Registry No. **1a**, 102687-64-9; **1b**, 139758-52-4; **2a**, 139732-09-5; **3a**, 139732-10-8; **3b**, 139732-15-3; **3b'**, 139732-16-4; **4**, 139732-11-9; **5a**, 139732-12-0; **5b**, 139732-17-5; **6**, 139758-51-3; **7**, 139732-13-1; **8**, 139732-14-2; 1,1,1-trifluoro-3-iodopropane, 460-37-7; benzenethiol, 108-98-5; 1-mercaptoheptane, 1639-09-4; styrene, 100-42-5; allyltrimethylsilane, 762-72-1; isobutenyltrimethylsilane, 18292-38-1; cyanotrimethylsilane, 7677-24-9; benzene, 71-43-2.

Supplementary Material Available: ^{1}H NMR spectra for **1b**, **4**, **5a**, **5b**, **6**, and **7** (6 pages). ordering information is given on any current masthead page.

Direct Polynitroaliphatic Alcohol Addition to Alkenes. 2. One-Step Synthesis of β-Substituted Polynitroalkyl Vinyl Ethers via an Alternative Transetherification Pathway[1]

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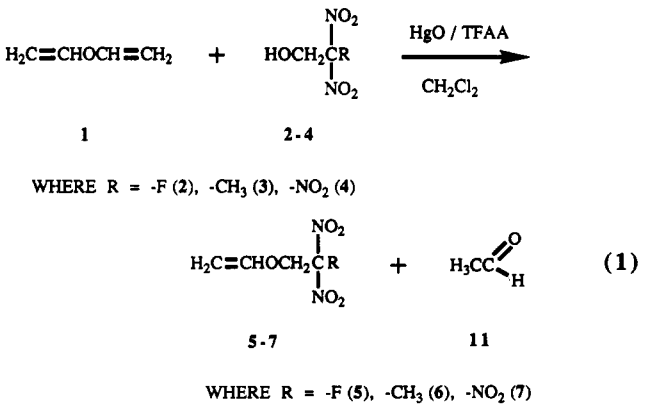
β-Substituted polynitroalkyl vinyl ether compounds represent monomeric polymer precursors which potentially could be useful chemical components in solid propellant or explosive formulations. Their preparation is limited by the inherent instability of the β-substituted polynitroalkyl structure in alkaline solution[2,3] and by the weak nucleophilic nature of the polynitroaliphatic alcohol precursors possessing either the geminal 2,2-dinitroalkyl or terminal 2,2,2-trinitroethyl structure.[3-6] This precludes using the common vinyl ether synthesis procedure where an alcohol and acetylene are reacted via base catalysis because these polynitroaliphatic alcohol reactants readily deformylate in alkaline solution forming formaldehyde plus their respective polynitroalkyl anion.[2,3] This paper reports our discovery of a novel reaction which permits the one-step, high-yield synthesis of β-substituted polynitroalkyl ethers under mild refluxing CH_2Cl_2 solvent conditions. Use of a mercury(II) oxide/trifluoroacetic acid (HgO/TFAA) cocatalyst and the divinyl ether (**1**) reactant with 2-fluoro-2,2-dinitroethanol (**2**), 2,2-dinitropropanol (**3**), and 2,2,2-trinitroethanol (**4**) produce their respective polynitroalkyl vinyl ethers through a nonreversible transetherification reaction (eq 1). While an inherent reversible

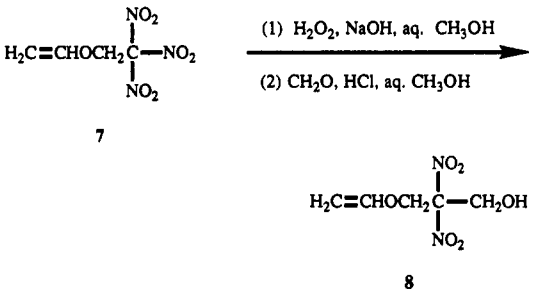


(1)

