spectral data were consistent with those reported;[51] IR (neat) 2210 (CN) and 1625 cm^{-1} (C═C); mass spectrum, *m/e* 143.0736; calcd for $C_{10}H_9N$, 143.0735. 4-Cyano-6-phenylhexanenitrile (0.137 g, 4%): bp 154 °C (0.38 mmHg); NMR ($CDCl_3$) δ 1.73–2.15 (m, CH_2, 4 H), 2.33–3.07 (m, $ArCH_2$, CHCN, and CH_2CN, 5 H), 7.03–7.47 (m, Ar, 5 H); IR (neat) 2230 cm^{-1} (CN); mass spectrum, *m/e* 198.1168; calcd for $C_{13}H_{14}N_2$, 198.1158. 2-Benzyl-4-phenylbutanenitrile (0.315 g, 15%): bp 150 °C (0.6 mmHg); NMR ($CDCl_3$) δ 1.70–2.03 (m, CH_2, 2 H), 2.50–3.10 (m, $ArCH_2$ and CHCN, 5 H), 7.03–7.46 (m, Ar, 10 H); IR (neat) 2230 cm^{-1} (CN); mass spectrum, *m/e* 235.1370; calcd for $C_{17}H_{17}N$, 235.1362.

Acknowledgment. We gratefully acknowledge support of this work by the Division of Chemical Sciences, Department of Energy (Contract No. DE-AC02-80ER10603).

Registry No. Ni, 7440-02-0; $C_6H_5CH_2Cl$, 100-44-7; $C_6H_5CH_2Br$, 100-39-0; 4-$CH_3C_6H_4CH_2Br$, 104-82-5; 3-$CH_3OC_6H_4CH_2Cl$, 824-98-6; 3-$F_3CC_6H_4CH_2Cl$, 705-29-3; 4-$ClC_6H_4CH_2Cl$, 104-83-6; 4-$BrC_6H_4CH_2Br$, 589-15-1; 4-$O_2NC_6H_4CH_2Cl$, 100-14-1; 4-$NCC_6H_4CH_2Br$, 17201-43-3; 4-$CH_3O_2CC_6H_4CH_2Cl$, 34040-64-7; 4-$HO_2CC_6H_4CH_2Br$, 6232-88-8; $C_6H_5CHBrCO_2H$, 4870-65-9; $C_6H_5CH_2CH_2C_6H_5$, 103-29-7; (4-$CH_3C_6H_4CH_2)_2$, 538-39-6; (3-$CH_3OC_6H_4CH_2)_2$, 1657-55-2; (3-$F_3CC_6H_4CH_2)_2$, 72390-22-8; (4-$ClC_6H_4CH_2)_2$, 5216-35-3; (4-$BrC_6H_4CH_2)_2$, 19829-56-2; (4-$O_2NC_6H_4CH_2)_2$, 736-30-1; (4-$NCC_6H_4CH_2)_2$, 4381-02-6; (4-$CH_3O_2CC_6H_4CH_2)_2$, 797-21-7; $C_6H_5CH_3$, 108-88-3; 4-$CH_3C_6H_4CH_3$, 106-42-3; 4-$ClC_6H_4CH_3$, 106-43-4; 4-$CH_3O_2CC_6H_4CH_3$, 99-75-2; 4-$HO_2CC_6H_4CH_3$, 99-94-5; $C_6H_5CH_2CO_2H$, 103-82-2; $(C_6H_5)_2CHCl$, 90-99-3; $(C_6H_5)_2CCl_2$, 2051-90-3; $C_6H_5CHBr_2$, 618-31-5; $C_6H_5CCl_3$, 98-07-7; *meso*-$C_6H_5CHBrCHBrC_6H_5$, 13440-24-9; *erythro*-4-$O_2NC_6H_4CHBrCHBrCO_2C_2H_5$, 41441-00-3; $C_6H_5CCl_2CCl_2C_6H_5$, 13700-81-7; $(C_6H_5)_2CHCH(C_6H_5)_2$, 632-50-8; $(C_6H_5)_2C{=}C(C_6H_5)_2$, 632-51-9; *cis*-$(C_6H_5)CH{=}CH(C_6H_5)$, 645-49-8; *trans*-$(C_6H_5)CH{=}CH(C_6H_5)$, 103-30-0; *cis*-$(C_6H_5)CCl{=}CCl(C_6H_5)$, 5216-32-0; *trans*-$(C_6H_5)CCl{=}CCl(C_6H_5)$, 951-86-0; *trans*-4-$O_2NC_6H_4CH{=}CHCO_2C_2H_5$, 24393-61-1; NiI_2, 13462-90-3; Li, 7439-93-2; methyl acrylate, 96-33-3; methyl 4-phenylbutanoate, 2046-17-5; acrylonitrile, 107-13-1; 4-phenylbutanenitrile, 2046-18-6; *cis*-4-phenyl-2-butenenitrile, 20067-97-4; *trans*-4-phenyl-2-butenenitrile, 20067-98-5; 4-cyano-6-phenylhexanenitrile, 89873-49-4; 2-benzyl-4-phenylbutanenitrile, 89873-50-7; (iodomethyl)benzoic acid, 31719-79-6; 1-(chloromethyl)naphthalene, 86-52-2; 2-(bromomethyl)naphthalene, 939-26-4; 9-bromofluorene, 1940-57-4; 1,2-bis(1-naphthyl)ethane, 15374-45-5; 1,2-bis(2-naphthyl)ethane, 21969-45-9; 9,9′-bi-9*H*-fluorene, 1530-12-7.

