mechanisms: (a) intermediate **3** or (b) another intermediate formed from **3** by loss of the leaving group is trapped by reaction with sulfite ion or thiamin. Consequently, simpler mechanism a is given in Scheme I. Incorporation of an additional step as required by pathway b does not change the kinetic form, only the collection of rate constants.

The derivation pertains to experimental conditions[3] where sulfite ion S is the limiting reagent under initial rate conditions and **1** is present in excess. The pH dependence is not expressed but it is to be understood that the conjugate acid of thiamin reacts with free sulfite ion while thiamin base is a nucleophile. Step k_3 is not included in the rate expression because one S is consumed and another is liberated. Note that S is liberated in step k_4 in which thiamin traps intermediate; the formation of oligomer is *catalyzed* by S, and so step k_4 must be included in the rate expression. Applying a steady-state assumption for **3** gives eq 2. This has the form of eq 1 in ref 3, $k_2 + k_4[1]$ being an apparent constant.

$$R = -\mathrm{d}[S]/\mathrm{d}t = k_1[1][S] - [3](k_2 + k_4[1])$$

$$R = \frac{k_1k_3[S]^2[1]}{k_2 + k_3[S] + k_4[1]} \qquad (2)$$

The k_2/k_3 ratio in ref 3 now becomes $(k_2 + k_4[1])/k_3$ and reduces to $k_4[1]/k_3$ if $k_2 < k_4[1]$. We actually prefer a scheme in which the two nucleophiles compete for an intermediate which already has lost the leaving group and therefore use different symbols k_B/k_S in eq 1 to express the competition. In this case no assumption needs to be made about the relative magnitudes of k_2 and $k_4[1]$.

Highly instructive is a consideration of the case where $k_4[1] > k_3[S]$; i.e., intermediate is trapped preferentially by **1**. As eq 3 shows, the rate of disappearance of sulfite ion now is second order in sulfite ion.

$$R = \frac{k_1k_3[S]^2[1]}{k_2 + k_4[1]} \qquad (3)$$

By use of our value for k_B/k_S and the concentrations given in ref 3 calculations show that sulfonate ion **2** is the major product at high pH. But as the acidity is lowered and the ratio of thiamin base to sulfite ion concentrations increases the major product becomes bispyrimidine **4** as the reaction becomes second order in sulfite ion.[10]

Registry No. 1·HCl, 67-03-8; **5**, 77028-14-9; sulfite ion, 14265-45-3.

(10) Buffer base also could trap intermediate, three being employed.[3] The good fit given by eq 1 suggests this process is not significant.

Vinylsilane-Mediated Spiroannulation. Synthesis of Spiro[4.5]decadienones

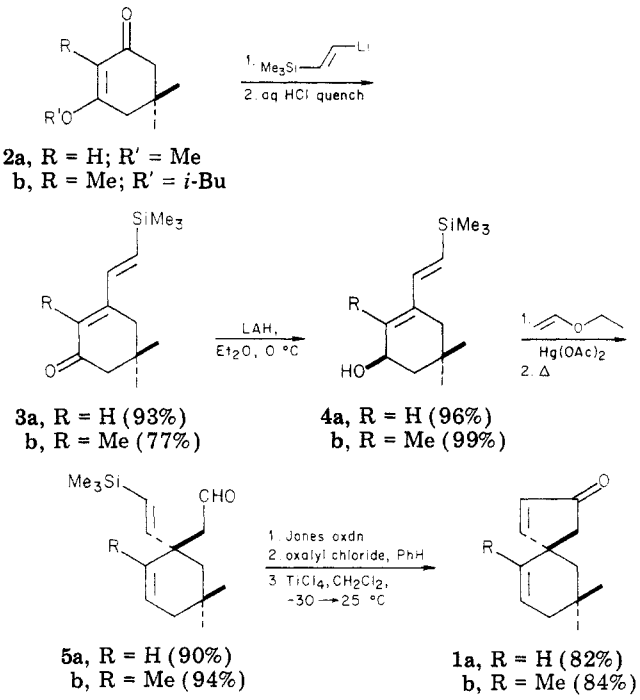
Steven D. Burke,* Charles William Murtiashaw, Meera S. Dike, Sharon M. Smith Strickland, and Jeffrey O. Saunders

