it is conceivable that the hydration rates of the different aldoses may be nearly identical. This is possible since the calculated hydration rate constants are critically dependent upon the value chosen for N_c (eq. 2).[8] The value of N_c is also necessary in calculations of the rate constants for the interconversions between the various ring forms.[8,17,22] The extremely small magnitude of N_c for most aldoses makes it quite difficult to obtain accurate values for this parameter.[8] In some cases it is possible that accurate measurements of N_c may be made using ultra-high-resolution NMR techniques. Such an important result has already been demonstrated for D-glucose.[23] Otherwise, the absence of precise measurements for sugars may limit the application of NMR[1,11,17,22] and other[8] techniques in the detailed elucidation of the kinetics of monosaccharide tautomerization.

Acknowledgment. This investigation was supported by U.S. Public Health Service Research Grant GM 27003 from the National Institute of General Medical Sciences and by instrumentation grants form the National Institutes of Health Division of Research Resources (RR01077 and NSF/BBS-8714258). We thank Dr. John M. Risley for helpful discussions and Dr. Claude R. Jones for his assistance with the NMR instrumentation.

Registry No. D-Ribose, 50-69-1; D-2-deoxyribose, 533-67-5; α-D-ribopyranose, 7296-59-5; β-D-ribopyranose, 7296-60-8; α-D-ribofuranose, 32445-75-3; β-D-ribofuranose, 36468-53-8; 2-deoxy-α-D-ribopyranose, 36792-85-5; 2-deoxy-β-D-ribopyranose, 22900-10-3; 2-deoxy-α-D-ribofuranose, 36792-87-7; 2-deoxy-β-D-ribofuranose, 36792-88-8.

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[23] Maple, S. R.; Allerhand, A. *J. Am. Chem. Soc.* **1987,** *109,* 3168-3169.

Dianions of 1,4-Bis(methylene)cyclohexane. Conformational Effects in Cyclic and Acyclic Dilithiated Hydrocarbons

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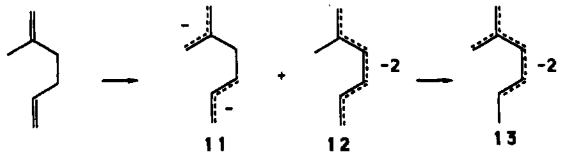
Dimetalation of 1,4-bis(methylene)cyclohexane results in formation of the *p*-xylene dianion via the linearly conjugated dianion 4. In contrast, 2-methyl-1,5-hexadiene, an acyclic analogue of 1,4-bis(methylene)cyclohexane, undergoes isomerization via the linearly conjugated dianion 12, rather than hydride elimination. MNDO calculations of the conformations of dilithiated 4 and 12 show that 4 is effectively planar, with a symmetrical distribution of charge. Dilithiated 12 is nonplanar, with an almost right angle bend in the π-system. The dianion can therefore be considered as two allyl anions which are orthogonal to each other. The difference in calculated conformations of 4 and 12 is advanced as the reason for the different reactivity of the two systems.

We have been interested for some time in the factors which control metalation in unsaturated hydrocarbons.[1] We have focused primarily on acyclic systems and have been particularly successful in predicting the preferential formation of "dianions"[2] in systems which allow the formation of more than one dianion by the use of REPA[3] calculations. We became interested in examining cyclic hydrocarbons to see if the same trends existed in those systems as in the acyclic systems. We chose to examine the metalation of 1,4-bis(methylene)cyclohexane (1) for two reasons. 1 can be considered a cyclic derivative of 2-methyl-1,5-hexadiene (2) whose metalation we have already examined.[1b] In addition, six-membered ring compounds with exocyclic or endocyclic double bonds in strongly basic reaction media undergo hydride elimination to yield benzene rings.[4] The observation was made that aromatization was facilitated by the incorporation of an isobutylene unit in the molecule, suggesting that a cross-conjugated dianion might be implicated. We were anxious to examine anion formation with a metalating system which would allow the opportunity to trap the anions before the formation of benzene rings from hydride elimination. We therefore report the characterization of anions from 1 by metalation with *n*-butyllithium/*N*,*N*,*N′*,*N′*-tetramethylethylenediamine (TMEDA) and their yield and behavior as a function of time.

Scheme I



Our working assumption was that the same types of anions found by metalation of 2 would be found in the metalation of 1. That is, metalation would yield the three anions (4, 6, and 8, Figure 1) analogous to those (11, 12, and 13) shown in Scheme I from metalation of 2. The anions formed from metalation of 1 with *n*-butyllithium-/TMEDA were characterized by quenching with *n*-propyl chloride. Ten monomeric products (Figure 2) were isolated in varying amounts depending on the age of the reaction mixture, indicated by time in Table I. They were characterized by ^{1}H NMR spectroscopy and mass spectroscopy, as shown in Table II. As Table I shows, aromatic product

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[1] (a) Thorstad, W. T.; Mills, N. S.; Buckelew, D. Q.; Govea, L. G. *J. Org. Chem.* **1989,** *54,* 773. (b) Mills, N. S. *J. Am. Chem. Soc.* **1982,** *104,* 5689. (c) Mills, N. S.; Rusinko, A. R. *J. Org. Chem.* **1986,** *51,* 2567. (d) Rusinko, A. R.; Mills, N. S.; Morse, P. *J. Org. Chem.* **1982,** *47,* 5198. (e) Mills, N. S.; Shapiro, J.; Hollingsworth, M. *J. Am. Chem. Soc.* **1981,** *103,* 1263.

