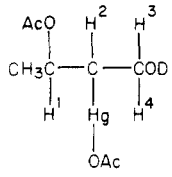

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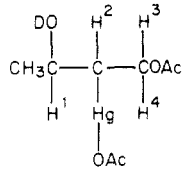

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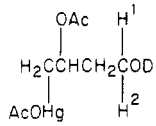

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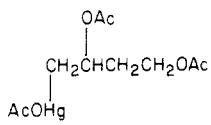

23

the presence of smaller quantities of **20** cannot be excluded. No crotyl acetate remained in the OM reaction mixture.

OM of 3-buten-1-yl acetate in a manner similar to that above showed the presence of 94% of the normal adduct. The remainder appeared to be a mixture of 2% of the acetoxy-interchanged mercurial **22** and 4% of the diacetoxy adduct **23**. However, the only evidence for **23** and the only basis of assigning a percentage to it was the integration of the CHOAc pentet at ca. δ 5.05, which integrated too high relative to the δ 3.46 triplet of H^1 and H_2 of **22** to be accounted for only on the basis of this material. Consequently, the presence of **23** was assumed.

Registry No. **1** (X = OH), 107-18-6; **1** (X = OCH_3), 627-40-7; **1** (X = OAc), 591-87-7; **2** (X = OH), 6117-91-5; *cis*-**2** (X = OCH_3), 10034-16-9; *trans*-**2** (X = OCH_3), 10034-14-7; **2** (X = OAc), 628-08-0; **3** (X = OH), 627-27-0; **3** (X = OCH_3), 4696-30-4; **3** (X = OAc), 1576-84-7; **4** (X = OH), 821-09-0; **4** (X = OCH_3), 1191-31-7; **4** (X = OAc), 1576-85-8; **5** (X = OH), 821-41-0; **5** (X = OCH_3), 5084-33-3; **5** (X = OAc), 5048-26-0; **6**, 32160-45-5; **17**, 75919-11-8; **18**, 75919-12-9; **19**, 75919-13-0; **20** (isomer 1), 75919-14-1; **20** (isomer 2), 75919-15-2; **21**, 75919-16-3; **22**, 75919-17-4; **23**, 75919-18-5; 1-methoxy-2-propanol, 107-98-2; 1-methoxy-3-propanol, 1589-49-7; 4-methoxy-1-butanol, 111-32-0; 1-methoxy-2-butanol, 53778-73-7; 5-methoxy-1-pentanol, 4799-62-6; 6-methoxy-1-hexanol, 57021-65-5; 1,2-propanediol, 57-55-6; 1,3-propanediol, 504-63-2; 1,3-butanediol, 107-88-0; 1,4-butanediol, 110-63-4; tetrahydrofuran, 109-99-9; 1,2-butanediol, 584-03-2; 2-methyltetrahydrofuran, 96-47-9; 1,4-pentanediol, 626-95-9; 1,5-pentanediol, 111-29-5; 1,5-hexanediol, 928-40-5; 1,6-hexanediol, 629-11-8; 2,3-butanediol, 513-85-9; 1,5-cyclooctadiene, 111-78-4; 5-methoxy-2-pentanol, 18423-18-2; 4-methoxy-2-butanol, 41223-27-2; 6-methoxy-2-hexanol, 75919-19-6.

Formation of Peralkylcyclohexadienyllithium Compounds

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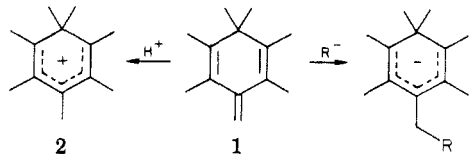
Received July 18, 1980

1,1,2,3,5,6-Hexamethyl-4-methylene-2,5-cyclohexadiene (**1**) reacts with alkyllithium compounds, RLi (R = *n*-Bu, *sec*-Bu, and *t*-Bu), at 20 °C in hydrocarbon solution or in the presence of ethers or tertiary amines, which act as ligands, to give stable, soluble 1,1,2,3,5,6-hexamethyl-4-alkylcyclohexadienyllithium compounds, **3a–c**. On heating, the latter aromatize to pentamethylalkylbenzenes, **4a–c**, with extrusion of methyllithium, while on hydrolysis of **3a–c** isomeric substituted cyclohexadienes are obtained. The effects have been investigated of varying RLi structure, ligand, and temperature on the rates of addition and aromatization reactions. Ligand metalation by RLi is a significant side reaction. Addition is faster with ligands known to reduce the association of alkyllithium compounds. Aromatization is faster in the presence of THF which favors formation of loose ion pairs and is slower with heavy substitution on the ring. It is proposed that large substituents (neopentyl) destabilize the transition states for aromatization due to steric interactions.

Introduction

In the study of ion pairing[1] in and among salts which contain carbanions, it would be desirable to find systems which form stable solutions in a variety of solvents and over a wide temperature range. In practice this is rarely achieved and thus many carbanion salts and their complexes are not amenable to solution spectroscopic investigation, specifically with NMR methods. This restriction has now been lifted with a series of substituted cyclohexadienylic lithium compounds.

The compound 1,1,2,3,5,6-hexamethyl-4-methylene-2,5-cyclohexadiene, **1**, is best known as the precursor of the



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heptamethylbenzenium ion,[2] **2**. We have now investigated the possible corresponding reaction with carbanionic substances. Ample precedent exists for the addition of organolithium compounds to polyenes.[3] It will be shown how alkyllithium compounds add to the methylene carbon of **1** to give stable soluble cyclohexadienylic lithium compounds both in the presence of ligands and unsolvated. This development makes possible comparative studies of ion-pairing effects in closely related anions and cations.[4] This paper mainly concerns the qualitative aspects of the reaction of triene **1** with different alkyllithium compounds—the effect of temperature and lithium ligands and an interesting aromatization reaction which involves the extrusion of methyllithium.

The list of abbreviations for lithium ligands is found at the beginning of the Experimental Section.

Results and Discussion

General Observations. Triene **1** was found to react smoothly at room temperature with alkyllithium com-

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(2) W. Doering, M. Saunders, E. A. Earhart, E. F. Wadley, W. R. Edwards, and G. Laber, *Tetrahedron*, **4**, 178 (1958).

(3) (a) R. A. H. Casling, A. G. Evans, and N. H. Reese, *J. Chem. Soc. B*, 519 (1966); (b) R. Waack and M. Doran, *J. Organomet. Chem.*, **29**, 329 (1971); (c) Y. Okamoto and H. Yuki, *ibid.*, **32**, 1 (1971); (d) A. G. Evans and D. B. George, *J. Chem. Soc.*, 4653 (1961); (e) *ibid.*, 141 (1962); (f) R. Waack, M. A. Doran, and P. E. Stevenson, *J. Am. Chem. Soc.*, **88**, 2109 (1966); (g) C. R. Hauser and D. N. Van Eenam, *ibid.*, **79**, 5512 (1957); *ibid.*, **79**, 5520 (1957).

(4) M. Hallden-Abberton, Ph.D. Thesis, The Ohio State University, 1979.

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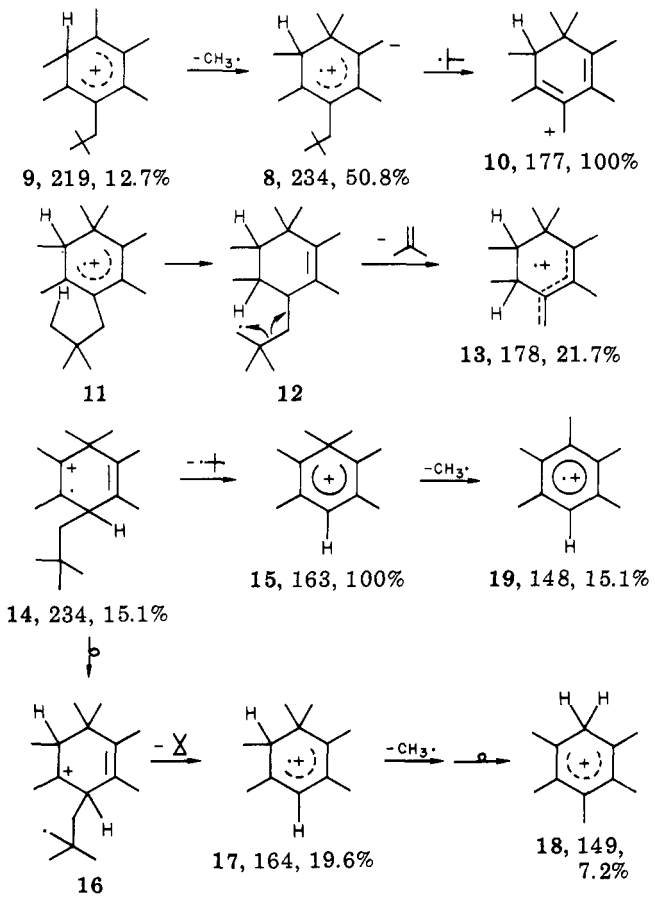
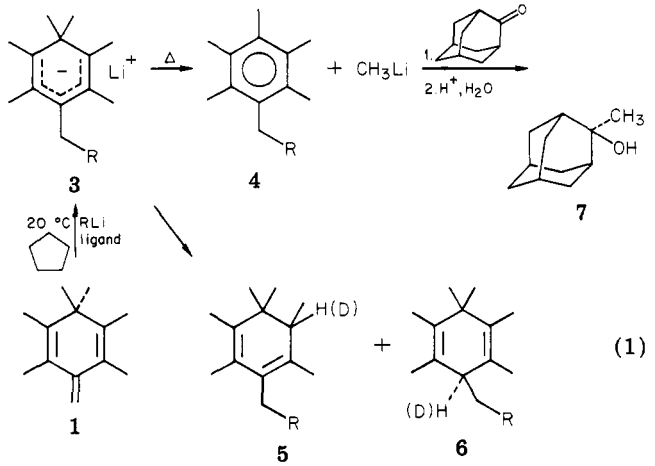
Scheme I



