.

**X-ray Structure Determination of 5a ($C_{24}H_{30}N_2$).** The crystallographic data are as follows: triclinic, $P\bar{1}$, $a$ = 5.893 (1) Å, $b$ = 12.825 (3) Å, $c$ = 14.199 (3) Å, $\alpha$ = 96.15 (2)°, $\beta$ = 100.28 (2)°, $\gamma$ = 99.16 (2)°, $V$ = 1032.2 (4) $Å^3$, $D_x$ = 1.12 g $cm^{-3}$ for $Z$ = 2. A total of 2796 independent reflections were measured (Syntex $P2_1$ diffractometer, graphite monochromatized Cu K$\alpha$ radiation, $2\theta_{max}$ = 114°) of which 2457 with $I \geq 2.5\sigma$ ($I$) were considered as having been observed. The structure was solved by direct methods using MULTAN80.[24] The H atoms were located in computed positions. Anisotropic least-squares refinement was carried out with the SHELX76 program.[25] The H atoms were refined with an overall isotropic temperature factor ($B$ = 6.7 $Å^2$). The final conventional $R$ index was 0.051. The lists of final atomic coordinates, atomic thermal parameters, and molecular dimensions have been deposited as supplementary material.

**Registry No. 3a**, 50743-11-8; **3b**, 111583-31-4; **3c**, 63742-29-0; **3d**, 26149-14-4; **3e**, 111583-32-5; **3f**, 71804-62-1; **3g**, 111583-33-6; **3h**, 111583-34-7; **3i**, 63742-28-9; **3j**, 111583-35-8; **3k**, 63742-38-1; **4**, 111583-40-5; **5a**, 111583-36-9; **5g**, 111583-37-0; **5h**, 111583-38-1; **5i**, 111583-39-2; **5j**, 111615-34-0; **14**, 4185-21-1; **15**, 111583-41-6; $PhCH_2CN$, 140-29-4; $EtOC(O)CH_2CN$, 105-56-6; $(CH_3)_2CHCN$, 78-82-0; $Ph_2CHCN$, 86-29-3; $ClCH_2CN$, 107-14-2; $CH_3CN$, 75-05-8; $CH_3CH_2CN$, 107-12-0; $CH_3(CH_2)_2CN$, 109-74-0; $CH_3(CH_2)_3CN$, 110-59-8; $CH_3(CH_2)_7CN$, 2243-27-8; $CH_2$═$CHCH_2CN$, 109-75-1; $t$-BuCl, 507-20-0; $i$-PrCl, 75-29-6; isobutyronitrile, 78-82-0; piperidine, 110-89-4.

**Supplementary Material Available:** Tables of atomic coordinates, thermal parameters, and bond lengths and angles for **5a** (3 pages). Ordering information is given on any current masthead page.

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(24) Main, P.; Fiske, S. J.; Hull, S. E.; Lessinger, L.; Germain, G.; Declercq, J. P.; Woolfson, M. M. "MULTAN80: A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data"; Universities of York, England, and Louvain-la-Neuve, Belgium, 1980.

(25) Sheldrick, G. M. SHELX76: Program for Crystal Structure Determination; University of Cambridge, England, 1976.

(26) Motherwell, S.; Clegg, W. "PLUTO"; University of Cambridge, England, 1978.

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# TiCl$_4$-Catalyzed Addition of HN$_3$ to Aldehydes and Ketones. Thermolysis and Photolysis of $\alpha$-Azido Ethers[1]

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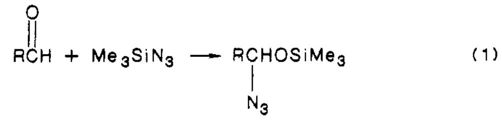
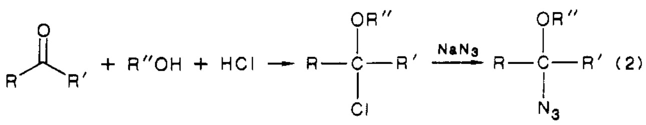
Aldehydes react with hydrazoic acid and alcohols in the presence of catalytic amounts of $TiCl_4$ to produce $\alpha$-azido ethers. The conversion of simple ketones to methyl $\alpha$-azido alkyl ethers can be accomplished by means of hydrazoic acid and methyl orthoformate. Both gas-phase thermolysis and photolysis of representative $\alpha$-azido ethers were studied and shown to produce mainly imino ethers. In the thermolysis, migratory preference decreases in the series H ≫ $CH_3$ > Ph ≫ OR.

## Introduction

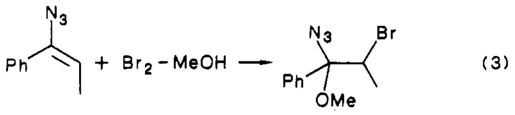
Compared to other organic azides, azido ethers represent a little studied class of compounds.[2] The two known methods of synthesis of azido ethers are addition of trimethylsilyl azide to aldehydes (eq 1) and azide substitution on $\alpha$-halo ethers (eq 2). However, these methods are not free of shortcomings. Trimethylsilyl azide reacts well with aldehydes but does not add to ketones;[3-5] furthermore, one is limited to formation of the trimethylsilyl ether. The reaction of $\alpha$-halo ethers with azide ions is applicable to both aldehydes and ketones but the method necessitates first the synthesis of $\alpha$-halo ethers.[6]



$$\overset{\mathrm{O}}{\overset{\|}{\mathrm{RCH}}} + \mathrm{Me_3SiN_3} \longrightarrow \underset{\underset{\mathrm{N_3}}{|}}{\mathrm{RCHOSiMe_3}} \qquad (1)$$



Another entry into such compounds, specifically into $\beta$-halogenated $\alpha$-azido ethers, involves addition of bromine in methanol to vinyl azides (eq 3).[7]



Recently, we found that $HN_3$ addition proceeds readily to enol ethers (eq 4) as well as to silyl enol ethers, although in the latter case the products were sometimes a mixture of azide and carbonyl compound (eq 5).[8] To other alkenes, $HN_3$ adds only in the presence of Lewis acids, preferably $TiCl_4$.[8]

**Synthesis of Azido Ethers from Aldehydes.** Though $HN_3$ does not react with aldehydes readily, we now report that this can be facilitated by addition of catalytic amounts of $TiCl_4$. For instance, when 0.05 equiv of $TiCl_4$ was added

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(1) Synthetic Methods. 25. For paper 24, see: Hassner, A.; Murthy, K. K. S. *Tetrahedron Lett.* **1987**, *28*, 683.

(2) Biffrin, M. F. C.; Miller, J.; Paul, D. B. *The Chemistry of The Azido Group*; Patai, S., Ed.; Wiley: London, 1971; Chapter 2.

(3) Birkofer, L.; Kaiser, W. *Justus Liebigs Ann. Chem.* **1975**, 266.

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(8) Hassner, A.; Fibiger, R. F.; Andisik, D. *J. Org. Chem.* **1984**, *49*, 4237.

