Table I. Activation Energies ($\Delta E^{\ddagger}$, kcal/mol) for $H_3CSCH_3 + CH_3 \rightarrow [(H_3C)_3S]^{\ddagger} \rightarrow CH_3 + H_3CSCH_3$

level	ΔE^{a}	$\Delta E(\text{spin})^{b}$	$\Delta E^{\ddagger c}$
SCF	26.54	19.46	19.19
MBPT(2)	19.23	13.48	13.21
MBPT(3)	20.06	16.15	15.88
DQ-MBPT(4)	20.25		
SDTQ-MBPT(4)	17.32	13.41	13.14

[a] Interaction energies calculated as $\Delta E = E(AB) - (E(A) + E(B))$. [b] Using spin-projected molecular energies[11] after annihilation of unwanted spin states. Fourth-order spin annihilation correction was estimated as $E_{PMBPT4} - E_{MBPT4} \approx E_{PMBPT3} - E_{MBPT3}$. [c] Thermodynamic corrections (zero point and thermal energies) were estimated by standard statistical mechanical techniques using unscaled frequencies.

Figure 2. Intramolecular displacement reaction of 4-(alkylthio)butyl radicals.[6]

corrections were estimated by open-shell many-body perturbation theory (MBPT) through fourth order at the SCF determined geometries. Spin-corrected total energies had their unwanted spin contaminants removed using the Löwdin spin annihilator operator,[11,12] with the spin correction to the fourth-order perturbation energy estimated from the third-order method.[13] Vibrational frequencies were evaluated using analytical second derivatives at the SCF level and thermodynamic quantities estimated by standard statistical mechanical techniques.[14]

Results and Discussion

The optimized geometries of the trial sulfuranyl species, $(H_3C)_3S^{\bullet}$, $(H_3C)_2HS^{\bullet}$, and $H_3S^{\bullet}$, are summarized in Figure 1. Relative energetics for the symmetric displacement reaction of methyl radical and dimethyl sulfide are collected in Table I. Extensive geometry searches failed to reveal a stable 9-S-3 structure but did locate transition-state structures for the displacement reactions. The molecular structures resemble those of phosphoranyl radicals,[15] exhibiting a T-shaped molecular structure (⟨eq-S-axial ~90°, ⟨axial-S-axial ~175°), with both the sulfur lone pair and the singly occupied orbital assuming pseudoequatorial positions.[3] For the three structures, the vibrational frequency analysis has revealed one eigenvalue of 690i, 677i, and 1454i cm^{-1} for $(H_3C)_3S^{\bullet}$, $(H_3C)_2HS^{\bullet}$, and $H_3S^{\bullet}$, respectively. The eigenfunctions of these frequencies exhibit axial compression and displacements modes, consistent with a displacement-type reaction. In previous work, we have shown that the singly occupied molecular orbital (SOMO) of the trimethyl- and propyl-1,4-butylidenesulfuranyl radicals show antibonding interactions between the axial groups consistent with axial-axial displacements.[6] Thus, we conclude that alkyl radical displacement at dialkyl and alkyl sulfides procedes through an axial–axial transition state rather than a 9-S-3 intermediate, consistent with our kinetic studies[6] and other lines of experimentation.[15]

Although the activation energy for the trimethylsulfuranyl radical has not been experimentally determined, activation barriers for the closely analogous reactions of 4-(*n*-propylthio)butyl ($\Delta H^{\circ} = 2.1$ kcal/mol, $\Delta E^{\ddagger} = 12.2$ kcal/mol) and 4-(*tert*-butylthio)butyl radical ($\Delta H^{\circ} = -2.2$ kcal/mol, $\Delta E^{\ddagger} = 11.4 \pm 0.4$ kcal/mol) lead us to estimate a barrier of 12 ± 2 kcal/mol for the displacement reaction of methyl radical and dimethyl sulfide. For the theoretical treatment of the open-shell transition state, past experience for first-row reactions suggests that spin contamination will be a complicating effect. Our results (Table I) indicate that the barrier heights calculated at the UHF and MBPT levels without spin annihilation are also too high, but can offer good agreement after elimination of unwanted spin components. Both correlation energy corrections ($\Delta E \approx 6.3$–9.2 kcal/mol) and spin annihilation ($\Delta E \approx 3.9$–7.1 kcal/mol) in the unpaired electron species result in significant corrections to the activation energy. Consistent with previous studies on the $C_2H_2 + H^{\bullet}$ reaction, higher orders of perturbation theory recovers greater degrees of correlation energy, but only marginally improve the spin contamination problems.[13] Upon removal of the first spin contaminant, the S^2 value for the trimethyl sulfuranyl radical changes from 0.877 to 0.754. Thermochemical corrections for zero point energy and internal energy were calculated at the SCF level and result in a −0.27 kcal/mol difference. The resulting theoretical values at the MBPT(2) and MBPT(4) levels are in good agreement with the predicted experimental value (12 ± 2 kcal/mol).