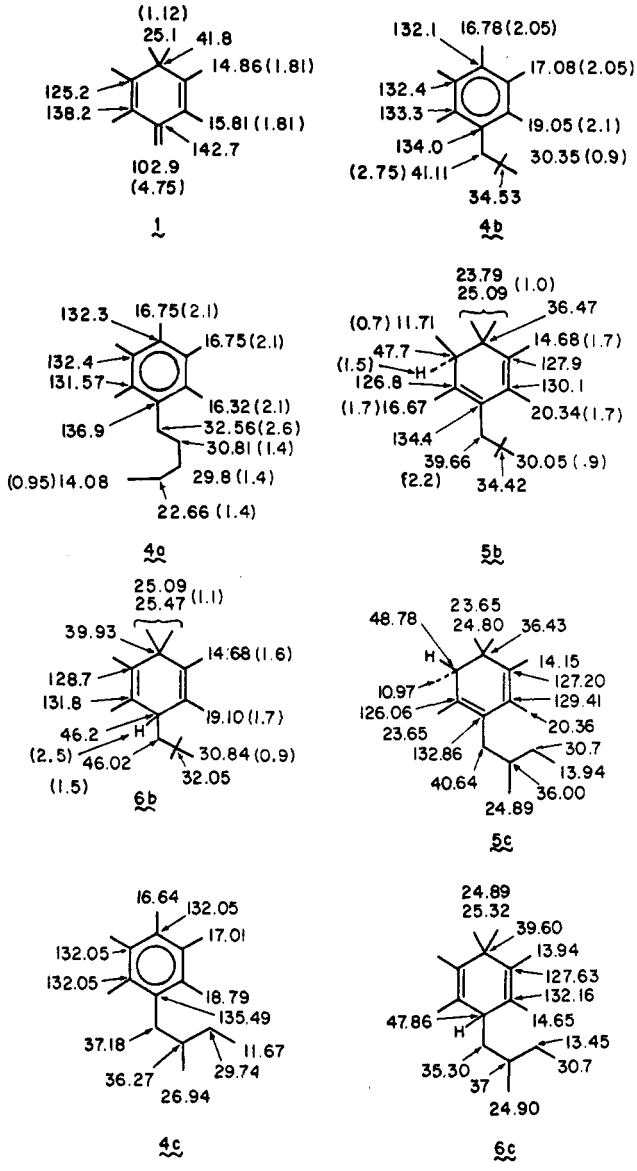
pounds in hydrocarbon solution alone or in the presence of ligands (ethers or amines) to give near quantitative conversion to soluble stable cyclohexadienyllithium compound **3**. This is shown by NMR and the products of hydrolysis reactions; see below. On heating to 80 °C, these



a, R = *n*-Bu; b, R = *t*-Bu; c, R = *sec*-Bu

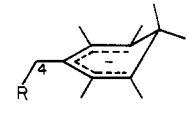
salts cleanly aromatize to methyllithium and the corresponding peralkylbenzene. For example, the reaction of 1.2 equiv of *tert*-butyllithium with 1 equiv of triene **1** in the presence of 2 equiv of *N*-methylpyrrolidine at 20 °C gave, after 30 min, >98% conversion to the salt **3**. Hydrolysis (water free of O_2) followed by distillation of the organic products yielded only two dienes, **5** and **6**, and small amounts of starting material **1** and neopentylpentamethylbenzene **4b** with less than 2% nonvolatile residue. All these products were separated by gas chromatography and identified from their UV, NMR, and mass

Table I. Carbon-13 (Proton) NMR Shift Data (chloroform, Me_4Si, ppm)



spectral properties (see Experimental Section). The dienes were differentiated by their UV maxima, 1,4, **6**, at 209 nm and 1,3, **5**, at 283 nm. Those assignments are consistent with the ^{13}C NMR data, Table I, and the mass spectral fragmentation patterns shown in Scheme I. Workup with D_2O leads to mass spectral data also consistent with the above interpretation (99.5% mono- and 0.5% dideuterium incorporation).

The ratio of dienes 1,4/1,3 obtained by hydrolysis of **3a–c** (H_2O or D_2O) under numerous conditions and with all organolithium reagents used varied from 1.4 to 2.0 except when the proton donor was an organic molecule. For instance, Me_2SO slowly protonated **3b** to give a diene ratio of 2.7, showing reaction at the less hindered 4-carbon to be favored with bulky proton donors (see **20**).



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Heating the solution of **3b**, prepared in the presence of NMP, for 3 h at 88 °C gave >98% conversion to the aromatic product, **4b** (see Experimental Section). Alterna-

Table II. Reactions of Alkyllithium Compounds with Triene 1

temp, °C	RLi, R, M	(RLi)/(triene)	ligand	(ligand)/(triene)	time, h	volatile hydrolysate, % yield 1	6	5	4
88	*n*-Bu, 1.33	1.00			24	45	*a*	*a*	54
20	*n*-Bu, 1.34	1.05	NMP	2.0	96	29	7	13	51
88	*n*-Bu, 1.33	1.05	NMP	2.0	2	3	*a*	*a*	97
20	*n*-Bu, 1.63	1.40	THF	2.2	48	1	0.5	1.3	97
20	*n*-Bu, 2.14	1.4	TMEDA	1.1	1	0.7	41	55	3
55	*n*-Bu, 2.14	1.4	TMEDA	1.1	5.5	0.6	*a*	*a*	99
20	*n*-Bu, 1.28	1.1	DPE	1.0	3.5	95	0.3	4.5	*a*
25	*n*-Bu, 1.28	1.1	DPE	1.0	18	49	*a*	1.0	50
25	*t*-Bu, 1.8	1.05			96	1	26	58	15
88	*t*-Bu, 1.7	1.0			24	*a*	1.1	0.3	98
20	*t*-Bu, 1.3	1.05	NMP	2.0	0.5	*a*	39	61	*a*
88	*t*-Bu, 1.3	1.05	NMP	2.0	24	*a*	*a*	*a*	99
20	*t*-Bu, 1.5	1.4	THF	2.2	1	5	33	54	9
20	*t*-Bu, 1.5	1.05	THF-d_8	2.2	1	2	35	56	7
20	*t*-Bu, 1.5	1.6	TMEDA	1.4	96	12	30	53	4
20	*t*-Bu, 1.5	1.05	THF	2.2	48	16	7	12	66
20	*t*-Bu, 1.4	1.05	THF-d_8	2.2	48	2	5	9	84
0	*t*-Bu, 0.96	1.1	DPE	1.0	4	30	28	41	1
20	*t*-Bu, 1.2	1.1	Et_2O	2.0	0.08	11	31	57	0.5
20	*t*-Bu, 1.09	1.1	Et_3N	2.0	0.08	16	39	44	1
0	*sec*-Bu, 0.95	1.1			54	41	25	42	4
20	*sec*-Bu, 0.80	1.1	NMP	2.0	1.8	9	38	52	1

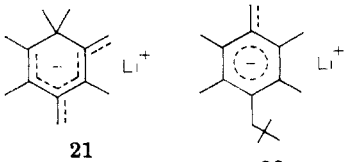
[a] < 0.3%.

tively reacting equimolar quantities of triene 1 and *tert*-butyllithium in cyclohexane at 80 °C for 8 h resulted in neopentylpentamethylbenzene **4b** (see Table II) and methyllithium, the latter identified by its adduct, **7b**, with adamantanone.[5]

The reactions of different alkyllithium compounds with triene 1 were carried out under a variety of conditions including variation of concentration, temperature and ligand. This led to the optimized conditions in Table II which gave the highest yields of salt **3** or aromatic product **4**.

The course of each reaction was monitored by gas chromatographic separation of hydrolysis products, sampled periodically during the course of the reaction. The yield of nonvolatile residue never exceeded 2%, based on 1. In this system total diene detected, **5** and **6**, represents the yield of cyclohexadienylic lithium compound. Table II lists the fractions of starting material, aromatic product, and dienes separated from these hydrolyzed reaction mixtures. Figure 1 illustrates the course of a typical reaction, showing consumption of 1, appearance of intermediate **3b**, and buildup of aromatic product, **4b**.

One further detail not revealed by H_2O hydrolysis of reaction mixtures comes from mass spectra of deuterolysis products from the reaction of *tert*-butyllithium and 1 in the presence of THF-d_8. In addition to the expected monodeuterated dienes **5b** and **6b** it was observed that about one-third of the aromatic product and of the small amount of remaining triene contained one deuterium per molecule. This implicates the deprotonation of triene 1 and aromatic product **4b** by unreacted *tert*-butyllithium to such species as **21** and **22**. These metalations are still a minor reaction compared to eq 1.