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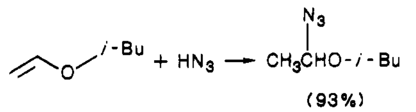
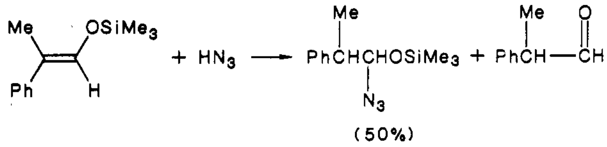
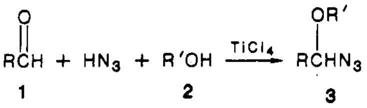


$$CH_2{=}CHO\text{-}i\text{-}Bu + HN_3 \rightarrow CH_3CH(N_3)O\text{-}i\text{-}Bu \quad (93\%)$$ (4)



$$Me(Ph)C{=}CH(OSiMe_3) + HN_3 \rightarrow PhCH(Me)CH(N_3)OSiMe_3 + PhCH(Me)CHO \quad (50\%)$$ (5)

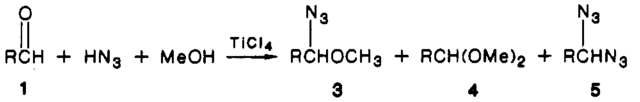
to a mixture of 1 equiv of aliphatic aldehyde **1**, an excess of $HN_3$, and an excess of alcohol **2**, azido ethers **3** were obtained in good to excellent yields (see Table I). Benzaldehyde reacted poorly to give little or no azido ether.



$$\underset{\mathbf{1}}{RCHO} + HN_3 + \underset{\mathbf{2}}{R'OH} \xrightarrow{TiCl_4} \underset{\mathbf{3}}{RCH(OR')N_3}$$

**a**, R = $Ph_2CH$, R′ = Me
**b**, R = $C_9H_{19}$, R′ = Me
**c**, R = $C_9H_{19}$, R′ = Et
**d**, R = Et, R′ = Me
**e**, R = *i*-Pr, R′ = Me
**f**, R = PhCH(Me), R′ = Me

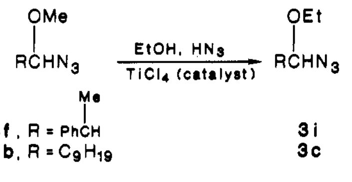
Depending on reaction conditions, the dimethyl acetal **4** or the diazide **5** was observed as a side product. The amount of side products can be controlled by using appropriate ratios of $HN_3$ and MeOH, as was demonstrated with diphenylacetaldehyde (**1a**) and decanal (**1b**) as substrates (see Table I). Increased amounts of MeOH lead to more acetal **4**, while a larger $HN_3$/MeOH ratio produced diazide **5**. For this reason, we adopted an optimum ratio of aldehyde/MeOH/$HN_3$ of 1:3:9 in the synthesis of the α-azido ethers **3**.



$$\underset{\mathbf{1}}{RCHO} + HN_3 + MeOH \xrightarrow{TiCl_4} \underset{\mathbf{3}}{RCH(N_3)OCH_3} + \underset{\mathbf{4}}{RCH(OMe)_2} + \underset{\mathbf{5}}{RCH(N_3)N_3}$$

A plausible mechanism that rationalizes formation of the products in illustrated in Scheme I; the catalytic species could be $TiCl_4$, $TiCl_2(OMe)_2$, $TiCl_2(N_3)_2$, or another mixed Ti species. Alternatively, HCl (formed in the reaction of $TiCl_4$ with MeOH or $HN_3$) could be the catalyst, but this appears less likely since addition of 1 equiv of 2,6-di-*tert*-butylpyridine did not inhibit the reaction.

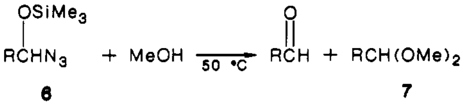
In accord with Scheme I is the fact that the methoxy group of methyl α-azidoalkyl ethers **3a** and **3b** can be exchanged in the presence of ethanol, $TiCl_4$, and $HN_3$ to form ethyl α-azido ethers **3i** and **3c** in 90% and 94% yield.



$$RCH(OMe)N_3 \xrightarrow[TiCl_4\ (catalyst)]{EtOH,\ HN_3} RCH(OEt)N_3$$

**3f**, R = PhCH(Me) → **3i**
**3b**, R = $C_9H_{19}$ → **3c**

No exchange occurred in the absence of $TiCl_4$, but the presence of $HN_3$ was necessary; otherwise significant amounts (20%) of acetal was formed. The ether exchange is a useful reaction in view of Birkofer's findings that trimethyl silyl ethers **6** reacted with methanol to regenerate aldehyde and form small amounts of acetal **7**.[3]



$$\underset{\mathbf{6}}{RCH(OSiMe_3)N_3} + MeOH \xrightarrow{50\ °C} RCHO + \underset{\mathbf{7}}{RCH(OMe)_2}$$

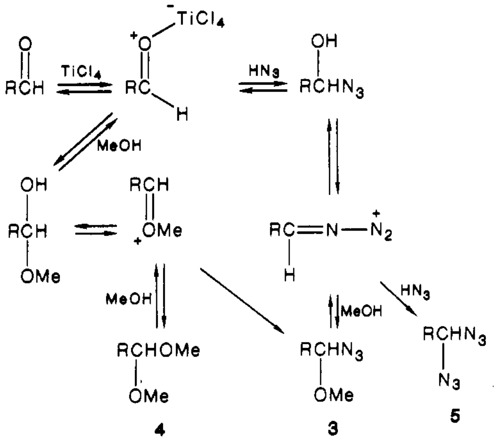
**Synthesis of Azido Ethers from Ketones.** Exposure of cyclohexanone or of 4-heptanone to the same reaction conditions ($HN_3$–$TiCl_4$–MeOH) as the aldehydes **1** did not yield azido ethers. Instead, tetrazole **8** was isolated from cyclohexanone, while amide **9**, a Schmidt reaction product, resulted from 4-heptanone. Apparently, the additional stabilization of the iminodiazonium intermediate derived from ketones leads to rearrangement rather than trapping by alcohol.