Department of Chemistry, University of South Carolina, Columbia, South Carolina 29208

Received September 19, 1980

The efficient construction of quaternary carbon centers remains as a fundamental test of synthetic methodology.[1] A popular arena for the probation of such technology is the construction of spiroannulated bicyclic carbon frameworks.[2] In connection with ongoing synthetic efforts in these laboratories, we required an efficient entry to spiro[4.5]decadienones of general structure **1**. The known and readily accessible dimedone derivatives **2** were seen as particularly attractive starting materials.[3] We report herein a vinylsilane-mediated spiroannulation sequence which effects the desired overall transformation of the vinylogous esters **2** to the spirodienones **1** in excellent yield.[4]

Scheme I[6]



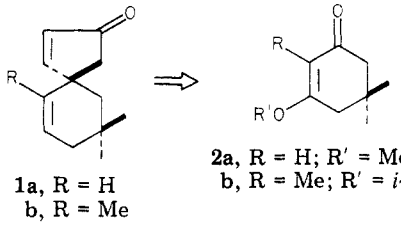
2a, R = H; R′ = Me
b, R = Me; R′ = *i*-Bu

3a, R = H (93%)
b, R = Me (77%)

4a, R = H (96%)
b, R = Me (99%)

5a, R = H (90%)
b, R = Me (94%)

1a, R = H (82%)
b, R = Me (84%)



1a, R = H
b, R = Me

2a, R = H; R′ = Me
b, R = Me; R′ = *i*-Bu

Treatment of dimedone methyl ether (**2a**) with *trans*-β-(trimethylsilyl)vinyllithium[5] (−78→25 °C) followed by a quench with 5% aqueous HCl provided the crystalline

(1) For a recent review of this topic, see: Martin, S. F. *Tetrahedron* **1980**, *36*, 419.

(2) The synthetic pursuit of a large variety of sesquiterpenes possessing a spiro[4.5]decane carbon skeleton has spawned much of this work. For a representative selection of papers describing various spiroannulation strategies, see: (a) Dauben, W. G.; Hart, D. J. *J. Am. Chem. Soc.* **1977**, *99*, 7307; (b) Corey, E. J.; Boger, D. L. *Tetrahedron Lett.* **1978**, 13; (c) Trost, B. M.; Hiroi, K.; Holy, N. *J. Am. Chem. Soc.* **1975**, *97*, 5873; (d) Semmelhack, M. F.; Yamashita, A. *Ibid.* **1980**, *102*, 5924; (e) Stork, G.; Danheiser, R. L.; Ganem, B. *Ibid.* **1973**, *95*, 3414; (f) Büchi, G.; Berthet, D.; Decorzant, R.; Grieder, A.; Hauser, A. *J. Org. Chem.* **1976**, *41*, 3208; (g) Martin, S. F. *Ibid.* **1976**, *41*, 3337; (h) Marx, J. N.; Norman, L. R. *Ibid.* **1975**, *40*, 1602; (i) Oppolzer, W.; Mahalanabis, K. K.; Battig, K. *Helv. Chim. Acta* **1977**, *60*, 2388; (j) Ruppert, J. F.; Avery, M. A.; White, J. D. *J. Chem. Soc., Chem. Commun.* **1976**, 978; (k) Altenbach, H.-J. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 940. For a review on the chemistry of spirosesquiterpenes, see: Marshall, J. A.; Brady, S. F.; Anderson, N. H. *Fortschr. Chem. Org. Naturst.* 1974, *31*, 283. For general reviews on spirocycle synthesis, see: Krapcho, A. P. *Synthesis* **1978**, 77; *Ibid.* **1976**, 425; *Ibid.* **1974**, 383.

(3) Clark, R. D.; Ellis, J. E.; Heathcock, C. H. *Synth. Commun.* **1973**, *3*, 347.