[2] Although the species reported will often be referred to as dianions, they are dilithiated hydrocarbons, with an appreciable covalent character in the carbon-lithium bond.

[3] (a) Hess, B. A.; Schaad, L. J. *Pure Appl. Chem.* **1980,** *52,* 1471. (b) Bates, R. B.; Hess, B. A.; Ogle, C. A.; Schaad, L. J. *J. Am. Chem. Soc.* **1981,** *103,* 5052.

[4] Wilhelm, D.; Clark, T.; Friedl, T.; Schleyer, P. von R. *Chem. Ber.* **1983,** *116,* 751.

0022-3263/91/1956-0947$02.50/0

Table I. Product Formation as a Function of Time[a]

time, h	ratio of *metalating* system to 1	1	14	15	16	17	18	19	20	21	22	23	24	25	26	other
6	2:1	89	–	5	–	<1	<1	<1	–	–	2	1	–	–	–	4
	3:1	83	–	5	–	<1	<1	<1	–	1	2	2	–	–	–	5
24	2:1	82	–	8	–	1	1	1	1	1	2	4	–	–	–	–
	3:1	60	–	8	<1	2	1	1	2	6	6	9	–	1	<1	4
48	2:1	72	–	10	–	2	1	1	3	1	2	7	–	1	–	4
	3:1	53	–	7	1	3	1	<1	4	6	7	11	–	2	1	5
216	2:1	29	7	15	12	2	2	2	16	–	3	2	1	6	2	<1
	3:1	26	11	11	10	2	2	1	20	<1	2	1	2	5	4	2

[a] Tetradecane was used as internal standard in the quantification of the product yields by capillary gas chromatography.

Table II. Spectral Data on Quench Products

compd	^{1}H NMR chemical shifts[a]	selected mass spectral fragments
15	0.89 (t, *J* = 6.8 Hz, 3 H), 1.21 (m, 4 H), 1.95 (dd, *J* = 6, 12 Hz, 1 H), 2.22 (m, 5 H), 2.36 (dd, *J* = 6, 12.6 Hz, 1 H), 4.67 (d, *J* = 1.8 Hz, 2 H), 4.72 (d, *J* = 1.8 Hz, 2 H)	*m/z* 150 (P, 8), 108 (60), 93 (100), 79 (87)
16	0.89 (t, *J* = 7.0 Hz, 3 H), 1.26–1.46 (m, 4 H), 1.66 (s, 3 H), 2.02–2.08 (m, 2 H), 2.15–2.32 (m, 2 H), 2.59 (br s, 1 H), 4.68 (d, *J* = 2.3 Hz, 1 H), 4.75 (d, *J* = 2.3 Hz, 1 H), 5.33 (br s, 1 H)	*m/z* 150 (P, 16), 107 (100), 91 (40), 79 (43)
17	0.90 (t, *J* = 7.2 Hz, 3 H), 1.36 (septet, *J* = 7.2 Hz, 2 H), 2.00 (q, *J* = 7.2 Hz, 2 H), 2.12–2.24 (m, 8 H), 4.66 (s, 2 H), 5.16 (t, *J* = 7.2 Hz, 1 H)	*m/z* 150 (P, 32), 93 (81), 79 (100)
18	0.89 (t, *J* = 7.2 Hz, 3 H), 1.20–1.22 (m, 4 H), 1.94 (t, *J* = 7.3 Hz, 2 H), 2.01–2.12 (m, 2 H), 2.30 (t, *J* = 6.4 Hz, 2 H), 2.73–2.78 (m, 2 H), 4.72 (s, 2 H), 5.34 (br s, 1 H)	*m/z* 150 (P, 7), 107 (25), 93 (100), 79 (66)
19	0.89 (t, *J* = 7.2 Hz, 3 H), 1.20–1.44 (m, 4 H), 1.76 (s, 3 H), 1.94 (t, *J* = 7.3 Hz, 2 H), 2.09 (br s, 4 H), 5.81 (br s, 2 H)	*m/z* 150 (P, 7), 107 (25), 93 (100), 79 (66)
20	0.89 (t, *J* = 7.3 Hz, 3 H), 1.35 (sextet, *J* = 7.3 Hz, 2 H), 1.58 (quintet, *J* = 7.3 Hz, 2 H), 2.31 (s, 3 H), 2.57 (t, *J* = 7.6 Hz, 2 H), 7.08 (s, 4 H)	*m/z* 148 (P, 21), 105 (100)
21	0.87 (t, *J* = 7 Hz, 3 H), 1.22 (m, 4 H), 1.42 (m, 2 H), 2.11 (dd, *J* = 9.0, 4.9 Hz, 2 H), 4.64 (br s, 2 H), 4.75 (br s, 2 H)	*m/z* 192 (P, 11), 150 (40), 149 (41), 107 (84), 93 (100), 91 (45), 81 (31), 77 (32)
22	0.89 (t, *J* = 7.2 Hz, 3 H), 0.90 (t, *J* = 7.1 Hz, 3 H), 1.21–1.22 (m, 8 H), 1.95 (t, *J* = 6.7 Hz, 2 H), 2.01–2.08 (m, 2 H), 2.16–2.31 (m, 2 H), 2.61 (br s, 1 H), 4.67 (d, *J* = 2.2 Hz, 1 H), 4.74 (d, *J* = 2.2 Hz, 1 H), 5.33 (br s, 1 H)	*m/z* 192 (P, 15), 149 (47), 93 (100), 91 (30), 79 (48)
23	0.92 (t, *J* = 7.3 Hz, 6 H), 1.35 (sextet, *J* = 7.3 Hz, 4 H), 1.52–1.63 (m, 4 H), 2.57 (t, *J* = 7.6 Hz, 4 H), 7.08 (s, 4 H)	*m/z* 190 (P, 20), 147 (100), 91 (49)