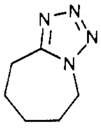
**Table I. Synthesis of α-Azido Ethers 3 from Aldehydes 1[a] and the Effect of MeOH/HN$_3$ Ratio on Formation of Acetal 4 and Diazide 5 Side Products**

| | R | 3 yield, % | MeOH/HN$_3$ | 3/4/5[b] |
|---|---|---|---|---|
| a | $Ph_2CH$ | 84 | 1:4 | 96:4:0 |
| a | $Ph_2CH$ | | 1:2 | 88:12:0 |
| a | $Ph_2CH$ | | 2:1 | 65:35:0 |
| a | $Ph_2CH$ | | 3:1 | 45:55:0 |
| b | $C_9H_{19}$ | 90 | 1:3 | 95:5:0 |
| b | $C_9H_{19}$ | | 1:7 | 67:0:33 |
| b | $C_9H_{19}$ | | 3:5 | 88:12:0 |
| c | $C_9H_{19}$[c] | 90 | | |
| d | $C_2H_5$ | 92 | | |
| e | *i*-Pr | 80 | | |
| f | $Ph_2CH(Me)$ | 75[d] | | |

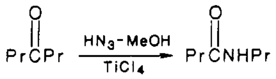
[a] The relative ratio of aldehyde to alcohol was 1:3. [b] Ratio by NMR integration. [c] Ethyl ether instead of methyl ether. [d] see ref 8.

**Scheme I**





**8**



$$PrCOPr \xrightarrow[TiCl_4]{HN_3\text{-}MeOH} PrCONHPr$$

**9**

However, we did succeed in preparing α-azido ethers from ketones by modifying an enol ether synthesis developed by Wohl.[9] According to Wohl, formation of enol ethers can be achieved by reaction of ketones with methyl orthoformate in the presence of *p*-toluenesulfonic acid followed by a tedious separation through a spinning band column.[9] We had shown that $HN_3$ addition to enol ethers proceeds readily (eq 4).[8] We now discovered that if hydrazoic acid was added to the ketones **10** along with the methyl orthoformate and tosic acid, azido ethers **11** were obtained directly in excellent yield (see below).

The reaction was complete in ca. 1 h, and workup was easily accomplished by passing the reaction mixture down a short 3-cm column of alumina. Unfortunately, there are certain limitations on the generality of this reaction. The hindered *tert*-butyl methyl ketone reacted very slowly to give only rearranged products, while acetophenone led to

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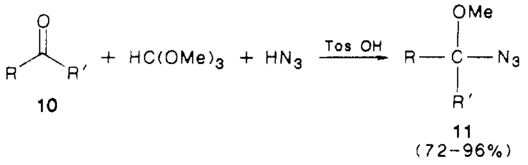
[9] Wohl, R. A. *Synthesis* **1974**, 38.

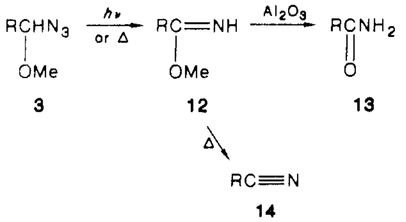


a, R = R′ = $C_2H_5$
b, R = *i*-Pr, R′ = Me
c, R,R′ = $(CH_2)_5$
d, R = Ph, R′ = Me

a diazide and much starting material along with the desired azido ether. Attempts to apply the methyl orthoformate–TosOH method to aldehyde **1e** led only to small amounts of azido ether **3e**, the major products being acetal and diazide.

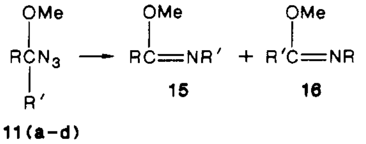
**Photolysis and Thermolysis of Azido Ethers.** There are very few studies of thermolysis of $\alpha$-azido ethers,[3,6] and no photolysis of such compounds has been reported. Boehme et al.[6] studied pyrolysis of some azido ethers derived from formaldehyde and found only hydrogen migration. Birkhofer et al.[34] pyrolyzed trimethylsilyl $\alpha$-azido ethers and observed amide formation with migration of silicon from oxygen to nitrogen. Since the siloxy compound probably represented a special case, it was of interest to examine the migratory aptitudes of substituents in $\alpha$-azido ethers *3* and *11* under both photolytic and pyrolytic conditions.

The pyrolyses were carried out in the vapor phase by passing the compounds at reduced pressure through a 1 in. × 12 in. heated Pyrex tube and trapping the products at −196 °C. The photolyses were achieved by irradiation with 3000-Å light in dilute benzene solution in a quartz vessel. Thermolysis of $\alpha$-azido ether **3f** at 300 °C gave cleanly the imidate **12f**, a product of H migration. The latter was converted to amide **13f** on treatment with deactivated alumina or to the nitrile **14f** on prolonged heating above 100 °C. The imidate **12f** was also the only isolable product from the photolysis reaction. Other aldehyde-derived azido ethers (**3d,e**), likewise, gave imidates **12** as the major product. Nitriles **14** were important byproducts, especially in the photolytic decomposition.



d, R = $C_2H_5$
e, R = $Me_2CH$
f, R = $\underset{\mathrm{Me}}{\mathrm{PhCH}}$

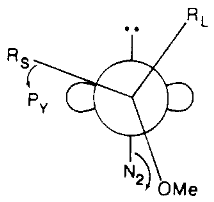
In the case of symmetrical ketone-derived azido ethers **11a** and **11c**, both thermolysis and photolysis led to imidates **15** by alkyl migration, with photolysis yields being essentially quantitative.



During thermolysis (360 °C) of the unsymmetrical azido ether **11b** (R = *i*-Pr, R′ = Me), methyl migration dominated over isopropyl migration, with a 3:1 ratio of **15b**/**16b**, but both were equally effective during photolysis. Similarly methyl migration was preferred over phenyl migration in the thermolysis of **11d** at 330 °C (**15d**/**16d** = 2:1). No methoxy migration was observed.

The preference for hydrogen over alkyl migration agrees with previous observations.[6,10] However, in $\alpha$-azido ketones,[10] phenyl migration predominated over methyl migration, while in our $\alpha$-azido ethers the opposite occurred. In thermolysis of tertiary alkyl azides[11] mainly intramolecular nitrene trapping products had been obtained, and the small amounts of imine formed indicated a migratory preference of Ph/Me of 1.9. Photolysis of such azides showed a Ph/Me preference of 0.75 and was interpreted as proceeding by loss of $N_2$ with concomitant group migration.[12] In thermolysis of $\alpha$-azido thioethers, sulfur migration occurred in preference to H or Ph migration.[13] Though in our $\alpha$-azido ethers oxygen migration was not observed, the alkoxy group appears to have a profound effect on the mode of decomposition of these azides.

Of the two major pathways that have been advanced for 1,2-migrations during alkyl azide decomposition, (a) concerted loss of nitrogen with 1,2 migration[14,15] and (b) formation of a discreet nitrene intermediate followed by migration,[11] we feel that the picture developed by Kyba and Abramovitch[12] may be applicable to explain our results. For the thermolysis of **3** and **11**, we assume that the lone electron pair on N is smaller than N═N and that a lone pair–methoxy interaction is unfavorable because of electron repulsion; hence, the preferred ground state conformation should be as shown in **17** (where $R_S$ = small group, $R_L$ = large group). Overlap between the bonding orbital of the migrating group $R_S$ and the electron-deficient $P_Y$ orbital of N from which $N_2$ departs, predicts a predominance of H migration, which is observed. Methyl migration should be favored over isopropyl or phenyl migration, which is also observed.



