Isomerization and Aromatization of the 1,3-Di-*tert*-butylcyclohexadienes in Strongly Basic Media[1]

N. Venkatasubramanian, Adrian Hawkins, and Samuel Siegel*

Department of Chemistry and Biochemistry, University of Arkansas, Fayetteville, Arkansas 72701

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The five isomeric 1,3-di-*tert*-butylcyclohexadienes are equilibrated in *t*-BuOK/Me_2SO at 30–55 °C. In lithium ethylamide in ethylamine at 0 °C, equilibration is accomplished within the set of three dienes which possess a tertiary hydrogen or between the other two dienes; however, one set is not transformed to the other. Aromatization accompanies the equilibration of the set of three but not the set of two. With a large excess of KAPA, the diene is transformed rapidly to the salt which aromatizes. With an excess of diene, the interconversion of all of the dienes accompanies aromatization (intraset isomerization being faster than interset interchange). In KAPA at 0 °C, the introduction of dicyclohexyl-18-crown-6 inhibits aromatization; however, after a time reaction slows although the basicity of the solution remains strong enough to abstract a proton from a tertiary carbon. The effect of the base system upon the competitive reactions of cyclohexadienyl carbanions is understood in terms of the differing interactions of the carbanionic salts with the medium.

Our interest in determining the relative stability of the isomeric cyclohexadiene derivatives of 1,3-di-*tert*-butylbenzene[2] has led us to examine how several strongly basic media, including solutions of lithium ethylamide in ethyl amine,[3] potassium 3-aminopropylamide (KAPA) in 1,3-diaminopropane (DAP),[4] and potassium *tert*-butoxide in dimethyl sullfoxide (Me_2SO),[5] affect these dienes. In general, our results are consistent with those of previous investigators and illustrate some of the structural features which govern the relative rates of cyclohexadiene isomerization and aromatization.[3-7] The effects of counterion, solvent, and a crown ether upon the relative rates of the competing reactions are striking and current views of the role of ion pairs in proton and hydride ion transfers are used to account for the observed phenomena.[8]

Scheme I

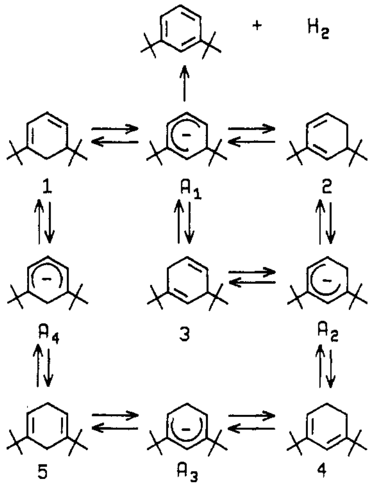

Table I. Equilibrium Distributions of the Isomeric 1,3-Di-*tert*-butylcyclohexadienes

base system	initial diene	distribution of dienes, % 1	2	3	4	5
t-BuOK/ Me_2SO						
55 °C	1	8.0	3.9	4.9	76.2	7.0
	2	7.1	2.3	4.5	80.0	5.7
	(AVE)[a,b]	(49.0)[a]	(20.0)[a]	(31.0)[a]	(93.0)[b]	(7.0)[b]
30 °C	1	7.8	1.9	4.3	79.7	6.1
LEA/EA						
0 °C	1[c]	47.7	24.6	27.7		
	2[c]	48.3	24.4	27.3		
	3[c]	48.7	24.8	26.5		
	5				93.2	6.8

[a] Distribution within group I, dienes **1**–**3**. [b] Distribution within group II, dienes **4** and **5**. [c] Accompanied by formation of arene **6**.

Unlike the previous investigations of cyclohexadienic hydrocarbons,[4,5,6,9,10] other than the parent compounds 1,3- and 1,4-cyclohexadiene,[9] the present study is limited to changes within the cycle. Two exceptions are Burgstahler, Chien, and Abdel-Rahman's description of the isomerization of 2,3-di-*tert*-butyl-1,4-cyclohexadiene to 1,6-di-*tert*-butyl-1,3-cyclohexadiene by refluxing the 1,4-diene for 1 h with lithium ethylamide in ethylamine[3] and the isomerization of 1,4-di-*tert*-butyl-1,4-cyclohexadiene to an 11:89 mixture with 1,4-di-*tert*-butyl-1,3-cyclohexadiene without the formation of 1,4-di-*tert*-butylbenzene after a 3-h reflux in the same base.[11] The five isomeric 1,3-di-*tert*-butylcyclohexadienes, whose preparation and properties have been published previously,[2] are illustrated in Scheme I. They can be divided into two sets. In the one which includes 1,5-di-*tert*-butyl-1,3-cyclohexadiene (**1**), 2,6-di-*tert*-butyl-1,3-cyclohexadiene (**2**), and 1,3-di-*tert*-butyl-1,4-cyclohexadiene (**3**), each diene bears a tertiary hydrogen; in the other [1,3-di-*tert*-butyl-1,3-cyclohexadiene (**4**) and 1,5-di-*tert*-butyl-1,4-cyclohexadiene (**5**)] this structural feature is absent. This division into two sets is expressed in the competitive rates of aromatization and isomerization affected by the strong bases.