[a] $CDCl_3$, 300 MHz.

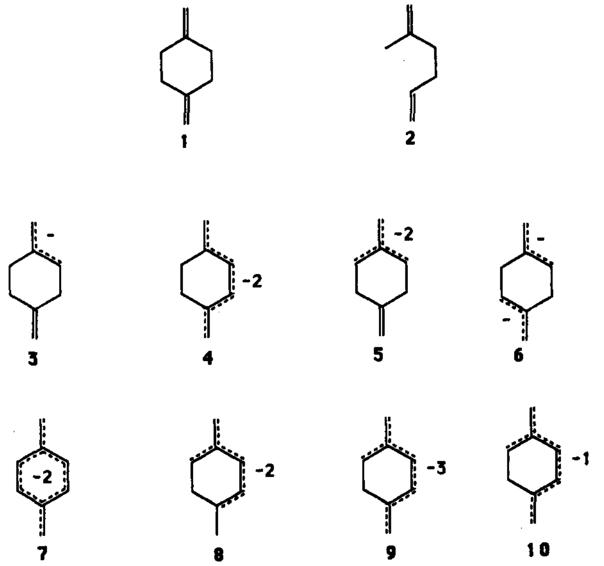

Figure 1. Possible mono- and polyanions from 1.

is barely visible after 2 h and continues to increase with time, reaching a maximum at 216 h. The products grouped into the category of "other" were those generally formed in less than 5% of the reaction mixture. When the mechanism for conversion of 1 to 7 is discussed (see below), those products are considered as unlikely candidates for the major pathway leading to dianion 7. In the quenches which occurred after 24 h of contact with the metalating system, three products (**24**, **25**, **26**) were observed which were derivatives of dimers of 1. Mass spectral analysis showed them to possess molecular weights of 214, 258, and 256, respectively. As shown by the ^{1}H NMR data in Table III, products **24** and **26** are clearly *p*-xylene derivatives.

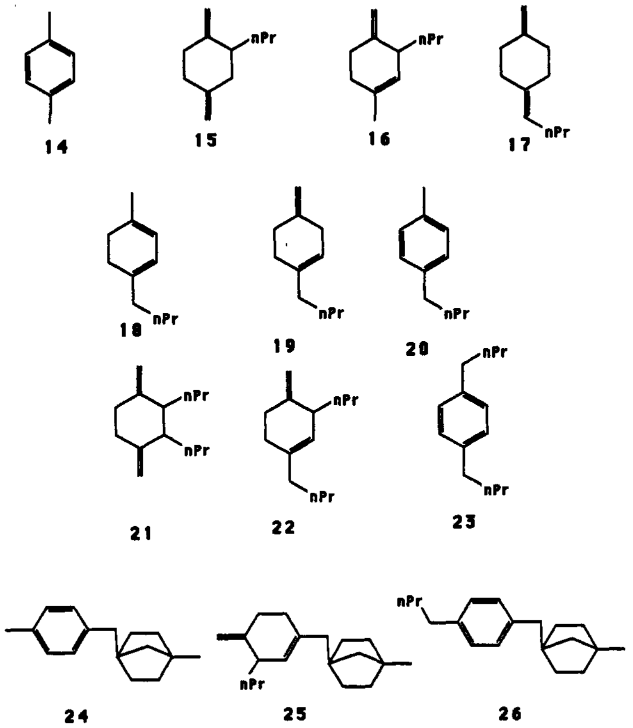

Figure 2.

Although the ^{1}H NMR spectra of each consisted of overlapping regions of peaks, we believe them to be the bicyclo[2.2.1]heptyl derivatives shown from the simplicity of the ^{13}C NMR spectra, especially that of **24**,[5] and from the

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[5] Because of the similarity of the ^{1}H NMR spectra of **24** and **26**, we did not obtain the ^{13}C NMR spectrum of **26**.