**17**

The equal facility of Me vs Ph and Me vs *i*-Pr migration during photolysis of azido ethers **11b** and **11d** may indicate a discrete nitrene intermediate in these instances. Photolysis of **11d** in the presence of the triplet sensitizer acetophenone did not change the ratio of methyl to phenyl migration, but the reaction time was increased by a factor of three, which may indicate involvement of a singlet nitrene in these reactions. Further work is in progress to shed light on these transformations and to exploit their synthetic potential.

## Experimental Section

Melting points (taken on Fisher-Johns block) are uncorrected. Infrared spectra were recorded on a Perkin-Elmer PE-457 spectrometer. $^1H$ NMR spectra were recorded on a Varian EM 360 (60 MHz) or Bruker AM 300 (300 MHz) spectrometer using TMS as an internal standard. Chemical shifts are reported in

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[10] Boyer, J. H.; Straw, D. *J. Am. Chem. Soc.* **1952**, *74*, 4506; **1953**, *75*, 2683.

[11] Abramovitch, R. A.; Kyba, E. P. *J. Am. Chem. Soc.* **1974**, *96*, 480.

[12] Kyba, E. P.; Abramovitch, R. A. *J. Am. Chem. Soc.* **1980**, *102*, 735.

[13] Jarvis, B. B.; Nicholas, P. E.; Midiwo, J. O. *J. Am. Chem. Soc.* **1981**, *103*, 3878.

[14] Abramovitch, R. A.; Kyba, E. P. *J. Am. Chem. Soc.* **1971**, *93*, 1537.

[15] Moriarty, R. M.; Reardon, R. C. *Tetrahedron* **1970**, *26*, 1379.

$\delta$ downfield from TMS, and coupling constants are given in Hz. The following notations are used for multiplicity: s, singlet; d, doublet; t, triplet; q, quartet; br s, broad singlet; m, multiplet. $^{13}$C NMR spectra were recorded at 75.5 MHz on a Bruker AM 300 instrument. Mass spectra were taken on a Varian M.A.T. CH-5 or Finnigan-4021 instrument. Gas chromatographic analyses were carried out on a Varian Aerograph 200. Elemental analyses were performed by Atlantic Microlab Inc, Atlanta, GA, or at the Hebrew University, Jerusalem. Commercially available reagents and solvents were usually reagent grade and distilled or recrystallized prior to use. Purification by distillation was deemed unsafe for most liquid azides; hence spot checks on elemental analyses were performed.

**Formation of Azido Ethers from Aldehydes. General Procedures.** The aldehyde (8 mmol) and the alcohol (30 mmol) were mixed in methylene chloride (50 mL), which was 1.7 N in hydrazoic acid (85 mmol)[7] followed by addition of titanium tetrachloride (0.3 mmol). The reaction mixture was stirred at room temperature for 3 h and then passed down a 3 cm × 3 cm column of alumina, by eluting with methylene chloride. The solvent was removed to yield the product, as a colorless oil, which generally contained 5–10% aldehyde and 5% acetal as impurities. In some cases these impurities were separated from azido ether by careful distillation through a spinning-band column and usually were found in the early fractions from the distillation.

**1-Azido-2,2-diphenyl-1-methoxyethane (3a)** was prepared as a colorless liquid from 2,2-diphenylethanal (MeOH, 84%): IR (liquid film), 3065, 3035, 2980, 2940, 2110, 1580, 1480, 1440, 1032, 757, and 703 cm$^{-1}$; $^1$H NMR (CDCl$_3$) $\delta$ 7.30 (br s, 2 Ph, 10 H), 4.97 (d, $J$ = 7.5 Hz, C-2, 1 H), 4.28 (d, $J$ = 7.5 Hz, C-1, 1 H), 3.42 (s, OCH$_3$); MS, $m/e$ (relative intensity) 226 (1), 225 (M − N$_2$, 6.5), 224 (1), 211 (M − N$_3$, 2.6), 210 (M − HN$_3$, 9), 193 (23), 182 (8), 168 (12), 167 (3), 166 (10), 165 (24), 152 (9), 105 (10.5), 86 (12), 84 (18.5), 77 (17), 75 (13), 58 (36), 51 (17), 49 (26), and 43 (100).

**1-Azido-1-methoxydecane (3b)** was prepared as a colorless liquid from decanal (MeOH, 90%): IR (liquid film), 2910, 2860, 2110, 1465, 1380, 1240, and 1110 cm$^{-1}$; $^1$H NMR (CDCl$_3$) $\delta$ 4.28 (t, $J$ = 6 Hz, C-1, 1 H), 3.47 (s, OCH$_3$), and 1.80–0.70 (m, remaining 19 H); MS, $m/e$ (relative intensity) 171 (M − N$_3$, 14), 170 (M − HN$_3$, 8), 124 (18), 73 (32), 71 (100), 68 (44), 57 (38), 55 (54), 54 (34), 43 (66), and 41 (98).

**1-Azido-1-ethoxydecane (3c)** was prepared as a colorless liquid from decanal (EtOH, 90%): IR (liquid film) 2930, 2860, 2110, 1465, 1380, 1345, 1225, 1105, and 780 cm$^{-1}$; $^1$H NMR (CDCl$_3$) $\delta$ 4.33 (t, $J$ = 6 Hz, C-1, 1 H), 3.67 (q, $J$ = 7 Hz, CH$_2$ in Et group), and 1.87–0.6 (m, remaining 19 H); MS, $m/e$ (relative intensity), 186 (13), 185 (M − N$_3$, 87) 171 (21), 155 (21), 101 (100), 98 (31), 86 (17), 84 (63), 70 (48), 58 (44), 56 (52), 44 (65), and 42 (52).

**1-Azido-2-methyl-1-methoxypropane (3e)** was prepared as a colorless liquid from isobutyraldehyde, bp 112 °C (625 mm) (MeOH, 80%): IR (liquid film), broad 2890–2970, 2840, 2110, 1470, 1395, 1385, 1305, 1250, 1225, 1160, 1100, 995, 980, 955, 855, and 760 cm$^{-1}$; $^1$H NMR (CDCl$_3$) 4.06 (d, $J$ = 6 Hz, C-1, 1 H), 3.49 (s, OCH$_3$), 1.94 (d, q, $J$ = 6, 7 Hz, C-2, 1 H), 0.98 (d, $J$ = 7 Hz, 6 H, 2 CH$_3$); $^1$H NMR (C$_6$D$_6$) $\delta$ 3.69 (d, $J$ = 6 Hz), C-1, 1 H), 3.09 (s, OCH$_3$), 1.79 (d, q, $J$ = 6, 7 Hz, C-2, 1 H), 0.87 (d, $J$ = 7 Hz, 6 H, 2 CH$_3$); $^{13}$C NMR (CDCl$_3$) $\delta$ 99.2 (d, C-1), 57.1 (q, OCH$_3$), 33.6 (d, C-2), 17.6 and 17.5 (2 q, 2 CH$_3$); MS, $m/e$ (relative intensity) 101 (M − N$_2$, 10), 100 (12), 87 (M − N$_3$, 2), 86 (M − HN$_3$, 100), 75 (28), 73 (10), 71 (8), 70 (18), 68 (20), 59 (12), 58 (65), 55 (20), 54 (8), 44 (12), 43 (65), 42 (26), 41 (50), and 39 (20). Anal. Calcd for C$_5$H$_{11}$ON$_3$: C, 46.49; H, 8.58; found C, 46.33; H, 8.36.