Results

***t*-BuOK in *t*-BuOH and Me_2SO.** To avoid the complication of aromatization, our initial attempt to isomerize

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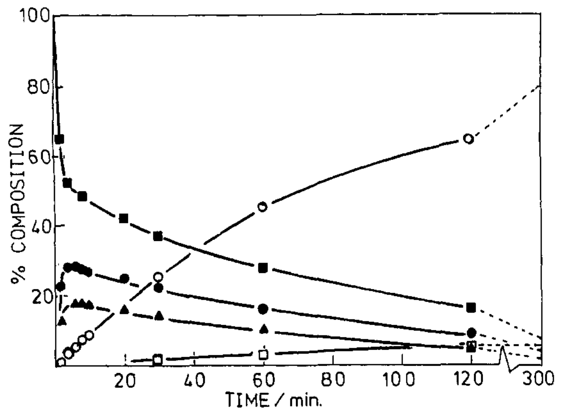

Figure 1. The isomerization of diene 1, 0.02 M, by potassium *tert*-butoxide in Me_2SO, 1.0 M, at 30 °C; (■) 1; (▲) 2; (●) 3; (○) 4; (□) 5.

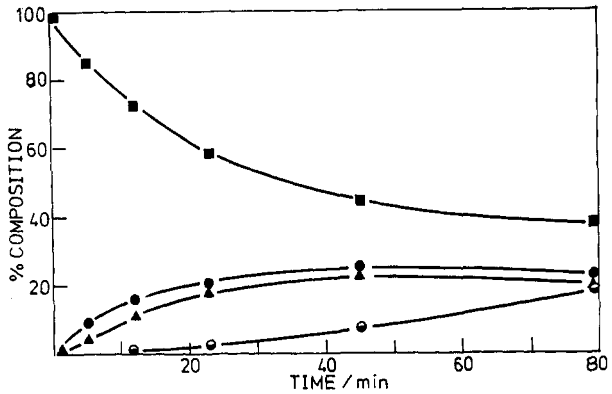

Figure 2. The isomerization and dehydrogenation of diene 1, in LEA at 0 °C; [LEA], 0.10 M; $[\text{diene}]_0$, 0.001 M; (■) 1; (▲) 2; (●) 3; (⊖) 1,3-di-*tert*-butylbenzene.

the dienes used potassium *tert*-butoxide in *tert*-butyl alcohol because it is reported to catalyze (55 °C) the reversible isomerization of 1,3- and 1,4-cyclohexadienes without the accompaniment of either aromatization or disproportionation.[9] This base system, however, had no effect on diene 1 at 60 °C (0.5 M *t*-BuOK). We chose to avoid raising the temperature to 200 °C, a temperature at which the isomeric *p*-menthadienes have been equilibrated without appreciable aromatization (<3%).[10]

A solution of potassium *tert*-butoxide in dimethyl sulfoxide (Me_2SO)[9] did bring about the equilibration of the dienes. The process is faster at 55 °C than at 30 °C but results in virtually the same distribution of isomers (Table I). The amount of arene produced is small (<2% at 55 °C). The rate of interconversion within the set of three dienes (1–3) or the set of two (4 and 5) is faster than the conversion of one set to the other (Figure 1).

The Action of LEA. In a solution of lithium ethylamide (LEA) in ethylamine at 0 °C, dienes 1–3 are readily converted to the same distribution of isomers, while concurrently, but more slowly, aromatization to 1,3-di-*tert*-butylbenzene (6) takes place (Figure 2). The arene appears to be an initial product from the 1,4-diene 3 but not of the 1,3-dienes 1 or 2. Neither diene 4 nor 5 is formed from any one of the set of three (dienes 1–3). At the same temperature, dienes 4 and 5 are interconverted, although more slowly than the set of three, without producing any of the latter or the arene.

