CH_3CN (180 mL) at 40 °C was added hexamethyldisilazane (12 mL, 0.057 mol). The mixture was refluxed 20 h, and after removal of NH_3 with vacuum (30 mmHg, 30 min) the solution was used for the preparation of **12a**,**b**.

1-(2-Deoxy-2-fluoro-3,5-di-*O*-benzoyl-D-arabinofuranosyl)thymine (12a,b). The silylation mixture containing **10b** (13.8 g, 0.051 mol) was stirred with a solution of **9** (17.6 g, 0.042 mol) in CH_3CN (30 mL) at reflux 1.5 h. The reaction was quenched in ice–water and extracted with CH_2Cl_2. The extract was washed with water, dried (Mg_2SO_4), and concentrated to give 19.4 g (99% yield) of crude product **12a**,**b** ($\alpha/\beta = 1/3$).[14b] The crude solid was stirred with 50 mL of CH_2Cl_2 and filtered, giving 4.9 g of the β-anomer **12a**: mp 120–122 °C; IR (KBr) 3190 (NH), 1605, 715 (Ar), 1720, 1670 (COOR, CONHCO), 1265 (COOR); ^1H NMR (Me_2SO-d_6) 8.2–7.4 (m, 12 H, Ar H, NH), 6.37 (dd, 1 H, C_1H), 5.68 (dd, 1 H, C_3H), 5.58 (dd, 1 H, $J_{HF} = 50$ Hz, C_2H), 4.69 (m, 3 H, C_4H, C_5H_2), 1.65 (s, 3 H, CH_3). Anal. ($C_{24}H_{21}N_2O_7F$) C, H, N.

1-(2-Deoxy-2-fluoro-β-D-arabinofuranosyl)thymine (β-FMAU; 2a). A slurry of 50% aqueous methanol (220 mL) and the anomeric mixture of dibenzoyl-FMAU (**12a**,**b**) ($\alpha/\beta = 2/3$, 14.5 g, 0.031 mol) was adjusted to pH 10.5 with 3 N NaOH and maintained at that pH for 16 h. The solvent was evaporated and the residue dissolved in water (150 mL), neutralized (pH 6.5–7.0) with concentrated HCl, and evaporated to dryness. Addition of CH_3CN (50 mL) precipitated the inorganic salts, which were removed by filtration. The filtrate was evaporated to yield 7.3 g (90%) of **2a**,**b** ($\alpha/\beta = 2/3$). A sample of the pure β-anomer was obtained by cooling a solution of the mixture in 10 mL of water for 16 h: mp 187–188 °C IR (KBr) 3460, 3400, 3000 (NH, OH), 1690, 1660 (CONHCO), 1035 (C–O); ^1H NMR (CD_3OD) 7.74 (m, 1 H, Ar H), 6.18 (dd, 1 H, C_1H), 5.0 (m, 1 H, $J_{HF} = 50$ Hz, C_2H), 4.32 (m, 1 H, C_3H), 4.0–3.8 (m, 3 H, C_4H, C_5H_2), 1.86 (s, 3 H, CH_3). Anal. ($C_{10}H_{13}N_2O_5F$) C, H, N.

Registry No. **1a**, 69123-98-4; **2a**, 69256-17-3; **2b**, 97672-34-9; **4**, 22224-41-5; **5a**, 7702-26-3; **5c**, 97614-41-0; **5d**, 97614-42-1; **5e**, 97614-50-1; **6**, 97614-43-2; **7** (Y = CH_2CH_2OH), 97614-49-8; **7** (Y = $CH(CH_3)CH(CH_3)OH$), 97614-51-2; **7** (Y = $C(CH_3)_2C(CH_3)_2OH$), 97614-52-3; 8 (Y = CH_2CH_2OH), 94-33-7; 8 (Y = $CH(CH_3)CH(CH[3)OH)$, 59517-16-7; 8 (Y = $C(CH_3)_2C(CH_3)_2OH$), 71380-60-4; **9**, 97614-44-3; **10a**, 38953-72-9; **10b**, 7288-28-0; **11a**, 97614-45-4; **11b**, 97614-46-5; **12a**, 97614-47-6; **12b**, 97614-48-7; 5-iodouracil, 696-07-1; thymine, 65-71-4; 2,3-butanediol, 513-85-9; pinacol, 76-09-5; ethylene glycol, 107-21-1.