**1-Azido-1-methoxypropane (3d)** was prepared as a colorless liquid from propanal, bp 100–105 °C (625 mm) (MeOH, 92%): IR (liquid film) 2950, 2850, 2110, 1470, 1370, 1260, 1220, 1200, 1140, 1090, 920, and 845 cm$^{-1}$; $^1$H NMR (CDCl$_3$) $\delta$ 4.25 (t, $J$ = 6 Hz, C-1, 1 H) 3.48 (s, OCH$_3$), 1.77 (d, q, $J$ = 6, 8 Hz, C-2, 2 H), and 0.97 (t, $J$ = 8 Hz, C-3, 3 H); MS, $m/e$ (relative intensity) 87 (M − N$_2$, 24), 86 (28), 73 (M − N$_3$, 100), 58 (29), 54 (32), 56 (25), 45 (16), and 41 (41).

**Exchange of Ether Groups. Conversion of 3a into 1-Azido-2,2-diphenyl-1-ethoxyethane (3i).** Azido ether **3a** (0.50 g, 2.0 mmol) and ethanol (3.0 g, 65 mmol) were mixed in chloroform (25 mL), which was 2.3 N in hydrazoic acid (58 mmol), followed by the addition of titanium tetrachloride (0.1 g, 0.5 mmol). The reaction mixture was stirred for 3 h and then passed down a 3 cm × 3 cm column of alumina, by eluting with chloroform. Removal of the solvent yielded the ethyl ether **3i**[8] (0.52 g, 97%) as a clear liquid with less than 10% of the acetal and no methyl ether as impurities.

**Conversion of 3a into 3i without Hydrazoic Acid Present.** Azido ether **3a** (0.65 g, 2.6 mmol) and ethanol (0.83 g, 18 mmol) were mixed in methylene chloride (25 mL), followed by the addition of titanium tetrachloride (0.05 g, 0.25 mmol). The reaction mixture was stirred at room temperature for 4 h and then passed down a 3 cm × 3 cm column of alumina, by eluting with methylene chloride. The solvent was removed to yield 0.67 g of a mixture of the azido ether **3i** and diphenylethanal diethyl acetal (80:20 by NMR), as a colorless liquid.

**Conversion of 3b into 3c.** Azido ether **3b** (0.44 g, 2 mmol) and ethanol (1 g, 21 mmol) were mixed in methylene chloride (25 mL), which was 1.7 N hydrazoic acid (43 mmol), followed by the addition of titanium tetrachloride (0.05 g, 0.25 mmol). The reaction mixture was stirred for 2.5 h and then passed down a 2 cm × 3 cm column of alumina, by eluting with methylene chloride. Removal of the solvent yielded azido ether **3c** (0.45 g, 98%) as a colorless liquid which contained (by NMR) no methyl ether and only 6% of the diethyl acetal as an impurity.

**Formation of Tetrazole 8.** Cyclohexanone (1.0 g, 10 mmol) and methanol (2 g, 62 mmol) were mixed in chloroform (50 mL), which was 1.7 N in hydrazoic acid (85 mmol), followed by the addition of titanium tetrachloride (0.50 g, 2.6 mmol). The reaction mixture was stirred at room temperature for 20 h, followed by the addition of excess water. The layers were separated, and the organic layer was dried over sodium sulfate. Removal of solvent yielded a yellow liquid (2.2 g). The addition of petroleum ether bp 40–60 °C left a yellow solid, which on trituration with petroleum ether and chloroform yielded tetrazole **8** (0.53 g, 40%), mp 53–54 °C, identical with an authentic sample.[16]

**Reaction of 4-Heptanone with HN$_3$.** 4-Heptanone (1.0 g, 8.8 mmol) and methanol (1.5 g, 47 mmol) were mixed with chloroform (50 mmol), which was 1.7 N in hydrazoic acid (85 mmol), and titanium tetrachloride (0.50 g, 2.6 mmol) was added to the solution. The reaction mixture was stirred for 48 h at room temperature, followed by the addition of excess water. After 10 min the layers were separated, and the organic layer was dried over sodium sulfate and the solvent removed to yield a clear oil (1.31 g), identified as $N$-propylbutyramide (**9**), by $^1$H NMR, IR, and MS (70% yield).

**The Synthesis of Azido Ethers from Ketones. General Procedure.** The ketone (20 mmol) and methyl orthoformate (20 mmol) were mixed in methylene chloride (35 mL), which was 1.5 N in hydrazoic acid (52 mmol), followed by the addition of $p$-toluenesulfonic acid (0.01 mmol). The solution was stirred at room temperature for 4 h and then passed down a 4 cm × 3 cm column of alumina, by eluting with methylene chloride. Removal of the solvent yielded the azido ether as a colorless liquid with 4–9% of the dimethyl ketal as an impurity (by NMR).

**1-Azido-1-methoxycyclohexane (11c)** was prepared as a colorless liquid from cyclohexanone. The yield was 86% with 4% of the ketal as an impurity: IR (liquid film) 2940, 2865, 2110, 1450, 1250, 1195, 1160, 1100, 1040, 910, 860, and 835 cm$^{-1}$; $^1$H NMR (CDCl$_3$) $\delta$ 3.27 (s, OCH$_3$), 2.27 (t, $J$ = 6 Hz, C-2 and C-6, 4 H), 1.35–1.83 (m, 6 H); $^{13}$C NMR (CDCl$_3$) $\delta$ 94.0 (s, C-1), 49.2 (q, OCH$_3$), 41.8 (t, C-2 and C-6) 33.7 (t, C-3 and C-5), 26.9 (t, C-4); MS, $m/e$ (relative intensity) 127 (M − N$_2$, 28), 113 (53), 112 (69), 111 (53), 97 (44), 84 (81), 43 (100), and 41 (87).