The Action of KAPA. Seeking a stronger base which would interconvert all five dienes at 0 °C, we turned to the "super base", potassium 3-aminopropylamide (KAPA) in the solvent 1,3-diaminopropane.[4,12] With diene 1 and a very large excess of KAPA at 30 °C, only small amounts of the isomeric dienes are detected in the quenched solutions (Table II), indicating that aromatization is faster than the deprotonation of the diene. A moderate excess of KAPA rapidly converts dienes 1 or 2 to a salt which forms mainly the 1,4-diene 3 upon quenching with water (Table II, entry 2).[13] 1,3-Di-*tert*-butylbenzene (6) and dihydrogen are the final products.[4] In excess KAPA, the log of the arene concentration increases linearly with time and is a measure of the rate of decomposition of the carbanion salt. The rate constants obtained from the plots are 5.7×10^{-3} and 1.7×10^{-4} s^{-1} at 30 and 0 °C, respectively.

If the concentration of diene 1 is much greater than the concentration of KAPA, isomerization is faster than aromatization (Table II, entry 4). Dienes 2 and 3 are the principal initial products, but dienes 4 and 5 are formed

Table II. Reactions of 1,5-Di-*tert*-butyl-1,3-cyclohexadiene (1) in KAPA at 30 °C. The Composition of Water Quenched Samples

$[D_1]$/ $[KAPA]^a$	time, min	products, mol %[b]				
		1	2	3	4	6[c]
0.001/0.04	0.7	57				43
	1.5					100
0.004/0.03	1.8	13		51		36
	5.8			25		75
0.02/0.07	1.0	7.6	5.2	53.7	4.9	28.7
	3.9			24.8		75.2
	7.3			8.9		91.4
0.02/0.007	0.7	86.8		13.2		
	2.7	67.1	7.9	24.9		
	6.8	41.0	13.3	29.1	6.8	9.9
	15.5	20.5	6.1	18.4	23.2	31.7
	30.0	5.0		5.5	30.8	58.6
	60.0				19.9	80.1

[a] The ratio of molar concentrations of diene to KAPA. This series of experiments used procedure B. [b] The absence of entries indicates less than 0.5% of the particular compound was observed. Diene 5 formed in amounts of <8% of diene 4. [c] 1,3-Di-*tert*-butylbenzene.

Table III. Effect of Crown Ether and $K^+B(Ph)_4^-$ on the Isomerization and Aromatization of Diene 1 in Solutions of KAPA at 0 °C.[a] The Composition of Water Quenched Samples

additive	time, min	products, mol %[b]				
		1	2	3	4	6[c]
none[d]	1.0	23.9	7.8	60.8	1.3	6.3
	4.1	16.2	8.2	64.9	3.3	7.4
	29.8	10.0	4.8	49.4	15.5	20.2
	60.0	6.8	3.9	38.5	16.8	34.0
	136.0	2.8	2.0	22.1	6.2	66.9
none	1.0	96	0.5	3.8	t	t
	4.0	81.0	2.8	15.4	0.6	0.2
	10.0	54.0	17.2	23.8	2.8	1.3
	20.0	28.2	14.8	22.0	15.2	15.0
	50.0	0.6	0.3	1.0	14.3	83.5
crown ether	3.8	82.9	4.1	12.9	0.0	0.0
	12.0	44.5	20.9	31.2	1.4	0.0
	100.0	38.9	17.6	26.9	9.8	0.0
$KBPh_4$	2.5	91.0	1.4	7.0	0.0	0.6
	5.0	81.2	4.9	10.2	0.0	3.6
	20.0	44.4	20.1	25.0	1.1	9.2
	50.0	4.2	2.3	2.5	2.9	87.7

[a] Diene 1 (0.05 M); KAPA (~0.01 M); using procedure A except for the first entry. [b] Dienes 5 formed in amounts <8% of diene 4. t = trace. [c] 1,3-Di-*tert*-butylbenzene. [d] Diene 1 (0.020 M); KAPA (0.027 M); using procedure B.

