condensed in a 100-mL round-bottom flask equipped with a dry ice condenser. Lithium shot (0.07 g, 0.010 mol), cleaned by rinsing in pentane, was then added and the base solution stirred until the blue color was discharged. To standardize the solution, a 1.00-mL aliquot was diluted to 10.00 mL with water. The resulting solution was used to titrate a weighed amount of potassium acid phthalate in water to the bromothymol blue end point.

Potassium 3-Aminopropylamide (KAPA). Procedure A. In a 100-mL three-neck, round-bottom flask (equipped with gas inlet adaptor, gas outlet which could be connected to a gas buret, and a rubber septum) potassium hydride (10 drops of a 20–25% suspension in oil, Alfa Products) was freed from its storage oil by washing with pentane several times and drying in a stream of dry nitrogen. 1,3-Diaminopropane (10.0 mL) was then added through the septum. The concentration of the base solution was calculated from the amount of hydrogen evolved and was adjusted, when desired, by adding a measured quantity of solvent. Unless the titer of a 1.00-mL aliquot of the base solution (see the preparation of LEA/EA solutions) agreed within 5% the solution was discarded. However, the concentration of KAPA in these solutions must be less than the titers indicate because the quenched early samples contain much less of the unconjugated diene **3** than is obtained in experiments with an excess of KAPA. With excess diene, the rate of aromatization is almost constant after the intermediate carbanion reaches its steady-state concentration, which, in turn, is approximately equal to the initial concentration of KAPA. Three independent preparations of 0.05 M KAPA (titer) gave steady-state rates of forming arene from initially 0.05 M diene of 1.3 ± 0.3% min^{-1}. Judged by the maximum concentration of diene **3** obtained in these experiments (Table III) the solutions contained 20–30% of the observed titer. The solutions, to which crown ether or potassium tetraphenylborate was added, were prepared by this procedure.

KAPA. Procedure B. This procedure differed from A in that the reaction vessel was a cylindrical tube (50-mL capacity) fitted with two stopcocks and a male ₮ 24/40 joint which could be closed with a rubber septum. The transfer to the tube of four to five drops of a 35 wt % potassium hydride suspension in mineral oil (Aldrich Chemical Co.) was done in a dry nitrogen swept glovebag. The reaction tube was then closed with a tight fitting septum and connected to the souce of dry nitrogen and to an automatic gas buret. The remainder of the procedure was the same as in A. The concentration of the amide formed was calculated from the volume of gas generated.[14]

***t*-BuOK/Me_2SO.** Potassium *tert*-butoxide (1.1 g) was transferred to the cylindrical reaction tube, described above as in procedure B. Under a flow of nitrogen, 10.0 mL of dry dimethyl sulfoxide was injected through the septum, and the mixture was stirred. The clear solution of *t*-BuOK/Me_2SO (≃1.0 M) was maintained at the required temperature (30 or 55 °C), and the diene (**1** or **2**, 50 μL) was injected into the base along with 25 μL of *tert*-butylbenzene.

Enolate Equilibria and Force Field Parameters

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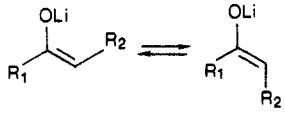
Lithium enolates with differing degrees of alkyl substitution were prepared and geometrically equilibrated by using catalytic phenylmercuric chloride in tetrahydrofuran. With the the resulting thermodynamic data, MM2 force field parameters were evaluated by using an automatic force field refinement program.

Introduction

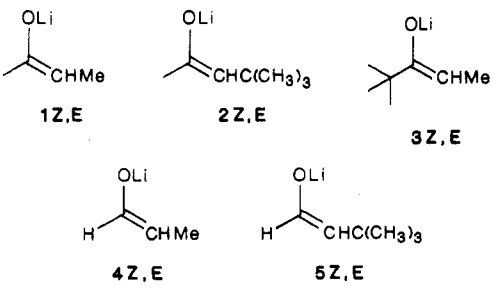
Geometrical equilibration of acyclic enolates from the often kinetically favored *E* isomer to the more stable *Z* isomer is a common method for controlling enolate stereochemistry. While studies by House[2] and Rathke[3]



demonstrated that the *Z* isomer is favored thermodynamically by approximately 1 kcal/mol for enolates where R_1, R_2 = CH_3, CH_2R, or CHR_2, little is known about the geometrical preferences of more hindered systems or enolates derived from aldehydes. Such information is important not only because it extends the scope of the equilibration process but also because it helps distinguish the nonbonded properties of the alkoxide with its associated counterion and bound solvent from the intrinsic torsional preferences of the enolate double bond. In this paper we describe equilibration of five conformationally well-defined lithium enolates in tetrahydrofuran, including those having R_1 or R_2 = *tert*-butyl. These studies were made possible by the development of a new enolate equilibration method and led to a preliminary assignment of force field parameters for ketone and aldehyde lithium enolates in the context of the MM2 molecular mechanics force field.[4]

Results and Discussion

The enolates we chose to study are those shown below. These enolates were selected because of their structural diversity and the threefold symmetry of their olefinic substituents which provide conformationally homogeneous enolates.



(1) NIH Postdoctoral Fellow, 1984–1986.
(2) (a) House, H. O.; Kramar, V. *J. Org. Chem.* **1963**, *28*, 3362. (b) House, H. O.; Trost, B. M. *J. Org. Chem.* **1965**, *30*, 1341.
(3) Fataftah, Z. A.; Kopka, I. E.; Rathke, M. W. *J. Am. Chem. Soc.* **1980**, *102*, 3959.
(4) Allinger, N. L. *J. Am. Chem. Soc.* **1977**, *99*, 8127.

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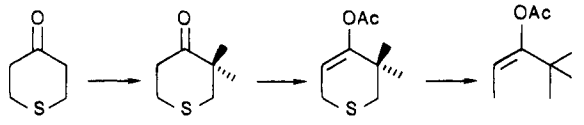
In preparation for the equilibration experiments, stereochemically enriched mixtures of both the *Z* and *E* enol trimethylsilanes or acetates of **1–5** were prepared. For **1** and **4**, enol trimethylsilanes were prepared as previously reported[5] and the geometrical isomers were separated by preparative VPC. In the case of **2**, conjugate addition of lithium dimethylcuprate to mesityl oxide followed by trapping with acetic anhydride gave a 3:1 mixture of *E* and *Z* enol acetates, which were separated by chromatography on silica gel. The isomerically pure enol acetates were then converted to their enol silanes by treatment with MeLi followed by addition of chlorotrimethylsilane. For **5**, conjugate addition of lithium dimethylcuprate to 3,3-dimethylacrolein with in situ trapping by chlorotrimethylsilane gave an 88:12 mixture of *E* and *Z* enol silanes[6] that readily resolved by flash chromatography. Stereochemical assignments were made by NMR. Thus aldehyde enol silanes **4** and **5** showed HC=CH coupling constants of 6–6.5 Hz and 12 Hz, which were assigned to the *Z* and *E* isomers, respectively. Methyl ketone enol silanes **1** and **2** exhibited upfield ^{13}C γ effects for the α' methyl of 5.2 and 4.2 ppm as expected for the *E* (methyl/alkyl cis) isomers.