In summary, we conclude that radical displacement at sulfur lacking electronegative ligands proceed through 9-S-3 transition states, rather than hypervalent reaction intermediates. The application of many-body perturbation methods allows one to approach thermochemical quality in second-row free-radical systems, with MBPT(2) capturing the majority of the correlation energy. Spin contamination of the wavefunction presents a major problem for accurately predicting the relative energetics for these species.

Registry No. H_3CSCH_3, 75-18-3; CH_3, 2229-07-4.

Supplementary Material Available: Molecular structures of $H_3S^{\bullet}$, $(H_3C)_2HS^{\bullet}$, and $(H_3C)_3S^{\bullet}$ (2 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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Formation of Sterically Hindered Primary Vicinal Diamines from Vicinal and Geminal Dinitro Compounds

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Vicinal diamines find wide application in synthesis as both synthons and catalysts.[1,2] While tertiary diamines such as *N,N,N′,N′*-tetramethylethylenediamine are common in catalysis,[3,4] the secondary and primary diamines

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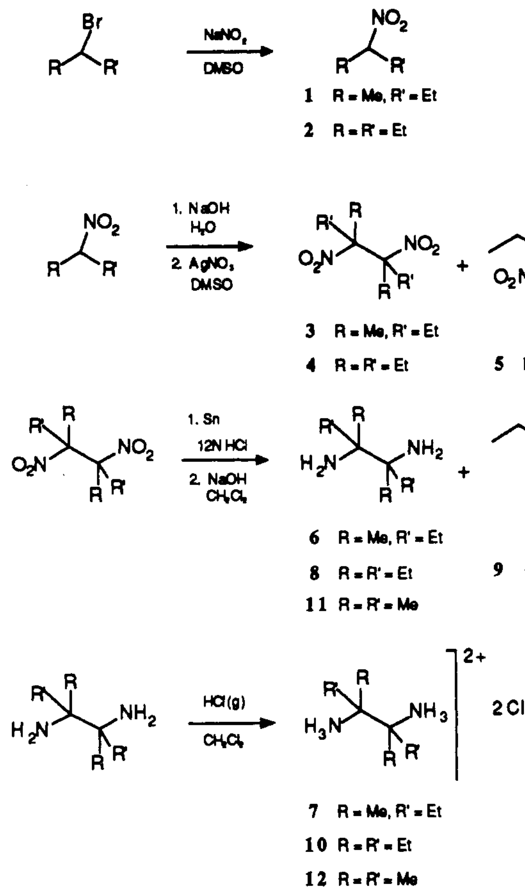
Scheme I



are widely used in condensation reactions. These diamines are common precursors for inclusion compounds, such as macrocyclic Schiff bases and various imaging agents.[5] We are interested in sterically hindered primary vicinal diamines as a means to prepare sterically hindered Schiff-base metallates.

Tetraalkyl-substituted primary vicinal diamines can be prepared via nitroalkyls by dimerization, using the Shechter method,[6] followed by reduction using the method of Sayre.[7] We describe herein modifications of these two methods leading to the improved synthesis of 2,3-diamino-2,3-dimethylbutane (11) and the synthesis of 3,4-diamino-3,4-dimethylhexane (6) and 3,4-diamino-3,4-diethylhexane (8) (Scheme I). The literature regarding preparation and characterization of these amines and nitro compounds is scattered and incomplete; therefore experimental details and characterization data are included for the known as well as the new compounds.

Experimental Section

General. The haloalkanes, 2,3-dimethyl-2,3-dinitrobutane, and 20-mesh granular tin were used as received from Aldrich. Mass spectra were recorded by Dr. David Thomas of SRI International and elemental analyses were performed by Galbraith and Desert Laboratories.

2-Nitrobutane (1). The 2-bromobutane (82 g, 0.60 mol) was added to a solution of sodium nitrite (72 g, 1.0 mol) in DMSO (450 mL), and the mixture was mechanically stirred under N_2 in an ambient temperature bath for 5.5 h. Ice water (200 mL) followed by water (750 mL) were added to the stirred white slurry, and the organic phase was collected by extraction with pentane (5 × 130 mL). The combined pentane extracts were washed with water (2 × 200 mL), dried over $MgSO_4$, and evaporated to a pale greenish-blue liquid (crude yield 40%) that was distilled at 60 mm (1, third fraction, 68–70 °C, 20 g, 0.19 mol, 32%). Beilstein: bp_{747} 138–139 °C.