**3-Azido-3-methoxypentane (11a)** was prepared as a colorless liquid from 3-pentanone. The yield was 91% with 9% ketal as an impurity: IR (liquid film) 2980, 2960, 2900, 2860, 2110, 1465, 1250, 1170, 1125, 1095, and 895 cm$^{-1}$; $^1$H NMR (C$_6$D$_6$) $\delta$ 3.04 (s, OCH$_3$), 1.55 (q, $J$ = 7 H$_2$, C-2 and C-4, 4 H), 0.73 (t, $J$ = 7 Hz, C-1 and C-5, 6 H); $^{13}$H NMR (C$_6$D$_6$) $\delta$ 96.9 (s, C-3), 48.5 (q, OCH$_3$), 26.2 (t, C-2 and C-4), 6.9 (q, C-1 and C-5); MS, $m/e$ (relative intensity) 115 (M − N$_2$, 28), 114 (11), 101 (44), 100 (100), 71 (98), 58 (50), 57 (67), 56 (56), 55 (61), 43 (67), and 41 (78).

**2-Azido-2-methoxy-3-methylbutane (11b)** was prepared as a colorless liquid from 3-methyl-2-butanone. The yield was 85% with 5% of the ketal as an impurity: IR (liquid film) 2960, 2840,

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[16] Nishiyama, K.; Watanabe, A. *Chem. Lett.* **1984**, 455.

2110, 1465, 1385, 1250, 1150, 1085, and 850 cm$^{-1}$; $^{1}$H NMR ($\mathrm{CDCl_3}$) $\delta$ 3.33 (s, $\mathrm{OCH_3}$), 2.02 (q, $J$ = 7 Hz, C-3, 1 H), 1.28 (s, C-1, $\mathrm{CH_3}$), 0.96 and 1.00 (2 d, $J$ = 7 Hz, 2 $\mathrm{CH_3}$); $^{13}$C NMR ($\mathrm{CDCl_3}$) $\delta$ 97.8 (s, C-2), 49.9 (q, $\mathrm{OCH_3}$) 35.1 (d, C-3), 17.3 (q, $\mathrm{CH_3}$), 17.1 (q, $\mathrm{CH_3}$), 16.6 (q, $\mathrm{CH_3}$); MS, $m/e$ (relative intensity) 115 (M − $\mathrm{N_2}$, 23), 100 (77), 85 (100), 72 (53), 55 (43) 53 (23), 43 (73) 42 (57), and 41 (27).

**Addition of $\mathrm{HN_3}$ to Acetophenone.** Acetophenone (1.0 g, 8.3 mmol) and methyl orthoformate (1.0 g, 9.4 mmol) were mixed in methylene chloride (20 mL), which was 2.0 N in hydrazoic acid, followed by the addition of *p*-toluenesulfonic acid (0.01 g, 0.05 mmol). The solution was stirred at room temperature for 6.5 h, followed by the addition of water. After 5 min of stirring, the layers were separated, and the organic layer was dried over sodium sulfate and the solvent removed to yield a yellow liquid (1.33 g). $^{1}$H NMR and IR showed this to be a mixture of starting material (30%), (1-azido-1-methoxyethyl)benzene (**11d**) (43%) and diazide (28%). The presence of diazide was inferred from the aromatic $^{1}$H integration and a third methyl absorption at $\delta$ 1.77.

**Photolysis of Azido Ethers. General Procedure.** The azido ether (6 mmol) was mixed with spectral grade benzene (60 mL) and irradiated with 300-nm light in a Rayonet reactor until all of the starting material had disappeared, as indicated by NMR. The product was isolated by removing the solvent. Volatile products were not isolated, but their spectra (NMR and IR) were compared with authentic samples or with samples obtained from the thermolysis of the same azido ethers.

**Thermolysis of Azido Ethers. General Procedure.** In general, the azido ether (5–10 mmol) was placed in the round-bottom flask, and a vacuum (0.1–0.3 mmHg) was applied to the system. As the vacuum was being applied, the azido ether was either heated or cooled, to control the rate of evaporization, so that all of the azido ether passed through the heated 12-in. tube in a Lindberg Mini-Mite furnace during approximately 30 min. The products of the thermolysis were collected in a liquid nitrogen trap. Because of the large amount of dead space after the oven, not all of the product was recovered in the bottom of the trap. This may explain the less than quantitative recovery of products. Isomeric imidates were difficult to separate by distillation or chromatography.

**Photolysis of Azido Ether 3f.** The photolysis took 3 days to give methyl 2-phenylpropanimidate (**12f**) (78%) bp 120–126 °C (24 mmHg); IR (liquid film) 3090, 3070, 2980, 2950, 1655, 1605, 1500, 1460, 1445, 1390, 1360, 1295, 1265, 1235, 1200, 1190, 1090, 965, 860, 780, and 717 cm$^{-1}$; $^{1}$H NMR ($\mathrm{CDCl_3}$) $\delta$ 7.67 (br s, NH) 7.20–7.38 (m, Ph, 5 H), 3.71 (s, $\mathrm{OCH_3}$), 3.65 (q, $J$ = 7 Hz, C-2, 1 H), 1.48 (d, $J$ = 7 Hz, $\mathrm{CH_3}$); $^{13}$C NMR ($\mathrm{CDCl_3}$) $\delta$ 175.0 (s, C-1), 141.2 (s, Ph), 128.4 (d, Ph), 126.4 (d, Ph) 126.0 (d, Ph), 52.9 (q, $\mathrm{OCH_3}$), 42.7 (d, C-2), 18.6 (q, $\mathrm{CH_3}$); MS, $m/e$ (relative intensity) 163 (61), 162 (12), 149 (10), 148 (45), 120 (6), 107 (6), 106 (25), 105 (100), 91 (40), 85 (10), 75 (22), 58 (12). Anal. Calcd for $\mathrm{C_{10}H_{13}ON}$: C, 73.59; H 8.03. Found: C, 73.90; H, 7.66.

Heating imidate **12f** at 160 °C for 44 h caused a 60% conversion to 1-phenylpropionitrile. When imidate **12f** was chromatographed on alumina, by eluting with methanol, 2-phenylpropionamide was isolated, mp 86–88 °C (20%).

**Thermolysis of Azido Ether 3f to Imidate 12f.** The azido ether was heated to 55 °C and the column to 300 °C. The vacuum was 0.04 mmHg, and the thermolysis took 3 h to yield pure imidate **12f** as a colorless oil (86%).

**Photolysis of Azido Ether 3e.** The reaction was run for 2 days. Methyl 2-methylpropanimidate (**12e**) and isobutyronitrile were obtained in a 2.5:1 ratio (95% yield). The imidate was identified by its characteristic spectra (see thermolysis of **3e**), and the nitrile was identified by comparison with an authentic sample.