Reactions of *tert*-Butyllithium with α,ω-Dihaloalkanes. Evidence for Single-Electron-Transfer-Mediated Metal–Halogen Interchange Involving Alkyl Radical–Halide Ion Adducts

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The reactions of *tert*-butyllithium (*t*-BuLi) with primary α-iodo-ω-haloalkanes and α,ω-dibromoalkanes have been investigated in experiments conducted at −23 °C in *n*-pentane–diethyl ether (3:2 by volume) solution. It has been found that production of an α-lithio-ω-haloalkane (**1**) by metal–halogen interchange at one end of a 1,3-, 1,4-, or 1,5-dihalide results in intramolecular coupling to give cycloalkanes in high yield. As the chain length of the dihalide is increased beyond five carbon atoms the production of an α,ω-dilithio species by interchange at both ends of the dihalide ceases to be excluded by cyclization of **1** and a precipitous drop in the yield of cycloalkane was found to occur in reactions of 1,6-diiodoalkanes with *t*-BuLi. Metal–halogen interchange was the exclusive process observed in reactions of α,ω-dihalides with *t*-BuLi provided at least one halogen of the substrate was an iodine. By contrast, similar treatment of α,ω-dibromoalkane provided only minor amounts of product attributable to metal–halogen interchange. Under conditions that provide an essentially quantitative yield of carbocyclic product from reductive cyclization of **1** generated from 1,5-diiodo-3,3-dimethylpentane, the corresponding 1,5-dibromide was converted to a mixture composed of cycloalkane, products from Wurtz-type coupling with *t*-BuLi, and quantities of parent alkane from formal reduction of the dihalide. The mechanism of the metal–halogen interchange was further probed by using 6-halo-1-hexene substrates. Observation of cyclized product from the reaction of *t*-BuLi with 6-bromo- and 6-iodo-1-hexene demonstrated that the interchange between *t*-BuLi and primary alkyl bromides and iodides occurs predominantly via a single-electron-transfer (SET) process. Incorporation of alkyl radical–halide ion adducts with halogen dependent lifetimes as intermediates following SET from alkyllithium to alkyl halide serves to explain the disparate behavior of alkyl bromides and iodides when treated with *t*-BuLi. A unified SET-mediated mechanism for metal–halogen interchange and Wurtz coupling is presented.

The exchange of halogen and lithium atoms in the reaction of an organic halide with an organolithium is known as the metal–halogen interchange. The reaction, discovered independently and virtually simultaneously by the groups of Gilman[2] and Wittig,[3] has attracted considerable attention over the past forty years[4] and the vast literature on this topic has been extensively reviewed.[5-10] Despite continued interest in the metal–halogen interchange as a

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(1) Taken in part from the Ph.D. Dissertation of R. Paul Gagnier, University of Connecticut, Storrs, CT, 1981.

(2) (a) Gilman, H.; Jacoby, A. L. *J. Org. Chem.* **1938**, *3*, 108. (b) Gilman, H.; Langham, W.; Jacoby, A. L. *J. Am. Chem. Soc.* **1939**, *61*, 106.

(3) Wittig, G.; Pockels, U.; Droge, H. *Chem. Ber.* **1938**, *71*, 1903.

(4) The metal–halogen interchange was observed but not recognized as such at least a decade before the pioneering work of Gilman and Wittig. For example, although Marvel and co-workers [Marvel, C. S.; Hager, F. D.; Coffman, D. D. *J. Am. Chem. Soc.* **1927**, *49*, 2323] reported that treatment of *o*- and *m*-bromotoluene with *n*-butyllithium gave toluene in yields of 65% and 87%, respectively, the observation was not exploited.

