amorphous solid which separated from the reaction mixture was collected on a funnel and washed with acetonitrile. The bromides could not be purified due to their intense hygroscopic nature and were submitted as obtained to the reductions. Analytical data are given in Table III.

Preparation of the Bis(NAH)s 8–13. Sodium dithionite (12.5 g, 85% purity, 61 mmol) was added to a solution of the bis(nicotinium)dibromides **2–7** (2 mmol) in a carbon dioxide saturated solution of sodium bicarbonate (3 g, 36 mmol) in water (50 mL), and the mixture was stirred vigorously. When foaming had ceased, additional water (50 mL), anhydrous sodium carbonate (17.5 g, 165 mmol), and chloroform (100 mL) were added, and the mixture was stirred for 5 h at ambient temperature in the dark. The chloroform layer containing the bis reductant was washed with water, dried over anhydrous sodium sulfate, and used as such for the asymmetric reduction of substrates. The bis reductants showed a single spot on TLC analysis (Kieselgel 60F_{254}, Merck Art. 5714, chloroform–methanol) with characteristic fluorescence of dihydronicotinamide.

Procedure for Asymmetric Reduction of Substrates. A solution of the bis reductant (0.35 mmol), anhydrous magnesium perchlorate (0.35 mmol), and substrate (0.35 mmol) in a mixture of dry acetonitrile (60 mL) and dry chloroform (20 mL) was stirred at room temperature for 17 h in the dark. After the reaction was quenched by addition of water, the reduction product was extracted with methylene chloride or ether. Isolation procedures are as follows: for **21**, see ref. 1; for **22**, purification by preparative VPC (5% polyethylene glycol succinate, 120 °C); for **23**, liquid chromatography (Kieselgel 60, 230–400 mesh) eluted with benzene–ethyl acetate; for **24**, preparative VPC (20% Apiezon L, 170 °C); for **25**, preparative VPC (2% silicon DC QF-1, 150 °C); for **26**, preparative VPC (20% Apiezon L, 130 °C).

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Registry No. **1**, 85084-02-2; **2**, 85084-03-3; **3**, 85084-04-4; **4**, 85084-05-5; **5**, 85096-99-7; **6**, 85097-00-3; **7**, 85097-01-4; **8**, 85084-06-6; **9**, 85084-07-7; **10**, 82946-92-7; **11**, 82946-93-8; **12**, 82946-94-9; **13**, 82946-95-0; **15**, 1603-79-8; **16**, 1122-62-9; **17**, 91-02-1; **18**, 5447-87-0; **19**, 13031-04-4; **20**, 434-45-7; **21**, 10606-72-1; **22**, 27911-63-3; **23**, 5583-33-5; **24**, 61925-48-2; **25**, 599-04-2; **26**, 10531-50-7; *N*-nicotinoyl-(*S*)-proline ethyl ester, 85097-02-5.

Nitromethylation of Alkenes

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Radical additions to alkenes have been studied extensively, in large part due to their importance to the polymer industry.[1] Carbon radicals, generated by manganese(III)- or cerium(IV)-promoted oxidative deprotonation of carboxylic acids,[2,3] acetone,[4,5] and other carbonyl compounds[5–7] have been added to olefins to give a variety of products with a larger carbon skeleton.[8] A number of these same radicals have been substituted onto simple aromatic compounds under similar conditions.[5,9–11] Recently we discovered that a similar oxidative deprotonation process could be used to generate nitromethyl radicals from nitromethane and successfully substitute them onto aromatic hydrocarbons.[12–14] The goal of this study was to explore the reaction of nitromethyl radicals, generated by way of oxidative deprotonation, with various olefins.

