Stereochemical Control of Reductions. 6.[1] The Hydroxymethyl Group as a Hinge for Internal Reagent Delivery[2]

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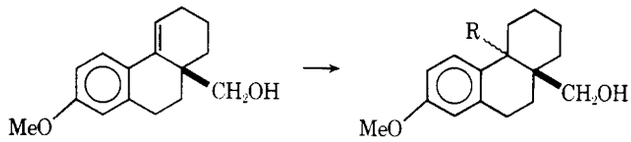
Esters of 7-methoxy-1,2,3,9,10,10a-hexahydrophenanthrene-10a-carboxylic acid have been synthesized by two routes. Reduction provided 7-methoxy-10a-hydroxymethyl-1,2,3,9,10,10a-hexahydrophenanthrene (1), whose cis (2) and trans (3) reduction products have previously been characterized. Treatment of 1 with $LiAlH_4$ in refluxing dibutyl ether gave 90% of a 95:5 mixture of 2 and 3, implying internal hydride transfer and a cyclic Al species. The extreme slowness of this reaction compared to the analogous reduction of cinnamyl alcohol is attributed to the *p*-methoxyl group, the trisubstituted styrene, and particularly the requirement of a seven-center hydride transfer. Reduction of 1 and of its salts with insufficiencies of N_2H_2 gave 48–60% conversions to mixtures containing the following ratios of 2 and 3: 1 (pure 2), Li (99:1), Na (58:42), K (52:48). These results are discussed in terms of attractive electrostatic vs. repulsive steric interactions.

We have already reported instances of the use of substrate hydroxymethyl groups to control the sterochemistry of olefin reduction in heterogeneous[1,3] and homogeneous[4] catalytic hydrogenation. The availability of compound 1 and its cis and trans reduction products 2 and 3 in connection with some of these studies,[1,4] prompted us to examine several methods of using the hydroxymethyl group in 1 as a reagent