Conversion of Alkenes to 1,2-Diazides and 1,2-Diamines

William E. Fristad,* Timothy A. Brandvold,[1a] John R. Peterson,[1b] and Scott R. Thompson

Department of Chemistry, University of Minnesota, Minneapolis, Minnesota 55455

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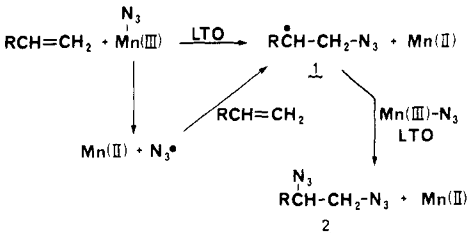
In this paper we wish to report the direct conversion of alkenes into 1,2-diazides as shown in eq 1. This manganese(III) method of vicinal difunctionalization is similar to a method of alkene chlorination reported previously by us[2] and represents one of the very few methods of introducing vicinal diazide functionality. Previously, Fe(III)[3] and Pb(IV)[4a] have been used to convert alkenes to 1,2-diazides, and Pb(IV) has converted 1,3-dienes to 1,4-diazides.[4b] Electrochemical oxidation of the azide anion can also be conducted in the presence of an excess of alkene to generate mono- and diazides in addition to dinitrogen.[5] However, the most common method of introducing vicinal diazides has been via a series of standard S_N2 displacements utilizing the highly nucleophilic azide anion.[6]

$$RCH{=}CH_2 + 2Mn(III) + 2N_3^- + RC(N_3)HCH_2N_3 + 2Mn(II) \quad (1)$$

Scheme I. Proposed Mechanism for Double Azide Addition



We had already demonstrated that manganese(III) acetate hydrate, $Mn_3O(OAc)_7(HOAc){\cdot}5H_2O$, and a chloride salt produced a Mn(III)–Cl species which was capable of oxidatively transferring a Cl ligand directly to an alkene without the intermediacy of free chlorine radicals.[2,7] Because N_3^- has a low E_0 value (variously described as 0.88,[5b] 0.78,[5c] and 0.6[8] V vs. SCE), we felt that it should be easily oxidized and that it may undergo the same type of ligand-transfer oxidation as chlorine or simply add to the alkene as a free $N_3{\cdot}$ radical. Thus the initial step in the mechanism of double azide addition may be either production of azide radicals or a direct ligand-transfer addition to generate the β-azidoalkyl radical 1 (Scheme I). While we did not determine whether free azido radicals were formed by Mn(III) oxidation, several reaction features were noted. If $N_3{\cdot}$ radicals were formed, they were trapped very efficiently by the alkene and did not lead to large amounts of molecular nitrogen. More importantly, Mn(III) oxidation of N_3^- in a control experiment conducted in the absence of alkene required 80 min to go to completion, whereas the identical reaction with stoichiometric 1-octene was complete in 10 min. This rate enhancement necessitates that the alkene be intimately involved in Mn(III) reduction and strongly argues for the ligand-transfer oxidation rather than the intermediacy of free azide radicals. The β-azidoalkyl radical 1 apparently reacts with a second Mn(III)–N_3 species in a typical ligand-transfer[9] fashion to complete the double addition.