(4) For applications of vinylsilanes in intermolecular acylation–cyclopentenone annulation sequences, see: (a) Cooke, F.; Moerck, R.; Schwindeman, J.; Magnus, P. *J. Org. Chem.* **1980**, *45*, 1046; (b) Paquette, L. A.; Fristad, W. E.; Dime, D. S.; Bailey, T. R. *Ibid.* **1980**, *45*, 3017.

(5) Prepared from the corresponding vinylstannane: Cunico, R. F.; Clayton, F. J. *J. Org. Chem.* **1976**, *41*, 1980.

0022-3263/81/1946-2400$01.25/0

dienone **3a** (mp 46–48 °C) in 93% yield (Scheme I).[6] Careful reduction of **3a** with an ethereal suspension of lithium aluminum hydride at 0 °C gave the chromatographically pure allylic alcohol **4a** in very high (96%) isolated yield.[7] Subjection of this alcohol to the standard mercuric ion catalyzed exchange reaction with ethyl vinyl ether and thermolysis in a sealed tube resulted in a smooth and efficient Claisen rearrangement sequence,[8] yielding the aldehyde **5a** (90%). The requisite quaternary center of eventual spirofusion was thus secured in three steps, with an overall yield in excess of 80% for the conversion of dimedone methyl ether (**2a**) to aldehyde **5a**.

The penultimate stage of the spiroannulation sequence required an upward adjustment of the carbonyl oxidation state[9] and activation. This was easily effected without purification of the intermediates by Jones oxidation[10] to the acid followed by treatment with oxalyl chloride in benzene[11] to give the corresponding acid chloride.

A variety of Lewis acid catalysts were screened for efficacy in the spiroannulation step. Of these, $TiCl_4$ and $SnCl_4$ provided the most satisfactory results, with $TiCl_4$ being the most effective. Treatment of the crude acid chloride derived from **5a** with 3 equiv of $TiCl_4$ in methylene chloride at −30 °C followed by allowing the reaction mixture to warm to 25 °C provided the desired spiro[4.5]decadienone **1a** in 79% yield from the aldehyde **5a**. *The overall yield for the transformation of* ***2a*** *to* ***1a*** *was 64%.*

In strict analogy, the sequence was also executed by starting with 2-methyldimedone isobutyl ether (**2b**). The conversion of **2b** to **1b** proceeded straightforwardly in the yields given in Scheme I. This second sequence proceeded in comparable efficiency, affording the spiro[4.5]decadienone **1b** in 60% overall yield. As described in the Experimental Section, the spiroannulation can be readily executed on milligram or multigram scales.

Experimental Section[12]

General Procedures. Melting points were recorded on a Büchi capillary melting point apparatus. Melting and boiling points are uncorrected. Infrared (IR) spectra were recorded on a Beckman IR 4210 spectrometer. Proton magnetic resonance (^1H NMR) spectra were recorded at 60 MHz (Varian EM 360), 90 MHz (Perkin-Elmer R-32 or Varian EM 390), or 400 MHz (Bruker WH-400) as indicated. Carbon magnetic resonance (^{13}C NMR) spectra were recorded on a Varian CFT-20 spectrometer. Chemical shifts for proton and carbon resonances are reported in parts per million (δ) relative to Me_4Si (δ 0.0).

Analytical thin-layer chromatography (TLC) was done on Analtech precoated TLC plates with silica gel GHLF, 250-μm layer thickness. Column chromatography was done with E. Merck silica gel 60, 70–230 mesh ASTM, Baker silica gel, 40–140 mesh, or Fisher Florisil, 100–200 mesh.

"Dry" solvents were prepared as follows. Diethyl ether (Et_2O) and tetrahydrofuran (THF) were distilled from sodium benzophenone ketyl immediately before use; ethyl vinyl ether was distilled from sodium; benzene was distilled from calcium hydride and stored over sodium; methylene chloride was passed through alumina or distilled from phosphorus pentoxide. All reactions were run under an atomosphere of dry nitrogen.

Elemental analyses were performed by Robertson Laboratory, Florham Park, NJ.