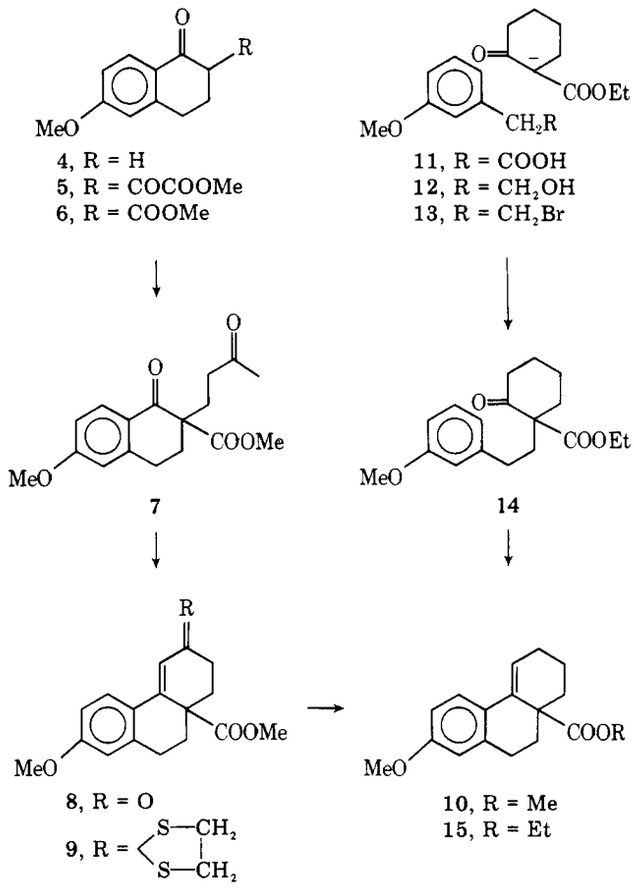
1 2, R = —H 3, R = ··· H

guide or "hinge" in other olefin reduction processes. Compound 1 seemed well suited to this kind of study for reasons similar to those which had made it attractive for hydrogenation studies,[1] viz., planarity (apart from the CH_2OH) so that both sides of the molecule are accessible, stereochemical simplicity, and positional stability of the styrene double bond. In addition, 1 combines a reasonable degree of crystallinity with sufficiently low molecular weight to allow VPC analysis and is readily available by reduction of the corresponding esters 10 and 15. As indicated in Scheme I, these esters were synthesized by two independent routes, the previously reported[5] Friedel–Crafts cyclization providing 15 in an overall yield of 23% from 11, and the alternate route through compounds 4–9 giving 10 in 26% yield; the relationship of 10 and 15 was demonstrated by transesterification. We have previously described the sequences used to establish the stereochemistry of the cis and trans reduction products 2 and 3.[1]

The reactions we wished to examine were ones for which reports exist of successful utilization of a hydroxyl group as an internal proton donor or reagent hinge. However, in both of the instances reported here the use of the hydroxyl group for stereo- or even regioselective control has been successfully demonstrated in only a single case or single series of compounds. We have examined these reactions mechanistically and for wider utility by applying them to system 1.

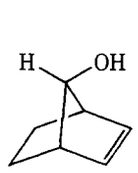
Lithium Aluminum Hydride Reduction of 1. The general rule that alkenes are not reduced by $LiAlH_4$ at ordinary pressures and temperatures[6] has a number of exceptions.[7] Almost all involve conjugated double bonds which are polarizable in such a way as to provide stabilization for the negative charge localized on the carbon where a C–Al bond is formed. Thus in essence these exceptions entail conjugate addition of hydride. Several of the systems involved, such as α,β-unsaturated carbonyl compounds,[8] are ones providing such good

Scheme I



anion stabilization that they normally undergo a wide variety of other conjugate additions. Others, such as diphenylethylenes,[9] do not and require generally higher reaction temperatures, while some compensate for poorer anion stabilization by permitting intramolecular hydride addition and incorporation of the C–Al bond into relatively unstrained rings.[10] The well known cinnamyl case,[7,11] in which carbonyl reduction precedes alkene reduction, falls into the last category.

The only examples we are aware of involving reactions at "normal" temperatures which do not involve such conjugate addition also fall into the last category and happen as well to be the sole examples which demonstrate regio- or stereochemical control by the group which confers intramolecularity. These are all reductions on variants of the homallylic systems 16 and 17.[12] The reactivity of 16 and 17 is evidently the result of a fortuitous arrangement of bonds and angles in a highly



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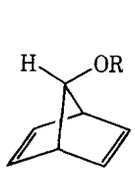
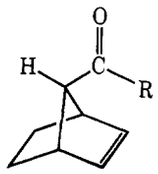


17a, R = H
17b, R = COMe



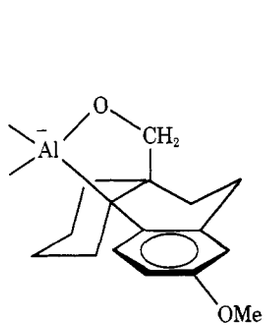
18a, R = H
18b, R = OMe

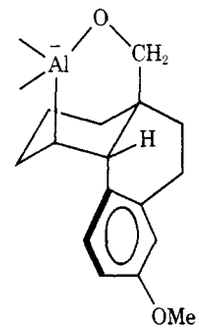
rigid system, and possibly also a result of the strained character of such alkenes.[6c,12c]

In **1** we were able to examine a case which, like cinnamyl systems, has only modest carbanion stabilization by a single phenyl, combined with the geometry for formation of a 5-membered Al ring. However **1** differs markedly from cinnamyl systems in the requirement of a 7-center hydride-transfer process in place of a 5-center one. Our results indicate that this change is drastically detrimental to olefin reduction. Successive attempts at reduction of **1** with $LiAlH_4$ in Et_2O, THF, DME, and dioxane established that the reaction does not proceed at a synthetically useful rate at the reflux temperatures of these solvents. However, in refluxing dibutyl ether (142 °) the reduction proceeded with a half-life on the order of 4 h, so that after 24–30 h the reaction was essentially complete and 90% yields of a mixture of **2** and **3** were isolable. Although several groups have reported increased rates of alkene reduction in more basic ethereal solvents,[11c,13] we desired a system whose temperature would be self-regulated by reflux and so did not explore the use of diglyme (bp 162 °C). We observed no evidence of the cyclopropane formation encountered in high-temperature $LiAlH_4$ treatment of cinnamyl systems.[14]