Other oxidized metal–azide complexes have previously been shown to thermally[10] or photochemically[11] generate $N_3{\cdot}$ which could be trapped or allowed to dimerize and produce molecular nitrogen. It was anticipated that any Mn(III)–N_3 complex would be very unstable, and therefore

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Table I. Manganese(III) Azidation of 1-Decene

entry	1-decene, M	Mn(III), equiv	NaN_3, equiv	1,2-diazide yield, %	di/monoazide[a] ratio
1	0.2	2.0	2.5	11	1.9
2	0.2	2.0	5.0	11	0.6
3	0.2	2.0	8.0	30	1.0
4	0.2	2.0	12.0	38	1.6
5	0.2	2.0	15.0	42	2.4
6	0.2	3.0	15.0	34	4.4
7	0.2	3.0	20.0	51	5.5
8	0.2	4.0	15.0	34	3.1
9	0.4	3.0	15.0	68	33.7

[a] This ratio was determined by GC integration and was not corrected for the appropriate response factor.

Table II. Preparation of 1,2-Diazides[a]

alkene	reaction temp, °C	trans/cis ratio	isolated diazide, yield, %
1-decene	116		2, 68
(*E*)-4-octene	70		3, 76
5-butyl-4-nonene	80		4, 72
cyclohexene	85	4:1	5, 59
cyclooctene	85	6:1	6, 51

[a] The mole ratio of reactants was alkene:manganese(III) acetate:sodium azide, 1:1:15. This represents a 50% excess of Mn(III) over a perfectly stoichiometric reaction.

no attempts were made to isolate this material from the reaction conditions or to synthesize it in some other way. For comparison, $Cu(N_3)_2$ has been prepared, and it detonates when dry.[12] Manganese(II) azide complexes are known;[13] however, the present method of generating Mn(III)–N_3 species slowly in situ appears to be a simple and safe way of generating a labile complex which performs useful synthetic organic chemistry.

The 1,2-diazides were prepared by heating a brown solution of manganese(III) acetate, sodium azide, and the alkene in glacial acetic acid until the solution turned colorless, which indicated the reduction of Mn(III) to Mn(II). The yield of 1,2-diazide was highly dependent on the reactant concentrations as shown in Table I. The major side product in the reaction was the 1-azidoalkane. This mono addition product was a particular problem at low alkene and Mn concentrations. Presumably monoazide was produced via hydrogen abstraction by radical intermediate **1** rather than further ligand-transfer oxidation to diazide **2**. Higher reactant concentrations (entry 9), however, allowed good selectivity for the double addition product, and these conditions were employed for the synthetic results listed in Table II. The reaction temperature was not crucial as addition proceeded satisfactorily between 116 and 70 °C over the course of 10–30 min. The yields for the double addition were higher than those reported by other methods.[3,5a,6a,14] The material balance was made up of monoazide, triazide, and dimeric products. The mono-, di-, and triazide products were isolated by medium-pressure chromatography and most usefully characterized by IR and chemical ionization mass spectrometry (CI-MS). Electron impact mass spectrometry invariably led to fragmentation and no parent ions could be observed. CI-MS with NH_3 as ionization gas gave characteristic results for mono-, di-, and triazide products which included in the positive ion spectrum ions corresponding to $M + NH_4^+$, $M - N_3^-$, and $M - N_3^- - N_2$ and in the negative ion spectrum $M + N_3^-$ or $M^- - N_2$. The exact nature of the triazide products could not be ascertained from the CI-MS data, and these minor components were not further investigated.