5,5-Dimethyl-3-[*trans*-β-(trimethylsilyl)vinyl]cyclohex-2-en-1-one (3a). To a solution of 12.22 g (31.4 mmol) of *trans*-1-(trimethylsilyl)-2-(tri-*n*-butylstannyl)ethylene in 45 mL of dry THF at −78 °C was added 31 mL of 0.96 M *n*-BuLi (29.8 mmol). After the mixture was stirred for 50 min at −78 °C and 50 min at −33 °C, the solution was again cooled to −78 °C and 4.47 g (29 mmol) of the vinylogous ester **2a**[2] in 9 mL of THF was added dropwise. The reaction was allowed to gradually warm to room temperature over a 4.5-h period. The solution was then cooled to 0 °C and quenched with 10 mL of 5% aqueous HCl and allowed to stir at ambient temperature overnight. The mixture was extracted with Et_2O and the combined extracts were dried ($MgSO_4$) and concentrated. The crude product was purified by chromatography on 700 g of silica gel. Elution with 10:1 hexanes–ether gave 6.00 g (93%) of crystalline dienone **3a**: mp 46–48 °C; R_f 0.51 (1:2 ether–hexanes); IR (CCl_4) 1667 (C=O), 1603 (C=C), 1568 cm^{-1} (C=C); ^1H NMR (60 MHz) ($CDCl_3$) δ 6.51 (AB q, 2 H, J_{AB} = 19 Hz, $\Delta\nu_{AB}$ = 12.6 Hz), 5.91 (t, 1 H, J = 1.5 Hz), 2.36 (d, 2 H, J = 1.5 Hz), 2.27 (s, 2 H), 1.08 (s, 6 H), 0.16 (s, 9 H); ^{13}C NMR ($CDCl_3$) δ 199.85, 154.36, 144.08, 137.95, 126.64, 51.08, 38.09, 32.71, 27.99, −1.88. Sublimation [bath temperature 60 °C (0.30 mmHg)] provided an analytical sample of **3a**.

Anal. Calcd for $C_{13}H_{22}OSi$: C, 70.20; H, 9.97. Found: C, 70.26; H, 10.02.

5,5-Dimethyl-3-[*trans*-β-(trimethylsilyl)vinyl]cyclohex-2-en-1-ol (4a). To a suspension of 2.21 g (0.058 mol) of lithium aluminum hydride in 300 mL of dry diethyl ether at 0 °C was added dropwise a solution of 12.00 g (0.054 mol) of dienone **3a** in 35 mL of ether. The reaction was allowed to stir for 4 h at 0 °C, at which time were added 2.0 mL of water, 2.2 mL of 15% aqueous sodium hydroxide, and finally 6.0 mL of water.[13] The resulting granular precipitate of aluminum salts was removed by filtration and the filtrate was dried ($MgSO_4$) and concentrated. The product thus obtained was eluted through a column of silica gel with ether to yield 11.62 g (96%) of the allylic alcohol **4a** as a viscous, colorless oil, homogeneous by TLC and spectroscopic analysis: R_f 0.62 (1:2 hexanes–ether); IR (film) 3313 (OH), 1632 (C=C), 1580 cm^{-1} (C=C); ^1H NMR (60 MHz) ($CDCl_3$) δ 6.19 (AB q, 2 H, J_{AB} = 19 Hz, $\Delta\nu_{AB}$ = 42.6 Hz), 5.74 (br s, 1 H), 4.37 (br s, 1 H), 2.66 (br s, 1 H), 2.00 (br s, 2 H), 1.86–1.20 (m, 2 H), 1.09 (s, 3 H), 0.93 (s, 3 H), 0.13 (s, 9 H); ^{13}C NMR ($CDCl_3$) δ 146.25, 136.91, 131.24, 127.23, 66.05, 44.90, 37.55, 31.55, 30.46, 25.76, −1.38.