While the *Z* enol acetate of **3** was prepared with >99% stereochemical purity by deprotonation with $LiN(i\text{-}Pr)_2$ (THF, −78 °C) followed by acetylation with acetic anhydride, the labile *E* isomer required a more lengthy preparation. Thus the lithium enolate of tetrahydrothiapyran-4-one[7] was dimethylated to **6** by a stepwise procedure ((1) LDA, THF, CH_3I, −40 °C; (2) Me_3SiI, HMDS, CH_2Cl_2; (3) (a) MeLi, THF–HMPA, −20 °C; (b) CH_3I), converted to enol acetate **7** ((a) LDA, THF; (b) Ac_2O), and then desulfurized (W-2 RaNi, THF, 25 °C).[8] While the desulfurization was accompanied with some geometrical isomerization, the product contained approximately 84% of the desired *E* isomer. The *E* enol acetate could be distilled but was rapidly hydrolyzed upon attempted purification by silica gel chromatography.



6 **7** **8E**

Although a variety of methods for enolate equilibration have been reported, including treatment with catalytic proton sources,[9] carbonyl compounds,[3] and oxygen,[10] none of the previously described procedures was successful with enolates **1–5**. The proton-exchange methods are among the most commonly used but in the case of the aldehyde enolates, aldol-related chemistry rapidly destroyed the enolate. In the case of enolate **2**, regioisomerization to the less substituted but more stable isomer was competitive with geometrical isomerization under all previously reported conditions.

Table I. Summary of Enolate Equilibration Data

enolate[a]	starting ratio (*Z*/*E*)[b]	final ratio (*Z*/*E*)
1	97:3	82:18[c]
1	71:29	82:18[c]
2	99.5:0.5	20:80[c]
2	1:99	20:80[c]
3[e]	>99.9:0.1	99.8:0.2[d]
3[e]	16:84	99.7:0.3[d]
4	99.9:0.1	65:35[c]
4	1:99	65:35[c]
5	>99.9:0.1	4:96[c]
5	<0.1:99.9	3:97[c]

[a] All runs were performed by using the enol trimethylsilane enolate precursor unless otherwise noted. [b] Starting ratios measured by ^1H NMR and/or VPC. [c] Final ratios measured by ^1H and/or ^{13}C NMR. [d] Final ratios measured by VPC of Ac_2O enolate trapping products; the *E* isomer could not be detected by NMR. [e] Enol acetate used as enolate precursor.

What was needed was a method that allowed for rapid enolate stereoisomerization with retention of positional integrity. One approach to this objective makes use of a reversible reaction at carbon. Aldol chemistry with carbonyl compounds like benzophenone has been used previously[3] for this purpose, but with the enolate **2**, no carbonyl compound could be found that rendered the equilibration fast enough to compete with enolate regioisomerization and decomposition.

Among the electrophiles that could give fast, reversible carbon addition with enolates are the mercuric halides. It is known that mercury(II) electrophiles give α-mercurio ketones[11] on reaction with enol derivatives and also that organomercurials undergo rapid exchange reactions with organolithiums.[12] We therefore treated the *Z* and *E* lithium enolates of **1–5** with 0.5–1.0 mol % of phenylmercuric chloride at 25 °C. Using enolate trapping with acetic anhydride and capillary VPC analysis, we found that the enolates under study underwent clean geometrical equilibration with half-lives of approximately 15 s. Before the equilibration/trapping method was used to evaluate the equilibrium *Z*/*E* ratio of **1–5**, several experiments were conducted to establish validity of the procedure. First, it was verified that the *Z*/*E* ratio of product enol acetates with **5** was invariant with enolate concentration (0.1–1.0 M) and with the amount of PhHgCl used (0.5–20.0 mol %). Second, by comparing the NMR-measured *Z*/*E* ratios of the enolates themselves (see below) with the Ac_2O trapping results, it was shown that with aldehyde enolates, the NMR and trapping results were indistinguishable. With certain ketone enolates, however, the situation was more complex. Enolate **2**, for example, gave significantly different results with the two analytical methods where Ac_2O trapping and enolate NMR, respectively, provided *Z*/*E* ratios of 65:35 and 20:80. Furthermore, the Ac_2O trapping ratio varied somewhat with changes in the amount of phenylmercuric chloride used in the equilibration experiments. These discrepancies likely stem from the rapidity of the mercury-catalyzed equilibration which becomes

(5) (a) Heathcock, C. H.; Buse, G. T.; Kleschick, W. A.; Pirrung, M. L.; Sohn, J. E.; Lampe, J. *J. Org. Chem.* **1980**, *45*, 1066. (b) Schraml, J.; Sraga, J.; Hrnciar, P. *Collect. Czech. Chem. Commun.* **1983**, *48*, 3097.

(6) (a) Corey, E. J.; Boaz, N. W. *Tetrahedron Lett.* **1985**, *26*, 6019. (b) Alexakis, A.; Berlan, J.; Besace, Y. *Tetrahedron Lett.* **1986**, *27*, 1047.

(7) Tetrahydrothiapyran-4-one was prepared in two steps in 45% overall yield by alkylation of *N*-methyl-4-piperidone with methyl iodide in ether followed by treatment of the iodide salt with a two-phase mixture of aqueous $Na_2S{\cdot}9H_2O$ and $CHCl_3$.

(8) (a) Kondo, K.; Negishi, A.; Matsui, K.; Tunemoto, D.; Masamune, S. *JCS Chem. Comm.*, **1972**, 1311. (b) Stotter, P. L.; Hornish, R. E. *J. Am. Chem. Soc.* **1973**, *95*, 4444.