There are three obvious sources for this large diminution in the rate of reduction of **1** compared to cinnamyl alcohol: the presence of a deactivating *p*-methoxyl group, an additional alkyl substituent on the double bond, and the requirement of a 7-centered process for hydride transfer. Consistent with the accepted intramolecular mechanism, presence of para electron-donating groups has been found to decrease the rate of such styrene reductions by $LiAlH_4$. Two studies provide direct rate data on ethereal $LiAlH_4$ reduction of cinnamyl vs. *p*-methoxycinnamyl alcohols.[13,15] Both indicate that the decrease in rate when this substituent is introduced can be compensated for by a temperature rise of 30–40 °C, more probably the lower of these two values. Less information appears to exist concerning the effect of adding an alkyl group at the olefin being reduced. The only useful data we are aware of deals with the preparative reduction of 2-methylcinnamic acid with $LiAlH_4$ in ether.[16] This reaction proceeded in high yield with no alkene reduction when carried out at 0 °C for 24 h. Since "at higher temperatures a mixture of the allylic and saturated alcohols was obtained", it appears that the introduction of this methyl group adds an energy barrier which, again, can be overcome by raising the temperature perhaps 30–40 °C. Even taken together, these two factors fail to account adequately for the extremely high temperature required for reduction of **1**. Since stereochemical evidence (*vide infra*) indicates the reaction to be intramolecular, we believe that the third factor mentioned, the apparently unfavorable stereochemistry of the hydride-transfer process, must be invoked to explain this very low reactivity.

At least two examples of alkene reduction are known which involve direct comparison of homologs and which may be pertinent. The previously noted reduction of system **16** and its variants proceeds by way of a 6-center hydride transfer to yield a 5-membered Al species.[12c] When the conditions for these reactions were applied to **18**, in which the cyclic process and species contain one more member, no alkene reduction product was detectable (2 h, 35 °C, Et_2O).[17] It is also reported that alkyne reduction in 4-phenyl-3-butynol was undetectable even after many hours under conditions where reduction of its lower homolog, phenylpropargyl alcohol, was 50% complete in 5 min (20 °C, Et_2O).[15] While both of these cases possess special features which may qualify any generalities drawn, it seems safe to conclude that the rates of these reactions must be very sensitive functions of the stereochemistry of the hydride-transfer process. Consistent with this, the reduction of coumarin is reported to proceed without olefin involvement under conditions which lead to complete double bond saturation when ethyl *o*-coumarate is reduced.[18]





19 20

Our reduction of **1** with $LiAlH_4$ in refluxing Bu_2O produced a mixture of **2** and **3** in the ratio of 95:5, clearly implying internal hydride transfer and the intermediacy of an internally bonded species like **19** or **20**. The mechanism represented by the latter structure, involving a less disadvantageous, 6-center hydride transfer, would also require a less conventional addition to the styrene bond, but one which would be aided instead of hindered by the resonance effects associated with the *p*-methoxy group.

In **20**, where ring-juncture stereochemistry is presumably fixed during hydride transfer, the small amount of trans product observed could only be due to intermolecular reactions. If **19** is the intermediate, trans material could arise either from intermolecular reactions or from incomplete retention in the C–Al bond hydrolysis. Such hydrolyses are almost certainly kinetically controlled, since they are known to be extremely fast and they have been shown to be highly stereoretentive, at least in the case of vinylalanes[6e,19] and of **16** and **17**.[12c]

While present evidence does not allow us to distinguish conclusively between the mechanisms represented by **19** and **20**, we are inclined to favor the former. In either case our conclusion concerning **1** is that, while hydroxy groups can be used as reagent hinges for stereochemical control of olefin reduction by $LiAlH_4$ in carefully selected cases, such reactions are generally limited by extreme stereochemical sensitivity of the hydride-transfer process and by narrow requirements of other aspects of the reaction, such as carbanion stabilization and perhaps Al ring size.