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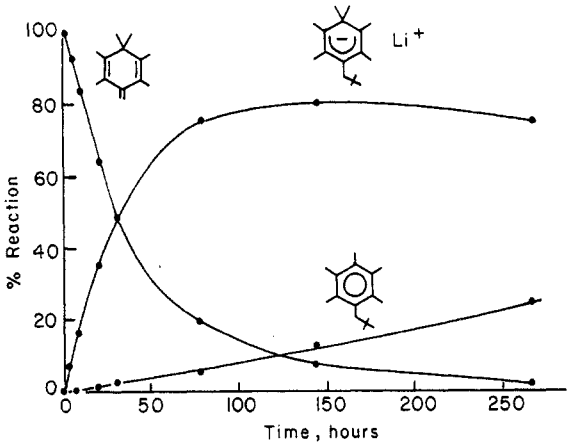
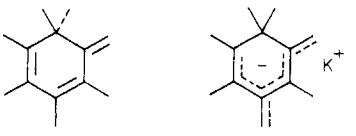


Figure 1. Reaction of triene 1, 0.96 M, with *tert*-butyllithium, 1.2 M, in cyclopentane at 20 °C.

Deprotonation of triene 1 was also observed in an attempt to vary the counterion in **3a**. Thus *n*-butyllithium and triene **2** with potassium *tert*-butoxide, allowed to react in cyclopentane (15 min, 0 to 20 °C), gave on hydrolysis 53% **4a**, 39% recovered triene 1, and 7% of an isomeric triene assigned to be **24** from metalated triene, **23**. This



24 23

reaction is much faster than with unsolvated *n*-butyllithium. However, no potassium salt **3aK** could be detected by NMR in this experiment, due probably to its low solubility. In a second experiment a solution of **3b** in cyclopentane containing 2 equiv of NMP was treated with potassium *tert*-butoxide at −75 °C for 15 min. In this preparation ^{13}C resonances of **3b** complexed to NMP are replaced by a new set of peaks with similar shifts, implying the existence in solution of a different cyclohexadienyl metal compound. From Schlosser's work these experimental conditions are claimed to favor metathesis to the organopotassium compound, **3bK**.[6,7]

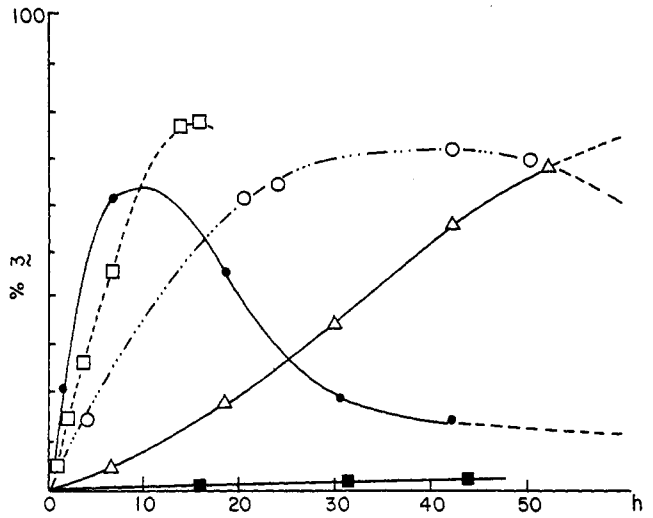


Figure 2. Formation of 3 in RLi additions to 1: (●) R = *sec*-Bu (1 M), 1 (0.19 M), cyclopentane, 25 °C; (□) *t*-Bu (1.7 M), 1 (1.5 M), benzene, 25 °C; (○) *t*-Bu (1.6 M), 1 (1.5 M), cyclopentane, 25 °C; (△) *sec*-Bu (1.0 M), 1 (0.9 M), cyclopentane, 0 °C; (■) *n*-Bu (1.0 M), 1 (0.9 M), cyclopentane, 25 °C.

Formation of Unsolvated Lithium Compounds. In order to assess the activating influence of ligands in reaction 1 we first investigated the system in hydrocarbon solution alone. As seen in Table II and/or Figure 2, at room temperature *sec*-butyllithium and *tert*-butyllithium add readily to 1, giving high conversion to the salts **3b** and **3c** while *n*-butyllithium hardly reacts at all. At 88 °C aromatic product **4a** forms slowly but the intermediate salt **3a** is not detected. Interestingly, also, the addition reaction (*t*-BuLi) is noticeably faster in benzene compared to cyclopentane. Note that Brown and co-workers have observed that carbon–lithium bond exchange rates are faster in benzene compared to alkanes.[8]

By use of initial rates of disappearance of 1 the apparent activation energy for *tert*-butyllithium addition to 1 in cyclopentane is found to be 22 kcal/mol. This compares to 15.5 kcal/mol for *tert*-butyllithium addition to 1,1-diphenylethylene.[9]

Initial rates of addition of alkyllithium compounds (RLi) to 1 decrease in the order R = *sec*-Bu (cyclopentane) > *t*-Bu (benzene) > *t*-Bu (cyclopentane) ≫ *n*-Bu (cyclohexane).

In addition reactions of alkyllithium compounds with π-carbon systems the less associated organolithium compounds generally react faster.[10] The higher reactivity of *sec*-butyllithium and *tert*-butyllithium compared to *n*-butyllithium correlates with their states of association—the first two are tetramers[11,12] in hydrocarbon solution while the third is a hexamer.[13] That this principle applies here also is confirmed by the results of RLi additions to 1 in the presence of ligands; see below.

In summary unsolvated alkyllithium compounds add to 1 to produce stable *solutions* containing cyclohexadienylic lithium compounds which on heating lose methyllithium to give aromatic compounds. This also constitutes an attractive route to generate unsolvated methyllithium.

Catalysis of the Addition of Alkyllithium Compounds to Triene 1. As seen in Table II the addition reactions of alkyllithium compounds to 1 are catalyzed by ethers and tertiary amines. All three cyclohexadienylic lithium compounds can be generated at room temperature and they all aromatize at elevated temperatures, or on extended storage at 20 °C.

The rates of addition of RLi species to 1 and the resulting distribution and yields of products depend on ligand, temperature, and the nature of alkyllithium used. The results are also influenced by deprotonation of ligand by the alkyllithium compound, which can be competitive with addition to 1.

The conditions listed in Table II are those which were found to give the maximum conversion to salt **3** or aromatic product **4**. Typically this involved the use of, per equivalent of triene 1, 1.05 to 1.4 equiv of alkyllithium and 1 to 2 equiv of ligand per 1 equiv of alkyllithium. Bulk solvent was always hydrocarbon. Salts **3a–c** are best formed around 20 °C since below this temperature the addition reaction is too slow while above it aromatization becomes significant. Qualitatively the rates of addition of *tert*-butyllithium to 1 with different ligands decrease in the order DEE ≃ TEA > NMP ≃ DME > THF ≫ DPE ≃ TMEDA. Highest yields of **3b** were obtained by using NMP (>98%), THF (87%), and DEE (88%). For *n*-butyllithium addition to 1 in the presence of ligands relative rates, M h^{-1}, 20 °C, in parentheses, are as follows: TMEDA (790), THF-d_8 (121), DPE (9.3, 25 °C), NMP (5.1). Here the highest yield of **3b** is obtained in the presence of TMEDA (97%). These results are influenced by competing metalation of ligand by the alkyllithium compound.[14] This lowers the concentration of alkyllithium and also introduces lithium alkoxides or amides which are known inhibitors of addition reactions of organolithium to π systems.[15] Inspection of ^{13}C and proton NMR spectra of reaction mixtures containing THF or TMEDA shows noticeable ligand cleavage (4%). However, we find *N*-methylpyrrolidine to be unreactive to *tert*-butyllithium even at 65 °C over 3 h; hence, it is a useful ligand in these reactions. Altogether ligand metalation is a less significant reaction in the case of *n*-butyllithium addition to 1, compared to *tert*-butyllithium. Thus TMEDA is effective in producing **3a** both rapidly and in high yield but is not useful for preparing **3b**. Metalation phenomena are also responsible for the efficacy of THF-d_8 as a catalyst over normal protio THF. As seen in Table II after the addition reaction, catalyzed by THF, there remained 14% unreacted triene, 1, while THF-d_8 gave almost total conversion to aromatic product **4b** and salt **3b**. Clearly the kinetic isotope effect in THF metalation must be responsible for these results.

Altogether the role of ligand in catalyzing these addition reactions of RLi compounds to 1 can only be understood qualitatively. Complexes of alkyllithium compounds with

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Table III. Rates of Aromatization of Salts 3a-c in Cyclopentane

temp, °C	salt	concn, M	ligand	concn, M	rate, M $h^{-1} \times 10^{-3}$
20	3b	0.77			6.8
25	3b	1.29			7.4
20	3b	1.25	NMP	2.5	1.1
20	3b	1.08	THF	2.4	21.2
20	3c	0.56			1.0
20	3a	1.48	TMEDA	1.6	32
20	3a	0.26	NMP	2.6	6.5
20	3a	0.40	THF	3.0	81

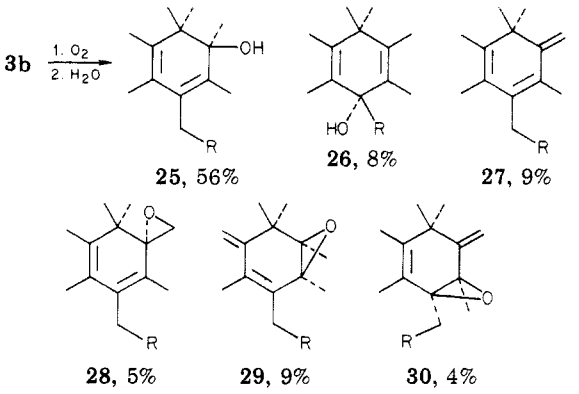
amines and ethers are known to catalyze addition reactions to numerous π systems.[16] These complexes are claimed to contain fewer RLi units than the corresponding unsolvated alkyllithium aggregates. This reduced association has come to be connected with higher reactivity in these addition reactions. Further understanding of these reactions requires some knowledge of the structure of the alkyllithium ligand complexes as well as of the ligand salt (**3a–c**) complexes.