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(12) (a) Makarova, L. G.; Nesmeyanov, A. N. *Methods of Elementoorganic Chemistry*; Nesmeyanov, A. N., Kocheschkov, K. A., Eds.; North-Holland: Amsterdam, 1967, Vol. 4. (b) Straub, H.; Zeller, K. P.; Leditschke, H. *Houben-Weyl's Methoden der Organischen Chemie, Band XIII, 2b*; Thieme Verlag: Stuttgart, 1974. (c) Makarov, L. *Organomet. React.* **1971**, *1*, 119; **1971**, *2*, 335.

competitive with trapping with hindered enolates such as **2**.

Thus with rapid equilibration methods like the one described here, the most reliable method for equilibrium ratio determination is direct measurement by a nonperturbing method like NMR. These measurements were carried out in THF-d_8 at 25 °C by using long relaxation times with both ^1H and ^{13}C NMR to monitor the progress of the equilibrations of **1–5**. Since the equilibrations were accompanied with varying amounts of solid formation, an internal standard was used to verify that one isomer was not being removed by selective precipitation.

The equilibrium ratios of the lithium enolates of **1–5** at 25 °C in tetrahydrofuran were measured starting in each case from both sides of the equilibrium position using the phenylmercuric chloride equilibration procedure described above. Table I summarizes the results.

The most obvious result of these equilibrations is the previously noted[2,3] preference for the *Z* isomers except in systems (**2**, **5**) bearing sterically demanding *tert*-butyl α substituents. The equilibrium ratio for the 2-butanone enolate (Z/E = 82:18) is similar to that reported by Rathke[3] for the lithium enolate of 3-pentanone in THF (Z/E = 84:16). The results above support the notion that there is an intrinsic thermodynamic preference for the *Z* isomers of enolates and further suggest that, when steric effects dominate the equilibrium, the steric requirements of enolate alkoxide with its bound counterion/solvent are intermediate between those of methyl and *tert*-butyl.

To generalize the above data and make the results useful for the molecular modeling of enolates, we used the experimentally determined energy differences in conjunction with available X-ray structural data to parameterize a simple molecular mechanics enolate model. Since only a meager amount of pertinent experimental data was available, the number of force field parameters that could be evaluated was quite small. The model we used was thus a crude one consisting only of the monomeric enolate anion itself. Such a model is obviously simplistic in light of recent X-ray[13] and NMR[14] studies of lithium enolates that show them to be well-defined oligomeric complexes of the enolate, lithium counterion, and solvent. It should be noted, however, that while the counterion and solvent are not explicit in our model, their effect can be implicitly incorporated into the force field parameters whose associated potential functions most closely resemble the actual potential surface. Thus, in fitting the model to the data, we would expect that the effective van der Waals radius of the enolate alkoxide to be enlarged in the optimized model, thereby representing alkoxide and its associated ligands as a single large sphere or superatom.

The most common method for finding the best values of force field parameters is repetitive manual adjustment until the calculated results cannot be significantly improved by further parameter adjustment. This method was used to establish the natural length of the enolate C–O bond to reproduce the experimental bond length found in the X-ray structure of pinacolone.[13] While the manual method works well when only a few parameters are to be optimized and the experimental data consist of only one or two points, simultaneous optimization of many parameters to fit a larger body of data is best carried out by a more automated procedure. To carry out such a refinement, we defined an error function (*F*), which reflected both energetic and geometrical errors as follows:

$$F = \sum(\text{energetic error})^2 + \sum(\text{geometrical error}) \times 100$$

The energetic error above is the difference between the calculated and experimental Z/E enolate energy differences for **1–5** and the geometrical error is the root-mean-square (rms) deviation for the least-squares superimposition[15] of the non-hydrogen atoms for the calculated and X-ray structures of the pinacolone enolate. Energetic errors in kJ/mol are squared, making the function sensitive to the most serious errors in energy and geometrical rms deviations are multiplied by 100 to make an 0.1 angstrom deviation correspond to a 10 kJ/mol energetic error. The geometrical errors are not squared to reflect our bias toward reproducing Z/E energy differences rather than the details of the X-ray crystal structure of pinacolone enolate.

Given the error function *F* which summarizes the extent to which the force field reproduces all of the experimental data, we used a program developed here that computes numerical derivatives of *F* with respect to the force field parameters and uses an iterative, steepest descent method with line-searching to find optimized values for the parameters giving the minimum possible value of *F*.[16] Thus we optimized the van der Waals, bending angle and certain torsional parameters involving the enolate alkoxide to give the final parameter set (Chart I).

The enolate C–O natural bond length (1.34 Å) was taken directly from the X-ray structure of the pinacolone enolate[13] and the remaining force field parameters were not optimized but simply set to the values of the corresponding parameters of the MM2 treatment of enol ethers.[17] While the paucity of data upon which this optimization was based makes analysis of the individual terms unwarranted, it is interesting to note that the major difference between the optimized enolate field and the enol ether field lies in the van der Waals parameters. Thus the united atom alkoxide that emerges is approximately twice the radius of the MM2 ether oxygen and is only 1% as hard.

Until more experimental data is available, the above parameters must be regarded as tentative but, as the

Chart I

bending:	
$C(sp^2)=C(sp^2)OLi$	$\theta_0 = 114.7°$
$C(sp^3)C(sp^2)OLi$	$\theta_0 = 102.3°$
$HC(sp^2)OLi$	$\theta_0 = 94.4°$
torsion:	
$C(sp^3)C(sp^2)=C(sp^2)OLi$	$V_1 = -1.2$ kcal/mol
van der Waals:	
OLi	$R = 3.58$, eps = 0.0007

Chart II

	$E - Z$, kcal/mol	
enolate	experimental	calculated
1	−0.90	−0.88
2	0.82	0.38
3	−3.29	−2.99
4	−0.37	−0.28
5	2.06	2.39

(13) (a) Amstutz, R.; Schweizer, W. B.; Seebach, D.; Dunitz, J. D. *Helv. Chim. Acta* **1981**, *64*, 2617, 2622. (b) Laube, T.; Dunitz, J. D. Seebach, D. *Helv. Chim. Acta* **1985**, *68*, 1373. (c) Seebach, D.; Amstutz, R.; Laube, T.; Schweizer, W. B.; Dunitz, J. D. *J. Am. Chem. Soc.* **1985**, *107*, 5403. (d) Williard, P. G.; Carpenter, G. B. *J. Am. Chem. Soc.* **1985**, *107*, 3345. (e) Williard, P. G.; Carpenter, G. B. *J. Am. Chem. Soc.* **1986**, *108*, 462.