Diimide Reduction of 1 and Its Salts. In 1967 Baird, Franzus, and Surridge[20] demonstrated in the reactions of diimide with the same norbornadienyl system cited above (**17**) a selectivity which ran counter to expectations based on steric grounds and thus appeared to involve an electrostatic complexation of the C-7 oxygen atom with N_2H_2. Since rates of olefin reduction with diimide fall off sharply with increasing substitution,[21] relatively few instances of reduction of tri- or tetra-substituted alkenes have been reported. Consequently, as far as we are aware no use has been made of this principle in regio- or stereoselectively controlling olefin reduction aside from the case of **17**. However, the evident enhancement in rate for N_2H_2 addition where such chelative effects operate, plus the possibility of further rate enhancement based on anion

Table I. Products from Reduction of 1 and Its Salts with HN=NH

Group	% Isolated yield	Composition of product mixture Ratio of 1:2:3[a]	Ratio of 2:3[a]
CH_2OH[b]	91	37:63:0	100:0
CH_2OH	90	37:63:0	100:0
CH_2OLi	90	47:52.5:0.5	99:1
CH_2ONa	90	33:39:28	58:42
CH_2OK	90	34:34:32	52:48

[a] Nonzero values considered accurate to ±2%, e.g., 37 ± 2:63 ± 2:0. [b] First (91%) determination carried out in refluxing diglyme, all others in refluxing 3:1 Bu_2O–diglyme.

formation, prompted us to examine the reaction of diimide with 1 and its salts.

The results, shown in Table I, clearly suggest for compound 1 and its Li salt the sort of chelative effect observed with 17. None of the results with the salts offer evidence that increased electron density on oxygen favors this effect. On the contrary, while the Li salt gives stereochemical results comparable to those from 1 itself, it appears that beyond Li, stereochemistry is increasingly controlled by the demands of cation size. This is consistent with what is already known about the sensitivity of N_2H_2 reductions to steric factors.[21,22]

Our experiments with 1 and its salts were not carried out to complete reduction (3 equiv of N_2H_2) and did not involve any appreciable excesses of base. Since toluenesulfinic acid ($pK_a \sim 1.66$) is a by-product of the thermal elimination of diimide from our precursor (*p*-toluenesulfonyl hydrazide), and since alkoxides are stronger bases than hydrazines, the alkoxy salts of 1 originally present obviously became protonated as these reactions proceeded. This change in the composition of the starting materials with reaction progress would cause the results with the salts to resemble those for neutral 1 more closely than if pure salts persisted throughout. Nevertheless the loss of stereochemical control for the Na and K salts is quite marked and is consistent only with much smaller chelative effects than for 1 or the Li salt.

It should be noted that the stereoselectivity exhibited in reduction of 1 and its Li salt is greater than for any other method of reduction we have attempted except homogeneous catalytic hydrogenation of the alkali metal salts.[1,4] Hence, although enhanced selectivity based on chelation with alkoxide ions did not materialize in our system, control of diimide reductions by internal chelation with hydroxyl groups is confirmed as a powerful stereochemical tool.

Experimental Section[23]

10a-Carbethoxy-7-methoxy-1,2,3,9,10,10a-hexahydrophenanthrene (15).[5] In a modification of a literature procedure,[24] a solution of 5.32 g (47 mmol) of KO-*t*-Bu in 104 mL of dry *t*-BuOH was stirred under N_2 during addition of 7.99 g (47 mmol) of 2-carbethoxycyclohexanone in 150 mL of *t*-BuOH. After 15–20 min, a solution of 10.2 g (47 mmol) of 3-methoxyphenethyl bromide (13)[25] in 100 mL of *t*-BuOH was added with stirring and the mixture was refluxed for 80 h and worked up as described.[24] Fractional distillation gave 7.3 g (53%) of 14 as a liquid, bp 130–155 °C at 0.08 mm (lit.[5] bp 150–160 °C at 0.1 mm); NMR δ 1.25 (3Ht, *J* = 7 Hz), 1.2–3.0 (12H complex), 3.75 (3Hs), 4.1 and 4.15 (2H, 2q, each *J* = 7), 6.5–7.3 (4H complex).