3-Nitropentane (2). Compound 2 was prepared as for 1, except from 3-bromopentane with a reaction time of 8 h. The final product was collected at ca. 15 mmHg at 77–80 °C (24 g, 0.20 mol, 34%). Anal. Calcd for $C_5H_{11}NO_2$: C, 51.26; H, 9.46; N, 11.96. Found: C, 51.12; H, 9.72; N, 11.63. ^1H NMR ($CDCl_3$): δ 4.42 (m, 1 H), 1.97 (m, 4 H), 1.03 (t, J = 7.3 Hz). MS (CI): m/e 135 (M + NH_4^+). Beilstein: bp_{746} 152–155 °C.

3,4-Dimethyl-3,4-dinitrohexane (3). A mixture of 1 (25 g, 0.24 mol) and NaOH (9.6 g, 0.24 mol) in water (56 mL) was stirred at ambient temperature under N_2 until homogeneous. A solution of $AgNO_3$ (46 g, 0.27 mol) in water (8 mL) was prepared at 50 °C under N_2 and then diluted with DMSO (475 mL). The solution of 1 was added to this DMSO solution, and the mixture was stirred in the dark at 40–50 °C for 6 h. Fine Ag metal was removed by filtration through Celite. Water (1 L) was added to the filtrate, and the resulting white suspension was cooled in ice–water for 45 min with occasional shaking. The crude crystals of 3 were collected by suction filtration, washed with water, and suction dried (48% crude yield). ^1H NMR spectroscopy and GC/MS showed a 1:1 mixture of two diastereomers in the crude product. This material was spectroscopically pure and suitable for use in the reduction step. Fractional recrystallization from diethyl ether/hexane gave white plates in a total yield of 34% (crop 1, 30%, 55%:45% meso:rac; crop 2, 4%, 17%:83% meso:rac). Anal. Calcd for $C_8H_{16}N_2O_4$: C, 47.05; H, 7.90; N, 13.72. Found (crop 1): C, 47.19; H, 8.08; N, 13.70. Found (crop 2): C, 47.15; H, 8.08; N, 13.64. ^1H NMR ($CDCl_3$): δ (crop 2) 2.05 (m, meso + rac, 2 H, CH_2), 2.52 (m, meso + rac, 2 H, CH_2), 1.56 and 1.55 (pseudodoublet, meso, 5 H, CH_3), 1.62 and 1.61 (pseudodoublet, rac, 1 H, CH_3), 0.89 (t, J = 7.25 Hz, meso + rac, 6 H, CH_3). MS (CI): m/e 222 (M + NH_4^+).

3,4-Diethyl-3,4-dinitrohexane (4). (a) From 3-Pentanenitronate and Silver Nitrate. The procedure was as for 3, using 2 (20.6 g), NaOH (7.0 g in 40 mL water), and $AgNO_3$ (30.3 g in 12 mL water followed by 400 mL DMSO) at 40–50 °C for 5 h. After the aqueous quench, the mixture was extracted with ether (4 × 140 mL), the extracts were dried over $MgSO_4$, and the solvent was removed to give a yellow liquid (9 g) containing 2, 4, and 3,3-dinitropentane (5) (vide infra) in a molar ratio of 1.2:1:1.7. The starting material was removed by stirring with NaOH (7.0 g) in water (40 mL) for 3 h, extraction with pentane, and evaporation to give a yellow liquid containing 5 and 4 in a molar ratio of 2.0:1.0. This mixture was chromatographed using CH_2Cl_2/hexane. Crystallization from the upper band gave white plates of 4 (2.25 g, 9.7 mol, 11%). Anal. Calcd for $C_{10}H_{20}N_2O_4$: C, 51.71; H, 8.68; N, 12.06. Found: C, 51.64; H, 8.64; N, 11.75. ^1H NMR ($CDCl_3$, 400 MHz): δ 0.90 (t, J = 7.36 Hz, 12 H), 2.15 (q, J = 7.51 Hz, 2 H), 2.19 (q, J = 7.32 Hz, 2 H), 2.35 (qd, J_q = 7.83 Hz, J_d = 0.65 Hz, 2 H), 2.39 (qd, J_q = 7.55 Hz, J_d not resolved, 2 H). MS (CI): m/e 250 (M + NH_4^+). IR (film on NaCl): ν (selected, cm^{-1}) 1547 (vs, br), 1473 (shld), 1457 (s), 1392 (m), 1358 (s), 1333 (s). The lower band gave a colorless liquid that quickly yellowed. Bulb-to-bulb vacuum distillation in the dark under reduced pressure gave colorless 5 (1.81 g, 11.2 mmol, 6%). Anal. Calcd for $C_5H_{10}N_2O_4$: C, 37.04; H, 6.22; N, 17.28. Found: C, 37.30; H, 6.21; N, 17.16. ^1H NMR ($CDCl_3$): δ 2.61 (q, J = 7.4 Hz, 2 H), 1.06 (t, J = 7.4 Hz, 3 H). MS (CI): irreproducible, no parent. IR (film on NaCl): ν (selected, cm^{-1}) 1559 (vs, br), 1464 (s), 1446 (s), 1393 (m), 1375 (s), 1389 (shld), 1334 (s, sym). In addition to the pure fractions, 3.51 g of mixed fractions were collected.