**Thermolysis of Azido Ether 3e.** The azido ether was cooled to −15 °C to lower its volatility so that vacuum (0.1 mmHg) could be applied to the system. The column temperature was 320 °C, and the thermolysis took 30 min. The sole product isolated was imidate **12e** (74%): IR (liquid film) 3100–3700, 2980, 2880, 1640, 1470, 1445, 1390, 1360, 1280, 1200, 1182, 1090, 990, 910, and 857 cm$^{-1}$; $^{1}$H NMR ($\mathrm{C_6D_6}$) $\delta$ 7.37 (br s, NH), 3.67 (s, $\mathrm{OCH_3}$), 2.21 (q, $J$ = 7 Hz, C-2, 1 H), 0.90 (d, $J$ = 7 Hz, 2 $\mathrm{CH_3}$); $^{13}$C NMR ($\mathrm{C_6D_6}$) $\delta$ 172.6 (s, C-1), 52.0 (q, $\mathrm{OCH_3}$) 34.3 (d, C-2), 19.8 (q, 2 $\mathrm{CH_3}$); MS, $m/e$ (relative intensity) 101 (36), 100 (32), 87 (9), 86 (98), 75 (15), 73 (22), 70 (36), 68 (25.4), 58 (100), 56 (28), 54 (34), 45 (35.6), 44 (63), 43 (49), 42 (59), and 39 (32).

**Photolysis of Azido Ether 3d.** The reaction time was 56 h. Methyl propanimidate **12d**, propanenitrile and unknown compounds were observed in a ratio 50:30:20. The imidate was identified by its characteristic spectra, and the propanenitrile was identified by comparison with an authentic sample. Imidate **12d**: IR (liquid film) 3100–3700 (NH), 1650 (C=N), and 1190 (C–O) cm$^{-1}$; $^{1}$H NMR ($\mathrm{CDCl_3}$) $\delta$ 3.67 (s, $\mathrm{OCH_3}$), 2.26 (q, $J$ = 7 Hz, C-2, 2 H) 1.13 (t, $J$ = 7 Hz, C-3, 3 H); MS, $m/e$ (relative intensity) 87 (82.5) and 58 (100).

**Thermolysis of Azido Ether 3d.** The azido ether was cooled to −14 °C to lower its volatility so that vacuum (0.3 mmHg) could be applied to the system. The column temperature was 370 °C, and the thermolysis took 30 min. A mixture of imidate **12d** and propanenitrile, 61% and 24%, respectively, was collected in the trap.

**Photolysis of Azido Ether 11c.** The photolysis took 40 h to give 2-methoxy-4,5,6,7-tetrahydro-$^{3}$*H*-azepine (**15c**) as the only product (95%): bp 70–72 °C (22 mmHg); IR (liquid film) 2940, 2860, 1670, 1440, 1370, 1345, 1250, 1200, 1155, 1095, 1050, 1010, 995, 815, 760, and 695 cm$^{-1}$; $^{1}$H NMR ($\mathrm{CDCl_3}$) $\delta$ 3.57 (s, $\mathrm{OCH_3}$), 3.42 (m, C-7, 2 H), 2.40 (m, C-3, 2 H), 1.45–192 (m, C-4, C-5, C-6, 6 H); $^{13}$C NMR ($\mathrm{CDCl_3}$) $\delta$ 170.0 (s, C-2), 52.4 (q, $\mathrm{OCH_3}$), 48.6 (t, C-7), 32.1 (t, C-3), 31.2 (t), 27.9 (t), 23.4 (t); MS, $m/e$ (relative intensity) 128 (8), 127 (52), 126 (20), 112 (100), 99 (30), 98 (30), 84 (21), 69 (44), 55 (46), and 54 (42). Anal. Calcd for $\mathrm{C_7H_{13}NO}$: C, 66.10; H, 10.30. Found: C, 65.82; H, 9.98.

**Thermolysis of Azido Ether 11c.** The azido ether was vaporized at room temperature under reduced pressure (0.3 mmHg) and passed through the column (300 °C) in 35 min to give imino ether **15c** (83%) as the only product.

**Photolysis of Azido Ether 11a.** The photolysis took 46 h and gave methyl *N*-ethylpropanimidate (**15a**) as the only product (100%): IR (liquid film) 2980, 1675, 1440, 1290, 1235, 1100, and 1085 cm$^{-1}$; $^{1}$H NMR ($\mathrm{C_6D_6}$) $\delta$ 3.67 (s, $\mathrm{OCH_3}$), 3.18 (q, $J$ = 7 Hz, *N*-ethyl, $\mathrm{CH_2}$), 2.20 (q, $J$ = 7 Hz, *C*-ethyl, $\mathrm{CH_2}$), 1.24 (t, $J$ = 7 Hz, *N*-ethyl, $\mathrm{CH_3}$), 1.00 (t, $J$ = 7 Hz, *C*-ethyl, $\mathrm{CH_3}$); $^{13}$C NMR ($\mathrm{C_6D_6}$) $\delta$ 173.2 (s, C=N), 51.0 (q, $\mathrm{OCH_3}$), 41.93 (t, *N*-ethyl, $\mathrm{CH_2}$), 20.78 (t, *C*-ethyl, $\mathrm{CH_2}$), 16.41 (q, *N*-ethyl, $\mathrm{CH_3}$), 9.78 (q, *C*-ethyl, $\mathrm{CH_3}$).

**Thermolysis of Azido Ether 11a.** The azido ether was vaporized at 4 °C under reduced pressure (0.1 mmHg) and passed through the column (300 °C) in 25 min to give imidate **15a** as the only product (86%).

**Photolysis of Azido Ether 11b.** The photolysis took 4 days and gave a mixture of isopropyl and methyl migrated products **16b** and **15b** in 1.1:1 ratio in 75% yield. Methyl *N*-isopropylacetimidate (**16b**): $^{1}$H NMR ($\mathrm{C_6D_6}$) $\delta$ 3.67 (s, $\mathrm{OCH_3}$), 2.69 (sept, $J$ = 6 Hz, 1 H), 1.61 (s, $\mathrm{CH_3}$), 1.03 (d, $J$ = 6 Hz, isopropyl, 2 $\mathrm{CH_3}$). Methyl *N*,2-dimethylpropanimidate (**15b**): $^{1}$H NMR ($\mathrm{C_6D_6}$) $\delta$ 3.63 (s, $\mathrm{OCH_3}$), 2.99 (s, $\mathrm{NCH_3}$), 1.91 (sept, $J$ = 6 Hz, 1 H), 1.16 (d, $J$ = 6 Hz, isopropyl, 2 $\mathrm{CH_3}$). $^{13}$C NMR [of the mixture **16b** and **15b**] ($\mathrm{C_6D_6}$) $\delta$ 169.3, 166.2, 51.1, 50.8, 48.3, 46.4, 25.9, 23.8, 17.1, 16.7; IR [mixture of **16b** and **15b**] (liquid film) 2960, 1670, 1465, 1270, 1100, and 750 cm$^{-1}$.

**Thermolysis of Azido Ether 11b.** The azido ether was cooled to −60 °C and vaporized under reduced pressure (0.08 mmHg) and passed through the column (330–360 °C) in 2 h to give a mixture of imidates **15b** and **16b** in a ratio 3:1 and in 88% yield.