Aromatization of the Salts 3a–c. The lithium salts **3a–c** are stable at −78 °C for at least 1 year but aromatize slowly at 0 °C with extrusion of methyllithium. This constitutes a new method to prepare methyllithium in the presence of many different ligands. Table III gives qualitative information on aromatization of **3a–c** to **4a–c**. Adding ligand to preformed unsolvated salts **3b,c** gave solutions of solvated **3b,c** largely uncontaminated by **4b,c** as happens when 1, ligand, and organolithium compound are mixed at the same time. Note that **3a** (from *n*-butyllithium) could not be obtained unsolvated since it decomposes as fast as it is formed. The initial rates of aromatization of salts **3a–c** depend on structure as well as ligand. For the unsolvated salts rates of aromatization are R = *n*-Bu ≫ *sec*-Bu > *t*-Bu. Table III lists initial rates of aromatization of salts **3a–c** under different conditions. With ligands one sees the trend, decreasing rates, R = *n*-Bu, THF ≫ NMP, and, R = *t*-Bu, THF > NMP. The salts **3a–c** appear from preliminary NMR studies to be bent around the saturated C_1 carbon; see **20** above.

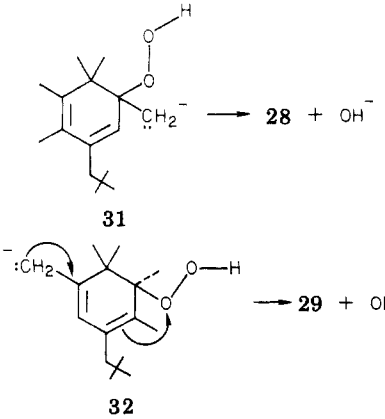
The transition state for aromatization necessarily involves some flattening of **3**. This entails increased periplanar interactions among the methyl groups aggravated by buttrerssing by the larger alkyl group at C_4. Thus aromatization should be energetically less accessible for larger groups at C_4; hence the stabilities of the salts in decreasing order run *t*-Bu > *sec*-Bu > *n*-Bu.

Also initial NMR studies of the salts **3** show that oxolane favors the formation of solvent-separated ion pairs.[17] The fastest rates of aromatization for each species were obtained in the presence of THF. This is consistent with Grovenstein's finding that fragmentation reactions of carbanionic substances are much faster under conditions favorable to solvent-separated ion pairs.[18]

Reaction of 3b with O_2. When O_2 was not rigorously excluded during the hydrolysis of **3b** several extra products were detected in addition to **4**, **5**, **6**, and recovered triene, **1**. That the new products came from oxidation of **3b** was confirmed by the results of reacting **3b** with dry oxygen. Thus **3b** from *tert*-butyllithium and triene **1** with *N*-methylpyrrolidine at 20 °C was reacted with a current of dry oxygen, and the products were hydrolyzed, separated by gas chromatography, and investigated by use of mass spectroscopy. Dienes **5** and **6**, the normal hydrolysis products of **3**, were not detected among the products of the oxidation reaction. Instead, six products were obtained: two alcohols, **25** (56%) and **26** (8%); a triene **27** (9%); three compounds, probably epoxides **28–30**, in 5%, 9%, and 4% yields, respectively. Products **25–27** gave



m/e values of 232 (triene **27** or ROH–H_2O). Treatment of the product mixture with LiOH–H_2O–diethyl ether resulted in the reduction of the proportions of **25** and **26** and a corresponding increase in the fraction of **27**. Thus **27** is the triene. The mass spectrum of alcohol **25** is nearly identical with that of triene but differs from that of **26**. This assigns the site of OH in **25** to the 2-position and in **26** to C_4. This is consistent with the observed fragmentation patterns. Products **28–30**, in low yield, have *m/e* of 248 (triene **27** + O) and are likely to be epoxides (see Experimental Section) obtained via base-catalyzed internal displacements on oxygen in the intermediate hydroperoxides. These assignments are consistent with the mass spectra but must be considered tentative.



Conclusions

We have described how alkyllithium compounds add to triene **1** in hydrocarbon solvents, or in the presence of ligands, to give stable solutions of cyclohexadienyllithium compounds, **3a–c**. The reaction is catalyzed by ethers and tertiary amines, particularly DEE, TMEDA, THF-d_8, and

(16) (a) A. G. Evans and D. B. George, *J. Chem. Soc.*, 4653 (1961); (b) S. Bywater and D. J. Worsfold, *Can. J. Chem.*, **40**, 1564 (1962); (c) M. Morton, L. J. Fetters, and E. E. Bostick, *J. Polym. Sci., Part C*, **1**, 311 (1963); (d) R. Waack and P. West, *J. Organomet. Chem.*, **5**, 188 (1966); (e) R. Waack, M. Doran, and P. E. Stevenson, *J. Am. Chem. Soc.*, **88**, 2109 (1966); (f) R. A. H. Casling, A. G. Evans, and N. H. Reese, *J. Chem. Soc. B*, 519 (1966); (g) P. West and R. Waack, *J. Am. Chem. Soc.*, **89**, 2764 (1967); (h) T. L. Brown, *Pure Appl. Chem.*, **23**, 447 (1970); (i) H. L. Lewis and T. L. Brown, *J. Am. Chem. Soc.*, **92**, 1955 (1970); (j) Y. Okamoto and H. Yuki, *J. Organomet. Chem.*, **29**, 329 (1971); (k) C. M. Selman and H. C. Hsieh, *J. Polym. Sci., Part B*, **9**, 219 (1971); (l) J. N. Hay, J. F. McCabe, and J. C. Robb, *J. Chem. Soc., Faraday Trans. 1*, **68**, 1 (1972).

(17) G. Fraenkel and M. Hallden-Abberton, to be published.

(18) See E. Grovenstein, *Angew. Chem., Int. Ed. Engl.*, **17**, 313 (1978).

NMP. The efficacy of NMP lies in its resistance to metalation, an effect which also explains the advantage of THF-d_8 over protio THF.

By choice of suitable ligands, **3a,c** may be produced in nearly quantitative yield. Unsolvated **3b,c** may also be obtained and all solvated species **3a–c** are soluble in hydrocarbons over a wide range of temperature.

Hydrolysis of the salts **3a–c** gives dienes **5a–c** and **6a–c**. Heating salts **3a–c** results in aromatization to **4a–c** with extrusion of methyllithium. The results are understood in terms of the relative rates of addition of RLi to **1**, aromatization of **3**, and metalation of ligands. The stability order of salts **3a–c** is proposed to derive from steric interactions among the alkyl substituents which raises the energy of the transition state for aromatization when the substituent at C_4 is bulky.

Experimental Section

Abbreviations. The following abbreviations are used: diethyl ether (DEE), glyme (DME), 1,2-dipiperidylethane (DPE), triethylamine (TEA), tetrahydrofuran (THF), *N,N,N,N'*-tetramethylethylenediamine (TMEDA), and *N*-methylpyrrolidine (NMP).

Solvents, Apparatus, and General Techniques. THF and diethyl ether were dried over and distilled from *n*-butylmagnesium bromide under an argon atmosphere. THF-d_8 was stored over Na–K alloy for several days with intermittent shaking, and was then bulb-to-bulb distilled into a new flask containing more Na–K, and the process was repeated. The second distillate was collected in a graduated storage vessel equipped with an in-line Kontes high-vacuum stopcock and stored under argon prior to use.

Glyme–2,*N,N,N',N'*-tetramethylethylenediamine and *N*-methylpyrrolidine were dried over sodium sand and distilled under reduced pressure. Pyridine, triethylamine (TEA), and 1,2-dipiperidylethane (DPE) were distilled from finely ground KOH under reduced pressure. Pure cyclopentane was obtained by stirring reagent-grade cyclopentane (Aldrich Chemical Co.) over 97% H_2SO_4 overnight, washing with water, drying over finely ground KOH, filtering, distilling the cyclopentane through a spinning-band column, and collecting the fraction boiling from 49.2 to 49.3 °C (760 torr). Cyclopentane was then redistilled from $LiAlH_4$ under an argon atmosphere. Cyclohexane was purified in a similar fashion. Benzene was dried and purified by distillation and redistillation from Na sand. All glassware used in organometallic reactions was cleaned in an alcoholic KOH bath followed by thorough rinsing with water and drying at 130 °C for 2–24 h prior to use. Glassware was removed, hot, from the drying oven and allowed to cool in the port of a Kewanee nitrogen glovebox under a flow of nitrogen, after which the glassware was assembled in the glovebox. Portions of air-sensitive triene **1** or delinquescent compounds such as KO-*t*-Bu were sealed in the glassware at this time, and the closed apparatus was removed from the glovebox. Final purging of the nitrogen atmosphere with extremely dry argon preceded each reaction. Argon was deoxygenated with metallic copper on asbestos (BSAF BR3-11 pellets) and dried by passage through 97% sulfuric acid, KOH pellets, and 4-A molecular sieves (dried by heating at 380 °C). This argon atmosphere was suitable for the storage of sublimed *t*-BuLi with *no* detectable alkoxide formation (<0.5% by Gilman double Titration).[19] Alkyllithium solutions were analyzed by this double titration procedure in the following manner. Dry, degassed ether (10 mL) under argon was placed in each of two 50-mL Erlenmeyer flasks equipped with serum caps. 1,2-Dibromomethane (1 mL) was added to one of the flasks and a 0.60-mL aliquot of RLi solution was added to each. After 1 min, each solution was hydrolyzed and 0.1 N standardized hydrochloric acid solution was added until phenophthalein was colorless. The solutions were then back titrated with 0.1 N sodium hydroxide solution. The concentration of alkoxide was given by the base concentration of the solution containing 1,2-dibromoethane and the concentration of RLi was given by the difference in base concentration of the two solutions. Alkoxide usually represented 1–2% of the total base. Operations requiring an inert atmosphere were carried out in either a Kewanee Scientific Equipment Co. 2C281-20 glovebox or a Vacuum Atmosphere Co. HE-43 glovebox under N_2 or argon atmosphere, respectively.