(b) From 3-Pentanenitronate and 5. A mixture of 2 (0.177 g, 1.51 mmol) and aqueous NaOH (0.15 g, 3.8 mmol in 0.6 mL) was stirred at room temperature until homogeneous and then added to a solution of 5 (0.24 g, 1.48 mmol) in DMSO (2 mL) under Ar. The resulting bright yellow solution was stirred at 50 °C for 5 min and then at ambient temperature for 21 h. The solution was brought to pH 7 with 1 N HCl, extracted with diethyl ether (5 × 15 mL), and evaporated to a light yellow oil containing

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multiple products but none of either starting material (TLC, 3:1 CH_2Cl_2/hexane). The major product was collected by chromatography with 2:1 CH_2Cl_2/hexane. Crystallization of the first band gave spectroscopically pure, white 4 (0.60 g, 0.26 mmol, 17%).

3,4-Diamino-3,4-dimethylhexane (6). Compound 3 (5.2 g, 25.5 mmol) was suspended in 12 N HCl (46 mL) in an ice bath and mechanically stirred as tin (55 g, 0.46 mol) was added in five equal portions at 30-min intervals. The reaction was then stirred at ambient temperature until the white, water-insoluble foam had dissipated, ca. 1 h. The solution phase was stirred in an ice bath and carefully basified with NaOH pellets to pH ca. 12. The gray mass was extracted by pouring CH_2Cl_2 (6 × 120 mL) into the Erlenmeyer flask, stirring vigorously with a glass rod, and then pouring the cloudy organic phase off of the top. The organic phase was dried over NaOH, suction filtered through Celite, and evaporated to a colorless or pale yellow oil. The dihydrochloride salt of 6 was precipitated by bubbling excess HCl through a stirred CH_2Cl_2 (100 mL) solution of the crude product. White 3,4-diammonio-3,4-dimethylhexane dichloride (7) was collected by filtration under N_2, after refrigeration to coagulate the precipitate, and dried under vacuum (4.52 g, 20.8 mmol, 82% overall yield, 1.0:1.0 meso:rac). Anal. Calcd for $C_8H_{22}N_2Cl_2$: C, 44.24; H, 10.21; N, 12.90; Cl, 32.76. Found: C, 44.15; H, 10.10; N, 12.74; Cl, 32.65. Fractional crystallization of this material from methanol/ethanol gave a 32% recovery of 7 as a single diastereomer (A). ^{1}H NMR (DMSO-d_6) Isomer A (meso): δ 8.62 (s, 6 H), 1.67 (q, J = 7.3 Hz, 4 H), 1.26 (s, 6 H), 0.99 (t, J = 7.3 Hz, 6 H). Isomer B (rac): δ 8.64 (s, 6 H), 1.66 (m, 4 H), 1.31 (s, 6 H), 1.01 (pseudoquartet, 6 H).

3,4-Diamino-3,4-diethylhexane (8). Analytically pure 4 (1.99 g, 8.57 mmol) was suspended in 12 N HCl (15 mL) under Ar and stirred in an ice bath as tin (1.78 g, 15.0 mmol) was added. The mixture was allowed to come to ambient temperature, and more tin (13.54 g, 114 mmol) was added in three portions as well as additional 12 N HCl (10 mL) over the next 2.5 h while the mixture was stirred in a 55 °C bath. The mixture was next heated in a 65 °C bath until all of the white solid had dissolved, ca. 2.5 h, and then treated as described for 6 to give a colorless oil (0.97 g). The molar composition of this crude product was 1.9:1.0 compound 8 to 3-pentanone oxime (9) (vide infra). The oil was dissolved in CH_2Cl_2 and stirred as excess HCl was bubbled through to give a milky white precipitate. The 3,4-diammonio-3,4-diethylhexane dichloride (10) was collected by filtration under N_2, after refrigeration to coagulate the precipitate, and dried under vacuum (0.88 g, 3.6 mmol, 42% overall yield). Anal. Calcd for $C_{10}H_{26}N_2Cl_2$: C, 48.98; H, 10.69; N, 11.42; Cl, 29.13. Found: C, 48.62; H, 10.57; N, 11.42; Cl, 28.91. ^{1}H NMR (DMSO-d_6): δ 8.52 (br s, 6 H), 1.77 (q, J = 7.3 Hz, 8 H), 0.99 (t, J = 7.3 Hz, 12 H).