Table III. Spectral Data on Quenched Dimers

compd	^1H NMR chemical shifts	^{13}C NMR chemical shifts	selected mass spectral fragments
24	1.06 (s, 3 H), 1.54–1.24 (m, 10 H), 2.32 (s, 3 H) 2.71 (s, 2 H), 7.03 (q, J = 8.7 Hz, 4 H)	20.98, 21.29, 35.71, 37.62, 42.03, 49.41, 128.42, 129.72, 134.60	214 (P, 57), 185 (57), 143 (22), 109 (70), 105 (100), 93 (21), 91 (21), 81 (37), 79 (43), 77 (39)
25	0.90 (t, J = 6.6 Hz, 3 H), 1.08 (s, 3 H), 1.54–1.21 (m, 15 H), 2.10 (s, 3 H), 2.19 (m, 2 H), 2.64 (br s, 2 H), 4.67 (s, 1 H), 4.74 (s, 1 H), 5.28 (d, J = 3.9 Hz, 1 H)	14.11, 20.38, 21.32, 29.78, 33.22, 36.21, 37.66, 38.48, 42.63, 43.82, 107.31, 118.6, 127.50	258 (P, 28), 135 (67), 93 (100), 91 (61), 81 (94)
26	0.93 (t, J = 7.2 Hz, 3 H), 1.06 (s, 3 H), 1.64–1.21 (m, 14 H), 2.58 (t, J = 7.7 Hz, 2 H), 2.71 (s, 3 H), 7.04 (q, J = 7.2 Hz, 4 H)		256 (P, 83), 227 (98), 213 (42), 147 (64), 129 (30), 128 (28), 109 (100), 91 (51), 81 (46)

Table IV. Anion Formation as a Function of Time[a]

time, h	ratio of metalating system to 1	starting material (1)	products from anion **3 (15, 17, 19)**	products from anion **4 (16, 18, 21, 22, 25)**	products from anion **7 (14, 20, 23, 24, 26)**	other
6	2:1	89	~6	~2	~1	4
	3:1	85	~5	~3	~2	5
24	2:1	82	~10	~2	~5	–
	3:1	65	~10	~12	~10	4
48	2:1	72	~13	~4	~10	<1
	3:1	56	~10	~14	~14	5
216	2:1	29	~20	~22	~28	<1
	3:1	26	~14	~20	~38	2

[a] Percentages do not always equal 100% because of round-off procedures.

similarity of the ^{13}C NMR spectra to that of known bicyclo[2.2.1]heptanes.[6] The proposed structure of **25** is suggested by similarities in its ^1H NMR spectrum to those of **22** and **24**/**26**.

A more effective way of evaluating the progress of the reaction than considering the relative amounts of each quench product lies in determining which anions would give rise to the products shown and then examining the anion formation as a function of time. Monoanion **3** and dianions **4**–**6** are accessible through direct metalation of **1**, dianion **7** would be the dianion from hydride elimination and deprotonation, and dianion **8** would be the dianion formed from the the type of rearrangement observed in the metalation of **2**. An examination of the products formed shows that **21** and **22**, the only nonbenzylic dialkylated products, could only arise from dianion **4**. Aromatic products **14**, **20**, **23**, **24**, and **26** could only arise from dianion **7**. The formation of **14** and **20** implicates proton abstraction from either *n*-propyl chloride or TMEDA. While we have observed some proton abstraction during an analogous quench with *n*-butyl chloride,[1a] the decrease in yield of **23** after long periods of time suggests to us that deprotonation of TMEDA is the most likely source of protons. Considering that monoalkylated product could arise from either monoanion, from partially protonated dianion, or from monoalkylation of dianion followed by protonation, the following conclusions can be drawn about the origin of monoalkylated product. Products **15**, **17**, and **19** can with accuracy only be attributed to monoanion **3**, with **17** arising from alkylation to give **19** followed by proton abstraction from **19** to give the resulting product. Monoalkylated product **18** must arise from dianion **4**. Monoalkylated product **16** could arise from either dianion **4** or **8**, but in the absence of any other evidence for **8**, we conclude that the most reasonable assumption is that the only dianion formed directly from starting material is **4**. Grouping the yields of products together in terms of anion of origin gives Table IV, which shows clearly the initial formation of monoanion, followed by formation of dianion **4**, which reaches a maximum of ~28% (with 2 equiv of metalating system) after 216 h of contact with the metalating system. We see an increase in **3**, **4**, and **7** at the expense of starting material. Considering the change in concentration of anions with time, it appears reasonable that **7** is formed from **4** presumably by loss of hydride and deprotonation to give the aromatic system.

Table V. Thermodynamic Stability of Potential Anions from 1

calculational method	4	5	6	8
REPA	0.028B	0.026B	0.055B	0.065B
MNDO ($\Delta\Delta H_{\text{formation}}$), kcal/mol	79.02	88.27	64.05	68.42

Our original inquiry addressed the questions of whether anion formation in cyclic systems paralleled their formation in acyclic systems and could be predicted from REPA calculations, and whether the pathway leading to the formation of aromatic products by hydride elimination in cyclohexyl systems could be determined by use of a relatively mild metalating system. Wilhelm et al.[4] found that elimination of hydride from a metalated starting material occurred much more effectively when the starting material contained an exocyclic double bond or was a 1-methyl-1-cycloalkene. They surmised that it was the inclusion of an isobutylene unit in the substrate which strongly favored the elimination reaction, as they had previously suggested.[7] Their mechanisms suggest the formation of cross-conjugated dianions as important intermediates in the elimination of hydride. We have found that in the metalation of **1**, neither the cross-conjugated dianion obtained by direct metalation of **1** (**5**) nor the cross-conjugated dianion obtained by rearrangement (**8**) are observed in the reaction medium. We therefore note that cross-conjugated dianions are not required for efficient elimination reactions.