(14) (a) Jackman, L. M.; Szeverenyi, N. M. *J. Am. Chem. Soc.* **1977**, *99*, 4954. (b) Jackman, L. M.; Lange, B. C. *J. Am. Chem. Soc.* **1981**, *103*, 4494. (c) Jackman, L. M.; Lange, B. C. *Tetrahedron* **1977**, *33*, 2737.

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(16) For a previous molecular mechanics force field refining scheme, see: Hagler, A. T.; Huler, E.; Lifson, S. *J. Am. Chem. Soc.* **1974**, *96*, 5319.

(17) Dodziuk, H.; von Voithenberg, H.; Allinger, N. L. *Tetrahedron* **1982**, *38*, 2811.

summary below shows, the calculated and experimental data compare well for the lithium enolates in tetrahydrofuran described here (Chart II).

Conclusion

While previous methods for the geometrical equilibration of enolates are problematic with certain systems, the phenylmercuric halide method described here operated efficiently with all systems studied. These systems included both methyl ketones and aldehydes and yields of equilibrated enolates were high in all cases. In a single experiment, we also found that the method works well with ester enolates and gives essentially the same E/Z ratio as does the standard LDA/HMPA procedure. We consider the catalytic phenylmercuric chloride scheme described here to be the method of choice for the stereochemical isomerization of enolates.

The use of automated parameterization schemes to optimize molecular mechanics force fields is advantageous when more than one or two parameters must be simultaneously adjusted or when multiple pieces of experimental data are being simultaneously fitted. Although experimentally underdetermined at this point, the molecular mechanics enolate model described above was readily defined by the automated optimization scheme described and fits the available data well.[20]

Experimental Section

(*E*)- and (*Z*)-2-Acetoxy-4,4-dimethyl-2-pentene. To a slurry of 10.3 g (54 mmol) of CuI in 25 mL dry THF at 0 °C under argon was added 83 mL (108 mmol) of 1.3 M MeLi in Et_2O. After stirring for 30 min, 5.1 mL (45 mmol) of mesityl oxide was added dropwise. After being stirred for 15 min, the reaction mixture was cooled to −78 °C, and 8.5 mL (90 mmol) of acetic anhydride was added in a single portion. The solution was warmed to room temperature, diluted with 100 mL of pentane, and filtered through Celite. The Celite was washed with 1 L of pentane. Combined organics were carefully stripped to a clear oil and filtered through silica gel (50 mm × 130 mm) with 10% ether/pentane to yield a 3:1 E/Z mixture of enol acetates. Flash chromatography (70 mm × 130 mm, 5% ether/pentane) separated the faster eluting E isomer from the Z isomer, yielding 2.41 g (34%) of the E isomer and 0.72 g (10%) of the Z isomer. Spectra were as previously reported.[18]

(*Z*)-2-[(Trimethylsilyl)oxy]-4,4-dimethyl-2-pentene. To a solution of 15 mL (19.2 mmol) of 1.3 M ethereal MeLi in 20 mL THF at 0 °C was added 1.15 mL (1.0 g, 6.41 mmol) of Z enol acetate. The ice bath was removed and the reaction mixture was stirred for 15 min. It was then cooled to 0 °C and 5.4 mL (21.4 mmol) of a 1:1 chlorotrimethylsilane/triethylamine mixture was added. After 15 min, the solution was diluted with 30 mL of petroleum ether and washed twice with *cold* saturated aqueous $NaHCO_3$. Drying over $MgSO_4$, filtration, and careful concentration at reduced pressure gave the crude product. Kugelrohr distillation (60 mmHg, 100–110 °C) gave 1.13 g (95%) of pure Z enol silane: IR (neat, cm^{-1}) 2955, 1665, 1479, 1379, 1339, 1254, 1228, 1162, 1043, 989, 846, 754, 677; ^1H NMR (270 MHz, $CDCl_3$) δ 4.27 (q, 1 H, J = 1.0 Hz, C=C*H*), 1.75 (d, 3 H, J = 1.0 Hz, C=CC*H*$_3$), 1.05 (s, 9 H, (C*H*$_3$)$_3$C), 0.20 (s, 9 H, (CH$_3$)$_3$Si); ^{13}C NMR (70 MHz, $CDCl_3$) δ 145.3 (C=*C*OSi(CH$_3$)$_3$), 117.4 (C=*C*H), 30.7 (C(CH$_3$)$_3$), 31.0 (*C*(CH$_3$)$_3$), 23.8 (C=C(OSi(CH$_3$)$_3$)*C*H$_3$), 1.0 ((*C*H$_3$)$_3$Si); MS (EI, relative intensity, m/e) 186 (10, M^+), 171 (100), 73 (90); HRMS (EI), calcd for $C_{10}H_{22}OSi$ 186.144, found 186.147.

(*E*)-2-[(Trimethylsilyl)oxy]-4,4-dimethyl-2-pentene. The E isomer was obtained by following the above procedure: IR (neat, cm^{-1}) 2959, 1660, 1463, 1384, 1362, 1253, 1233, 1159, 1037, 1000, 885, 843, 754; ^1H NMR (270 MHz, $CDCl_3$) δ 4.78 (q, 1 H, J = 1.0 Hz, C=C*H*), 1.81 (d, 3 H, J = 1.0 Hz, C=CC*H*$_3$), 1.07 (s, 9 H, (C*H*$_3$)$_3$C), 0.15 (s, 9 H, (C*H*$_3$)$_3$Si); ^{13}C NMR (70 MHz, $CDCl_3$) δ 146.7 (CH$_3$*C*=), 120.5 (C=*C*H), 31.5 (C(CH$_3$)$_3$), 30.2 (*C*(CH$_3$)$_3$), 19.6 (C=C*C*H$_3$), 0.34 ((*C*H$_3$)$_3$Si); MS (EI, relative intensity, m/e) 186 (10, M^+), 171 (100), 115 (10), 73 (100), 57 (12); HRMS (EI), calcd for $C_{10}H_{22}OSi$ 186.144, found 186.148.