Table I. Comparison of Product 5, 9, and 10 Percentages as Function of Catalyst

DVE/FDNEOH reactant ratio	catalyst/cocatalyst	% 5	% 9	% 10
1.00	HgO/TFAA	90.5	0	9.5
1.00	$HgSO_4$/TFAA	11.0	5.3	83.7
1.00[3]	$HgSO_4$	3.7	35.1	61.2
2.00[3]	$HgSO_4$	5.6	73.4	21.0

equilibrium in the transetherification reaction is responsible for the low (27–32%) yields obtained with more nucleophilic 2-nitroalkyl alcohols,[7] this particular transetherification reaction uniquely circumvents the equilibrium condition because the chemical structure of **1** does not permit formation of a conjugate alcohol. The 2-fluoro-2,2-dinitroethyl vinyl ether (**5**) and 2,2-dinitropropyl vinyl ether (**6**) compounds are known;[2,8] the 2,2,2-trinitroethyl vinyl ether (**7**) and its 3-hydroxy-2,2-dinitropropyl vinyl ether (**8**) derivative are reported for the first time (eq 2).



(2)

Results and Discussion

Two previous methods are reported which provide **5** and **6**.[2,8] The first reported synthesis produces **5** and **6** in 51 and 60% yields, respectively, and is achieved by heating **2** or **3** with vinyl acetate using mercury(II) acetate and concentrated H_2SO_4 in catalytic amounts.[8] A more recent procedure provides **5** in 88% yield and **6** in a 94% yield by heating their respective aldehyde bis[2,2-dinitroalkyl] acetal in the presence of anhydrous $NaHSO_4$.[2] While this pyrolysis reaction produces **2** or **3** as a recyclable byproduct for preparing more acetal reactant, the initial acetal preparation makes this a two-step process. The subject transetherification where **1** is reacted with either **2** or **3** in the presence of the HgO/TFAA cocatalyst produces vinyl ethers **5** and **6** in approximately 75–78% yields, respectively, prior to purification by vacuum distillation (eq 1). Reaction of **1** with **4** using the HgO/TFAA cocatalyst results in the first synthesis of **7** in a 26% yield which, in turn, is a precursor for the new compound **8** (eq 2). A one-pot procedure forms **8** via alkaline dinitrosation of **7** followed by an acidic formalation. Compound **8** represents a novel β-substituted 2,2-dinitroaliphatic structure since it possesses two different terminal functional reaction sites, a vinylic bond and a hydroxyl moiety.[10] Although the yield of **8** is not optimized, its formation demonstrates a synthetic strategy for obtaining a new type of difunctional polynitroaliphatic compound. Figure 1 compares the characteristic ^{1}H NMR spectra of the four vinyl ethers **5–8**

(1) Shackelford, S. A.; McGuire, R. R.; Cochoy, R. E. US Patent 4,426,540, Jan 17, 1984; *Chem. Abstr.* **1984**, *100*, 121764.
(2) Coburn, M. D. *Synthesis* **1977**, 570.
(3) Cochoy, R. E.; McGuire, R. R.; Shackelford, S. A. *J. Org. Chem.* **1990**, *55*, 1401–1406.
(4) Shipp, K. G.; Hill, M. E.; Kamlet, M. J. *NOLTR* 62-68, April 1962.
(5) Adolph, H. G.; Kamlet, M. J. *J. Org. Chem.* **1968**, *34*, 45–50.
(6) Cochoy, R. E.; McGuire, R. R. *J. Org. Chem.* **1972**, *37*, 3041–3042.
(7) Watanabe, W. H.; Conlon, L. E. *J. Am. Chem. Soc.* **1957**, *79*, 2828–2833.
(8) Adolph, H. G. US Patent 3,808,182, Apr 30, 1974; *Chem. Abstr.* **1975**, *82*, 58493.
(9) Shipp, K. E.; Hill, M. E. *NAVORD Report 6752*, 5 Jan 1960, 14–17.
(10) The suggestion for attempting the synthesis of **8** from **7** was provided by Dr. M. J. Kamlet (deceased Feb 1988).