In our previous work with dianions of 2-methyl-1,5-hexadiene (**2**)[1b] we observed formation of three dianions, **11**, **12**, and **13**. The increase in the percentage of **13** with time suggested that it was thermodynamically the most stable dianion in the reaction mixture. The preference for formation of **13** over **11** and **12** was discussed in terms of their respective resonance energies per atom (REPA).[3]

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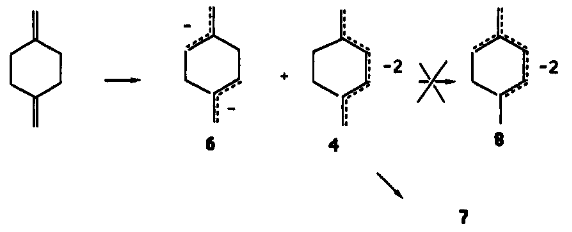
(6) (a) Poindexter, G. S.; Kropp, P. J. *J. Org. Chem.* **1976**, *41*, 1215. (b) Bohlmann, F.; Zeisberg, R.; Klein, E. *Org. Magn. Reson.* **1975**, *7*, 426. (c) Weigand, E. F.; Schneider, H.-J. *Org. Magn. Reson.* **1979**, *11*, 637.

(7) (a) Clark, T.; Schleyer, P. v. R. *J. Chem. Soc., Chem. Commun.* **1976**, 798. (b) Wilhelm, D.; Clark, T.; Schleyer, P. v. R. *Tetrahedron Lett.* **1982**, *23*, 4077.

Scheme II



The REPA's for **13**, **11**, and **12** are 0.065B, 0.055B, and 0.028B, respectively.[1b] For continuity with our previous work, we tabulate the REPA values in Table V. However, one problem with REPA calculations is that they take into account neither substitution on the substrate nor conformation. In addition, REPA calculations do not include the effect of the counterion on the energy and geometry of the "anionic" species. Alkyl substitution on the dianions being considered has not appeared to be a problem in previous systems examined,[1] but because conformational effects would seem to be important in this system, we examined the stability of the various dianionic systems possible by more sophisticated calculations. We chose to calculate $\Delta H_{\text{formation}}$ for dilithiated **4–6** and **8** using Dewar's MNDO program[8] because of its improved lithium parameterization.[9] We must note that the $\Delta H_{\text{formation}}$ calculated with the MNDO method for lithiated hydrocarbons does not give energies which are correct in any absolute sense.[10] However, the energies calculated for the sets of dilithiated hydrocarbons should be reliable in a comparative sense. In Table V we also tabulate the relative $\Delta\Delta H_{\text{formation}}$ in going from starting hydrocarbons to dilithiated **4–6** and **8**. By this means of comparison, the order of stability of the potential dianions from **1** is **6** > **8** > **4** > **5**. Although the order of stability suggested by these calculations differs from the order predicted by REPA calculations, in both cases the dianion formed is not the most stable one. We appear to be dealing with a system in which the thermodynamically most stable dianions do not form, a system in which the kinetically formed dianions are diverted and are not allowed to isomerize to the more stable dianions. In similar studies of dianion formation from methylenecycloalkanes of varying ring sizes,[11] we again see a preference for formation of dianions which are not those calculated to be the thermodynamically most stable. We are suggesting with this study and with others to be reported shortly that metalation in cyclic systems does not necessarily result in formation of the thermodynamically most stable dianion as the major dianionic species in solution.

The original basis for this study was a comparison of the formation of dianions from acyclic and cyclic hydrocarbon precursors. Metalation of **2** with either *n*-butyllithium/TMEDA or potassium *tert*-butoxide/*n*-butyllithium resulted in the formation of the dianions in Scheme I.[1b] In the metalation of **2** with potassium *tert*-butoxide/*n*-butyllithium (Scheme I), the isomerization of the initially formed dianions to **13** was determined to occur via **12** because a quench of the supernatant above the solid di- and monopotassioalkene revealed only the dialkylated products from **12**. One would expect that the isomerization of dianions from **1** would take the same course (Scheme II), resulting in the formation of dianion **8**. Instead, loss of hydride/deprotonation results ultimately in the formation of **7**. Hydride loss can occur from a dilithiated "dianionic" species such as **4**, **5**, **6**, or **8** or from a trilithiated "trianionic" species such as **9**. The high energy calculated for **9** ($\Delta\Delta H_{\text{formation}}$ = 215.07 kcal/mol) argues against its intermediacy in the formation of **7**. In addition, use of 3 equiv of metalating system does not give rise to any species which can unequivocably be derived from trianion. While **5**, **6**, or **8** could lose hydride to result ultimately in the formation of **7**, we argue against hydride elimination from those dianions because no evidence is found in the quench results to suggest their existence. While one could argue that **4** isomerizes to **8** in analogy to the isomerization of **12** to **13**, with **8** then losing hydride to yield **7**, the calculated energies of **4** and **8** make it difficult to postulate **8** as a relatively unstable intermediate which undergoes hydride elimination so rapidly as to be undetected. We therefore suggest that the most likely candidate for hydride elimination is **4**.