Table I. Nitromethylation of Alkenes[a]

alkene	products	yield, % $Mn(OAc)_3$ + $Cu(OAc)_2$	yield, % $Mn(OAc)_3$
cyclohexene	3-(nitromethyl)-cyclohexene	38	
	1-(nitromethyl)-cyclohexene	2	
	cyclohexen-3-yl acetate	8	8
cyclopentene	3-(nitromethyl)-cyclopentene	11	
	1-(nitromethyl)-cyclopentene[a]	3	
	cyclopenten-3-yl acetate	3	
	cyclopenten-3-ol	7	
1-pentene	pentenyl acetates	9	8
1-octene	minor products[b]		
styrene	minor products[b]		
α-methyl-styrene	1-nitro-3-phenyl-3-butyl acetate	35	32[c]
	nitromethylated α-methylstyrene[d]	8	6

[a] Tentative identification based on product mixture spectral properties. [b] Unidentified. [c] With $Ce(NH_4)_2(NO_3)_6$ (10 mmol) instead of $Mn(OAc)_3$ this product was found in 13% yield, and additional byproducts were produced. [d] Tentative, could be side chain or nuclear substitution product.

Results

Excess alkene, nitromethane, and acetic acid were refluxed with manganese(III) acetate as the limiting reagent until complete reduction to manganese(II) occurred. A second series of reactions with a copper(II) acetate additive (equimolar to manganese(III) acetate) was also carried out. The products and yields obtained after the workup are summarized in Table I.

Cycloalkenes. Low yields of products not containing a nitro group resulted when either cyclohexene or cyclopentene were reacted with nitromethane and manganese(III) acetate. In the former case the only product formed to any extent (8%) was cyclohexen-3-yl acetate. In the latter, just trace quantities of unidentified compounds resulted. However, when copper(II) acetate was included as a cooxidant the products changed rather dramatically. The major product from cyclohexene was identified as 3-(nitromethyl)cyclohexene (38%) on the basis of its NMR and IR spectra and elemental analysis. A minor amount of 1-(nitromethyl)cyclohexene was also found. The analogous nitromethylated products [3-(ni-

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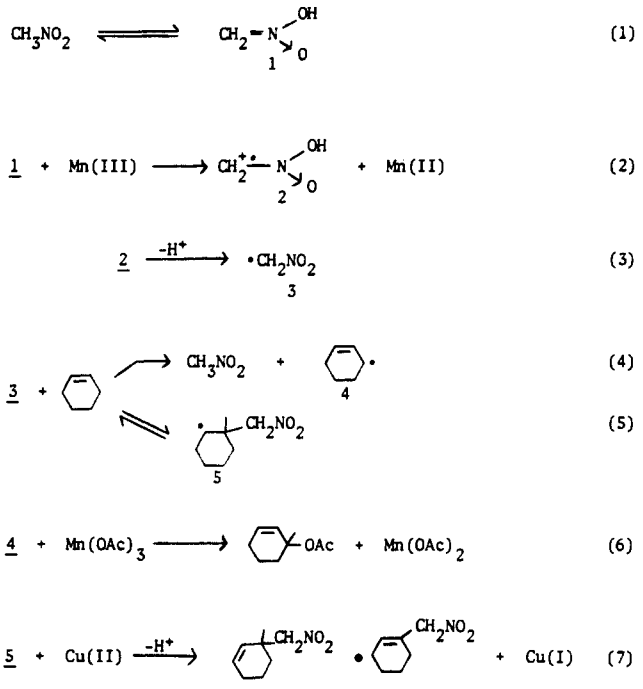
Scheme I



tromethyl)cyclopentene and 1-(nitromethyl)cyclopentene] were produced in 11% and 3% yields, respectively, from cyclopentene.

Alkenes. No evidence of nitromethylated products was detected with either 1-pentene or 1-octene as the substrate. With 1-pentene, an alkenyl acetate, presumably 1-penten-3-yl acetate, was produced. Little difference was noted between the reactions run with and without the copper(II) acetate cooxidant.

Arylalkenes. Both styrene and α-methylstyrene gave complex product mixtures upon attempted nitromethylation, which were not fully characterized. Minor unidentified products were found for the styrene–nitromethane reaction in the presence and absence of the copper(II) acetate cooxidant, as in both cases the product mixture after workup was quite viscous, indicating that polymerization may have occurred. The product mixtures from α-methylstyrene with and without copper(II) acetate were fairly similar. The major product was 1-nitro-3-phenyl-3-butyl acetate (32–35%) while a byproduct (6–8%) seemed to be a nitromethylated α-methylstyrene ($C_{10}H_{11}NO_2$) (either nuclear or side chain). Quite a few other byproducts (1–8%) were also detected in these complex product mixtures but were not identified. One reaction in which cerium(IV) ammonium nitrate was utilized instead of manganese(III) acetate yielded 13% of 1-nitro-3-phenyl-3-butyl acetate and an increased number of byproducts.