The above product (4.0 g, 13 mmol) was cyclized by refluxing in HOAc–HCl–H_2O according to the described procedure[5] to yield 3.3 g (86%) of solid 15, whose melting point after two recrystallizations from MeOH was 85 °C (lit.[5] mp 87–88 °C); IR 1720 cm^{-1}; UV 220, 261.5, 296 nm; NMR δ 1.05 (3Ht, *J* = 7 Hz), 1.2–2.9 (10H complex), 3.7 (3Hs), 4.0 (2Hq, *J* = 7), 6.1 (1 Ht, *J* = 4), 6.35–6.75 (2H complex), 7.4 (1 Hd, *J* = 9); MS *m/e* 286 (85%, M^+), 213 (100%), 212 (87%).

2-Carbomethoxy-2-(γ-ketobutyl)-6-methoxy-1-tetralone (7). 2-Methoxyoxalyl-6-methoxy-1-tetralone (5)[26] was thermally decarbonylated to provide 2-carbomethoxy-6-methoxy-1-tetralone (6);[26] NMR δ 2.0–3.2 (5H complex). 3.75 (3Hs), 3.8 (3Hs), 6.6–7.0 (2H complex), 8.0 (1 Hd, *J* = 8.5 Hz). A solution of 19.2 g (82 mmol) of 6 in 100 mL of dry benzene was added to a solution prepared by dissolving 1.90 g (82.5 mg-atoms) of Na in 100 mL of dry MeOH. The reaction of 25.0 g (174 mmol) of 1-diethylamino-3-butanone with 25.0 g (176 mmol) of MeI for 30 min at 0 °C gave a precipitate which was washed twice with dry Et_2O to remove excess MeI.[27] A solution of this methiodide in 100 mL of dry MeOH was added to the solution of sodium enolate described above. The resulting mixture was stirred overnight at 25 °C under N_2, refluxed 2 h, and worked up in the usual way to provide 21.6 g (87%) of 7 as the crude solid. Recrystallization from EtOAc–MeOH gave material melting 85 °C; IR 1725, 1680 cm^{-1}; UV 212.5, 230, 280 nm; NMR δ 2.0–3.2 (8H complex), 2.1 (3Hs), 3.65 (3Hs), 3.8 (3Hs), 6.55–7.0 (2H complex,) 8.0 (1 Hd, *J* = 9 Hz); MS *m/e* 304 (19%, M^+), 234 (94%), 202 (58%), 148 (100%), 120 (55%).

Anal. Calcd for $C_{17}H_{20}O_5$: C, 67.09; H, 6.62. Found: C, 67.12; H, 6.72.

10a-Carbomethoxy-7-methoxy-1,9,10,10a-tetrahydrophenanthren-3(2*H*)-one (8). A solution of 20.0 g (66 mmol) of 7 in 1 L of dry MeOH was added under N_2 to a solution prepared by dissolving 21.23 g (923 mg-atoms) of Na in 1 L of dry MeOH. The solution was stirred overnight at 25 °C and then refluxed 2 h under N_2, becoming dark and cloudy. The benzene extracts from the cooled mixture, when neutralized, dried, and concentrated, provided 14.2 g (75%) of 8 as the crude solid, mp 153 °C after recrystallization from EtOAc; IR 1730, 1663 cm^{-1}; UV 243.5, 330 nm; NMR δ 1.65–3.1 (8H complex), 3.65 (3Hs), 3.8 (3Hs), 6.6 (1 Hs), 6.6–6.95 (2H complex), 7.75 (1 Hd, *J* = 9 Hz); MS *m/e* 286 (97%), M^+), 230 (79%), 227 (100%), 226 (77%), 215 (60%), 171 (73%).