Table VI. Bond Lengths and Angles for 27

	bond lengths, Å	bond angles, deg	dihedral angles, deg
C_1–C_2 (C_5–C_6)	1.49		
C_2–C_3 (C_4–C_5)	1.40		
C_3–C_4	1.47		
C_1–C_2–C_3 (C_4–C_5–C_6)		121	
C_2–C_3–C_4 (C_3–C_4–C_5)		122	
C_1–C_2–C_3–C_4/C_3–C_4–C_5–C_6			179.0
C_2–C_3–C_4–C_5			9.5
Li–C_3–C_4–Li			178.0

Table VII. Bond Lengths and Angles for 28

	bond lengths, Å	bond angles, deg	dihedral angles, deg
C_1–C_2 (C_5–C_6)	1.49		
C_2–C_3 (C_4–C_5)	1.40		
C_3–C_4	1.47		
C_1–C_2–C_3 (C_4–C_5–C_6)		121	
C_2–C_3–C_4 (C_3–C_4–C_5)		122	
C_1–C_2–C_3–C_4/C_3–C_4–C_5–C_6			179.0
C_2–C_3–C_4–C_5			–8.0
Li–C_3–C_4–Li			–9.3

At first thought, hydride elimination from **4** to give **7** seems perfectly reasonable because **7** contains a benzene ring whose formation could serve as the driving force for the reaction. However, loss of hydride from any "dianion" would result in the formation of a *nonaromatic* monoanion. Deprotonation of the monoanion would give **7**. Since loss of hydride to give monoanion presumably would be an irreversible reaction, the formation of a benzene ring cannot be the driving force for hydride elimination. Since the loss of hydride in **4** does not occur to form a species containing a benzene ring directly, why is hydride loss from cyclic **4** so facile as to preclude the formation of any other dianions, while acyclic **12** isomerizes to **13** rather than eliminate hydride?

The obvious difference in the course of reactions must be due to a conformational factors. When **4** is a part of a ring, its conformational mobility is severely restricted. Acyclic dianion **12** is free to assume the energetically most favorable conformation. If there is a great difference in the geometry of the lowest energy conformers, that difference could explain the different product outcomes. One way to gain insight into the conformational behavior of the cyclic and acyclic species is to model their structure with molecular orbital calculations. Semiempirical calculations (MNDO) have been shown to reproduce and even to predict the general geometrical features of organolithium compounds shown by X-ray structures quite well.[12] Ta-

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[8] Dewar, M. J. S.; Thiel, W. *J. Am. Chem. Soc.* **1977**, *9*, 4899, 4907.

[9] Thiel, W. *QPCE* **1982**, *2* (No. 438), 63.

[10] Schleyer, P. v. R. *Pure Appl. Chem.* **1983**, *55*, 355.

[11] Meyer, S. D.; Mills, N. S.; Kersten, S. D.; Ruud, C. C., manuscript in preparation.

Table VIII. Bond Lengths and Angles for Dilithiated 12

	bond lengths, Å	bond angles, deg	dihedral angles, deg
C_1-C_2 (C_5-C_6)	1.39		
C_2-C_3	1.47		
C_3-C_4	1.53		
C_4-C_5	1.39		
C_5-C_6	1.56		
C_1-C_2-C_3		130	
C_2-C_3-C_4		122	
C_3-C_4-C_5		127	
C_4-C_5-C_6		122	
C_1-C_2-C_3-C_4/C_3-C_4-C_5-C_6			18.3
C_2-C_3-C_4-C_5			-92.2
C_3-C_4-C_5-C_6			2.1
LI-C_3-C_4-Li			66.0

bles VI and VII show the MNDO results for dilithiated **4**. The structure reported in Table VI and represented by **27** has the coordinated lithium ions located above and below the "plane" of the ring. The molecule demonstrates a high degree of symmetry. Most importantly, the dihedral angles for the ring reveal that the π-system is very close to planar. The carbon framework of the structure reported in Table VII and represented by **28** is very similar to that of **27**. Although the coordinated lithium ions are cis in structure **28**, the difference between the calculated heats of formation is only 1.2 kcal/mol. This suggests that the most stable conformation of **4** is controlled primarily by the carbon framework, with the lithium counterions having little influence on the conformation.