**Photolysis of Azido Ether 11d.** The photolysis took 137 h and gave imidates **15d** and **16d** in equal portions (90% yield). Methyl *N*-methylbenzimidate **15d**: $^{1}$H NMR ($\mathrm{CDCl_3}$) $\delta$ 7.40 (m, Ph, 5 H) 3.80 (s, $\mathrm{OCH_3}$), and 1.80 (s, $\mathrm{CH_3}$). Methyl *N*-phenylacetimidate (**16d**): $^{1}$H NMR ($\mathrm{CDCl_3}$) $\delta$ 7.40 (m, Ph, 5 H), 3.08 (s, $\mathrm{OCH_3}$), and 2.80 (s, $\mathrm{CCH_3}$). IR [mixture of **15d** and **16d**] (liquid film) 3060, 2950, 1670, 1595, 1438, 1280, 1210, 1110, 1040, 790, 760, and 715 cm$^{-1}$.

**Thermolysis of Azido Ether 11d.** The azido ether was vaporized at room temperature under reduced pressure (0.1 mmHg) through the column (330 °C) over a 3-h period to give imidates **15d** and **16d** (82%), in a ratio of 2:1, respectively.

**Photolysis of Azido Ether 11d with Acetophenone.** The azido ether (0.10 g, 0.56 mmol) and acetophenone (0.19 mmol) were dissolved in benzene (2 mL) and irradiated at 300 nm. The reaction took 215 h to reach 90% completion and gave a 1:1 ratio of methyl and phenyl migrated products **16d** and **15d**, respectively.

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**Registry No.** **1a**, 947-91-1; **1b**, 112-31-2; **1d**, 123-38-6; **1e**, 78-84-2; **3a**, 111238-39-2; **3b**, 111238-40-5; **3c**, 111238-41-6; **3d**, 111238-42-7; **3e**, 111238-43-8; **3f**, 91633-37-3; **3i**, 111238-45-0; **4a**, 51936-06-2; **4b**, 7779-41-1; **5b**, 111238-44-9; **7c**, 933-40-4; **8**, 54-95-5; **9**, 5129-73-7; **10a**, 96-22-0; **10b**, 563-80-4; **10c**, 108-94-1; **10d**, 98-86-2; **11a**, 87272-11-5; **11b**, 111238-47-2; **11c**, 111238-46-1; **11d**, 65501-11-3; **12d**, 20258-22-4; **12e**, 41796-01-4; **12f**, 111238-49-4; **13f**, 1125-70-8; **14d**, 107-12-0; **14e**, 78-82-0; **14f**, 1823-91-2; **15a**, 24433-77-0; **15b**, 111238-50-7; **15c**, 2525-16-8; **15d**, 1775-61-7; **16b**, 111238-51-8; **16d**, 24433-81-6; $HN_3$, 7782-79-8; $Ph_2CHCH(OEt)_2$, 67820-48-8; $Me(CH_2)_8CH(OEt)_2$, 34764-02-8; $Pr_2CO$, 123-19-3; $Et_2C(OMe)_2$, 25636-49-1; *i*-PrC(Me)$(OMe)_2$, 59554-08-4; PhC-$(OMe)(CH_2N_3)N_3$, 111238-48-3.

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# Intramolecular Azide–Olefin Cycloadditions. A Novel Synthesis of 2,5-Dihydrooxazoles[1]

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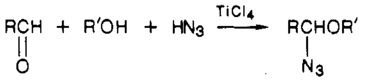
A facile synthetic route from aldehydes to allyl α-azidoalkyl ether **2** is described. Thermolysis of **2** proceeds by intramolecular azide–olefin cycloaddition via triazolines and provides a novel synthesis of 2,5-dihydrooxazoles **6**. The use of silica gel in the chemoselective conversion of the intermediate triazolines to bicyclic aziridines **7** is described.

## Introduction

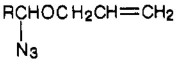
In the accompanying paper,[2] we have shown that α-azido ethers **1** can be prepared from an aldehyde, an alcohol, and hydrazoic acid using titanium tetrachloride as the catalyst (eq 1).



$$\underset{\underset{O}{\|}}{RCH} + R'OH + HN_3 \xrightarrow{TiCl_4} \underset{\underset{N_3}{|}}{RCHOR'} \quad (1)$$

1

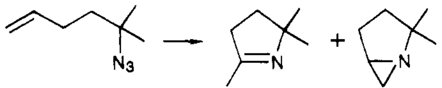
We reasoned that by employing an unsaturated alcohol such as allyl alcohol as the R′OH component, it should be possible to prepare allyl α-azidoalkyl ethers of type **2**, if the olefinic double bond can be made to survive the acid-catalyzed reaction conditions.



$$\underset{\underset{N_3}{|}}{RCHOCH_2CH{=}CH_2}$$

2

Such unsaturated azido ethers are molecules that set the stage for an intramolecular 1,3-dipolar cycloaddition.[3] In fact, Logothetis[4] had studied the thermal intramolecular azide–olefin cycloaddition (IAOC) of 5-azido-5-methyl-1-hexene (**3**) and observed the formation of a mixture of imine **4** and aziridine **5**. Recently we showed that IAOC reactions of azido vinyl β-lactams lead primarily to fused triazolines.[5] Thermolysis of azido ethers in the absence of a double bond produces imidates.[2] Hence, allyl α-azidoalkyl ethers **2** on cyclization should result either in fused triazolines, in imidates, in aziridines, or in the title compounds **6**.



3 4 5

While $\Delta^2$-oxazolines are well-known, their $\Delta^3$-isomers, the 2,5-dihydrooxazoles **6**, are a rare class of compounds, and there are only few methods known for their preparation.[6] A synthetic approach to this class of molecules is also desirable since various substituted 2,5-dihydrooxazoles have been used as artificial flavors.[7]

## Results and Discussion

We herewith report the synthesis of allyl α-azidoalkyl ethers **2** and their utility in a new approach to 2,5-dihydrooxazoles. The reaction of an aldehyde with an allyl alcohol and $HN_3$ in a ratio of 1:3:9 was carried out in the presence of $TiCl_4$, as a catalyst and produced azido ethers **2** in yields of 70–90%. The ratio of reagents is critical[2] to ensure a high yield of azido ether and prevent formation of acetal and diazide side products. These reaction conditions do not affect the olefinic double bond.

The allyl azido ethers **2** were somewhat unstable compounds, but chromatography on basic alumina provided analytically pure samples in many cases. Yields of 70–88% were achieved before chromatography, and the products were pure enough for the cycloaddition step. Intramolecular cycloaddition was studied in chloroform, benzene, and toluene at reflux temperature. Benzene was found to be the solvent of choice, because it gave cleaner products.

Thermolysis of azidoalkenes **2a–g** in benzene for 6–20 h led to 2,5-dihydrooxazoles **6** as the major products in 66–90% yield. In some cases triazolines **8** were observed (by NMR) as byproducts.

Structure proof for oxazolines **6** was provided by $^1H$ and $^{13}C$ NMR, mass spectra, and elemental analysis. For instance, **6a** showed the imino methyl signal at δ 2.08 with

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