Reduction of 1,2-diazides would constitute a simple two-step route to 1,2-diamines, which are difficult to obtain by other straightforward techniques.[15] Alkylazides have been reduced to amines by a variety of conditions including the following: $NaBH_4$;[16] Pd/C, H_2, $CHCl_3$, EtOH;[17] 1,3-propanedithiol, Et_3N, MeOH;[18] Na, NH_3, MeOH;[19] BH_3·THF;[20] $LiAlH_4$.[21] In our hands reduction of 1,2-diazides proved to be much more problematic, and all the above methods failed to completely reduce 1,2-diazidodecane **2** without polymer formation. Hydrogenation of **2** with Pd/C in acetic acid/acetic anhydride did lead to the formation of the 1,2-diacetamide **7** in 44% yield.[22] Satisfactory reduction of the diazide to the diamine was, however, finally accomplished in 73% crude yield by hydrogenation over Lindlar's catalyst.[23] The diamine was purified as the dibenzamide **8**.[24] Swift and Swern have also shown that Adam's catalyst can be used to reduce 1,2-diazides to the corresponding 1,2-diamine.[6b] Thus, 1,2-diamines can be produced in two steps from the corresponding alkene by double azide addition followed by hydrogenation.

Experimental Section

Melting points were determined with an Electrothermal apparatus and are uncorrected. ^1H NMR spectra were obtained on a Varian HFT-80 (80 MHz). Chemical shifts are reported in parts per million relative to internal $(CH_3)_4Si$ in $CDCl_3$. Mass spectra were obtained with an AE1 Kratos MS-30 (electron impact) or a Finnigan 4000 (chemical ionization) spectrometer. Infrared spectra were obtained on a Beckman 4250 spectrophotometer. Gas chromatography was performed with a Varian 3700 model gas chromatograph equipped with a FID's and a Hewlett-Packard 3390A integrator. The columns used were 5% Carbowax 20M on 100/120 mesh Chromosorb W, 0.3 cm × 6 m, and 10% SF-96 on 80/100 mesh Chromosorb W, 0.3 cm × 6 m. Products were isolated by medium-pressure liquid chromatography (FMI pump, silica gel column, refractive index detector, Altex model 156). Manganese(III) acetate hydrate was prepared by the literature method.[25]

Caution: All reactions employing azides and Mn(III) were conducted in a hood behind a safety shield. We have never experienced problems with *sodium azide/Mn(III) mixtures*, however, care should be exercised with azides and oxidizing agents. An explosion did occur while cooling the *clear solution after diazidation of styrene*. At the time of explosion all the oxidant had been reduced. The cause of this explosion was not further investigated, but the styrene used was a commercial sample inhibited with 4-*tert*-butylcatechol. The expected product 1,2-diazido-1-phenylethane has been previously prepared.[3c] No other

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mishaps occurred in over 50 reactions with other alkenes.

General Procedure for Data in Table I. 1-Decene (5.0 mmol), manganese(III) acetate hydrate, and sodium azide were refluxed in glacial acetic acid at the concentrations specified until the dark brown color had disappeared (<30 min). The reaction was allowed to cool, poured into 30–60 °C petroleum ether, washed with water (2×) and saturated bicarbonate solution, and dried ($MgSO_4$). Yields for entries 1–8 were determined by GC comparison (dodecane internal standard) with the isolated yield of 68% for entry 9.

Representative Procedure for Diazide Formation. 1-Decene (0.50 g, 4.8 mmol), sodium azide (4.46 g, 72 mmol), manganese(III) acetate (3.86 g, 4.80 mmol, 14.4 mequiv of Mn(III)), and glacial acetic acid (25 mL) were placed in a 50-mL, round-bottomed flask equipped with a magnetic stirrer, reflux condenser, and nitrogen inlet. The mixture was heated to 70–116 °C whereupon the salts dissolved. The heating was continued until the solution lightened from dark brown to clear, or light yellow (10–30 min). The mixture was cooled to room temperature, diluted with water (200 mL), and extracted with 30–60 °C petroleum ether (4 × 25 mL). The combined extracts were washed with saturated bicarbonate solution, dried ($MgSO_4$), and evaporated. The residue was chromatographed (5% EtOAc:Hexane) to yield 1,2-diazidodecane **2** (0.73 g, 3.3 mmol, 68%).