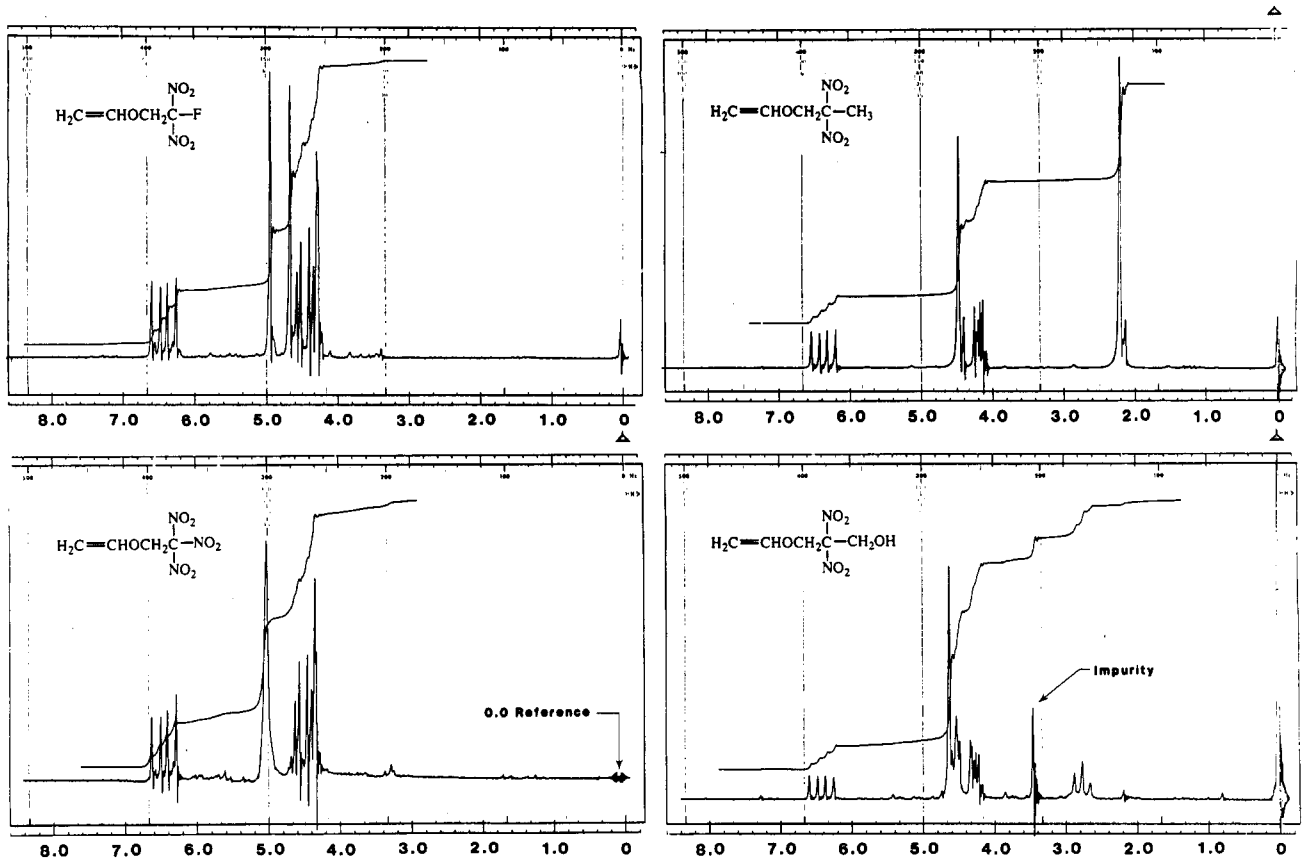
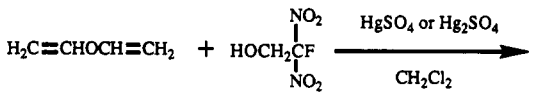


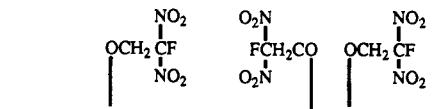
Figure 1. NMR (60-Hz) spectra of vinyl ether products 5–8.

obtained in this new transetherification.