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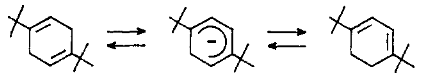
initially in greater amounts when starting with diene **3** than from dienes **1** or **2**. Aromatization which accompanies the isomerization of diene **1** proceeds slowly at first, accelerates to a steady rate as the distribution of dienes **1–3** approach the equilibrium value, and finally declines as the conversion of dienes to arene approaches completion (Table III, entry 2). The addition of dicyclohexyl-18-crown-6 to the solution of KAPA before diene **1** is injected has little effect upon the initial rate of disappearance of the diene; however, the reaction slows markedly after 40–50% of the diene has been converted to its isomers (Table III, entry 3). Diene **4** (and **5**) continues to be formed but much more slowly than in the absence of the crown ether; however, *the arene is not detected*. The solution remains more basic than LEA as judged by its ability to abstract a proton from a tertiary carbon which is required to transform one set of dienes to the other.[14] Apparently the interaction of KAPA and the crown ether is more complicated than the expected rapid complexation with the potassium ion.[15] The relative rate of aromatization to isomerization of diene **1** is increased if potassium tetraphenylborate is added to the solution of KAPA, a slowed rate of deprotonation of **1** being accompanied by an increased rate of forming the arene **6** (Table III, entry 4).[16] The cycloalkenes 1,3-, 1,5-, and 3,5-di-*tert*-butylcyclohexenes were not detected in any of the experiments, indicating that disproportionation does not occur.[2]

Discussion of Results

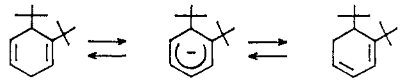
The relative concentrations of the dienes at equilibrium fall in the order **4** ≫ **1** > **5** > **3** > **2**. If account is taken of the greater symmetry of diene **5** over the other dienes and assuming that otherwise their entropy would be the same, the relative energies of the dienes follows the same order except for the interchange of the positions of dienes **1** and **5**. With this correction the dienes which have both alkyl groups attached to vinyl carbons are of lower energy than those with only one group so attached. Conjugation is a stabilizing factor; however, the unconjugated diene **3** appears to be more stable than conjugated diene **2** although the difference is small. Results like this have been recorded previously and attributed in part to a possible direct electronic interaction between the 1- and 4-double bonds which balances stabilization through 1,3-conjugation.[17] Hoffman has furnished a theoretical model for an electronic coupling of the two double bonds in planar 1,4-cyclohexadiene which involves hyperconjugative interaction with the methylene groups.[18]

The Effect of Dienic Structure upon Proton and Hydride Transfers. As noted in the introduction, the isomeric 1,3-di-*tert*-butylcyclohexadienes fall into two structural categories; in the one set (**1–3**) each diene has a tertiary hydrogen which is lacking in the dienes in the second set (**4** and **5**). The distinction is exhibited strikingly in solutions of lithium ethyl amide in ethyl amine (LEA) at 0 °C in which isomerization proceeds readily within each set but interconversion between the sets is not observed. Aromatization competes with isomerization in the first set but not in the set of two. Interestingly, aromatization does not accompany the catalyzed interconversion of 1,4-di-*tert*-butyl-1,4-cyclohexadiene (**7**) and 1,4-di-*tert*-butyl-1,3-cyclohexadiene (**8**) which also lack a tertiary hydrogen.[2]


7 8

(1)

Although the interconversion of 2,3-di-*tert*-butyl-1,4-cyclohexadiene (**9**) to 1,6-di-*tert*-butyl-1,3-cyclohexadiene (**10**) probably proceeds via a cyclohexadienyl carbanion that does possess a tertiary hydrogen, the dissociation of this hydride would generate the highly strained 1,2-di-*tert*-butylbenzene, and accordingly the absence of evidence of aromatization is not surprising.[3] In *t*-BuOK in Me_2SO


9 10

(2)

at 30–55 °C and in KAPA at 0 °C, the conversion from one set of dienes to the other takes place but more slowly than intragroup isomerization. Presumably, inductive and steric effects are involved.[19]

Inspection of the differences in structure of the likely carbanionic intermediates leads to a plausible contributing factor for these differences (Scheme I). The carbanions A_1, which is a common intermediate for the interconversion of dienes **1–3**, and A_3, which is produced by the loss of a proton from either **4** or **5**, are of lower energies than the intermediates A_2 and A_4, which interconnect the set of three dienes with the set of two. This statement is supported by recent calculations which show that a methyl group (electron donating relative to hydrogen) destabilizes the carbanion to a greater extent when attached to the 1-, 3-, or 5-positions then when attached to the 2- or 4-position.[20] Accordingly one should expect the relative energies of the carbanionic structures to increase in the order $A_1 < A_3 < A_4 < A_2$.