3-Methyltetrahydrothiapyran-4-one. To a solution of 15 mL (7.5 mmol) of a 0.5 M solution of LDA in THF at −78 °C was added dropwise a solution of 858 mg (7.4 mmol) of tetrahydrothiapyran-4-one (Aldrich) in 3 mL of THF. After being stirred for 30 min, the solution was added dropwise to a flask containing 691 μL (11.1 mmol) of methyl iodide in 2 mL of THF at −40 °C. This was allowed to stir for 3 h at which point the reaction mixture was diluted with ether and washed with saturated $NaHCO_3$ and brine. The ethereal extracts were combined, dried over Na_2SO_4, decanted, and concentrated in vacuo to give a yellow oil. The crude oil was purified by flash chromatography on a 45 mm × 200 mm silica gel column, eluting with 10% ethyl acetate/petroleum ether, giving 683 mg (71%) of 3-methyltetrahydrothiapyran-4-one: IR (neat, cm^{-1}) 2980, 2940, 2920, 1715 (C=O), 1450, 1420, 1375, 1245, 1130, 975, 920, 815; ^1H NMR (270 MHz, $CDCl_3$) δ 2.83 (m, 7 H, SC*H*$_2$C*H*(CH$_3$)C(=O)C*H*$_2$C*H*$_2$S), 1.15 (d, 3 H, J = 7.0 Hz, C*H*$_3$CHC=O); ^{13}C NMR (70 MHz, $CDCl_3$) δ 209.8 (C=O), 47.3 (O=CCHCH$_2$S), 43.3 (CH$_2$C=O), 37.0 (SCH$_2$CHC=O), 30.4 (SCH$_2$CH$_2$C=O), 14.2 (CH$_3$CHC=O); MS (EI, relative intensity, m/e) 130 (100, M^+), 102 (12), 88 (51), 74 (30), 60 (47); HRMS (EI), calcd for $C_6H_{10}OS$ 130.04523, found 130.04680; TLC (silica gel, 10% ethyl acetate/petroleum ether) R_f 0.35.

1-[(Trimethylsilyl)oxy]-2-methyl-4-thiacyclohex-1-ene.[19] To a solution of 321 mg (2.47 mmol) of 3-methyltetrahydrothiapyran-4-one and 433 mg (603 μL, 2.96 mmol) of hexamethyldisilazane in 3.2 mL of CH_2Cl_2 at −20 °C was added 546 mg (385 μL, 2.72 mmol) of iodotrimethylsilane. After being stirred for 12 h at room temperature, the reaction mixture was diluted with pentane and washed with cold water followed by cold brine. The organic layers were combined, dried over Na_2SO_4, decanted, and concentrated in vacuo to give a pale yellow oil. The crude oil was purified by flash chromatography on a 20 mm × 200 mm silica gel column, eluting with 1% ether/pentane, yielding 477 mg (96%) of the desired product. Capillary VPC of the material indicated a 90:10 mixture of isomeric enol ethers.

Major isomer: IR (pentane, cm^{-1}) 2960, 1460, 1380, 1265, 1140, 1105, 910, 865; ^1H NMR (270 MHz, $CDCl_3$) δ 3.06 (bs, 2 H, SC*H*$_2$C(CH$_3$)=CO), 2.73 (t, 2 H, J = 7.0 Hz, SC*H*$_2$CH$_2$C=O), 2.28 (m of t, 2 H, J = 7.0 Hz, SCH$_2$C*H*$_2$C=O), 1.63 (s, 3 H, OC=CC*H*$_3$), 0.19 (s, 9 H, (C*H*$_3$)$_3$SiO); ^{13}C NMR (70 MHz, $CDCl_3$) δ 143.7 (SiOC=C), 110.1 (SiOC=*C*), 31.3 (SCH$_2$*C*H$_2$C=C), 29.8 (SCH$_2$CH$_2$C=C), 25.9 (SCH$_2$C=CO), 16.4 (SiOC=C*C*H$_3$), 0.4 ((CH$_3$)$_3$SiO); MS (EI, relative intensity, m/e) 202 (37, M^+), 187 (44), 174 (17), 159 (10), 141 (18), 112 (9), 91 (8), 73 (100); HRMS (EI) calcd for $C_9H_{18}OSiS$ 202.08475, found 202.07720; TLC (silica gel, 10% ethyl acetate/petroleum ether) R_f 0.88.

3,3-Dimethyltetrahydrothiapyran-4-one (6). To a solution of 235 μL (273 μmol) of 1.16 M MeLi in 250 μL of THF and 85 μL of HMPA was added at −20 °C, 50 mg (248 μmol) of 1-[(trimethylsilyl)oxy]-2-methyl-4-thiacyclohex-1-ene in 250 μL of THF. The mixture was allowed to stir for 45 min and then added dropwise to a microflask containing 30 μL of methyl iodide in 250 μL of THF at −78 °C. The resulting mixture was allowed to stir for 3 h and was diluted with ether, washed with water and brine, dried over Na_2SO_4, decanted, and concentrated at reduced pressure to give a yellow oil. The oil was purified by flash chromatography on a 5 mm × 100 mm silica column, eluting with 5% ethyl acetate/petroleum ether, giving 24 mg (67%) of **6**: IR (pentane, cm^{-1}) 2960, 2890, 2840, 1708, 1455, 1375, 1260, 1135, 905, 858; ^1H NMR (270 MHz, $CDCl_3$) δ 3.88 (t, 2 H, J = 6.9 Hz, CH$_2$C*H*$_2$C=O), 3.71 (t, 2 H, J = 6.9 Hz, C*H*$_2$CH$_2$C=O), 3.69 (s, 2 H, C*H*$_2$C(CH$_3$)$_2$C=O), 1.24 (s, 6 H, (C*H*$_3$)$_2$CC=O); ^{13}C NMR (70 MHz, $CDCl_3$) δ 212.3 (C=O), 46.7 (O=*C*C(CH$_3$)$_2$), 43.2 (*C*H$_2$C=O), 40.1 (SC*H*$_2$C(CH$_3$)$_2$), 30.6 (SC*H*$_2$CH$_2$C=O), 24.5 ((C*H*$_3$)$_2$CC=O); MS (EI, relative intensity, m/e) 144 (65, M^+), 116 (6), 89 (27), 60 (14), 56 (100); HRMS (EI), calcd for $C_7H_{12}OS$ 144.06088, found 144.06035; TLC (silica gel, 10% ethyl acetate/petroleum ether) R_f 0.47.