1,2-Diazidodecane (2): IR 2930, 2860, 2100, 1470, 1345, 1270 cm^{-1}; ^1H NMR δ 3.3 (br s, 3 H), 1.7–0.7 (m, 17 H); CI-MS (NH_3 ionization gas) for $C_{10}H_{20}N_6$ (positive) $M - N_3^- + NH_3$ 199, $M - 2N_3^- + NH_2^- + NH_3$ 173, $M - 2\,N_3^- + NH_2^-$ 156, (negative) $M + N_3^-$ 266.

4,5-Diazidooctane (3) Mixture of Diastereomers: IR 2960, 2925, 2870, 2110, 1460, 1260 cm–^{1}; ^1H NMR δ 3.3 (m, 2 H), 1.6–0.8 (m, 14 H); CI-MS (NH_3 ionization gas) for $C_8H_{16}N_6$ (positive) $M + NH_4^+$ 214, $M - N_3^- + NH_3$ 171, $M - N_2 + H^+$ 169, $M - 2N_3^- + NH_2^-$ 128, $M - N_3^- - N_2$ 126, (negative) $M + N_3^-$ 238, $M - N_2$ 168.

4,5-Diazido-5-butylnonane (4): IR 2960, 2930, 2880, 2100, 1470, 1250 cm^{-1}; ^1H NMR δ 3.15 (m, 1 H), 2.2–0.7 (m, 25 H); CI-MS (NH_3 ionization gas) for $C_{13}H_{26}N_6$ (positive) $M + NH_4^+$ 284, $M - N_2 + H^+$ 239, (negative) $M + N_3^-$ 308.

1,2-Diazidocyclohexane[5a,6a] **(5)**: 4:1 trans/cis mixture by GC: IR 2940, 2865, 2100, 1260 cm^{-1}; ^1H NMR δ 3.7–3.0 (m, 2 H), 2.3–0.9 (m, 8 H); CI-MS (NH_3 ionization gas) for $C_6H_{10}N_6$ (positive) $M - N_3^- + NH_3$ 266, $M - N_3^- - N_2 + NH_3$ 113, $M - 2N_3^- + NH_2^-$ 98, $M - N_3^- - N_2$ 96, (negative) $M - N_2 = 138$.

1,2-Diazidocyclooctane[5a] **(6)**: 6:1 trans/cis mixture by GC: IR 2930, 2860, 2100, 1465, 1445, 1255 cm^{-1}; ^1H NMR δ 3.75–3.3 (m, 2 H), 1.9–1.1 (m, 12 H); CI-MS (NH_3 ionization gas) for $C_8H_{14}N_6$ (positive) $M + NH_4^+$ 212, $M - N_2 + NH_4^+$ 184, $M - N_3^- + NH_3$ 169, $M - N_2 + H^+$ 167, $M - 2N_2 + H^+$ 139, $M - 2N_3^- + NH_2$ 126, (negative) $M - N_2$ 166, $M - 2N_2 - H^+$ 137.

Preparation of 1,2-Diaminodecane Diacetamide (7). A 25-mL, two-necked flask equipped with two gas valves and a hydrogen filled balloon was charged with **2** (0.50 g, 2.20 mmol), 10% palladium/carbon (0.25 g), glacial acetic acid (12 mL), and acetic anhydride (3 mL). After stirring at 25 °C for 7 h the mixture was filtered, poured onto water (150 mL), and extracted with chloroform (3 × 50 mL). The combined extracts were washed with saturated sodium bicarbonate (50 mL) and brine (50 mL), dried ($MgSO_4$), and evaporated. Trituration of the oil with diethyl ether/30–60 °C petroleum ether afforded a colorless solid which was filtered and washed with 30–60 °C petroleum ether (0.25 g, 0.98 mmol, 44%): mp 136–138 °C; IR 3290, 3095, 2915, 2850, 1630, 1540, 1370, 1290, 750, 715 cm^{-1}; ^1H NMR δ 6.45 (br, 1 H), 6.0 (br, 1 H), 4.1–3.65 (m, 1 H), 3.4–3.05 (m, 2 H), 1.95 (s, 6 H), 1.8–0.7 (m, 17 H).