The above procedure was also performed on a crude mixture of 4 and 5 (from which 2 had been removed). Using 15.15 g of 4 + 5 (1.0:2.2), 181 g of Sn, and 220 mL of 12 N HCl, the molar composition of the crude product was 1.0:2.0 8:9. The final yield of 10 was 2.44 g (9.9 mmol, 6% overall yield from 40.61 g of 2). Anal. Found: C, 48.63; H, 10.72; N, 11.28. The oxime was isolated from the supernatant of 10 as a yellow oil, bulb-to-bulb vacuum distillation of which gave colorless 9 (1.0 g, 10 mmol, 3% from 2). Anal. Calcd for $C_5H_{11}NO$: C, 59.37; H, 10.96; N, 13.85. Found: C, 59.73; H, 10.89; N, 13.79. ^{1}H NMR ($CDCl_3$): δ 9.32 (s, 1 H), 2.30 (q, J = 7.6 Hz, 2 H), 2.16 (q, J = 7.4 Hz, 2 H), 1.01 (t, J = 7.5 Hz, 6 H). IR (film on NaCl, selected, cm^{-1}): ν_{OH} 3275 (vs, vb), $\nu_{C=N}$ 1667 (m). MS: m/e 101. Beilstein: bp$_{763}$ 165 °C. A trace quantity of a third product was isolated from the supernatant of 10 that appeared to be 3-amino-3,4-diethyl-4-hexene [selected spectral data. ^{1}H NMR ($CDCl_3$): δ 5.60 (q, 1 H) and 3.3 (br s, 2 H). IR (film on NaCl, cm^{-1}): ν 3380 (m, shld), 3240 (br, m), and 1595 (m). MS: m/e 155].

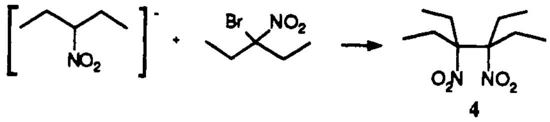
3-Pentanone Oxime (9). Tin (2 × 0.94 g, 15.8 mmol) was added under Ar over 2 h to a stirred suspension of 5 (0.17 g, 1.05 mmol) in 12 N HCl (3 mL) at ambient temperature. The solution phase was treated as described for 6 to give spectroscopically pure 9 (0.090 g, 0.89 mmol, 85%).

Results and Discussion

A variety of nucleophilic additions, coupling reactions, and reductions were examined to prepare the desired tetraalkyl-substituted diamines from alkyl halides. The tetramethyl-substituted primary vicinal diamine 11 has been prepared previously by reduction of the vicinal dinitro compound,[7,8] and more recently from 2,3-dimethyl-2-butene and nitric oxide at an organocobalt center.[9] The diethyl, dimethyl-substituted primary vicinal diamine 6 has been mentioned in the literature, also prepared by reduction of the corresponding vicinal dinitroalkyl.[10] The tetraethyl-substituted derivative 8 has not been reported as of this writing. The synthesis route for these three diamines from the corresponding alkyl halides is shown in Scheme I.

The highest yields of 11 and 6 were obtained by reduction of the corresponding dinitro compound with tin in HCl, and 8 could be obtained only by this method. We have adapted the tin chloride procedure of Sayre (76% yield of the oxalate derivative of 11)[7] to provide good yields of these diamines at large scale (e.g. 50 g). Compound 11 previously has been isolated from water only as an oil, turning to a brown liquid within a few days in dry air, or from THF as a paste. We obtained spectroscopically pure rosettes (mp 103 °C) of 11 in 75% yield by extraction of the basified reaction mixture directly with methylene chloride (as described in the Experimental Section for preparation of crude 6). A volatile solvent is required if solvent must be removed because 11 sublimes readily. Crystalline 11 obtained by this procedure can be stored in dry air for at least 3 years without change in melting point. Alternatively, the pure dihydrochloride salt of 11, compound 12, can be precipitated essentially quantitatively by bubbling HCl through the crude methylene chloride extracts.

Syntheses of the dinitro precursor to diamine 6, compound 3, have been described: from the mononitro compound 1 and silver,[11] from the alkyl halide and 2-butanenitronate,[12] or from 2-butanenitronate and sodium persulfate.[6] Recently the availability of the precursor to diamine 8, tetraethyl dinitroalkyl 4, from 3-bromo-3-nitropentane and 3-pentanenitronoate (eq 1), has been indicated.[13] We prepared compounds 3 and 4 from 1 and 2 by the Shechter method for oxidative coupling of nitroalkyls,[6] which were in turn generated by metathesis of the corresponding secondary alkyl halides with sodium nitrite.[14]



(1)

4

The oxidative coupling of 1 was performed using aqueous NaOH to form the 2-butanenitronate anion and then $AgNO_3$ in DMSO as oxidant, to give 1:1 meso:rac 3. Although the meso and rac isomers of 3 can be separated chromatographically,[15] we generally chose to proceed with the 1:1 mixture and effect isomeric separation at later stages. An isomerically enriched sample of 3 (17%:83%