All product mixture analysis and separations by vapor-phase chromatography were performed by using a Varian Aerograph A-700 chromatograph at 140–155 °C at a flow of 33 mL/min. Columns were either a 5 ft × –0.5 in. 20% SE-30 on firebrick (column A), 15 × 0.25 in. 20% SE-30 on Chrom P (column B), or most often 0.5% SF-96 silicone fluid (G.E.) on 80/120-mesh glass beads (column C). IR spectra were recorded on a Perkin-Elmer Model 457 grating spectrophotometer. Mass spectra were obtained on an AEI Model MS-9 spectrometer.

NMR Equipment. Continuous-wave proton spectra were obtained on the Varian HA-100 HX-90 (90 MHz) and WP-80 (80 MHz) spectrometers. Carbon-13 NMR with proton decoupling was carried out at 22.63 MHz, using HX-90 equipment, and at 15.09 MHz on a home-built multinuclear Fourier-Transform spectrometer with external proton lock. The system includes a Bruker power amplifier and decoupler (B-SVBB), field stabilizer (B-S N 15), Ortec 416 A gate with delay generator and 4610 program control units, Tektronix display 602, Hewlett-Packard 5105 A frequency synthesizer, and HA-60 Varian electromagnet. The data system consists of a Nicolet BHC 1080 E computer with 20 480 20-bit words of memory and a Diablo movable head disk. A proportionally controlled 300-W heater in conjunction with a platinum resistance thermometer served to thermostat the nitrogen gas which passed through the insert and thus controlled the temperature of the sample. The system was calibrated by use of a separate platinum resistance thermometer immersed in methanol in a spinning NMR tube. For critical temperature measurements this system was placed in the insert before and after each spectrum. With broadband decoupling it is necessary to turn off the decoupler during the temperature measurement.[20]

The reference for proton NMR spectra was Me_4Si. In the ^{13}C spectra either Me_4Si (0.00 ppm), cyclopentane (26.523 ppm), or cyclohexane (27.620 ppm) was used as a reference. The latter solvents were referenced to Me_4Si in a separate experiment.

Purification of Hexamethylbenzene. Hexamethylbenzene was purified by first dissolving 76.3 g in 280 mL of pure chloroform with 85 mL of absolute ethanol. This solution was filtered and the chloroform–ethanol–water azeotrope distilled out until the remaining solution just turned cloudy. Addition of 25 mL of chloroform to the hot solution gave, on cooling and drying (0.04 torr), 74.2 g of hexamethylbenzene, mp 164.3–165.6 °C.

Triene 1. A three-necked 250-ml Morton flask with condenser, addition funnel, mechanical stirrer (with air seal), and gas-inlet tube was thoroughly flamed out in a current of argon. Hexamethylbenzene (24.9 g, 153.6 mmol) and aluminum chloride (22.06 g, 169.5 mmol) were dissolved in 100 mL of bromobenzene in the flask. The solution was heated to 90 °C and dry chloromethane gas (by passage through 96% H_2SO_4, KOH, and $CaSO_4$) was introduced just below the surface at a rate of 326 mmol/h for 41 min (223 mmol), maintaining the temperature at 90 °C. The solution was allowed to cool to room temperature and was filtered through a glass-wool plug held in a large funnel directly into a flask containing powdered urea (30.5 g, 508.4 mmol) at –30 °C. To the well-stirred slurry was added 150 mL of water slowly with gradual warming to 0 °C, giving an aqueous solution of pH 1. Both layers were filtered under suction through a mat of Celite directly into a separatory funnel, and the bromobenzene layer was removed. Analysis of this solution by ^1H NMR indicated 94% triene and 6% hexamethylbenzene. The aqueous layer was extracted with 50 mL of pentane and after removal of the pentane in vacuo the residue was combined with the bromobenzene layer, which was rapidly extracted with 4 40-mL portions of *chilled* 37.5% aqueous HCl (total = 160 mL, 12 N HCl; 1.92 equiv). The acid extract was *immediately* poured into a 2-L flask (with mechanical-stirrer assembly) containing 400 g of ice and 200 mL of pentane, followed at once by the addition of a solution of 269.5 g of K_2CO_3, in 400 mL of water in a pressure-equalized dropping funnel. This addition must be slow enough to prevent foaming

(19) H. Gilman, *Org. React.*, 8, 265 (1954).

(20) B. E. Mann, *Adv. Organomet. Chem.*, 12, 135 (1974).

and avoid buildup of pressure. It is essential to work fast at this point to avoid decomposition of the carbocation. The evolved CO_2 purged gases from the flask via a capillary diffusion tube in the top of the dropping funnel. After being dried over 35 g of $CaSO_4$, the solution was filtered and the pentane removed by rotary evaporation, affording 25.2 g of a pale yellow oil which solidified upon standing. NMR analysis indicated that the crude product consisted of 95.1% **2**, 3.1% HMB, and 1.8% bromobenzene. After recrystallization from 78 mL of MeOH and 5 mL of Et_2O (with 5 mg of K_2CO_3) 20.68 g of triene 1 in 76.4% yield was obtained in two crops, mp 45.5–50.0 °C (lit.[2] mp 47 °C). NMR and VPC analysis indicated that this product was 97.8% triene 1 and 2.2% hexamethylbenzene. The third crop had a depressed melting point and further product was obtained by evaporating off the methanol and bromobenzene under reduced pressure and by passing the residue through an alumina column (2.2 × 22.0 cm, 70 g of "Certified Alumina-Brockman Activity 1" basic, 80–200 mesh, Fisher Scientific Co.). Elution with pentane began to give a residue after 75 mL of effluent was collected; the next 135 mL gave an inseparable mixture of triene 1 and traces of hexamethylbenzene; further elution with diethyl ether gave two unidentified products in low yields. After removal of the pentane and recrystallization of the first fraction from 6.5 mL of methanol and 0.3 mL of diethyl ether at 0 °C, 1.32 g of further triene plates was filtered off, bringing the total overall recovered yield to 22 g of 97.8% pure triene in 81.3% yield. Sublimation under residual argon atmosphere (25–31 °C, 1.3 torr) was nearly quantitative, giving white crystals of triene 1. Unsublimed samples of triene **2** were found to be of satisfactory purity for use in the reactions described below: IR (melt, between KBr plates, sealed edges) 3110 (m), 2966 (s), 2923 (s), 2867 (s), 1658 (w), 1612 (m), 1580 (w), 1544 (w), 1471 (s), 1437 (s), 1372 (s), 1354 (s), 1287 (m-sh), 1065 (s), 1003 (w), 908 (wv), 850 (s), 760 (w), 700 (w), 700 (m), 581 (s-sh) cm^{-1}; ^1H NMR (CCl_4, 100 MHz, internal Me_4Si) δ 1.083 (s, 6 H, *gem*-dimethyls), 1.80 (s, 12 H, ring methyls), 4.80 (s, 2 H, CH_2); ^{13}C NMR (Me_4Si, CCl_4, 90 MHz) 142.1 (C-4), 137.3 (C-3), 124.8 (C-2), 102.8 (=CH_2), 41.3 (1-**C**(CH_3)$_2$), 24.8 (1-C(**C**H_3)$_2$), 15.6 (3-CH_3), 14.7 (2-CH_3) ppm; mass spectrum, *m/e* (relative intensity) 176 (M^+, 27.8), 162 (-CH_3, 16.7), 161 (-CH_4, 100), 147 (161 - CH_2, 7.1), 133 (147 - CH_2, 4.8), 119 (133 - CH_2, 4.4), 105 (119 - CH_2, 4.7), 91 (105 - CH_2, 5.9), 41 (4.8), 39 (3.6).

Alkyllithium Solutions. The alkyllithium solutions used in our investigations were prepared from commercially available RLi solutions (Alfa Products, Ventron Corporation, and Matheson Coleman and Bell Company) by removing the pentane (*t*-BuLi) or hexane (*n*-BuLi) in vacuo and replacing the solvent with purified cyclopentane or cyclohexane (see previous discussion). Alkyllithium concentrations were all determined by the procedure previously mentioned. As a precaution we routinely sublimed samples of *t*-BuLi for use in the alkyllithium addition reactions. These highly purified samples gave the same addition rates and reaction products as the unsublimed stock solutions in all reactions examined. We therefore used unsublimed RLi in most of the reactions examined (alkoxide 2%).