This subject HgO/TFAA cocatalyzed transetherification (eq 1) contrasts markedly with the addition reaction followed by reactants 1 and 2 with either $HgSO_4$ or Hg_2SO_4 catalysis (eq 3).[3] Under the same conditions, the addition



1 2



(3)

9 10

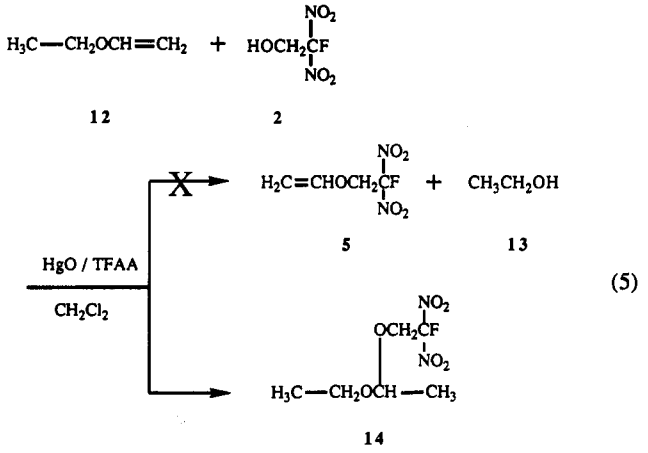
reaction produces mainly monoadduct 9 and diadduct 10 products (Table I). Transition from an addition reaction pathway to the transetherification is achieved by using the mercury(II) oxide catalyst in place of either mercury sulfate salt. Pure HgO catalyst with 1 and 2 produces 5 in 20–30% yield before product degradation occurs with prolonged reaction times.[3] Introduction of the trifluoroacetic acid cocatalyst, however, drastically increases the vinyl ether product yield (ca. 75% prior to distillation) and eliminates the product degradation problem. Direct isolation of the product oil by solvent removal followed by GLPC/MS analysis demonstrates how selectively this transetherification reaction proceeds. Without any purification, this crude product oil is comprised of 5 (81.6%), unreacted 2 (3.8%), and the diastereomeric[3] diadducts 10 (8.6%). The remaining 6.0% is the 2-[2-fluoro-2,2-dinitroethyl]ethyl ether which forms via a parallel transetherification between DVE and its ethanol stabilizer.[3] A GLPC/MS analysis of the crude oil following CH_2Cl_2 solvent removal obtained in the reaction of 1 and 3 reveals the analogous vinyl ether 6 (91.8%) plus only two other minor products comprising the remaining 8.2%. No unreacted alcohol 3 is detected. To ensure the mercury salt catalyst is the determining factor whether the transetherification or addition pathway occurs, 1 and 2 are reacted in the presence of an $HgSO_4$/TFAA cocatalyst under the same reaction conditions as the HgO/TFAA transetherification. Table I compares these results along with those of the previously reported $HgSO_4$-catalyzed addition reaction. Clearly, vinyl ether 5 selectively results because of the catalytic HgO salt, while formation of the mono- 9 and diadduct 10 products results from $HgSO_4$ salt catalysis, regardless of whether the TFAA cocatalyst is used or not.

The high transetherification yields of products 5 and 6 result from acetaldehyde 11 byproduct formation. Because transetherification normally is a reversible equilibrium reaction (eq 4), product formation must be driven by

$$R^1OCH{=}CH_2 + R^2OH \rightleftharpoons R^2OCH{=}CH_2 + R^1OH \quad (4)$$

continuous removal of the desired vinyl ether product ($R^2OCH{=}CH_2$) or the conjugate alcohol byproduct (R^1OH), especially when weakly nucleophilic monosubstituted 2-nitroaliphatic alcohol reactants are used. Even then, yields only from 27 to 32% are achieved.[7] The unique diene structure of 1 circumvents the problem of conjugate alcohol product formation by producing acetaldehyde instead. Formation of byproduct 11 (eq 1), either directly or indirectly from an immediate tautomerization of ethenol ($H_2C{=}CH{-}OH$), removes the reversible equilibrium condition normally encountered in the vinyl ether transetherification and, thereby, drives it to completion. The significantly higher yields of 5 and 6 derived from the less nucleophilic 2,2-dinitroaliphatic alcohols 2 and 3 compared to monosubstituted 2-nitroaliphatic al-