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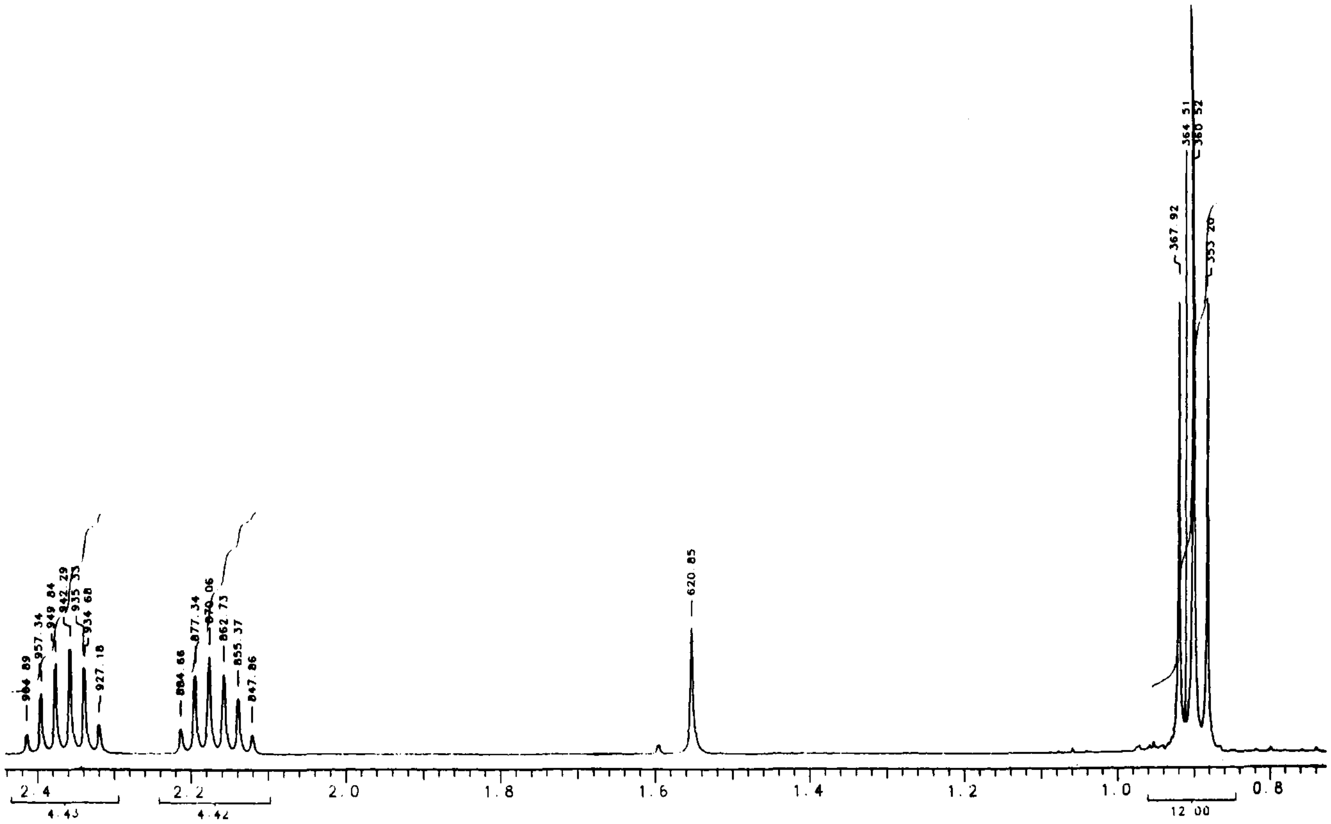
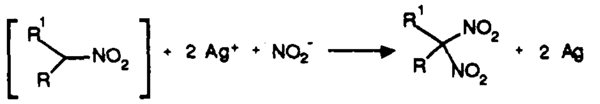


Figure 1. ^1H NMR spectrum of 3,4-diethyl-3,4-dinitrohexane (4).

isomers 1:2) that was reduced to 6 was unaltered in isomeric composition[10] and was used to show that isomer 1 of 3 corresponds to the meso isomer of 6. The stereochemistry of 3, prepared with persulfate, was not described by Shechter; however, rac products dominated when the primary nitronate anions 2-methyl-1-propanenitronate (4.5:1 rac:meso) and benzenenitronate (3.5:1 rac:meso) were oxidized with persulfate.[6] The lack of stereospecificity that we observed in the oxidative coupling of 2-butanenitronate may result from a decreased ability to distinguish sterically between two similar alkyl groups during bimolecular coupling of secondary nitronate fragments, as compared to the alkyl and hydrogen groups in primary nitronates.