Reactions of Organolithium Compounds with Triene. Workup Procedure. Normal workup refers to slowly syringing an organolithium product solution into 5 mL of deoxygenated H_2O under an argon atmosphere (5% aqueous HCl solutions were used to quench solutions of **3** containing an amine ligand). If only chromatographic analysis was to be performed, a sample of the hydrocarbon layer was withdrawn after the layers had thoroughly settled and injected onto a gas–liquid chromatograph (usually using column C); see below. If the sample was to be analyzed further, the desired product was isolated by dilution of the hydrocarbon layer with distilled benzene, separation of the layers and, after filtration, azeotropic removal of the benzene solvent to dry the isolated compound(s). The product was then pumped in vacuo (0.1 torr) to remove traces of benzene. The remaining material is referred to as the crude product and was isolated with minimum loss of compound by this procedure. On molecular distillation of this crude product at 0.001–0.01 torr, 30–120 °C, there remained less than 2% residue.

Gas Chromatographic Separations. Typically the crude hydrolysis mixture described above was taken up into pentane and analyzed by GLC using a $^1/_8$ in. × 10 ft stainless-steel column packed with 0.5% silicone fluid (SF-96; G. E.) on 80/120-mesh glass beads (column C) at 140–155 °C and a helium flow rate of 33 mL/min. Retention times increased in the order **1**, **6**, **5**, **27**, **4**, for both the *n*-butyl and *t*-butyl derivatives.

2-Methyladamantanol, 7. A 50-mL ₹ 14/20 flask with stirring bar, condenser, and side arm bearing a 2-mm straight-bore stopcock (protected with a serum cap) was flamed out in a current of argon. The flask was charged by syringe through the stopcock with *tert*-butyllithium in cyclohexane (2.4 mL, 6.2 mmol, 2.59 M) and then triene **1** (11 g, 6.2 mmol). This reaction mixture was heated with stirring at 80 °C under argon for 8 h. The reaction mixture first turns red and then gives a yellow-orange precipitate with colorless supernatant. After the system was cooled to room temperature the liquid phase was syringed out and the remaining precipitate treated at 0 °C with 2-adamantanone (0.94 g, 6.25 mmol) in 20 mL of dry diethyl ether. This mixture was stirred at 0 °C for 10 h. The resulting white precipitate was hydrolyzed with water. Removal of the ether phase, drying it with $MgSO_4$, and evaporation of solvent left a pale yellow oil. Recrystallization gave 0.78 g of 2-methyladamantanol in 75% yield (based on triene): mp 210 °C (uncorrected) (lit.[5] mp 207.8–209 °C); obsd *m/e* 166.136 188, calcd 166.135 756 9. The liquid phase from the original reaction mixture was found to contain neopentylpentamethylbenzene in >98% yield.

1,1,2,3,5,6-Hexamethyl-4-pentylcyclohexadienyllithium, 3a. The reaction vessel was a ₹ 14/20 25-mL flask with glass-covered stirring bar and side arm with 2-mm straight-bore stopcock, protected with a serum cap. The system was flamed out in a current of dry argon. *n*-Butyllithium (1.52 mL, 4.21 mmol, 2.77 N) in cyclopentane was syringed into the reaction vessel, through the stopcock. Then a solution of triene **1** (0.53 g, 3.01 mmol) in 0.45 mL of dry TMEDA was slowly added via syringe at 20 °C over 7 min to the well-stirred butyllithium. The solution, total volume 1.97 mL, was then stirred for an additional 50 min at 20 °C and a 3.0-mL portion was syringed into 10 mL of rapidly stirred deoxygenated 5% aqueous HCl solution under argon. GLC analysis of this hydrolysate mixture showed 0.7% **1**, 41.0% **6a**, 56% **5a** (97% anion), and 2% **4d**. All other *n*-butyllithium additions were performed and analyzed in similar fashion. Samples of **3a** TMEDA in solution were stored in vials, under argon, protected by straight-bore stopcocks, below 0 °C.

Pentamethylpentylbenzene. The remaining 1.37 mL of the solution of **3a**·TMEDA obtained above was heated at 55 °C under argon with stirring for 5.5 h before hydrolytic workup as described above. Analysis of the hydrolysate by GLC showed 0.6% **1** and 99% **4a** only. The crude product was sublimed at 0.01 torr and 60 °C to yield 0.51 g of the title compound in 77% yield, based on triene: mp 31–32 °C; UV (cyclohexane) λ_{max} 222 nm; IR (KBr, melt) 2958 (s), 2926 (s), 2875 (s), 2862 (s), 1510 (m), 1380 (w), 1620 (w), 1010 (vw), 800 (vw), 724 (vw) cm^{-1}; mass spectrum, *m/e* (relative intensity) 219 (P + 1, 6.4%), 218 (P, 31.5%), 176 (1.2%), 161 (100%), 148 (3.3%), 147 (9.8%), 143 (4.5%), 131 (4.2%), 105 (3.0%), 91 (4.2%), 85 (5.1%), 57 (3.3%), 55 (3.0%); ^1H NMR (60 MHz, CCl_4) δ 0.95 (1-CH_3), 1.40 (1,β,γ,δ-$(CH_2)_3$, 6 H), 2.13–2.15 (2–6-$(CH_3)_5$, 15 H), 2.57 (4α-CH_2, t); ^{13}C NMR (Me_4Si, 22.63 MHz, $CDCl_3$) 14.08 (1ϵ-CH_3), 16.32 (2,6-$(CH_3)_2$), 16.75 (3,4,5-$(CH_3)_3$), 22.66 (1δ-CH_2), 29.81 (1γ-CH_2), 30.81 (1β-CH_2), 32.56 (1α-CH_2), 131.57 (C-2, C-6-ring), 132.27 (C-4-ring), 132.40 (C-3, C-5-ring), 136.88 (C-4, ring) ppm. Anal. Calcd: C, 88.00; H, 12.00. Found: C, 88.00; H, 11.90.

1,1,2,3,5,6-Hexamethyl-4-pentyl-2,4-cyclohexadiene, 5a, and 1,1,2,3,5,6-Hexamethyl-4-pentyl-2,5-cyclohexadiene, 6a. From the reaction of 3 mmol of triene, 4.2 mmol of *n*-butyllithium, and 3.3 mmol of TMEDA in cyclopentane for 5.5 h, as described above, there was obtained on hydrolysis 0.87 g of a pale yellow oil. This consisted of 5.7% **1**, 38% **6a**, 52% **5a** (anion = 90%), and 4% **4a**. The two diene isomers were separated from each other by preparative GLC on a 0.75 in. × 5 ft Carbowax 2000 column at 146 °C with a flow rate of 45 mL/min. The dienes **5a** and **6a** were obtained in 98.5% and 94.0% purity, respectively (each containing a small amount of the other). Spectral parameters of **6a** (1,4-diene) follow: UV (cyclohexane) λ_{max} 208.5 nm; IR (KBr, neat) 2960 (s), 2936 (s), 2862 (s), 2826 (m), 1708–1735 (br, w), 1465 (s), 1380 (s), 1358 (m), 1150 (w), 1120 (w), 1105 (w), 1191 (m), 1176 (m) cm^{-1}, no diene C=C stretch at 1650 cm^{-1}, only *gem*-dimethyl C—C stretch in 1350–1380 region; mass spectrum, *m/e* (relative intensity) 234 (P, 0.9%), 219 (0.5%), 164 (13.7%), 163 (B, 100%),

150 (3.3%), 149 (22.8%), 148 (20.0%), 147 (13.2%), 133 (17.3%), 121 (4.8%), 119 (4.0%), 117 (2.3%), 115 (1.4%), 107 (2.4%), 105 (3.3%), 93 (1.4%), 91 (2.8%), 79 (1.4%), 77 (1.1%), 55 (1.3%); ^{1}H NMR (60 MHz, $CDCl_3$) δ 1.62 (2,3,5,6-$(CH_3)_4$, 12 H), 1.061 and 1.046 (1,1-$(CH_3)_2$, 6 H), 2.50 (4-H, 1 H), 0.99 (4ϵ-CH_3, 3 H), 0.80–1.60 (4β–δ-CH_2, 6 H).

Spectral parameters of **5a** (1,3-diene) follow: UV (cyclohexane) δ_{max} 267.9 nm (calcd 273 nm; inspection of models indicates some nonplanarity of the 1,3-diene unit due to steric effects, and in **5b,c** also); IR (KBr, neat) 2960 (s), 2925 (s), 2862 (s), 1648 (vw), 1454 (s), 1386 (m), 1363, 1355, 1110 (w), 1090 (w), 1065 (w), 1040 (w), 990 (w) cm^{-1}; mass spectrum, *m/e* (relative intensity) 235 (P + 1, 3.7%) 234 (P, 24.0%), 219 (P – CH_3, 12.5%), 192 (2.2%), 178 (3.4%), 177 (8.4%), 164 (9.5%), 163 (14.5%), 161 (6.7%), 150 (12.0%), 149 (B, 100%), 148 (6.7%), 147 (17.5%), 136 (9.0%), 135 (34.0%), 134 (9.0%), 133 (22.5%), 131 (6.4%), 129 (6.3%), 117 (9.0%), 108 (4.7%), 93 (12.0%), 91 (20.0%), 81 (4.2%), 79 (12.0%), 77 (9.5%), 70 (6.7%), 57 (6.4%), 55 (9.0%),; ^{1}H NMR (60 MHz, CCl_4) δ 0.754 (6α-CH_3, 3 H, d, J(HC–CH_3) = 6.90 Hz), 0.847 and 0.944 (1,1α-$C(CH_3)_2$, 6 H), 1.71 (br, 2α-, 3α-, and 5α-CH_3's, 9 H), 1.16–1.44 (4b–δ CH_2's, 6 H, 4ϵ obscured), 2.14 (4α-CH_2, 2 H).