Table VIII shows the MNDO results for dilithiated **12**. As would be expected, the molecule does not demonstrate the symmetry found in **4**. More striking, however, is the distinct lack of planarity in the π-system. The dihedral angle for the central four carbons of the π-system (92°) suggests strongly that the molecule is behaving as though it were two allylic anions, joined by a central carbon–carbon bond. Because the two anionic systems are almost orthogonal to each other, they should behave almost as two independent π-systems.[13] In this geometry may lie the explanation for the difference in the reactin paths. Hydride elimination from allylic anions is highly uncommon. Nonplanar dilithiated **12** can isomerize more easily than it can eliminate hydride.

The net atomic charges calculated by MNDO support very different electron distributions in dilithiated **4** and **12**. As shown in Figure 3, the electron distribution in dilithiated **4** reflects the symmetry of the molecule with negative charge calculated for all but the quaternary carbons. In contrast, the net atomic charges for dilithiated **12** suggest a much less symmetrical molecule. Interestingly, the sole quaternary carbon in **12** possesses a moderate amount of electron density.

In summary, dimetalation of 1,4-bis(methylene)cyclohexane results in formation of the *p*-xylene dianion via the linearly conjugated dianion **4**. Contrary to suggestions in the literature that loss of hydride occurs via cross-conjugated dianions, in this system we see no evidence for cross-conjugated dianion formation. We suggest that formation of benzene products from doubly unsaturated cyclohexanes by dimetalation probably occurs via linearly conjugated dianions. In addition the loss of hydride in the cyclic dianion is in sharp contrast to the behavior of dimetalated 2-methyl-1,5-hexadiene, an acyclic analogue of 1,4-bis(methylene)cyclohexane, which undergoes isomerization to the thermodynamically more stable cross-conjugated dianion via the linearly conjugated dianion **12**, rather than hydride elimination. Semiempirical molecular orbital calculations suggest that the only dianion observed is not the thermodynamically most stable one. MNDO calculations of the conformations of dilithiated **4** and **12** show that **4** is effectively planar, with a symmetrical distribution of charge. Dilithiated **12** is nonplanar, with an almost right angle bend in the π-system. The dianion can therefore be considered as two allyl anions which are orthogonal to each other. The difference in calculated conformations and electron distributions of the two systems is suggested as the reason for the different reactivity of the two systems.

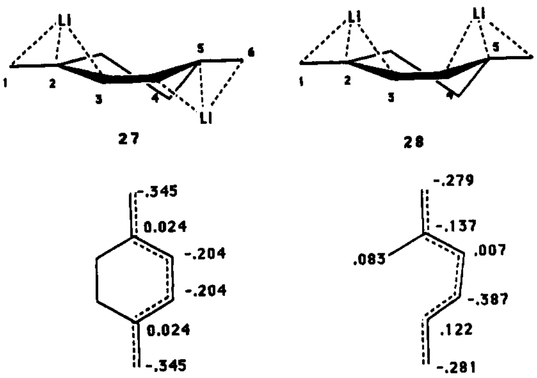

Figure 3.

Experimental Section

Apparatus and Materials. ^{1}H NMR spectra were recorded in $CDCl_3$ on a Varian VXR-300 MHz nuclear magnetic resonance spectrometer. Product distribution in reaction mixtures at varying periods of time were analyzed on a methyl silicone capillary column with a Hewlett-Packard 5890A gas chromatograph. Mass spectral data were obtained with a Hewlett-Packard 5995 GC/MS. Gas chromatographic separations for NMR analysis were performed on a Perkin-Elmer Sigma 3-B gas chromatograph. Pentane was obtained from Baker and dried by distillation from phosphorus pentoxide. TMEDA, from Aldrich Chemical Company, Inc., was distilled from the sodium/benzophenone ketyl. *n*-Butyllithium (1.6 M in hexane) was obtained from Fluka Chemical Corp. 1,4-Bis(methylene)cyclohexane was obtained from Wiley Organics.

Metalation with *n*-Butyllithium/TMEDA. For each set of timed quenches, *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TMEDA), *n*-butyllithium, 1,4-bis(methylene)cyclohexane, and tetradecane (internal standard) were combined in bulk in a septum-capped graduated cylinder under argon, and aliquots were transferred to Schlenk flasks to be stored until the appropriate quench time. Just prior to quench, the glass stopper was removed under a flow of argon and replaced with a rubber septum for addition of the quenching agent, *n*-propyl chloride. Each Schlenk flask contained 1.2 mL (8.0 mmol) of TMEDA, 5.0 mL (8.0 mmol) of *n*-butyllithium, 0.53 mL (4.0 mmol) of 1,4-bis(methylene)cyclohexane (**1**), and 250 μL (1.9 mmol) of tetradecane. After 24 h the reaction mixture had turned reddish-black. Each aliquot was quenched at the appropriate time with *n*-propyl chloride (1.26 mL, 1.43 mmol). Water was added to the test tube after 15 h until two layers were visible.