Discussion

Nitromethylation occurred best with cycloalkenes and required the presence of a cooxidant. A likely mechanism for this process is shown in Scheme I for cyclohexene. The mechanism (eq 1–3) for the formation of the nitromethyl radical via the aci form, **1**, and a radical cation, **2**, had been worked out earlier.[13] Once formed this radical, **3**, can apparently react in one of two ways with an alkene. Allylic hydrogen abstraction (eq 4) leads eventually to an alkenyl acetate (eq 6), the only product characterized in the reaction without copper(II). Alternately, attack onto the double bond forms a radical (**5**, eq 5) which is apparently oxidized less readily by manganese(III) than carbon radicals such as **4**.[4] With the good oxidant, Cu(II),[15] this radical adduct is converted to a cation which can lose a proton to form both nitromethylated isomers (eq 7). In the absence of the cooxidant Cu(II), this radical adduct reverts back to the reactants.

The poor nitromethylation results with the alicyclic alkenes might be due to the lessened attraction of the electrophilic nitromethyl radical[12,14] for these less electron-rich alkenes.

Nitroalkylation with α-methylstyrene apparently took on a different twist. Initial attack by nitromethyl gave a tertiary benzylic radical, $C_6H_5\dot{C}(CH_3)CH_2CH_2NO_2$, which was readily oxidized by either Mn(III) or Cu(II), adding acetate to give the addition product (Table I), rather than a product of oxidative deprotonation. Substitution by the nitromethyl radical also occurred with α-methylstyrene, but it was unclear as to whether it was the result of attack at the double bond or on the ring. At any rate the amount of C_{10}-nitro-containing product was not very significant.

With styrene it is likely that the initial radical adduct, $C_6H_5\dot{C}HCH_2CH_2NO_2$, adds quite readily to more styrene to cause polymerization even with Cu(II) cooxidant present. An analogous telomerization has been reported for the Mn(III)–Cu(II) cooxidants with ethylene.[16]

All in all, nitromethylation was accomplished with cycloalkenes by using a cooxidant and with α-methylstyrene. With terminal olefins and styrene nitromethylation was not a favorable process.

Experimental Section

GC analyses were performed on a Hewlett-Packard Model 5840A gas chromatograph equipped with flame-ionization detectors and a capillary inlet system (split mode) by using a 30 m × 0.22 mm SP2100 glass capillary column. Preparative gas chromatography was done on a Varian Model 90P gas chromatograph equipped with a 10 ft × 0.25 in. SS 15% SE-30 on Gas-Chrom Q (60–80-mesh) column. IR spectra were obtained with a Perkin-Elmer Model 710B spectrophotometer as thin films or as solutions (in $CDCl_3$) in a matched set (0.1 mm) of solution cells. A 60-MHz Hitachi Perkin-Elmer Model R-24B spectrometer was used to run NMR spectra ($CDCl_3$ solvent containing 1% Me_4Si). GC/MS analyses were performed on a Hewlett-Packard Model 5995B gas chromatograph–mass spectrometer by using a 50 m × 0.25 mm SE-54 fused silica capillary column (we are grateful to Mark Hartwig of Hewlett-Packard for running these samples). Elemental analysis were done by Micro-Analysis, Inc.

Manganese(III) acetate was prepared according to a literature procedure[12,17] and analyzed for purity by iodometry. Styrene and α-methylstyrene were vacuum distilled just before use. The remaining reactants and solvents were commercially available in high purity and were used directly.

Nitromethylation of Alkenes Promoted by Manganese(III) Acetate. General Procedure. Manganese(III) acetate (10 mmol), copper(II) acetate (10 mmol, where applicable), nitromethane (10 or 25 mL), and the alkene (10 mL) were mixed in acetic acid (40 mL) and refluxed under a nitrogen atmosphere until a color change (brown to white) indicated the metal ion had been reduced (1–4 h). After cooling, the reaction mixture was poured onto a mixture of water (50 mL) and either chloroform or ethyl ether (25 or 50 mL). The organic layer was separated, washed with water (50 mL) and aqueous 5% sodium carbonate (50 mL), dried over sodium sulfate, and concentrated to ~10 mL on a rotary evaporator for subsequent GC analysis. In some cases an appropriate internal standard (usually *p*-nitrotoluene) was added to a portion of the product mixture and quantitative analysis performed by GC.