1,1,2,3,5,6-Hexamethyl-4-neopentylcyclohexadienyllithium, 3b. All reactions were conducted under an argon atmosphere and all chemicals used were dry and freed of oxygen by argon ebullition. A typical procedure follows. First *tert*-butyllithium in cyclopentane (2.8 mL, 6.3 mmol, 2.25 M) was syringed into the reaction vessel described above. A mixture of sublimed triene **1** (1.06 g, 6.0 mmol) and dry *N*-methylpyrrolidine (1.02 g, 1.25 mL, 2 mmol) was then introduced dropwise into the well-stirred *tert*-butyllithium solution at 20 °C over a period of 8 min. After the resulting yellow solution (4.90 mL) was stirred for an additional 5–20 min at 20 °C, analysis by ^{1}H, ^{13}C, and ^{7}Li NMR showed nearly quantitative conversion to **3b** within the limits of detection. A 1.90-mL portion of the same solution was slowly quenched with 1.0 mL of deoxygenated D_2O under argon and gave 0.54 g (2.28 mmol, 98%) of a mixture of dienes **6b** and **5b** *exclusively*, in the ratio 63:100. Less than 0.1% **1** or aromatic product **4b** could be detected by GLC analysis of the deuterolysis mixtures.

All other solutions of **3b** with different ligands were prepared in the same manner, using an addition time of 5–8 min at a temperature of 15–20 °C. The exceptions were reactions without ligand and with TMEDA.

3b·TMEDA. By use of the apparatus described above a mixture of triene (1.08 g, 6.15 mmol) and TMEDA (0.91 mL, 0.79 g, 6.77 mmol) was added to *tert*-butyllithium in pentane (8.94 mL, 9.84 mmol, 1.10 M) at 20 °C over 8 min and the solution was stirred for an additional 15 min. Hydrolysis of a 0.2-mL aliquot revealed18% **1**, 32% **6b**, 47% **5b**, and 2% **4b**. Addition of more TMEDA (0.25 mL, 0.21 g, 1.85 mmol) and allowing the system to react for 17 min more gave the product mixture 12.2% **1**, 35.4% **6b**, 48% **5b**, and 4% **4b**. Pentane was removed from the main unhydrolyzed portion of the reaction mixture in vacuo and replaced by cyclopentane. The solution was set aside for NMR studies.

3b Unsolvated. The reaction vessel described above was charged, under argon, with a glass-covered stirring bar and triene (0.72 g, 4.07 mmol). Then at 25 °C a solution of *tert*-butyllithium (1.62 mL, 4.28 mmol, 2.64 M) in cyclopentane was syringed in with stirring. The initial pale yellow solution turned purple after 5 min, then red brown, and finally black. After being stirred at 25 °C for 96 h, the reaction mixture was quenched by adding 5 mL of deoxygenated water under a slow stream of argon. Alternatively, samples prepared in this manner were stored in the freezer prior to NMR investigation. Hydrolysis of a 0.1-mL aliquot of the product solution indicated 1% unreacted **1**, 58% **5b**, 26% **6b**, and 15% **4b**, as 84% anion and 15% aromatic products, respectively.

2,3,4,5,6-Pentamethylneopentylbenzene. Triene **1** (1.02 g, 5.79 mmol) was dissolved in 2.0 mL of dry cyclohexane and the resulting solution was added over a period of 40 min to a well-stirred solution of *tert*-butyllithium 5.09 mL, 11.58 mmol, 2.27 M) in cyclohexane at 70 °C. The solution became quite dark after the addition of only a few drops of triene solution. After the addition was completed, the temperature was raised to 88 °C over 20 min and stirring was continued at 88 °C for an additional 3 h until the solution was only a pale yellow red with much methyllithium precipitate. After standard workup, 1.26 g of a colorless oil was obtained which crystallized upon cooling to room temperature, mp 50.5–59 °C. This consisted of 2.3% dienes and 98% aromatic product **4b** based on GLC analysis. The crude product was easily recrystallized from 4 mL of Et_2O and 5 mL of MeOH at 5 °C to give 0.92 g of snow white crystals in two crops (mp 60.2–61.8 °C) which were recrystallized again to yield 0.80 g of product **4b**, mp 62.8–63.8 °C, in 63% yield based on **1**. The spectral data obtained from this sample follow: IR (KBr, melt) 3026 (m), 2956 (s), 1482 (s), 1468 (s), 1445 (m), 1393 (m), 1367 (s), 1234 (m), 1205 (w), 1159 (w), 1065 (m), 1048 (w), 1003 (m), 896 (vw), 815 (vw), 790 (vw) cm^{-1}; mass spectrum, *m/e* (relative intensity) 219 (P + 1, 1.8%), 218 (P, 11.6%), 203 (1.9%), 163 (3.1%)8 162 (28.3%), 161 (B, 100%), 160 (1.6%), 147 (7.3%), 145 (1.3%), 133 (1.0%), 131 (2.3%), 119 (1.0%), 115 (1.4%), 105 (1.5%), 91 (2.2%), 77 (1.0%); ^{1}H NMR (60 MHz, CCl_4) δ 0.87 (1-CH_3, 9 H), 2.09 (3,4,5-CH_3, 9 H), 2.14 (2,6-CH_3, 6 H), 2.70 (1-CH_2, 2 H); ^{13}C NMR (Me_4Si, 22.63 MHz, $CDCl_3$), 16.78 (4-CH_3), 17.08 (3,5-CH_3), 19.05 (2,6-CH_3), 30.35 (1-CH_3), 34.53 (1-**C**$(CH_3)_3$), 41.11 (1-CH_2), 132.11 (4-**C**CH_3), 132.40 (3, **C**CH_3), 133.32 (2, **C**CH_3), 134.02 (1-**C**$CH_2C(CH_3)_3$) ppm. Anal. Calcd: C, 88.00; H, 11.94. Found: C, 88.00; H, 11.94.

1,1,2,3,5,6-Hexamethyl-4-neopentyl-2,4-cyclohexadiene, 6b, and 1,1,2,3,5,6-Hexamethyl-4-neopentyl-2,5-cyclohexadiene, 5b. Triene **1** (0.35 g, 2 mmol) was reacted with *tert*-butyllithium (0.9 mL, 2.1 mmol, 2.25 M) in the presence of THF (0.29 g, 4 mmol) in cyclopentane at 20 °C over 25 min. After hydrolysis the organic layer was diluted with dry benzene, benzene–water was azeotroped out, and the remaining benzene was pumped out (0.1 torr) at room temperature. This yielded 0.3 g of crude product, shown by gas chromatography to consist of 13% recovered triene **1**, 31% **6b**, 40% **5b**, and 16% **4b**; see below. This mixture was placed on a high-pressure liquid chromatography (LC) column (3.1 × 61.3 cm, silica gel, 58-μm pore, Alpha Products, Ventron Corp., packed in cyclohexane) and the sample was eluted with distilled cyclohexane at a flow rate of 3.0 mL/min. After 340 mL of cyclohexane was collected the first product began to appear and samples were removed from the column in 10-mL portions. A 0.1-g (83%) sample of pure diene **5b** was collected from eluate volumes 340–400 mL, and a 0.074-g (83%) sample of pure diene **6b** from 525–675 mL. Samples were separated from cyclohexane by warming the effluent solutions under a rapid stream of dry argon in tared vials protected with serum caps. Since sample **5b** was extremely sensitive to air, treatment in this manner was necessary and gave good recovery of **5b**. The spectral data for **6b** (the 1,4-diene) follow: UV (cyclohexane) δ_{max} 217.5 nm; IR (KBr, neat) 2970 (s), 2918 (s), 2876 (s), 1697 (m), 1470 (m), 1480 (m), 1448 (m), 1396 (s), 1382 (s), 1366 (s), 1232 (w), 1155 (w), 1110 (w), 1092 (m), 1050 (w), 932 (w), 870 (w), 813 (vw), 772 (vw), 752 (vw), 590 (w) cm^{-1}; mass spectrum, *m/e* (relative intensity) 235 (P + 1, 0.4%), 234 (P, 2.3%), 219 (0.4%), 217 (0.7%), 178 (0.4%), 177 (1.6%), 164 (19.6%), 163 (B, 100%), 162 (2.2%), 161 (1.8%), 149 (7.2%), 148 (15.1%), 147 (9.2%), 135 (2.8%), 133 (10.1%), 121 (3.3%), 119 (2.5%), 107 (1.1%), 105 (2.6%), 93 (0.9%), 91 (2.7%), 79 (1.1%), 77 (1.2%), 71 (4.6%), 57 (1.6%). Monodeuterated **6b**: 235 (P, 0.86%), 234 (0.02%), 165 (14.9%), 164 (100%), 150 (6.6%), 149 (13.8%), 148 (4.3%), 147 (5.2%), 135 (2.6%), 134 (7.2%), 122 (2.3%), 121 (1.1%), 120 (1.7%), 119 (1.7%), 118 (1.1%), 106 (2.09%), 105 (1.1%), 92 (1.4%), 91 (1.4%), 71 (3.4%), 57 (2.0%), 55 (1.4%); ^{1}H NMR (100 MHz, $CDCl_3$) δ 0.912 (4-CH_3, 9 H), 1.074 (1-CH_3, 6 H), 1.549 (4 CH_2, 2 H, d, J(CH,CH_2) = 4.2 Hz), 1.63 (2,6-CH_3, 6 H), 1.68 (3,5-CH_3, 6 H), 2.46 (4-CH, 1 H); ^{13}C NMR (Me_4Si) 14.68 (2,6-CH_3), 19.10 (3,5-CH_3), 25.09 and 25.47 (1,1-CH_3), 30.84 (4-CH_3), 32.05 (4β-CH_2**C**), 39.93 (1-C ring) 46.02 (4-CH_2), 46.19 (4-C ring), 128.68 (2,6-C ring), 131.76 (3,5-C ring) ppm.