6,6-Dimethyl-1-acetoxy-4-thiacyclohex-1-ene (7). To a solution of 833 μL (416 μmol) of 0.5 M LDA in THF at −78 °C

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was added a solution of 50 mg (347 μmol) of **6** in 1 mL of THF. The solution was allowed to stir for 45 min and 65 μL (694 μmol) of acetic anhydride was added. After stirring for 10 min, it was warmed to room temperature and stirred for an additional 10 min. The reaction mixture was diluted with pentane and washed with cold saturated $NaHCO_3$. The pentane extracts were combined, dried over Na_2SO_4, decanted and concentrated in vacuo to give a colorless oil. The oil was purified by flash chromatography on a 10 mm × 150 mm silica gel column eluting with 2% ether/pentane, giving 44 mg (69%) of **7**: IR (pentane, cm^{-1}) 2960, 2820, 1752, 1455, 1420, 1380, 1265, 902, 855; ^1H NMR (270 MHz, $CDCl_3$) δ 5.45 (q, 1 H, J = 5.5 Hz), 3.19 (d, 2 H, J = 5.5 Hz, SCH_2CH=), 2.62 (s, 2 H, $SCH_2C(CH_3)_2$), 2.14 (s, 3 H, CH_3C=O), 1.14 (s, 6 H, $(CH_3)_2CC$=O); ^{13}C NMR (70 MHz, $CDCl_3$) δ 169.1 (CH_3C=O), 153.8 (O=COC=C), 113.2 (O=COC=C), 40.6 (SCH_2C=C), 35.6 ($SCH_2C(CH_3)_2C$=C), 25.9 ($(CH_3)_2CC$=C), 25.1 ($SCH_2C(CH_3)_2$-C=C), 21.0 ($OCOCH_3$); MS (EI, relative intensity, m/e) 186 (47, M^+), 144 (100), 111 (34), 98 (28), 88 (83); HRMS (EI), calcd for $C_9H_{14}O_2$ 186.07144, found 186.07124; TLC (silica gel, 10% ethyl acetate/petroleum ether) R_f 0.39.

(*Z*)-4,4-Dimethyl-3-acetoxypent-2-ene (8Z). To a solution of 1.08 mL (0.516 mmol) of a 0.5 M LDA solution in THF at −78 °C was added a solution of 52.6 mg (0.43 mmol) of *tert*-butyl ethyl ketone in 1.5 mL of THF. The solution was allowed to stir for 45 min and 81 μL of acetic anhydride was added. This was allowed to stir for 25 min before it was worked up by diluting with pentane and washing with cold saturated $NaHCO_3$. The organic layers were combined, dried over Na_2SO_4, decanted, and concentrated in vacuo to give a colorless oil. Flash chromatography on a 40 mm × 200 mm silica gel column eluting with 5% ether/pentane gave 59 mg (88%) of (*Z*)-4,4-dimethyl-3-acetoxypent-2-ene: IR (pentane, cm^{-1}) 2960, 2730, 2650, 1761, 1460, 1375, 902, 860; ^1H NMR (270 MHz, C_6D_6) δ 5.13 (q, 1 H, J = 7.0 Hz, vinylic), 1.85 (s, 3 H, O=CCH_3), 1.51 (d, 3 H, J = 7.0 Hz, CH_3CH=), 1.13 (s, 9 H, *t*-Bu)); ^{13}C NMR (70 MHz, C_6D_6) δ 167.9 (CH_3C=O), 156.6 (O=COC=C), 108.1 (OC=CCH_3), 36.7 ($C(CH_3)_3$), 28.6 (C(CH_3)$_3$), 20.8 (CH_3C=O), 12.0 (CH_3C=CO); MS (EI, relative intensity, m/e) 156 (4, M^+), 114 (63), 99 (100), 81 (24); HRMS (EI), calcd for $C_9H_{16}O_2$ 156.11502, found 156.11537; TLC (silica gel, 10% ethyl acetate/petroleum ether) R_f 0.54.

(*E*)-4,4-Dimethyl-3-acetoxypent-2-ene (8E). A slurry of 7.5 g of Raney Ni (Aldrich, equivalent to W-2 Raney Ni catalyst) in 10 mL of dry THF was prepared by washing the solution ten times with 20-mL portions of distilled water and ten times with 20-mL portions of dry THF. To this slurry under N_2 was added 473 mg (2.54 mmol) of 6,6-dimethyl-1-acetoxy-4-thiacyclohex-1-ene in 1.0 mL of dry THF. The solution was allowed to stir for 48 h at room temperature and then filtered through a plug of Celite and washed with pentane. The solvent was removed by reduced pressure distillation at aspirator pressure to give a yellow oil. Kugelrohr distillation of the residue at atmospheric pressure gave two fractions, one (50–70 °C) containing mostly solvent with some impurities and the other (70–110 °C) containing an 84:16 mixture of *E* and *Z* enol acetates (178 mg, 45%). Attempted flash chromatography on a 3% Et_3N slurry-packed silica gel column led to decomposition and hydrolysis.

8E: IR (pentane, cm^{-1}) 2960, 2730, 2660, 1749, 1460, 1375, 908, 860; ^1H NMR (270 MHz, C_6D_6) δ 5.13 (q, 1 H, J = 7.0 Hz, vinylic), 1.84 (s, 3 H, O=CCH_3), 1.68 (d, 3 H, J = 7.0 Hz, CH_3CH=), 1.27 (s, 9 H, *t*-Bu)); ^{13}C NMR (70 MHz, C_6D_6) δ 169.7 (CH_3C=O), 154.9 (O=COC=C), 113.8 (OC=CCH_3), 36.7 ($C(CH_3)_3$), 29.9 (C(CH_3)$_3$), 20.8 (CH_3C=O), 12.9 (CH_3C=CO); MS (EI, relative intensity, m/e) 156 (3, M^+), 114 (90), 99 (100), 81 (40); HRMS (EI), calcd for $C_9H_{16}O_2$ 156.11502, found 156.11430; TLC (silica gel, 10% ethyl acetate/petroleum ether) R_f 0.61.

(*E*)- and (*Z*)-3,3-Dimethyl-1-[(trimethylsilyl)oxy]but-1-ene.[6] To a slurry of 24.9 g (131.0 mmol) of cuprous iodide in 350 mL of dry THF at 0 °C was added 225.5 mL (261.6 mmol) of a 1.16 M solution of MeLi in Et_2O. The brownish grey solution was cooled to −50 °C and 14.2 g (16.55 mL, 130.3 mmol) of trimethyl chlorosilane was added. The solution was allowed to stir for 10 min and 10.0 g (119.0 mmol) of 3,3-dimethylacrolein was added in 20 mL of dry THF. This solution was stirred overnight at −50 °C and worked up by diluting with pentane and washing with cold water followed by cold, dilute NH_4OH. The pentane layers were combined, dried over Na_2SO_4, decanted, and concentrated to give a pale yellow oil. ^1H NMR analysis showed an 88:12 mixture of *E* and *Z* enol silanes. Flash chromatography of 3.0-g portions of the product on a 50 mm × 250 mm silica gel column eluting with 0.5% Et_2O/pentane gave the pure product. A total of 12.8 g (61%) of *E* enol silane and 1.72 g (9%) of *Z* enol silane were collected as colorless oils. The remainder of the material (30%) consisted of 1,2-addition product.