The Shechter coupling of 2 by silver nitrate gave both the expected vicinal dinitro compound 4 and another product, the geminal dinitro compound 5.[16] The formation of 5 might result from thermal decomposition of either the nitronate anion or the vicinal dinitro compound 4 in our system. Shechter attributed the formation of geminal dinitro coproducts during the oxidative coupling of primary nitronates to extrusion of free nitrite followed by reaction of this nitrite with nitronate (the Kaplan–Shechter reaction,[17] eq 2).[6b] Our results suggest that secondary nitronate anions also might decompose with release of nitrite. Alternatively, the vicinal dinitro product may eliminate nitrous acid to some degree under the reaction conditions (50 °C): Rüchardt and co-workers have reported that thermal decomposition of tetraalkyl-substituted vicinal dinitro compounds in solution occurs without C–C bond cleavage to give olefins and nitrous acid.[13]



(2)

It is interesting that while the geminal dinitro compound could result from decomposition of 4, the geminal species also can serve as an intermediate in formation of 4. When we reacted pure 5 with 3-pentanenitronate, 4 was isolated in 17% yield. Nucleophilic substitution of *gem*-dinitro compounds by nitronate anions has been described; the reaction apparently proceeds via radicals with an $S_{NR}1$ pathway.[18] The utility of this pathway for production of 4 under our particular conditions is limited, because 3-pentanenitronate becomes the limiting reagent once 5 has formed, but could be increased by adjusting the stoichiometry.

The four quartets of doublets observed in the 400-MHz proton NMR spectrum of 4 indicate that this compound contains eight different methylene protons and is rotationally rigid in solution at ambient temperature (Figure 1). The doublet we observed for the methyl substituents in the spectrum of *meso*-3 is indicative of rotational isomerism in solution for this compound as well; rotational isomerism in both the meso and rac isomers of 3 has been studied by Huang and co-workers in the solid and solution states using IR and Raman spectroscopy.[15]

We were surprised to find both the vicinal diamine 8 and the oxime 9 in crude reaction mixtures from reduction of 4, whether the *gem*/*vic*-dinitro mixture or pure 4 were employed. The ratio of oxime to diamine was much higher, however, when the gem/vic mixture was used. We monitored mixtures of the two dinitro compounds as well as mixtures of the diamine and oxime at ambient temperature by ^1H NMR and observed no interconversion over a two

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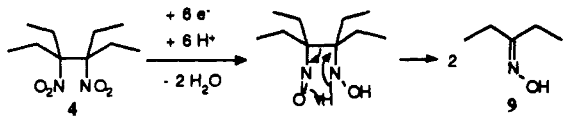
[16] We have found one reference to 5, prepared by oxidation of 3-nitro-3-nitrosopentane with CrO_3 in glacial acetic acid. Born, G. *Ber. Deutsch. Chem. Ges.* **1896**, *29*, 93. The geminal and vicinal dinitro mixture can be separated chromatographically; however, we found that pure 10 could be precipitated after the reduction step without prior separation of the two dinitro compounds.

[17] (a) Bahner, C. T. *Ind. Eng. Chem.* **1952**, 317. (b) Kaplan, R. B.; Shechter, H. *J. Am. Chem. Soc.* **1961**, *83*, 3535.

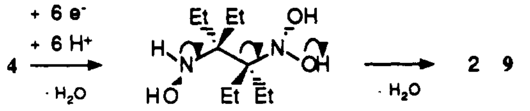
[18] Bowman, W. R. *Chem. Soc. Rev.* **1988**, *17*, 283.

Scheme II

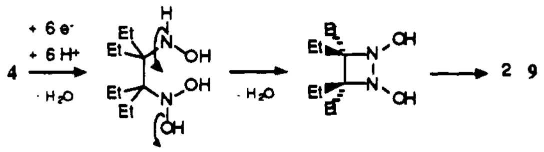
a) pericyclic rearrangement after 6-electron reduction



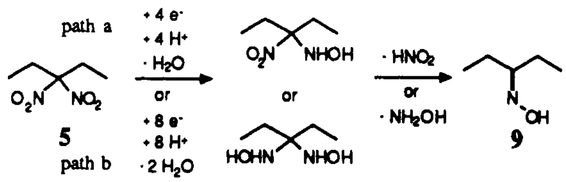
b) *trans*-elimination after 6-electron reduction



c) cleavage of diazetine after 6-electron reduction



Scheme III



week period. These results suggest that the oxime can form from the geminal dinitro compound **5** as well as from **4** during the reduction step. Accordingly, reduction of pure **5** under these conditions did give **9** in 85% yield.