The spectral data for **5b** (1,3-diene) follow: UV (cyclohexane) δ_{max} 266.6 nm; IR (KBr, neat) 2970 (s), 2958 (s), 2920 (s), 2876 (s), 1480 (m), 1462 (m), 1446 (m), 1392 (w), 1380 (w), 1368 (s), 1357 (w), 1238 (w), 1203 (w), 1158 (vw), 1100 (w), 1070 (vw), 1045 (vw) 990 (vw) cm^{-1}; mass spectrum, *m/e* (relative intensity) 235 (P + 1, 10.9%), 234 (P, 50.9%), 220 (2.2%), 219 (12.7%), 217 (2.1%), 178 (21.7%), 177 (B, 100%), 176 (4.5%), 164 (3.0%), 163 (21.1%), 162 (5.4%), 161 (6.9%), 150 (9.4%), 149 (63.9%), 148 (5.4%), 147 (16.3%), 136 (7.8%), 135 (44.4%), 133 (10.3%), 122 (7.2%), 121 (38.9%), 120 (3.7%), 119 (10.3%), 117 (3.1%), 77

(3.0%), 71 (36.1%), 57 (10.9%), 55 (7.8%). Monodeuterated **5b**: 236 (P, 11.3%), 234 (1.7%), 220 (15.7%), 218 (3.2%), 179 (21.4%), 178 (B, 100%), 177 (6.9%), 176 (2.9%), 165 (3.2%), 164 (22.5%), 163 (5.9%), 162 (7.5%), 161 (2.9%), 151 (10.2%), 150 (75.0%), 149 (7.8%), 148 (17.7%), 147 (6.8%), 136 (17.4%), 135 (39.2%), 134 (10.6%), 133 (6.9%), 122 (41.6%), 121 (7.6%), 120 (8.8%), 119 (5.9%), 108 (3.7%), 107 (5.3%), 106 (5.3%), 105 (5.5%), 94 (2.3%), 93 (3.1%)8 92 (4.2%), 91 (6.5%), 79 (2.6%), 77 (2.5%), 71 (38.1%), 57 (14.3%), 55 (3.2%); ^{1}H NMR (100 MHz, $CHCl_3$) δ 0.747 (6-CH_3, 3 H, J(CH,CH_3) = 6.8 Hz), 0.878 (4-CH_3, 9 H), 0.957 (1-CH_3, 6 H), 1.486 (6-CH, 1 H), 1.660 (5-CH_3, 3 H), 1.716 (2,3-CH_3, 6 H), 2.170 (4-CH_2, 2 H), ^{13}C NMR (Me_4Si, 22.63 MHz, $CDCl_3$) 11.71 (6-CH_3), 14.68 (2-CH_3), 16.67 (5-CH_3), 20.34 (3-CH_3), 23.79 and 25.09 (1-CH_3), 30.05 (4-CH_3), 34.42 (4-$C(CH_3)_3$), 36.47 (1-C ring), 39.66 (4-CH_2), 47.70 (6-C ring), 126.8 (5-C ring), 127.9 (2-C ring), 130.9 (3-C ring), 134.4 (4-C ring).[21]

Reaction of *sec*-Butyllithium with Triene 1. This reaction was carried out in similar fashion to those using *n*-butyllithium and *tert*-butyllithium. Thus *sec*-butyllithium (2.3 mL, 4.08 M, 9.48 mmol) in cyclopentane was reacted at 0 °C for 30 min with a solution of triene **1** (1.52 g, 8.02 mmol) in 3 g of dry THF. Quenching with degassed water and separation of products by gas chromatography gave 0.31 g of triene **1** (20.6%), 0.56 g of **5c** (37%), 0.4 g of **6c** (26.2%), and 0.25 g of **4c** (16.2%). Crude samples were purified by high-pressure LC (see above). NMR spectra are summarized in Table I. Mass spectral data: **4c**, *m/e* calcd 218.2034, obsd 218.2039; **5c**, *m/e* calcd 234.2347, obsd 234.2351.[21]

Reaction of 3b with O_2. The glassware consists of a 10-mL round-bottom flask with side arm protected by a 2-mm straight-bore stopcock with serum cap. A glass-covered stirring bar was introduced and the system flamed out in a current of argon. A mixture of triene **1** (0.67 g, 3.79 mmol) and *N*-methylpyrrolidine (0.79 mL, 7.58 mmol) was syringed in via the stopcock. To this solution, at 20 °C, was added by syringe *tert*-butyllithium in cyclopentane (1.5 mL, 2.64 M, 3.98 mmol) over a period of 8 min and the mixture was allowed to stir for an additional 20 min. A 0.4-mL aliquot from this reaction mixture was hydrolyzed with deoxygenated 5% aqueous HCl and the organic layer separated by gas chromatography (5 ft × 0.25 in. column with SE-30 on glass beads, 122 °. This showed >99% conversion to **3b**. Dry oxygen (through $CaSO_4$) was bubbled through the remaining solution of **3b**, which turned from yellow to red and then back to yellow. Samples were removed for NMR (^{1}H and ^{13}C) investigation. The rest was hydrolyzed with D_2O, treated with 10 mL of a solution of 5 g of ammonium chloride in 25 mL of water and the organic layer washed with 5% aqueous HCl. After being dried with sodium acetate and removal of solvent the organic layer gave 0.52 g of a yellow oil, 93% of which gave rise to six components: **25** (56%), *m/e* 232; **26** (8%), *m/e* 232; **27** (9%), *m/e* 232; **28** (5%), *m/e* 248; **29** (1%), *m/e* 248; **30** (14%), *m/e* 248.

(21) Dienes and dienols were insufficiently stable to survive transportation for analysis. However, their NMR spectra show no detectable impurities.

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Registry No. **1**, 3043-52-5; **2**, 27175-04-8; **3a**, 75961-59-0; **3b**, 75961-60-3; **3c**, 75961-61-4; **4a**, 75934-66-6; **4b**, 56909-25-2; **4c**, 75934-67-7; **5a**, 75948-79-7; **5b**, 75948-80-0; **5b-d**, 75948-81-1; **5c**, 75948-82-2; **6a**, 75948-83-3; **6b**, 75948-84-4; **6b-d**, 75948-85-5; **6c**, 75948-86-6; **7**, 702-98-7; **25** (R = *tert*-butyl), 75934-68-8; **26** (R = *tert*-butyl), 75934-69-9; **27** (R = *tert*-butyl), 75934-70-2; **28** (R = *tert*-butyl), 75934-71-3; **29** (R = *tert*-butyl), 75934-72-4; **30** (R = *tert*-butyl), 75934-73-5; butyllithium, 109-72-8; *tert*-butyllithium, 594-19-4; *sec*-butyllithium, 598-30-1; hexamethylbenzene, 87-85-4; 2-adamantanone, 700-58-3.

Mechanism of an Acid-Catalyzed Geometric Isomerization about a Carbon-Nitrogen Double Bond[1]

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The mechanism of the hydrogen chloride catalyzed geometric isomerization of (*E*)-*O*-methylbenzohydroximoyl chloride (**1a**) has been investigated. It has been determined that radioactive chloride ($^{36}Cl^-$) is incorporated into the hydroximoyl chloride at a rate equal to one-half the rate of the isomerization. It has also been found that the rate constant for $^{36}Cl^-$ incorporation into the (*E*)-hydroximoyl chloride (**1a**) during isomerization is about 210 times faster than the rate constant for $^{36}Cl^-$ exchange in the (*Z*)-hydroximoyl chloride (**2a**). Based on these observations, it is concluded that the isomerization of **1a** involves nucleophilic attack by $^{36}Cl^-$ on the conjugate acid of **1a** to give a tetrahedral intermediate. The tetrahedral intermediate undergoes stereomutation and thus has a 50–50 chance of losing either $^{36}Cl^-$ or nonradioactive Cl^- to give the conjugate acid of **2a**. The isomerization rates for five (*E*)-hydroximoyl chlorides (**1a–e**) gave a Hammett correlation with σ with a ρ value of –0.66. The rate of isomerization of **1a** was measured in deuterium chloride–dioxane solution and found to be about twice as fast as the isomerization of **1a** in hydrogen chloride (k_H/k_D = 0.44). The low Hammett ρ value and a deuterium isotope effect of 0.44 are consistent with a preequilibrium protonation of **1a** followed by nucleophilic attack by chloride ion. It was found that an *o*-methyl substituent (**1f**) considerably reduces the rate of isomerization.

A plethora of studies[3-13] has been carried out on the kinetics and mechanisms of uncatalyzed geometric isomerization of compounds containing a carbon–nitrogen double bond (imines). Although most of these investiga-

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(2) Taken in part from the Ph.D. Dissertation of E. A. Nalley, Texas Woman's University, May 1975, and the M.S. Thesis of N. M. Silk, Texas Woman's University, May 1978.

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