cohols[7] illustrate how effective byproduct 11 formation is in overcoming the reversible equilibrium condition (eqs 1 and 4). Byproduct 11 is detected in small amounts from reaction aliquots subjected to ^1H NMR analysis after CH_2Cl_2 solvent removal. Further verification of 11 formation is achieved by preparative GLPC analysis of the transetherification reaction of 1 and 2 where an isolated volatile, colorless liquid provides ^1H NMR, FTIR, and mass spectral data which is identical with an authentic acetaldehyde sample. The importance of surpressing this reversible equilibrium condition by producing acetaldehyde is further illustrated under conditions where 11 cannot be formed. When ethyl vinyl ether 12 is substituted for divinyl ether 1, reaction with 2 and the HgO/TFAA cocatalyst under the same conditions does not produce 5 (eq 1). Instead of transetherification, addition occurs and provides acetal 14 as the sole reaction product in a 70% isolated yield (eq 5). A GLPC/MS analysis of the crude



(5)

reaction product reveals only product 14. The highly nucleophilic character of the conjugate ethanol byproduct 13, which would form with 5 in a transetherification, prevents this reaction pathway by shifting the entire equilibrium to the reactant side (eq 4). This forces the addition reaction pathway to occur and produces the same acetal product 14 as one obtains using the $HgSO_4$ catalyst with reactants 12 and 2.[3] Compound 14 is confirmed by GLPC/MS and ^1H NMR comparison with a known sample.

A mercury(II) trifluoroacetate [$Hg(OTFA)_2$]/TFAA cocatalyst also produces vinyl ether 5 in a reasonably high conversion using CH_2Cl_2 or $ClCH_2CH_2Cl$ solvent with reactants 1 and 2. The $Hg(OTFA)_2$ compound[11] must have the TFAA cocatalyst present to form any detectable 5. No reaction results with a $Hg(OTFA)_2$/trifluoroacetic anhydride cocatalyst. While the $Hg(OTFA)_2$/TFAA cocatalyst in CH_2Cl_2 provides a high conversion to 5, ^1H NMR analysis reveals a noticeable presence of both the mono- 9 and diadduct 10 acetals. Three parallel $Hg(OTFA)_2$/TFAA cocatalyzed reactions conducted in the higher boiling $ClCH_2CH_2Cl$ solvent with reactants 1 and 2 in molar ratios of 3:1, 1:1, and 1:3, respectively, reveal a higher presence of the unwanted addition products 9 and 10 as the alcohol 2 stoichiometry is increased. Excess 1 or a 1:1 molar ratio of 1 and 2 provide a crude product oil containing 65–70% of 5 by ^1H NMR analysis. The remaining 25 to 30 percent is comprised of addition products 9 and 10. When 2 is present in a 3-fold excess, only 30–35% of 5 is present in the oil isolated directly from a reaction aliquot; the remaining 70–65% is compounds 9 and 10. Repeating this parallel stoichiometric reactant study in CH_2Cl_2 provides a similar result.

Conclusions

Highly nonnucleophilic β-substituted polynitroaliphatic vinyl ethers like 5 and 6 are synthesized in high yield by using the unique diene chemical structure of divinyl ether 1 to interrupt the reversible equilibrium normally present in transetherification reactions. The presence of an ethenoxy leaving group from 1 when reacted with polynitro alcohol 2 or 3 permits either a direct or immediate tautomeric formation of acetaldehyde in place of the usual conjugate alcohol. Because acetaldehyde cannot react with the vinyl ether product and produce a reversible equilibrium condition like the conjugate alcohol, this transetherification is driven to its product side. This synthetic strategy also produces the first synthesis of 2,2,2-trinitroethyl vinyl ether (7) by permitting the exceptionally nonnucleophilic 2,2,2-trinitroethanol (4) to react with 1 nonreversibly in the presence of the mercury(II) oxide/trifluoroacetic acid (HgO/TFAA) cocatalyst. While TFAA significantly enhances the yield of 2,2-dinitroalkyl vinyl ethers, the HgO catalyst actually causes the transetherification pathway to proceed in place of the addition pathway achieved with the $HgSO_4$ and Hg_2SO_4 catalytic salts. Preparation of polynitroalkyl vinyl ethers 5–7 is most cleanly and selectively accomplished via this transetherification pathway using the HgO/TFAA (trifluoroacetic acid) cocatalyst and CH_2Cl_2 solvent.