Of these intermediates, only A_1 has a tertiary hydrogen whose loss as a hydride ion yields the arene. Apparently a hydride ion is lost more slowly from a secondary carbon atom, but a quantitative comparison of the relative rates is not available from these experiments. In KAPA, the loss of hydride from a secondary carbon atom is clearly demonstrated by the rapid aromatization of 1,3-, or 1,4-cyclohexadiene by excess KAPA at 0 °C.[21]

Base-Catalyzed Reactions. The base systems used to affect the transformation of cyclohexadienes differ in their ability to abstract protons from the dienes to form cyclohexadienyl carbanions, but other characteristics of the systems affect the relative rates of the competing reactions: isomerization, aromatization, or disproportionation. Isomerization results from the reprotonation of the carbanion, aromatization, and disproportionation from the loss of a hydride ion or its direct transfer to a diene acceptor.

In principle, with a given diene, the stronger the base the higher the rate of deprotonation. If strong enough the base will neutralize an equivalent of the diene, and if in excess, either the carbanion is stable at the existing tem-

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[14] Venkatasubramian, N., unpublished results. The addition of 1,3-cyclohexadiene to solutions of KAPA generates a deep red color; however, this does not occur in solutions which contain the crown ether although the later solutions apparently convert both triphenylmethane and diphenylmethane to their conjugate bases as judged by the immediate formation of the color of these carbanions.

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perature or it forms an arene by the loss of a hydride ion which subsequently yields dihydrogen and restores the original base.[22] With excess diene, isomerization and, with certain dienes, disproportionation compete with aromatization. These characteristics of a very strong base describe the ways in which solutions of KAPA affects the di-*tert*-butylcyclohexadienes except that these substituted dienes are not observed to disproportionate. Arnett and Venkatasubramanian have shown that KAPA neutralizes both 1,3- and 1,4-pentadienes, the heats of neutralization ($\Delta H_{25\,°C}$) being −8.8 and −16.7 kcal mol^{-1}, respectively, the difference representing the heat of isomerization.[12] Apparently, solutions of KAPA at 0 °C also neutralize the cyclohexadienes.

The Isomerization of Dienes. In the base systems which catalyze the isomerization but not the aromatization of 1,3- or 1,4-cyclohexadiene, the cyclohexadienyl anions apparently are strongly solvated particularly by molecules of alcohol through hydrogen bonds.[23] Solutions of the potassium alkoxide in the corresponding alcohol have been used at 200 °C to affect diene isomerization with little aromatization.[10,13] In contrast, in solutions of *t*-BuOK in the nonhydroxylic solvents Me_2SO or dioxane, isomerization of 1,3-cyclohexadiene is fast and disproportionation to an equimolar mixture of cyclohexene and benzene is quantitative.[9] Similarly, the *p*-menthadienes are rapidly equilibrated in *t*-BuOK/Me_2SO at 55 °C while disproportionation to *p*-menthene and *p*-cymene occurs slowly; disproportionation is faster at higher temperatures.[5] Interestingly, lithium dimethylamide in hexamethylphosphoramide at room temperature rapidly converts 4-vinylcyclohexene to an equimolar mixture of ethylbenzene and 1-ethylcyclohexene.[5] The probable mechanism requires the initial abstraction of a tertiary proton leading via an intermediate carbanion to 1-ethyl-1,3-cyclohexadiene which rapidly disproportionates. Apparently, the disproportionation of the five isomeric di-*tert*-butylcyclohexadienes is inhibited by the substituents and allows the faster isomerization to proceed toward equilibrium.

Aromatization. Aromatization, like disproportionation, appears to require that the carbanion be weakly solvated, but the interaction of the solvent with the cation also appears to be important because aromatization is increasingly favored in media and under conditions which promote the formation of contact ion pairs.[24,25] In a given solvent, the equilibrium between contact and solvent separated ion pairs of a carbanion lithium favors the solvent separated form relative to the distribution for a potassium salt which reflects the greater attraction of the smaller cation for polar solvent molecules.[26]

The difference in the solvent character of ethylamine and 1,3-diaminopropane (DAP) is unlikely to reverse the difference in the attraction of Li^+ and K^+ for solvent molecules so that a cyclohexadienylpotassium in 1,3-diaminopropane should contain a higher proportion of contact ion pairs than a cyclohexadienyllithium.[27] The greater solubility of KAPA in DAP over potassium salts of monoalkylamides in excess monoamine has been attributed to the possibility that KAPA forms either a chelated ion pair or, through "internal solvation", forms an amide ion stabilized by an intramolecular hydrogen bond.[28] Independent evidence supports the later contention.[29] Presumably, contact ion pairs in DAP have the cation externally coordinated with the diamine.[30]