Anal. Calcd for $C_{17}H_{18}O_4$: C, 71.31; H, 6.34. Found: C, 71.33; H, 6.41.

7-Methoxy-1,9,10,10a-tetrahydrophenanthren-3(2*H*)-one. A 100-mg sample of 8 (0.35 mmol) in 10 mL of 50% aqueous MeOH was refluxed 30 min with 10 mg (0.15 mmol) of 85% KOH. The usual workup provided 68 mg (85%) of the decarbomethoxylated material, mp 115–116 °C after recrystallization from EtOH (lit.[28] mp 114–115.5 °C); IR 1670 cm^{-1}; NMR δ 1.2–3.1 (9H complex), 3.8 (3Hs), 6.5 (1 Hd, *J* = ca. 1 Hz), 6.55–6.95 (2H complex), 7.7 (1 Hd, *J* = 9). This NMR spectrum is identical with that of another sample of this material, mp 110–112 °C, obtained in this laboratory[29] as a by-product in the synthesis of 7-methoxy-3,4,9,10-tetrahydrophenanthren-1(2*H*)-one.[30]

10a-Carbomethoxy-3,3-ethylenedithio-7-methoxy-1,2,3,9,-10,10a-hexahydrophenanthrene (9). A mixture of 286 mg (1.0 mmol) of 8, 0.20 mL (2.40 mmol) of ethanedithiol, 5.0 mL of HOAc, and 0.10 mL of freshly distilled BF_3OEt_2 was prepared at 0 °C and allowed to stand overnight at 25 °C. The yellowish needles formed were recrystallized in the mixture by adding hot MeOH and cooling. The collected solid was washed twice with cold MeOH to give 300 mg (85%) of 9 as white needles, which melted at 167–167.5 °C after recrystallization from MeOH; IR 1730 cm^{-1}; UV 217, 277 nm; NMR δ 1.3–3.1 (8H complex), 3.4 (4Hm), 3.6 (3Hs), 3.8 (3Hs), 6.3 (1 Hs), 6.5–6.9 (2H complex), 7.6 (1 Hd, *J* = 9 Hz); MS *m/e* 362 (2%, M^+), 167 (37%), 149 (100%).

Anal. Calcd for $C_{19}H_{22}O_3S_2$: C, 62.95; H, 6.12. Found: C, 63.24; H, 6.16.

10a-Carbomethoxy-7-methoxy-1,2,3,9,10,10a-hexahydrophenanthrene (10) by Desulfurization of 9. A mixture of 100 mg (0.276 mmol) of 9, 1.00 g of W-4 Raney Ni which had been deactivated by refluxing 2.5 h in acetone, and 10 mL of absolute EtOH was refluxed 24 h. Filtration, concentration, and sublimation gave 37 mg (49%) of 10, mp 111.5–112 °C, identical with the subsequently described 10, prepared from 15, by comparison of spectra.

Preparation of 10 by Transesterification of 15. A solution of 429 mg (1.50 mmol) of 15 in 5.0 mL of dry MeOH was added to a solution prepared by dissolving 505 mg (22.0 mg-atoms) of Na in 25 mL of dry MeOH. After 24 h of refluxing under N_2, the mixture was neutralized, extracted, and concentrated to give 368 mg of crude solid. Recrystallization from MeOH provided 350 mg (85%) of 10 as short needles, mp 113–113.5 °C; IR 1725 cm^{-1}; UV 218, 264, 297.5 nm; NMR δ 1.1–2.85 (10H complex), 3.5 (3Hs), 3.7 (3Hs), 6.1 (1 Ht, *J* = 4 Hz), 6.3–6.7 (2H complex), 7.35 (1 Hd, *J* = 9); MS *m/e* 272 (95%, M^+), 214 (51%), 213 (96%), 212 (100%), 171 (61%).