E isomer: IR (pentane, cm^{-1}) 2980, 2910, 2860, 1659, 1460, 1380, 1255, 1145, 1030; ^1H NMR (270 MHz, $CDCl_3$) δ 6.13 (d, 1 H, J = 12.0 Hz, OC*H*=CH), 5.08 (d, 1 H, J = 12.0 Hz, OCH=C*H*), 0.98 (s, 9 H, $(CH_3)_3C$), 0.18 (s, 9 H, $(CH_3)_3Si$); ^{13}C NMR (70 MHz, $CDCl_3$) δ 136.5 (O*C*H=CH), 124.1 (OCH=*C*H), 29.9 ($(CH_3)_3C$), −0.9 ($(CH_3)_3Si$); MS (EI, relative intensity, m/e) 172 (11, M^+), 157 (89), 113 (11), 83 (11), 73 (100), 57 (17); HRMS (EI), calcd for $C_9H_{20}OSi$ 172.12833, found 172.12976; TLC (silica gel, 1% Et_2O/pentane) R_f 0.24.

Z isomer: IR (pentane, cm^{-1}) 2980, 2910, 2860, 1651, 1475, 1450, 1445, 1380, 1095, 910; ^1H NMR (270 MHz, $CDCl_3$) δ 5.96 (d, 1 H, J = 6.5 Hz, OC*H*=CH), 4.30 (d, 1 H, J = 6.5 Hz, OCH=C*H*), 1.09 (s, 9 H, $(CH_3)_3C$), 0.15 (s, 9 H, $(CH_3)_3Si$); MS (EI, relative intensity, m/e) 172 (14, M^+), 157 (100), 101 (5), 83 (14), 73 (98), 57 (23); HRMS (EI), calcd for $C_9H_{20}OSi$ 172.12833, found 172.12872; TLC (silica gel, 1% Et_2O/pentane) R_f 0.64.

Generation and Equilibration of Enolates. Procedure A (Acetic Anhydride Quench). To a solution of 290 μmol of enol silane in 1.3 mL of dry THF was added 0.17 mL of 1.36 M methyllithium in ether at 25 °C. After 30 min, 23 μL of an 0.1 M solution of phenylmercuric chloride in THF was added. After 30 s, 42 μL of Ac_2O was added and the resulting mixture was stirred for an additional 1 min. The solution was then poured into ether and washed with saturated $NaHCO_3$. The organic phase was dried over $MgSO_4$ and decanted and an aliquot was immediately analyzed by OV-101 capillary column VPC.

Procedure B (NMR Studies). A steady stream of dry argon was blown over a solution of 300 μL (348 μmol) of 1.16 M MeLi in Et_2O in a micro reaction vial until the Et_2O had evaporated. To the dry solid was added 114 μmol of enol silane (or 57 μmol of enol acetate) in 450 μL of THF-d_8. The vial was centrifuged and the supernatant liquid syringed into a flame-dried NMR tube that had been purged with argon. As an internal standard, a solution of purified mesitylene in THF-d_8 was added to the enolate solution and then the tube was sealed with parafilm. Portions of phenylmercuric chloride (2–5 mg) were added under Ar to the contents of the NMR tube and spectra were then recorded on either a JEOL FX-270 or a Bruker WM-300 spectrometer. NMR spectral data for the lithium enolates are given below.

(*Z*)-2-(Lithiooxy)but-2-ene (1Z): ^1H NMR (270 MHz, THF-d_8) δ 3.5 (vinyl H, obscured by solvent), 1.60 (bs, 3 H, =C(OLi)CH_3), 1.44 (d, 3 H, J = 6.0 Hz, CH_3CH=); ^{13}C NMR (70 MHz, THF-d_8) δ 158.3 (=COLi), 86.9 (=CH), 26.4 (CH_3C-(OLi)=), 11.54 (CH_3CH=).

(*E*)-2-(Lithiooxy)but-2-ene (1E): ^1H NMR (270 MHz, THF-d_8) δ 3.9 (q, 1 H, J = 7.0 Hz, vinyl H), 1.6 (bs, 3 H, =C-(OLi)CH_3), 1.46 (d, 3 H, J = 7.0 Hz, CH_3CH=); ^{13}C NMR (70 MHz, THF-d_8) δ 158.3 (=COLi), 86.8 (=CH), 20.0 (CH_3C(O-Li)=), 13.6 (CH_3CH=).

(*Z*)-4,4-Dimethyl-2-(lithiooxy)-2-pentene (2Z): ^1H NMR (270 MHz, THF-d_8) δ 3.54 (bs, 1 H, vinyl H), 1.73 (bs, 3 H, vinyl Me), 1.04 (s, 9 H, $(CH_3)_3C$); ^{13}C NMR (70 MHz, THF-d_8) δ 157.4 (=COLi), 102.7 (=CH), 32.2 (C(CH_3)$_3$), 31.4 ($C(CH_3)_3$), 28.2 (C(OLi)CH_3).

(*E*)-4,4-Dimethyl-2-(lithiooxy)-2-pentene (2E): ^1H NMR (270 MHz, THF-d_8) δ 4.18 (bs, 1 H, vinyl H), 1.73 (bs, 3 H, vinyl Me), 1.04 (s, 9 H, $(CH_3)_3C$); ^{13}C NMR (70 MHz, THF-d_8) δ 158.0 (=COLi), 105.3 (=CH), 33.4 (C(CH_3)$_3$), 30.4 ($C(CH_3)_3$), 22.7 (C(OLi)CH_3).

(*Z*)-4,4-Dimethyl-3-(lithiooxy)pent-2-ene (3Z): ^1H NMR (300 MHz, THF-d_8) δ 3.79 (q, 1 H, J = 7.0 Hz, vinylic), 1.49 (d, 3 H, J = 7.0 Hz, CH_3C=C), 1.00 (s, 9 H, $(CH_3)_3C$); ^{13}C NMR (70 MHz, THF-d_8) δ 170.7 (LiOC=C), 82.7 (LiOC=*C*), 38.4 ($(CH_3)_3C$), 30.9 ($(CH_3)_3C$), 14.8 (CH_3C=C).