3-(2-Oxoethyl)-3-[*trans*-β-(trimethylsilyl)vinyl]-5,5-dimethylcyclohex-1-ene (5a). To a solution of 3.40 g (15.2 mmol) of allylic alcohol **4a** in 300 mL of ethyl vinyl ether was added 4.0 g (12.5 mmol) of mercuric acetate. The reaction mixture was heated at reflux, and three 2.0-g (6.25 mmol) portions of mercuric acetate were added at 2 h intervals. After being refluxed overnight, the reaction was cooled to room temperature and 0.60 mL of glacial acetic acid was added. After being stirred for 3 h, the reaction mixture was diluted with 200 mL of ether and washed with 200 mL of 5% aqueous KOH. The organic layer was dried (K_2CO_3) and condensed. Elution through a column of Florisil with ether–hexanes (1:6) afforded 3.59 g (95%) of the corresponding allyl vinyl ether which was homogeneous by TLC and spectroscopic analysis, R_f 0.86 (1:2 ether–hexanes).

Into a sealable tube was placed 1.20 g (4.76 mmol) of the vinyl ether. After being sealed, the tube was heated at 187 °C for 5.75 h and at 200 °C for 30 min. The crude product was eluted through a column of Florisil with 1:15 ether–hexanes to yield 1.14 g (4.52 mmol, 95%) of the Claisen rearrangement product, aldehyde **5a**, as a colorless oil, homogeneous by spectroscopic analysis: R_f 0.69 (1:5 ether–hexanes); IR (CCl_4) 1723 (C=O), 1605 cm^{-1} (C=C); ^1H NMR (60 MHz) ($CDCl_3$) δ 9.64 (t, 1 H, J = 3.2 Hz), 5.89 (AB q, 2 H, J_{AB} = 19.2 Hz, $\Delta\nu_{AB}$ = 19.0 Hz), 5.77 (br s, 2 H), 2.39 (d, 2 H, J = 3.2 Hz), 1.87 (br s, 2 H), 1.63 (AB q, 2 H, J_{AB} = 14.4

(6) All yields reported are for chromatographically and spectroscopically pure material.

(7) If the reduction was carried out at temperatures greater than 0 °C, conjugate reduction became competitive.

(8) For general reviews of the Claisen rearrangement, see: (a) Rhoads, S. J.; Raulins, N. R. *Org. React.* **1975**, *22*, 1; (b) Ziegler, F. E. *Acc. Chem. Res.* **1977**, *10*, 227.

(9) Claisen rearrangement modifications which would give the higher oxidation state directly (e.g., Johnson ortho ester Claisen and Ireland ester enolate Claisen) proved unsatisfactory.

(10) Bowers, A.; Halsall, T. G.; Jones, E. R. H.; Lemin, A. J. *J. Chem. Soc.* **1953**, 2555.

(11) Adams, R.; Ulich, L. H. *J. Am. Chem. Soc.* **1920**, *42*, 599.

(12) Full experimental details are presented only for the sequence affording the spiro[4.5] decadienone **1a**. The procedures leading to **1b** were essentially identical, and the last step of that sequence is detailed below.

(13) This useful procedure, which greatly simplifies the workup of $LiAlH_4$ reductions, is described in: Fieser, L. F.; Fieser, M. "Reagents for Organic Synthesis"; Wiley and Sons: New York, 1967; Vol. I, p 584.

Hz, $\Delta\nu_{AB}$ = 12.70 Hz), 1.03 (s, 3 H), 0.90 (s, 3 H), 0.11 (s, 9 H).

9,9-Dimethylspiro[4.5]deca-1,6-dien-3-one (1a). To a solution of 1.67 g (6.68 mmol) of aldehyde **5a** in 20 mL of acetone at 0 °C was added 2.5 mL (6.68 mmol) of Jones reagent (2.67 M) dropwise via syringe. After being stirred at 0 °C for 2 h the reaction mixture was allowed to warm to room temperature over a 1-h period. The reaction was neutralized with aqueous sodium bicarbonate and extracted several times with ether. The combined ether extracts were washed with dilute aqueous HCl and brine, dried (Na_2SO_4), and concentrated under reduced pressure. Filtration of an ether solution of the crude product through a pad of silica gel provided 1.73 g (97%) of the carboxylic acid.