For gas chromatographic analysis, the water layer was extracted with pentane and the organic layers were combined and extracted with saturated ammonium chloride to remove TMEDA. Yield data was obtained on a 25-m Hewlett-Packard methyl silicone column under the following conditions: initial temperature 140 °C; initial time 5.00 min; rate 10°/min; final temperature 300 °C; final time 10.00 min. The internal standard showed a mass

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(13) The crystal structure of dilithiated hexatriene has been reported by Bates (Arora, S. K.; Bates, R. B.; Beavers, W. A.; Cutler, R. S. *J. Am. Chem. Soc.* **1975**, *97*, 6271) and is planar. We think that the combination of the symmetry of the species and crystal packing forces may impose planarity on the dilithiated hexatriene.

balance of 94–100% of starting material. For ^1H NMR analysis, the reaction mixture was concentrated by fractional distillation and the products were separated and collected by preparative gas chromatography on a 4-m OV-17 column.

Spectral data for all compounds reported at summarized in Tables II and III.

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Gas-Phase Analogues of Solvolysis. The Conjugate Acid of *n*-Propyl Phenyl Ether

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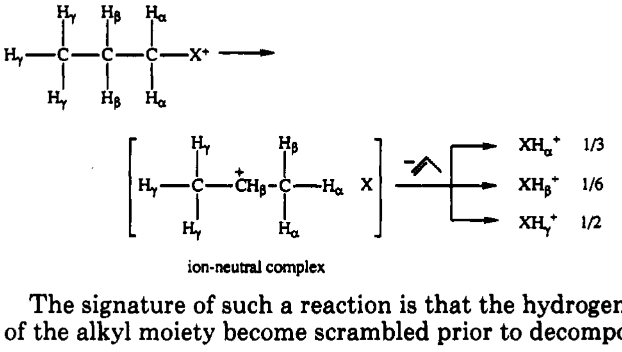
The analogy between first-order decomposition of gaseous ions via ion–neutral complexes and solvolytic elimination is explored using an MS/MS technique, chemical ionization-metastable ion kinetic energy spectroscopy (CI-MIKES). Expulsion of propene from M + 2 conjugate acid ions in the methane-d_4 CI-MIKES of *n*-propyl phenyl ethers shows isotopic exchange that is difficult to explain unless complexes containing propene and $PhOHD^+$ are formed reversibly. Comparison of the CD_4 CI-MIKES of $CH_3CD_2CH_2OPh$ (β-d_2), $CD_3CH_2CD_2OPh$ (α,γ-d_5), and $CH_3CH_2CH_2OPh$ (d_0) shows that further isotopic scrambling takes place, which is interpreted in terms of intermediates of the form [i-Pr^+ phenol]. Steady-state kinetic analysis of relative product yields shows that the ion–neutral complex [$CH_3CHCH_3^+$ PhOD] is at least 5 times more likely to yield free propene than to form a complex of the form [C_3H_6 $PhOHD^+$]. The complex [$CH_3CDCH_3^+$ PhOH] isomerizes to [$CDH_2CHCH_3^+$ PhOH] but is less than half as likely to do so as to yield free $CH_3CD{=}CH_2$. If the isotope effect for the proton transfer that yields free propene is assumed to be much larger than any other isotope effect in the reaction sequence, then its value is k_H/k_D = 1.5, which is consistent with proton transfer to the phenol ring.

In the gas phase, carbon–oxygen bonds of positive ions frequently heterolyze to produce ion–neutral complexes, as shown schematically by eq 1.[1–4] These contain electrically charged and uncharged fragments, which are not covalently bound but are held together by electrostatic attraction. Such heterolyses have been described as gas-phase analogues of solvolysis, since they represent the conversion of covalent to ionic bonds.[5] Transient electrostatically bound intermediates are frequently formed by gaseous cations derived from alkyl aryl ethers, as demonstrated by evidence from this laboratory ranging from photoionization studies[6,7] to analysis of the neutral alkenes formed by subsequent decomposition of the ion–neutral complexes.[2,8] The analogy to solvolytic elimination hinges on the intermediacy of [R^+ X], where at least one of the fragments in the complex enjoys virtually free rotation about axes perpendicular to the interfragment axis.[3,7] It is possible to draw other kinds of ion–neutral complexes as intermediates (such as the [alkene HX^+] complex that occurs downstream from [R^+ X] in the first-order decomposition of alkyl pyridyl ether radical cations[6]), but the comparison with solvolysis loses pertinence unless heterolysis to form [R^+ X] can be shown to intervene.

$$\underset{\text{molecular ion}}{RX^+} \rightarrow \underset{\text{ion–neutral complex}}{[R^+\ X]} \qquad (1)$$

The fragmentation pathway of an aryl alkyl ether is often independent of how charge is deposited. In 1976 Benoit and Harrison noted that *n*-propyl phenyl ether undergoes the same sort of decomposition process when it is protonated in the gas phase (chemical ionization or CI) as when an electron is removed from it by electron impact (EI).[9] CI produces the conjugate acid of the parent neutral, an even-electron ion that might have been expected to behave very differently from the odd-electron radical cation produced by EI. Yet both ions expel propene. Intermediacy of an ion–neutral complex in both cases accounts for the observed results, as eq 2 depicts. In EI the leaving group X is a phenoxy radical, while in CI X is phenol (a consequence of protonation on oxygen). Either can act as a Brønsted base, leading to the expulsion of propene, as the second step of eq 2 represents.



(2)

The signature of such a reaction is that the hydrogens of the alkyl moiety become scrambled prior to decompo-

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