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Cyclohexene. Preparative GC was used to isolate the products from cyclohexene. The major product was identified as 3-(nitromethyl)cyclohexene: NMR ($CDCl_3$) δ 5.6 (m, 2 H), 4.2 (d, 2 H), 2.9 (m, 1 H), 1.9–1.5 (m, 6 H); IR (neat) 3055, 2965, 1555, 1385 cm^{-1}. Anal. Calcd for $C_7H_{11}NO_2$: C, 59.57; H, 7.80; N, 9.93. Found: C, 59.94; H, 8.06; N, 9.96. A poorly resolved shoulder peak on the back of the major component appeared to be a nitro-containing compound, possibly 1-(nitromethyl)cyclohexene, on the basis of its weak spectra: IR (neat) 3075, 2980, 1545, 1390 cm^{-1}; NMR ($CDCl_3$) δ 5.7, 4.3, 1.9–1.6 (all poorly resolved). Another byproduct was identified as cyclohexen-3-yl acetate: NMR ($CDCl_3$) δ 5.8 (m, 2 H), 5.25 (m, 1 H), 2.0 (m, 6 H), 1.7 (s, 3 H); IR (neat) 3075, 2975, 1720, 1250, 1030 cm^{-1}.

Cyclopentene. The concentrated product mixture from the cyclopentene reaction after reactant removal contained 50% of a major component, ~10% each of three minor products, and very small amounts of other compounds. Preparative GC did not successfully separate the major components, so spectral analysis was done on the concentrated product mixture: NMR ($CDCl_3$) δ 5.9–5.7 (overlapping m), 5.05 (s, $C{=}CCH_2NO_2$) 4.4 (d, $CHCH_2NO_2$), 3.5–3.0 (overlapping m), 2.5–1.6 (overlapping m and s); IR (neat) 3470 (weak), 3090, 2880, 1785, 1730, 1550, 1380, 1240, 1200 cm^{-1}. The major product was 3-(nitromethyl)cyclopentene: mass spectrum, m/e 67 (100, $M^+ - CH_2NO_2$), 96 ($M^+ - HNO$), 68, 70, 95; NMR δ 5.8, 4.4, 1.8; IR 1550, 1380 cm^{-1} (NO_2 group). One minor product was cyclopenten-3-ol [mass spectrum, m/e 84 (M^+), 66 (100, $M^+ - 18$), 83, 67; IR 3470 cm^{-1} (O–H stretch)] while another was cyclopenten-3-yl acetate: mass spectrum, m/e 67 (100, $M^+ - CH_3CO_2$), 66 ($M^+ - CH_3CO_2H$), 83 ($M^+ - CH_3CO$), 84; IR 1730 (C=O), 1240 (CO) cm^{-1}. A minor product, not cleanly resolved by GC/MS, was likely 1-(nitromethyl)cyclopentene (NMR siglet at δ 5.05).

1-Pentene. Essentially only one product was obtained (low yield) and had a retention time fairly similar to that of the suspected acetate from cyclopentene. No nitro group stretches were observed in the IR of the concentrated product mixture.

1-Octene. A complex mixture of minor products (<1%) was found. No further efforts at product identification were attempted.

Styrene. GC analysis showed that the viscous product mixture from styrene contained relatively small amounts of a number of volatile products. NMR analysis of the product mixture showed small signals at δ 4.3 (t, $CH_2CH_2NO_2$), 2.5 (m), and 2.0 (s) in addition to signals related to the styrene structure. Though a nitromethylated styrene is implicated, the amount present was very little, as only weak nitro group stretches were observed in the IR. The high viscosity and NMR spectrum indicated some polystyrene.