Preparation of 1,2-Diaminodecane. A 250-mL pressure vessel was charged with **2** (1.63 g, 7.30 mmol), Lindlar's catalyst (1.63 g), and absolute ethanol (25 mL). After 23 h, at 50 psi H_2 and 25 °C the pressure was relieved and the mixture filtered through diatomaceous earth. The filtrate was diluted with 3 N hydrochloric acid (50 mL) and extracted with diethyl ether (3 × 15 mL). The combined ethereal extracts were washed with 3 N hydrochloric acid (2 × 15 mL) and the combined aqueous layers made basic with potassium hydroxide to pH 11. This solution was extracted with diethyl ether (4 × 25 mL) and the latter combined ethereal extracts washed with saturated sodium bicarbonate, dried (KOH), and evaporated to give the oily diamine (0.92 g, 5.32 mmol, 73% crude).

Benzoyl chloride (2 mL) was slowly added to a mixture of crude diamine (0.35 g, 2.03 mmol) in 10% sodium hydroxide. After 15 min at 25 °C the solution was adjusted to pH 9 and the precipitate filtered. Recrystallization from hot ethanol/water (3:1) afforded a solid (0.79 g, mp 145–148 °C) which was recrystallized from 95% ethanol to give 1,2-diaminodecane dibenzamide **8** (0.48 g, 1.3 mmol, 62%): mp 147–151 °C, lit.[24] mp 160–161 °C; ^1H NMR δ 7.9–7.1 (m, 10 H), 4.5–4.1 (m, 1 H), 3.75–3.4 (m, 2 H), 2.0–0.7 (m, 17 H), NH not observed.

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Registry No. **2**, 97644-75-2; (*threo*)-**3**, 97644-76-3; (*erythro*)-**3**, 97654-62-1; **4**, 97644-77-4; (*cis*)-**5**, 10027-79-9; (*trans*)-**5**, 57770-13-5; (*cis*)-**6**, 97644-78-5; (*trans*)-**6**, 97644-79-6; **7**, 97644-80-9; **8**, 97644-81-0; sodium azide, 26628-22-8; manganese(III) acetate, 993-02-2; 1,2-diaminodecane, 13880-30-3; 1-decene, 872-05-9; (*E*)-4-octene, 14850-23-8; 5-butyl-4-nonene, 7367-38-6; cyclohexene, 110-83-8; cyclooctene, 931-88-4.

Some Observations on the Iodination of 2-Naphthol and Its Methyl Ether

William B. Smith

Department of Chemistry, Texas Christian University, Fort Worth, Texas 76129

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While the bromination of 2-naphthol and its methyl ether were studied many years ago[1] and have served as the basis for an organic synthesis preparation of 6-bromo-2-naphthol,[2] the iodination of 2-naphthol or 2-methoxynaphthalene has received only brief study. Potts[3] iodinated a number of activated aromatic rings with iodine using ethylenediamine as the hydrogen iodide acceptor and reported a 96% yield of 1-iodo-2-naphthol from 2-naphthol. Jones and Richardson[4] in the same year reported a 90% yield of 1-iodo-2-methoxynaphthalene from 2-methoxynaphthalene using iodine, sodium iodide, and dichloroamine Wirth, Konigstein, and Kern[5] subsequently prepared the same compound (76% yield) in developing the use of iodic acid as an oxidizing agent for the hydrogen iodide produced during the reaction.

Recently, we required a reliable supply of 6-iodo-2-methoxynaphthalene. A survey of the literature suggested two potential routes from readily available starting materials. Takagi, Hayama, and Okamoto[6] have published a method for the replacement of bromine in an aryl bromide with iodine. The reaction requires heating the aryl bromide in dimethylformamide with an excess of potassium iodide in the presence of a small amount of nickel bromide and tributylphosphine. The exact role of

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