To a solution of 50 mg (0.188 mmol) of the carboxylic acid in 1 mL of dry benzene was added 73 μL (0.84 mmol) of oxalyl chloride dropwise via syringe. After the reaction mixture was stirred for 3 h at room temperature the benzene and excess oxalyl chloride were removed in vacuo and 3.0 mL of dry methylene chloride was added. After the solution was cooled to −30 °C, 62 μL (0.56 mmol) of titanium tetrachloride was added. The reaction mixture was stirred 2 h at −30 °C and was allowed to warm to room temperature and stir for 15 h, at which time the solution was poured into saturated aqueous sodium bicarbonate. The organic material was extracted with ether and the combined extracts were dried ($MgSO_4$) and concentrated. Purification was effected by chromatography on a column of silica gel. Elution with hexanes, followed by 1:8 ether–hexanes, afforded 27 mg (82%) of the desired spiro[4.5]decadienone **1a**, homogeneous by TLC and spectroscopic methods, as an oil (crystalline at subambient temperature): R_f 0.46 (1:1 ether–hexanes); IR (CCl_4) 1723 (C=O); ^{1}H NMR (400 MHz) ($CDCl_3$) δ 7.29 (d, 1 H, J = 5.50 Hz), 6.02 (d, 1 H, J = 5.50 Hz), 5.68 (ddd, 1 H, J = 9.68, 5.22, 2.90 Hz), 5.27 (br d, 1 H, J = 9.68 Hz), 2.34 (AB q, 2 H, J_{AB} = 18.77 Hz, $\Delta\nu_{AB}$ = 63.98 Hz), 1.78–1.86 (m, 2 H), 1.51 (AB q, 2 H, J_{AB} = 13.73 Hz, $\Delta\nu_{AB}$ = 85.87 Hz), 0.97 (s, 3 H), 0.92 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 208.67, 171.77, 131.00, 128.80, 126.40, 48.77, 46.46, 45.58, 37.78, 30.64, 28.89, 26.75. Distillation [bath temperature 80 °C (1.4 mmHg)] gave an analytical sample of **1a**.

Anal. Calcd for $C_{12}H_{16}O$: C, 81.77; H, 9.15. Found: C, 81.85; H, 9.23.

6,9,9-Trimethylspiro[4.5]deca-1,6-dien-3-one (1b). To a solution of 7.51 g (28.4 mmol) of aldehyde **5b** in 90 mL of acetone at 0 °C was added 10.65 mL (28.4 mmol) of 2.67 M Jones reagent in dropwise fashion. After being stirred for 2.5 h at 0 °C and 6 h at room temperature, the reaction mixture was neutralized with saturated aqueous bicarbonate and extracted repeatedly with ether. The combined ether extracts were dried ($MgSO_4$) and concentrated in vacuo to give 7.77 g (98%) of the corresponding carboxylic acid.

To a solution of 11.05 g (39.5 mmol) of this acid in 230 mL of dry benzene was added 12.5 mL (143 mmol) of oxalyl chloride. After the reaction mixture was stirred at room temperature for 8.5 h, the benzene and excess oxalyl chloride were removed in vacuo and 350 mL of dry methylene chloride was added. The solution was cooled to −30 °C and 12.95 mL (118 mmol) of titanium tetrachloride was added dropwise. After the solution had been stirred for 2 h at −30 °C and 14 h at room temperature, the reaction was poured into saturated aqueous sodium bicarbonate. The organic material was extracted with ether, and the combined extracts were dried ($MgSO_4$) and concentrated under reduced pressure. The crude product was purified by chromatography on silica gel. Elution with hexanes followed by 1:8 ether–hexanes afforded 6.30 g (84%) of the spiro[4.5]decadienone **1b**, homogeneous by TLC and spectroscopic criteria, as an oil (crystalline at subambient temperature): R_f 0.66 (1:1 ether–hexanes); IR (film) 1720 cm^{-1} (C=O); ^{1}H NMR (400 MHz) ($CDCl_3$) δ 7.29 (d, 1 H, J = 5.37 Hz), 6.14 (d, 1 H, J = 5.37 Hz), 5.50 (br s, 1 H), 2.39 (s, 3 H), 1.86 (AB q, 2 H, J_{AB} = 16.65 Hz, $\Delta\nu_{AB}$ = 39.96 Hz), 1.53 (AB q, 2 H, J_{AB} = 13.67 Hz, $\Delta\nu_{AB}$ = 116.19 Hz), 1.49 (s, 2 H), 0.98 (s, 3 H), 0.94 (s, 3 H).