α-Methylstyrene. The concentrated product mixture from α-methylstyrene after reactant removal was shown by GC to consist of about 50% of a major component and 15% of a second component, with the remaining 35% being composed of a complex mixture of more than ten minor components (1–5%). Preparative GC was unsuccessful in further purifying this mixture, so it was analyzed as is by NMR and IR. The IR showed strong bands at 3025, 2975 (CH), 1740, 1240 (OAc), 1555, 1380 (NO_2), and 760, 690 cm^{-1} (monosubstitution) plus other weaker signals. The NMR ($CDCl_3$) contained prominent signals at δ 7.2–7.3 (overlapping s, aromatic), 4.3 (t, 2 H, CH_2NO_2), 2.5–2.9 (overlapping m, 4 H), 2.0 (s, 3 H, CH_3), and 1.9 (s, 3 H, acetate methyl) and other smaller complex signals at δ 5.4–5.0 (C=CH and/or $ArCH_2NO_2$), 2.9–3.3, and 1.5–1.8.

The major product was 1-nitro-3-phenyl-3-butyl acetate: mass spectrum, m/e 237 (M^+), 91 (100, $C_7H_7^+$), 131 ($M^+ - CH_3CO_2H,NO_2$), 121, 115, 105, 77, 65, 51; the major IR and NMR signals were consistent with this structure. A minor product was a nitromethylated α-methylstyrene (either nuclear or side chain); mass spectrum, m/e 177 (M^+), 117 (100, $M^+ - CH_2NO_2$), 116, 135, 102, 91, 77.

Registry No. Cyclohexene, 110-83-8; cyclopentene, 142-29-0; 1-pentene, 109-67-1; 1-octene, 111-66-0; styrene, 100-42-5; α-methylstyrene, 98-83-9; 3-(nitromethyl)cyclohex-1-ene, 85097-24-1; 3-(nitromethyl)cyclopent-1-ene, 85097-25-2; 1-nitro-3-phenyl-3-butyl acetate, 85097-26-3; manganese(III) acetate, 993-02-2; copper(II) acetate, 142-71-2; nitromethane, 75-52-5.

Regioselective Cyanation of Pyridine 1-Oxides with Trimethylsilanecarbonitrile: A Modified Reissert–Henze Reaction[1]

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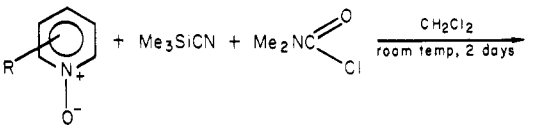
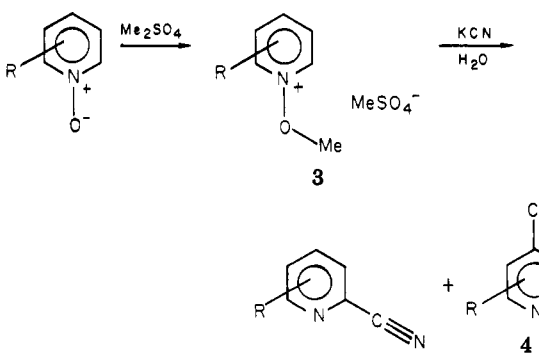
Treatment of pyridine 1-oxides **1** with equimolar quantities of trimethylsilanecarbonitrile and dimethylcarbamyl chloride in dichloromethane gives nearly quantitative yields of the corresponding 2-pyridinecarbonitriles **2** (eq 1, Table I). This new modification of the Reissert–Henze reaction[2] represents a significant improvement over previous methods for synthesis of 2-pyridinecarbonitriles, which often give low yields and cyanation at both the 2- and 4-positions of the pyridine (eq 2, Table I). It



a, R = H; **b**, R = 2-CH_3; **c**, R = 3-CH_3; **d**, R = 4-CH_3



is the first application of trimethylsilanecarbonitrile to the cyanation of pyridine 1-oxides. The use of trimethylsilanecarbonitrile in Reissert reactions of pyrimidine, quinoline, isoquinoline, and other fused, multiple-ring, nitrogen heterocycles has been reported recently.[3] It is especially noteworthy that unsubstituted, and 2- and 4-methylpyridine 1-oxides give exclusively the corresponding 2-pyridinecarbonitrile. Reaction of the 3-methyl derivative **1c** is almost as selective, producing 90% 3-methyl-2-pyridinecarbonitrile and 5% 5-methyl-2-pyridinecarbonitrile.[4]

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