Anal. Calcd for $C_{17}H_{20}O_3$: C, 74.97; H, 7.40. Found: C, 74.74; H, 7.37.

Reduction Procedures. Lithium Aluminum Hydride. A solution of 24.4 mg (0.10 mmol) of 1 in 3.0 mL of dry Bu_2O was added with stirring under N_2 to a suspension of 5.0 mg (0.125 mmol) of 95% $LiAlH_4$ in 1.0 mL of dry Bu_2O. After this mixture had been refluxed 30 h under N_2 it was worked up by anaerobic addition of saturated

aqueous Na_2SO_4. Separation and concentration of the organic portion gave an oil distilled at ca. 0.1 mm in a sublimation apparatus, whose cold finger was weighed immediately before and after removal of the distillate for subsequent VPC analysis. The product consisted of 22.2 mg (90%) of a liquid mixture of **2** and **3** in the ratio of 95:5.

Diimide. For reduction of the alcohol 18.6 mg (0.10 mmol) of *p*-toluenesulfonyl hydrazide was combined with 24.4 mg (0.10 mmol) of **1** in 4.0 mL of dry solvent (see Table I) and refluxed under N_2. For the salts 24.4 mg (0.10 mmol) of **1**, dissolved in a variable amount of dry solvent, was combined with 1.1 equiv of base under N_2; the mixture was stirred 2 min at 35 °C for formation of the Li salt (ethereal MeLi, no other solvent), refluxed for 24 h to produce the Na salt (NaH, 1 mL of diglyme), and refluxed 2 h in the case of the K salt (KH, 3 mL of Bu_2O). These procedures had previously been shown to give complete conversion to alkoxides.[1] For each salt the solvent was then adjusted to give a total of 4 mL of 3:1 Bu_2O–diglyme, 18.6 mg (0.10 mmol) of *p*-toluenesulfonyl hydrazide was added, and refluxing under N_2 was begun. For all reactions another 0.10-mmol portion of reagent was added after 3 h and again after 6 h of reflux. When each mixture had been refluxed 12 h under N_2, it was worked up by addition of water, aqueous HCl, and pentane. Separation and concentration of the organic portions gave an oil which was chromatographed on Al_2O_3 and then distilled and collected for VPC analysis as described above.

Analysis of Product Mixtures. The entire distillate was washed from the sublimator cold finger with solvent and this solution was used directly for VPC analysis. NMR did not provide adequate resolution of the appropriate peaks at 60 MHz to be useful for mixture analysis. Typical VPC retention times for **1**, **2**, and **3**, respectively, were 6, 10, and 13 min with the Apiezon column at 270 °C and 6, 13, and 16 min for the SE-30 column at 235 °C. Traces were integrated by planimeter and calibrated with traces from prepared mixtures of **2** and **3**.

Control Reductions. Except in one instance, control reactions to establish absence of equilibration were run on the trans product (**3**) since evidence indicates it is the less stable epimer.[1,30,31] These reactions employed $LiAlH_4$ with **2** and with **3**, and *p*-toluenesulfonyl hydrazide with **3** and with the K salt of **3**, utilizing 0.05-mmol quantities and the reduction procedures indicated above. Material recoveries were 96–100% and in no instance was evidence detected for epimerization.

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Registry No.—**1**, 53547-99-2; **1** (Li salt), 63215-76-9; **1** (Na salt), 63215-77-0; **1** (K salt), 63215-781; **5**, 6935-48-4; **6**, 40153-87-5; **7**, 63215-79-2; **8**, 63215-80-5; **9**, 63215-81-6; **10**, 63215-82-7; **13**, 2146-61-4; **14**, 63215-83-8; **15**, 59434-75-2; 2-carbethoxycyclohexanone, 1655-07-8; 1-diethylamino-3-butanone, 3299-38-5; 1-diethylamino-3-butanone methiodide, 43025-83-8; 7-methoxy-1,9,10,10a-tetrahydrophenanthren-3(2*H*)-one, 5869-03-4; ethanedithiol, 540-63-6.

References and Notes

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