Anal. Calcd for $C_{13}H_{18}O$: C, 82.06; H, 9.53. Found: C, 81.88; H, 9.63.

Acknowledgment. Grateful acknowledgment is extended to the donors of the Petroleum Research Fund, administered by the American Chemical Society, to Research Corporation, to the National Institutes of Health (Biomedical Research Support Grant 5 S07 RR07160), and to the American Cancer Society (Grant IN-107F, awarded to C.W.M.) for their generous support of this research. High-field NMR spectra were obtained through the National Science Foundation Regional NMR Center at the University of South Carolina (Grant CHE 78-18723).

Registry No. 1a, 76999-33-2; **1b**, 76999-34-3; **2a**, 4683-45-8; **2b**, 76999-35-4; **3a**, 76999-36-5; **3b**, 76999-37-6; **4a**, 76999-38-7; **4b**, 77011-22-4; **5a**, 76999-39-8; **5a** carboxylic acid, 76999-40-1; **5b**, 76999-41-2; **5b** carboxylic acid, 76999-42-3; *trans*-1-(trimethylsilyl)-2-(tributylstannyl)ethylene, 58207-97-9; ethyl vinyl ether, 109-92-2.

Effect of Benzyl Groups on Electron Loss from Tetraalkylhydrazines and 2-Tetrazenes

Stephen F. Nelsen,* Loretta A. Grezzo, and Valentine E. Peacock

S. M. McElvain Laboratories of Organic Chemistry, Department of Chemistry, University of Wisconsin, Madison, Wisconsin 53706

Received December 16, 1980

The thermodynamics of the tetraalkylhydrazine one electron oxidation equilibrium (eq 1) has been studied for

$$R_2NNR_2 \underset{+e}{\overset{-e}{\rightleftharpoons}} (R_2NNR_2)^{+\cdot} \quad (1)$$

a variety of alkyl groups by determining the formal potentials for electron transfer ($E^{\circ\prime}$), using cyclic voltammetry (CV).[1] Equation 1 provides an opportunity to study the effect of R group substitution on a reaction where these effects are unusually large. Changes in the thermodynamics for eq 1 with R group substitution have proven to be dominated by steric effects, although electronic and solvation effects are clearly also present. The alkyl groups on adjacent nitrogens are eclipsed in the radical cation, which has an olefin-like equilibrium geometry with a substantially shorter NN distance,[2] greatly increasing the vicinal R group interaction over that in the neutral form. The majority of this increase in vicinal steric interaction is removed in the tetraalkyl-2-tetrazene electron-transfer equilibrium (eq 2).[3] Comparison of $E^{\circ\prime}$ values for these

$$R_2NN{=}NNR_2 \underset{+e}{\overset{-e}{\rightleftharpoons}} [R_2NN{=}NNR_2]^{+\cdot} \quad (2)$$

equilibria with vertical, vapor-phase ionization potentials (IP_v) measured by photoelectron (PE) spectroscopy has allowed estimation of the importance of steric, electronic, and solvation changes with alkyl group substitution on these equilibria.[4] Our discussion of these factors has previously been limited to the effects of saturated alkyl substituents. We turn our attention here to considering

(1) Nelsen, S. F.; Peacock, V. E.; Weisman, G. R. *J. Am. Chem. Soc.* **1976**, *98*, 3281.
(2) Nelsen, S. F.; Hollinsed, W. C.; Kessel, C. R.; Calabrese, J. C. *J. Am. Chem. Soc.* **1978**, *100*, 7876.
(3) Nelsen, S. F.; Peacock, V. E. *J. Am. Chem. Soc.* **1977**, *99*, 8354.
(4) (a) Nelsen, S. F.; Peacock, V. E.; Kessel, C. R. *J. Am. Chem. Soc.* **1978**, *100*, 7017. (b) Nelsen, S. F. *Isr. J. Chem.* **1979**, *18*, 45.

0022-3263/81/1946-2402$01.25/0