Decomposition during reduction of **4** to **8** may result from an increase in the reduction potential, as electron-donating alkyl groups are added to the vicinal dinitro backbone and/or from an increased tendency for intramolecular decomposition imposed by the rotational rigidity of **4**. Scheme II shows mechanisms by which oxime **9** might form during reduction of the vicinal dinitro compound **4**. A six-electron reduction of **4** could produce the nitrosohydroxylamine, and then pericyclic rearrangement with cleavage of the central carbon-carbon bond would give 2 equiv of **9** (a). Both nitroso species and hydroxylamines have been proposed as intermediates during metal-halide reductions of nitro compounds.[3] A six-electron reduction of **4** to give the (hydroxylamino)dihydroxyamine followed by trans elimination of water gives 2 equiv of **9** (b). A third possibility is rearrangement of the six-electron reduction product to give a 1,2-diazetidine, which then cleaves to give **9** (c). Based on the work of Shustov and co-workers on oxidative cleavage of vicinal bis(hydroxylamines),[19] the trans elimination (b) appears most probable for reductive cleavage of vicinal dinitro compounds.

Scheme III shows two routes by which oxime **9** might form from the *gem*-dinitro compound **5**. Either a four-electron reduction of **5** followed by elimination of nitrous acid (path a) or an eight-electron reduction followed by loss of hydroxylamine (path b) gives **9**, which is apparently inert to further reduction by tin in strong acid.[20]

Conclusion

Tetraalkyl-substituted primary vicinal diamines are accessible from nitroalkyls via dimerization followed by reduction of the resultant vicinal dinitroalkyls. The geminal dinitroalkyl appears to be an intermediate in formation of the tetraethyl-substituted vicinal dinitro compound; further mechanistic studies are necessary to determine the generality of geminal dinitro intermediates in the Shechter reaction. Both inductive effects and rotational rigidity may make reduction of the tetraethyl-substituted dinitro compound subject to side reactions. The oxime, isolated as a side product from this reduction, is not a reaction intermediate; however, its formation supports the intermediacy of hydroxylamines in the reduction of nitro compounds by metals in mineral acids.

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[19] Shustov, G. V.; Tavakalyan, N. B.; Shustova, L. L.; Pleshkova, N. B.; Kostyanovskii, R. G. *Bull. Acad. Sci. USSR Div. Chem. Sci.* **1982**, *31*, 330.

[20] It is unknown whether the trace 3-amino-3,4-diethyl-4-hexene that was also isolated from the supernatant of **10** resulted from elimination of an ammonium cation during reduction of the vicinal dinitro compound or whether it represents the reduction product of a trace quantity of 3,4-diethyl-3-nitro-4-hexene in the starting dinitro mixture.

Synthesis of Optically Active 3-(1-Hydroxyalkyl)phthalides by Stereoselective Pinacol Cross-Coupling

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The vanadium(II)-promoted reaction between an aliphatic aldehyde and a "ligand accelerated" aliphatic or aromatic aldehyde recently reported by Pedersen et al.[1] represents the first synthetically useful approach to 1,2-diols via intermolecular[2] pinacol cross-coupling.[3] By the use of a chiral, nonracemic amide function as in **1** we were able to establish an enantioselective version of this extremely convenient process that allowed the synthesis of 3-(1-hydroxylalkyl)phthalides **2a,b**–**5a,b** in 75–84% enantiomeric excess (ee) and up to 91:9 syn/anti diastereoisomeric ratio[4] via the corresponding dihydroxyamides.

However, for the pinacol coupling to be a successful competitor with other methods to produce optically active 1,2-diols,[5-11] a higher level of enantiocontrol was required

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[1] (a) Freudenberger, J. H.; Konradi, A. W.; Pedersen, S. F. *J. Am. Chem. Soc.* **1989**, *111*, 8014. (b) Takahara, P. M.; Freudenberger, J. H.; Konradi, A. W.; Pedersen, S. F. *Tetrahedron Lett.* **1989**, 7177. (c) Park, J.; Pedersen, S. F. *J. Org. chem.* **1990**, *55*, 5924. (d) Konradi, A. W.; Pedersen, S. F. *J. Org. Chem.* **1990**, *55*, 4506.

[2] For an intramolecular version of this reaction see: Raw, A. S.; Pedersen, S. F. *J. Org. Chem.* **1991**, *56*, 830.

[3] Reviews: McMurry, J. E. *Chem. Rev.* **1989**, *89*, 1513. Pons, J. M.; Santelli, M. *Tetrahedron* **1988**, *44*, 4295.

[4] (a) Annunziata, R.; Cinquini, M.; Cozzi, F.; Giaroni, P. *Tetrahedron: Asymmetry* **1990**, *1*, 355. (b) Annunziata, R.; Cinquini, M.; Cozzi, F.; Giaroni, P.; Benaglia, M. *Tetrahedron* **1991**, *47*, 5737. In the original model the attack of the ketyl radical of the aliphatic aldehyde on **1** was hypothesized. However, as pointed out by one of the reviewers, attack of the ketyl radical of **1** on the aliphatic aldehyde could take place as well.

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