(5) Gilman, H.; Jones, R. G. *Org. React.* (*N.Y.*) **1951**, *6*, 339.

(6) Jones, R. G.; Gilman, H. *Chem. Rev.* **1954**, *54*, 835.

(7) Schollkopf, U. In "Methoden der Organischen Chemie"; Georg Thieme: Stuttgart, 1970; Vol. 13/1.

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method for the preparation of otherwise inaccessible organolithiums,[11] the mechanism of the reaction remains something of an enigma.

Early studies of the metal–halogen interchange revealed that the reaction, most readily accomplished with bromine and iodine containing halides,[5] is a reversible process[5,12,13] leading to an equilibrium mixture favoring the organolithium having an organic moiety best able to accommodate a negative charge.[5,7-10,13] Although the reaction is often represented (as here) in terms of monomeric organolithiums, these species are in fact aggregates whose degree of association may be affected by such factors as solvent, concentration, and temperature.[7-10,14]

$$\text{R–Li} + \text{R}'\text{–X} \rightleftharpoons \text{R–X} + \text{R}'\text{–Li}$$

Reaction of an organolithium with an organic halide is, of course, not confined to metal–halogen interchange. Wurtz-type coupling[15] leading to mixtures of hydrocarbons (i.e., R–R, R′–R, and R′–R′ for the general scheme shown above),[7-10,13] β-elimination,[5-10] α-metalation,[16] and formal reduction of the organohalide[17] are all possible outcomes. These competing reactions often compromise the metal–halogen interchange as a synthetic route to novel organolithiums and they are particularly troublesome in mechanistic studies of the process.

Due no doubt to the capricious behavior of organic halides when treated with organolithiums, there have been relatively few comprehensive studies of the interchange mechanism.[8,9] The most detailed studies have employed aryl halides as substrates since these species undergo exchange with organolithiums at a convenient rate with little side product formation.[18-20] The elegant work of Winkler and Winkler[18] on the metal–halogen interchange of aryl bromides with aryllithiums demonstrated that excess negative charge is developed in the transition state for the slow step of the reaction. This result was interpreted[18] in terms of a concerted exchange of lithium and halogen via nucleophilic attack of a carbanion-like aryllithium on the bromine atom of the aryl halide. A similar mechanistic conclusion was drawn in a more recent study of the aryl bromide–*n*-butyllithium interchange.[19]

In addition to the mechanism suggested by studies of aryl halide exchange, several other schemes have been proposed to account for metal–halogen interchange. Such mechanisms include concerted metathesis via a four-center transition state,[8,9] reversible formation of an ate–complex by nucleophilic attack of the organolithium on the halogen of the organic halide,[21] and various single-electron-transfer-(SET) mediated processes.[8,22-24] Although a rather detailed investigation of the metal–halogen interchange between ethyllithium and ethyl iodide has been reported (the findings implicate SET pathways),[25] there is a paucity of mechanistic data on the interchange reaction of simple alkyl systems. Support for the various mechanistic proposals has, for the most part, relied on stereochemical evidence,[26] spectroscopic probes for radical intermediates,[23,24,27] and inferences drawn from the results of studies of the reactions of organic halides with aromatic radical anions[28] and organostannyl alkalis.[29,30] Despite continued interest, no consensus exists as to the actual mechanism of the interchange and little is known about the relationship (if any) between this process and the Wurtz coupling reaction.[31]

In an attempt to circumvent some of the experimental difficulties associated with studies of the metal–halogen interchange, we have explored the behavior of primary, aliphatic α,ω-dihalides when treated with *tert*-butyllithium (*t*-BuLi). The rationale for the use of dihalides as substrates follows from the recent finding that α-lithio-ω-haloalkanes (**1**, $\text{LiCH}_2{\sim}\text{CH}_2\text{X}$) generated by interchange at one end of a 1,3-, 1,4-, or 1,5-dihalide undergo clean intramolecular coupling to give cycloalkanes.[32] Such cyclization effectively biases the interchange equilibrium by removing **1**. Thus, the extent of metal–halogen interchange and such competing reactions as intermolecular coupling, elimination, etc. is easily assessed by product analysis.

We report herein that such studies, coupled with data from experiments employing 6-halo-1-hexenes as substrates, demonstrate for the first time that the metal–halogen interchange between *t*-BuLi and primary bromides or iodides proceeds predominantly, and perhaps exclusively, via SET. The results also suggest that alkyl halide radical–anions (or, more precisely, alkyl radical–halide ion adducts[33]) may exist as intermediates during the interchange reaction. Differences in the lifetimes of such species prior to their dissociation to noninteracting alkyl radicals and halide ions may well play a role in determining

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(14) Brown, T. L. *Adv. Organomet. Chem.* **1965**, *3*, 365; *Acc. Chem. Res.* **1968**, *1*, 23; *Pure Appl. Chem.* **1970**, *23*, 447.