(*E*)-4,4-Dimethyl-3-(lithiooxy)pent-2-ene (3E): ^1H NMR (300 MHz, THF-d_8) δ 3.79 (q, 1 H, J = 7.0 Hz, vinylic), 1.62 (d, 3 H, J = 7.0 Hz, CH_3C=C), 1.05 (s, 9 H, $(CH_3)_3C$); ^{13}C NMR (70 MHz, THF-d_8) δ 171.1 (LiO*C*=C), 78.3 (LiOC=*C*), 36.1 ($(CH_3)_3C$), 30.9 ($(CH_3)_3C$), 11.6 (CH_3C=C).

(Z)-1-(Lithiooxy)prop-1-ene (4Z): ^{1}H NMR (270 MHz, THF-d_8) δ 6.69 (d, 1 H, J = 3.0, LiOC*H*=), 3.6 (vinyl H, obscured by solvent), 1.47 (d, 3 H, J = 6.0 Hz, vinyl Me).

(E)-1-(Lithiooxy)prop-1-ene (4E): ^{1}H NMR (270 MHz, THF-d_8) δ 6.72 (d, J = 11.0 Hz, LiOC*H*=), 4.08 (m, 1 H, MeC*H*=), 1.40 (d, 3 H, J = 5.9 Hz, vinyl Me).

(Z)-3,3-Dimethyl-1-(lithiooxy)but-1-ene (5Z): ^{1}H NMR (270 MHz, THF-d_8) δ 6.46 (d, 1 H, J = 6.5 Hz, LiOC*H*=CH), 3.37 (d, 1 H, J = 6.5 Hz, LiOCH=C*H*), 1.08 (s, 9 H, $(CH_3)_3C$); ^{13}C NMR (70 MHz, THF-d_8) δ 150.3 (LiO*C*=C), 108.6 (LiOC=*C*), 33.9 ($(CH_3)_3C$), 32.9 ($(CH_3)_3C$).

(E)-3,3-Dimethyl-1-(lithiooxy)but-1-ene (5E): ^{1}H NMR (300 MHz, THF-d_8) δ 6.75 (d, 1 H, J = 11.5 Hz, LiOC*H*=CH), 4.29 (d, 1 H, J = 11.5 Hz, LiOCH=C*H*), 0.96 (s, 9 H, $(CH_3)_3C$); ^{13}C NMR (70 MHz, THF-d_8) δ 150.5 (LiO*C*=C), 111.7 (LiOC=*C*), 33.0 ($(CH_3)_3C$), 31.7 ($(CH_3)_3C$).

Electrochemical Reduction of Phenylpropadiene at Mercury Cathodes in Dimethylformamide: Isomerization of the Allene to 1-Phenyl-1-propyne

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Polarograms and cyclic voltammograms exhibit two waves for reduction of phenylpropadiene at a mercury electrode in dimethylformamide containing tetra-*n*-butylammonium perchlorate; the first wave signals reduction of phenylpropadiene to 1-phenyl-1-propene and the second wave is attributable to reduction of 1-phenyl-1-propene to 1-phenylpropane. However, the first wave is abnormally small because phenylpropadiene undergoes substantial rearrangement to 1-phenyl-1-propyne, which is reducible to 1-phenylpropane at nearly the same potential as 1-phenyl-1-propene. Controlled-potential electrolyses of phenylpropadiene, 1-phenyl-1-propene, and 1-phenyl-1-propyne at mercury pool cathodes have verified the processes elucidated by means of polarography and cyclic voltammetry. In the presence of diethyl malonate (a proton donor), base-catalyzed isomerization of phenylpropadiene to 1-phenyl-1-propyne is blocked totally; at a potential corresponding to the first wave for reduction of phenylpropadiene, electrolysis products are *trans*-1-phenyl-1-propene, *cis*-1-phenyl-1-propene, and 1-phenyl-2-propene, whereas 1-phenylpropane and 1-phenyl-2-propene are obtained at a potential on the second reduction wave for phenylpropadiene.

Two recent reviews[1,2] have dealt extensively with the electrochemical reduction and oxidation of allenes. In general, the allene moiety is not electroreducible unless it is conjugated to one or more phenyl groups or unless it is bonded to another activating substituent.

Our interest in the electrochemistry of phenylpropadiene stems from a paper by Doupeux, Martinet, and Simonet[3] concerning the cathodic behavior of several haloallenes, among which was 1-phenyl-3-bromopropadiene. These authors observed that, in dimethylformamide containing 0.1 M tetraethylammonium bromide, reduction of 1-phenyl-3-bromopropadiene gives rise to four polarographic waves, the third and fourth being attributed to stepwise reduction of phenylpropadiene to 1-phenyl-1-propene and to 1-phenylpropane. As part of the same work, the polarographic and coulometric characteristics of 3-chloro-3-phenyl-1-propyne in dimethylformamide containing 0.1 M tetraethylammonium perchlorate were examined, and the starting material was postulated to undergo a sequence of electron-transfer and proton-transfer reactions having phenylpropadiene as an intermediate. In a brief survey of the electrochemistry of 1-phenyl-1-hydroxy-2-propyne in dimethylformamide containing 0.1 M tetra-*n*-butylammonium iodide, Lund and co-workers[4] implied that, in the presence of a proton donor, phenylpropadiene might be involved in the overall course of the reduction. In none of these investigations, however, was the existence of phenylpropadiene actually demonstrated. Moreover, there has been no publication pertaining to the electrochemistry of phenylpropadiene itself.

Accordingly, we report the results of the first study of the electrochemical reduction of phenylpropadiene at mercury in dimethylformamide containing 0.1 M tetra-*n*-butylammonium perchlorate and of the electrolytically induced isomerization of phenylpropadiene to 1-phenyl-1-propyne.

Experimental Section

Reagents. Dimethylformamide used as solvent and tetra-*n*-butylammonium perchlorate employed as supporting electrolyte were handled as described in a previous paper.[5] Triply distilled mercury (Troy Chemical Corp., Wood Ridge Chemical Division) was utilized as electrode material. All deaeration and drying operations were carried out with either Matheson PP or Air Products UHP nitrogen.

Instrumentation and Procedures. Cells for polarography, cyclic voltammetry, and controlled-potential electrolyses were similar to those described in earlier publications.[5-7] All potentials are quoted with respect to a reference electrode consisting of a saturated cadmium amalgam in contact with dimethylformamide saturated with both cadmium chloride and sodium chloride;[8,9] this electrode has a potential of -0.75 V vs. the aqueous saturated calomel electrode at 25 °C.

Controlled-potential electrolyses were performed with the aid of a Princeton Applied Research Corporation (PARC) Model 173

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