Experimental Section

General. *Caution! Reactants 2-fluoro-2,2-dinitroethanol (2), 2,2-dinitropropanol (3), and 2,2,2-trinitroethanol (4) are compounds which, although normally stable under routine handling conditions, can explode under the proper thermal, shock, friction, or electrostatic discharge stimuli. Additionally, 2 also causes severe burns to the skin. Proper shielding and skin protection should be used when handling these compounds or when working up reactions containing these reactants.* Most general experimental procedures used have been outlined previously.[3] Several later reactions were conducted in HPLC-grade CH_2Cl_2 solvent dried over CaH_2. The 2,2-dinitropropanol was provided by the Naval Surface Warfare Center/White Oak Laboratory, Silver Spring, MD. The 2,2,2-trinitroethanol (mp 76 °C) was synthesized from tetranitromethane, dried by azeotropic distillation, crystallized from a CCl_4–CH_2Cl_2 solution, and stored over CCl_4 in a freezer.[9] The trifluoroacetic acid was purchased from Eastman Organic Chemicals and the red HgO compound from J. T. Baker Chemical Company as "Baker Analyzed" reagent purity. All ^1H NMR spectra were taken in $DCCl_3$ solvent and are referenced to the TMS standard.

Synthesis of 2-Fluoro-2,2-dinitroethyl Vinyl Ether (Product 5). A 50-mL single-necked round-bottom flask was charged with 2.00 g (28.6 mmol) of divinyl ether (1), 50 mL of CH_2Cl_2, 4.40 g (28.6 mmol) of 2, and a Teflon-coated magnetic stirring bar. To the stirred solution was added 0.40 g of HgO followed by 200 μL of trifluoroacetic acid (TFAA). The reaction flask was fitted with a water-cooled reflux condenser topped with a Drierite-filled drying tube. The reaction was stirred at reflux temperature (bp CH_2Cl_2 at FJSRL elevation = 34–37 °C) for 16.5 h.[12] The CH_2Cl_2 solvent was removed by rotary evaporation leaving a yellowish oil. The oil was placed onto a short column prepared by packing 2.5 g of aluminum oxide (pH 6.9) slurried in CCl_4 into a 15-mL "coarse" glass-sintered Buchner funnel. Elution with 35 mL of CCl_4 and solvent removal by rotary

(11) The mercury(II) trifluoroacetate was prepared by refluxing HgO in a trifluoroacetic acid/trifluoroacetic anhydride suspension until all the HgO solid dissolved. Rotary evaporation produced a slightly off-white solid confirmed to be the trifluoroacetate salt by IR and X-ray fluorescence analyses. This preparation is similar to another reported procedure: Brown, H. C.; Rei, M-H. *J. Am. Chem. Soc.* **1969**, *91*, 5646–5647.

(12) The 16–17.5-h reaction time initially was for procedural convenience. Additional study indicates this reaction to form 5 and 6 is nearly complete in 5–7 h.