That contact ion pairs are the species that eliminates hydride ion is indicated by the failure of aromatization to take place in solutions of KAPA containing an equivalent or more of the crown ether. The crown ether is expected to decrease the fraction of contact ion pairs[31] in which the cation facilitates the extrusion of a hydride ion from the carbanionic intermediate through the electrostatic force acting between the oppositely charged entities. However, the slowed rate of interconversion of the two sets of dienes, which begins after about 50% conversion of the initial diene, suggests that other changes involving the crown ether lower the effective basicity of the solution.[14] Presumably, a cation-encapsulating agent[31] which is stable in the superbasic medium would accomplish the objective of allowing a rapid interconversion of all these dienes without causing their aromatization. The addition of potassium tetraphenylborate to the solution of KAPA, which increases the relative rate of aromatization to isomerization of diene **1**, is likely to increase the proportion of contact ion pairs through a common ion effect.[16] A large excess of KAPA over the diene could have the same effect.

Experimental Section

Reagents. Potassium *tert*-butoxide (Alfa Products) was sublimed before use. Dicyclohexyl-18-crown-6-ether (Dupont Lot #LR 3-301) was purified by means of its acetonitrile complex,[32] mp 69.0–69.5 °C (lit.[33] mp 69.0–69.5 °C). Potassium tetraphenylborate was prepared by following the procedure of Wittig and Raff.[34] The syntheses of the isomeric 1,3-di-*tert*-butylcyclohexadienes **1**–**5** have been described previously.[2] A Varian Model EM-360 NMR and a Perkin-Elmer 283 IR spectrophotometer were used to confirm the identity of the dienes. Phillips Petroleum 99.5% cyclohexane was used as received. 1,3-Diaminopropane was distilled from calcium oxide and stored over 3A molecular sieves. Dimethyl sulfoxide was kept over dry calcium sulfate overnight and distilled over calcium hydride under reduced pressure.

General. After a base solution was equilibrated thermally at the selected temperature (±0.5 °C), a specified amount of diene was introduced via a gas tight syringe. *tert*-Butylbenzene was added as the internal standard in amounts one-half that of the total diene concentration. In experiments using the crown ether, a specified amount was added to the solution of base before the addition of the diene. At selected intervals 0.20-mL aliquots of the reaction mixture were removed by means of a gas-tight syringe and immediately quenched in 1 mL of ice-cold water. These aqueous solutions were then extracted with 0.20 mL of cyclohexane and analyzed by GLC using a Varian Model 940 GC connected to a Laboratory Data Control Model 308 computing integrator. A 25 ft × $^1/_8$ in. column containing 10% Carbowax 750 in 60/80 mesh Chromosorb P was operated at 115 °C with nitrogen as carrier gas.

Preparation of Lithium Ethylamide in Ethylamine (LEA/EA). In a typical experiment, ethylamine (50 mL), after passage of the vapor through a potassium hydroxide tower, was

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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$_2$SO.** 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$_2$SO ($\simeq$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

Glen W. Spears, Craig E. Caufield,[1] and W. Clark Still*

Department of Chemistry, Columbia University, New York, New York 10027

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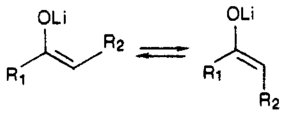
Lithium enolates with differing degrees of alkyl substitution were prepared and geometrically equilibrated by using catalytic phenylmercuric chloride in tetrahydrofuran. With the the resulting thermodynamic data, MM2 force field parameters were evaluated by using an automatic force field refinement program.

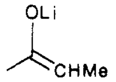
Introduction

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$_2$R, 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]

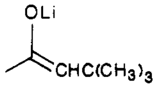


Results and Discussion

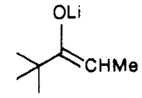
The enolates we chose to study are those shown below. These enolates were selected because of their structural diversity and the threefold symmetry of their olefinic substituents which provide conformationally homogeneous enolates.



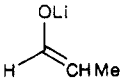
1Z,E



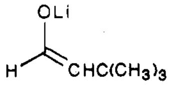
2Z,E



3Z,E



4Z,E



5Z,E

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