evaporation gave 4.75 g of a colorless oil. The colorless oil is purified by vacuum distillation at 34-35 °C (13 Torr) or 20-21 °C (0.6 Torr) via short-path vacuum distillation to provide 5 as a pure sample. A Kugelrohr bulb to bulb distillation at 65-68 °C (13 Torr) provides 1.66 g of 5 (64.0% overall yield) on a 14.3 mmol scale reaction of 1 and 2. Compound 5: ^{1}H NMR (dd, 6.42 with J_{H-H} = 7 Hz, 1 H), (d, 4.72 with J_{vic-HF} = 16 Hz, 2 H), (m, 4.36, 2 H); IR (neat film) cm^{-1} 3130, 3060 (=CH), 3000, 2940, 2900 (sat. CH), 1645 (C=C), 1600, 1300 (NO_2); mass spectrum m/e 181 (1.2) M + 1, 180 (19.3) M$^+$, 134 (5.6), 88 (16.4), 62 (24.9), 46 (33.4), 45 (79.8), 44 (27.5), 43 (21.2), 42 (30.9), 30 (100) base. Isolated acetaldehyde byproduct 11: ^{1}H NMR (quart, 9.74, 1 H), (d, 2.15, 3 H); IR (CCl_4 solution) cm^{-1} 3052, 2986 (CH and CH_3), 1730 (C=O); mass spectrum m/e 44 (45.5) M$^+$, 43 (29.1), 29 (100) base, 28 (44.0).

Synthesis of 2,2-Dinitropropyl Vinyl Ether (Product 6). A 250-mL single-necked round-bottom flask was charged with 3.50 g (50.0 mmol) of 1, 100 mL of CH_2Cl_2, 7.50 g (50.0 mmol) of 3, and a Teflon-coated magnetic stirring bar. To the stirred solution was added 0.50 g of HgO followed by 500 μL of TFAA. The reaction flask was fitted with a water-cooled reflux condenser topped with a Drierite-filled drying tube. The reaction was stirred at reflux temperature 17.5 h. The CH_2Cl_2 solvent was removed by rotary evaporation leaving a slightly yellow oil. The oil was placed onto a short column prepared by packing 15.0 g of neutral aluminum oxide (pH 6.9) slurried in CCl_4 into a 30-mL "coarse" glass-sintered Buchner funnel. Elution with 40 mL of CCl_4 and solvent removal by rotary evaporation gave 7.52 g of a slightly yellow oil. The crude oil is purified by vacuum distillation at 38.2-40.0 °C (0.2 Torr) giving 5.64 g (64.2%) of 6 as a colorless oil: ^{1}H NMR (dd, 6.42 with J_{H-H} = 7 Hz, 1 H), (s, 4.51, 2 H), (m, 4.27, 2 H), (s, 2.23, 3 H); IR (neat film) cm^{-1} 3110, 3060 (=CH), 2980, 2940, 2880 (sat. CH), 1640, 1625 (C=C), 1570, 1320 (NO_2); mass spectrum m/e 177 (0.8) M$^+$, 133 (7.2), 84 (68.6), 57 (46.2), 44 (35.5), 43 (57.1), 41 (100) base, 39 (83.4), 30 (75.7). Anal. Calcd for $C_5H_8N_2O_5$: C, 34.1; H, 4.54; N 15.9; O 45.5. Found: C, 33.8; H, 4.70; N, 16.0; O by difference, 45.4.

Synthesis of 2,2,2-Trinitroethyl Vinyl Ether (Compound 7). A 100-mL single-necked, round-bottom flask was charged with 1.50 g (21.4 mmol) of 1, 50 mL of CH_2Cl_2, 3.62 g (20.1 mmol) of 4, and a Teflon-coated magnetic stirring bar. To the stirred solution was added 0.10 g of HgO followed by 500 μL of TFAA. The reaction flask was fitted with a water-cooled reflux condenser topped with a Drierite-filled drying tube. The reaction was stirred at reflux temperature for 16.25 h.[13] The CH_2Cl_2 solvent was removed by rotary evaporation leaving an orange oil. The oil was placed onto a short column prepared by packing aluminum oxide (pH 7.3) slurried in CCl_4 in the manner already described. The unreacted alcohol 4, however, remained upon CCl_4 solvent removal. Hexane elution of the crude product oil through a 1.5- × 34.0-cm SiO_2 (60/200-mesh) chromatographic column followed. Hexane removal via rotary evaporation gave 1.59 g (25.9%) of 7 as a slightly yellow oil: ^{1}H NMR (dd, 6.44 with J_{H-H} = 8 Hz, 2 H), (s, 4.98, 2 H), (m, 4.43, 2 H); IR (neat film) cm^{-1} 3140, 3060 (=CH), 3000, 2940, 2900 (sat. CH), 1645 (C=C), 1600, 1300 (NO_2).

Synthesis of 3-Hydroxy-2,2-dinitropropyl Vinyl Ether (Compound 8).[14] A 250-mL three-necked, round-bottom flask was charged with 1.59 g (7.67 mmol) of 7, 20 mL of methanol, and 6 mL of 30% H_2O_2. One side neck was fitted with a 30-mL pressure-equalized addition funnel and the other side neck with a ground-glass thermometer assembly. The center neck was fitted with an overhead mechanical stirring motor and assembly. The stirred solution was cooled to -15 °C, and then a solution containing 3.50 g of NaOH in 7 mL of 1:1 H_2O/methanol was added dropwise to the stirred solution at a rate to keep the reaction temperature at -4 °C or lower. After addition was complete, the cold bath was removed and the reaction came to room temperature. Next, enough water was added to dissolve all solids and two layers formed.[15] Six mL of 37% formaldehyde solution was added dropwise to the stirred solution such that the reaction temperature remained at 33 °C or lower. The heterogeneous slurry homogenized into an orange solution which then was warmed gently to 40 °C. Enough concd HCl (37%) was added to effect pH 2 (pH Hydrion paper), and a lemon yellow solution appeared. The reaction solution was placed into a freezer (ca. -10 °C) over the weekend, and oil droplets formed in the reaction mixture. Most of the methanol was removed by rotary evaporation, and a CH_2Cl_2 extraction followed. The CH_2Cl_2 extract was dried over anhyd $MgSO_4$. Gravity filtration and CH_2Cl_2 removed by rotary evaporation produced 0.70 g of a yellow oil. The yellow oil was eluted through a 1.5- × 20.0-cm 60/200-mesh SiO_2 column packed with hexane. Elution was begun with hexane followed by incremental 10, 15, 20, 50, and 75% CH_2Cl_2-hexane enrichments. Early fractions produced 0.29 g (19.2%) of nearly pure 8. Compound 8 could be vacuum distilled with a molecular still at 55 °C (0.3 Torr): ^{1}H NMR (dd, 6.42 with J_{H-H} = 7 Hz, 1 H), (s, 4.64, 4 H),[16] (m, 4.44, 2 H), (broad t, 2.78, 1 H); IR (neat film) cm^{-1} 3500 (OH), 3060 (=CH), 2960, 2900 (sat. CH), 1640 (C=C), 1575, 1320 (NO_2); mass spectrum m/e 192 (M$^+$).

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(13) Aliquots taken during this reaction indicate it apparently proceeds much more slowly than the analogous reactions with alcohols 2 and 3.

(14) The denitrosation/formalation of 7 to form 8 was based upon a procedure described in: Hall, T. N.; Shipp, K. G. *NOLTR 61-2*, 21 Mar 1961, 10.

(15) Because H_2O_2 can react violently with aqueous formaldehyde solution, enough water is added to achieve complete solubility at room temperature (ref 9).

(16) The singlet at δ 4.64 has some overlap with the split multiplet at δ 4.44; however, the total integration of both spectral sets is the correct 6 H (Figure 1).

A New Class of Enantioselective Organoboron Reducing Agents. BH_3 Complexes with Chiral Terpenic 1,2-Azaboracyclohexanes†

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In the last few years, remarkable achievements have been made in the area of enantioselective boron reducing agents.[1,2] For example, chiral oxazaborolidines may be used as catalysts in the BH_3 reduction of ketones.[2] Herein we describe a new class of enantioselective boron reducing agents, BH_3 complexes of *N*-alkyl-10,10-dimethyl-5-aza-6-boratricyclo[7.1.1.0^{2,7}]undecanes.

It was found that various secondary nopylamines (4-8), easily prepared according to Scheme I from nopol (1)

† We dedicate this paper to Professor H. C. Brown on the occasion of his 80th birthday.

0022-3263/92/1957-2953$03.00/0