(15) The Wurtz reaction, involving formation of alkanes by dimerization of alkyl halides over sodium metal, is one of the oldest "name reactions" in organic chemistry [Wurtz, A. *Ann. Chim. Phys.* **1855**, *44*, 275; *Liebigs Ann. Chem.* **1855**, *96*, 364]. The name has come to be associated more generally with the formation of hydrocarbons via coupling of an organometallic and an organohalide. It is of some historical interest to note that organolithium compounds were implicated as intermediates in the Wurtz coupling [Spencer, J. F.; Price, G. M. *J. Chem. Soc.* **1910**, *97*, 385] well before authentic samples were prepared from either organomercurials [Schlenk, W.; Holtz, J. *Chem. Ber.* **1917**, *50*, 262] or directly from halides and lithium metal [Ziegler, K.; Colonius, H. *Liebigs Ann. Chem.* **1930**, *479*, 135].

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(19) Rogers, H. R.; Houk, J. *J. Am. Chem. Soc.* **1982**, *104*, 522.

(20) In contrast to the clean metal–halogen interchanges reported in ref 18 and 19, reaction of methyllithium with polyhalophenols leads to coupling of the aromatic halides. Cf., Huddle, P. A.; Perold, G. W. *J. Chem. Soc., Perkin Trans. 1* **1980**, 2617 and references therein.

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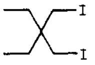
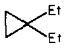
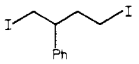
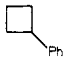
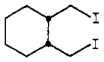
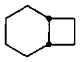
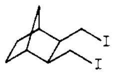
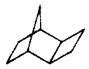
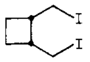
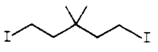
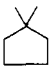
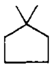
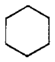
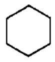
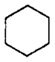
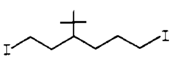
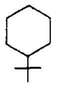
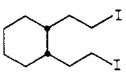
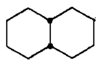
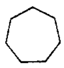
Table I. Reactions of α-Iodo-ω-haloalkanes with *tert*-Butyllithium[a]

entry	dihalide	cycloalkane	yield,[b] %	other products (yield,[b] %)
1			93	
2			87 (78)	
3			97	
4			99 (52)	
5				 (98)
6	I-$(CH_2)_5$-I		99	
7	I-$(CH_2)_5$-Br		98	
8	I-$(CH_2)_5$-Cl		99	
9	 3		93	
10	 4		95	
11	I-$(CH_2)_6$-I		~5	n-C_6H_{14} (55) + n-$C_{12}H_{26}$ (15) + n-$C_{18}H_{38}$ (3) + *e*
12	I-$(CH_2)_6$-I[c]		~2	n-C_6H_{14} (89) + n-$C_{12}H_{26}$ (8)
13	I-$(CH_2)_6$-I[d]		~2	n-C_6H_{14} (98)
14			14	*e*
15			16	*e*
16	#y		<2	n-C_7H_{16} + n-$C_{14}H_{30}$ + *e*

[a] Except where otherwise indicated, reactions were performed at −23 °C by slow addition of 2.0–2.2 equiv of *t*-BuLi to 0.1 M solutions of dihalide in *n*-pentane–diethyl ether (3:2 by volume). [b] Yields determined by GLC analysis of the reaction mixture using internal standards and correction for detector response. Isolated yields in parenthesis. [c] 1×10^{-2} M solution of diiodide. [d] 1×10^{-3} M solution of diiodide. [e] Other products present but not identified.

the course of the reaction between an organolithium and an organohalide.

Results and Discussion

Metal–halogen interchange reactions were performed at −23 °C by slow addition of 2.0–2.2 molar equiv[34] of *t*-BuLi to a 0.1 M solution of the α,ω-dihalide in *n*-pentane–diethyl ether (3:2 by volume). This solvent mixture, used by Applequist and O'Brien in their pioneering studies of exchange equilibria,[13] was found in preliminary experiments to afford clean metal–halogen interchange free from competing elimination reactions. The choice of −23 °C as the reaction temperature was dictated by practical considerations: a number of dihalides are not completely soluble at lower temperatures and consumption of *t*-BuLi by reaction with diethyl ether complicates product analysis when reactions are run at a higher temperature. Although the degree of association of *t*-BuLi in the *n*-pentane–diethyl ether solvent system has not been determined, it seems probable that tetrameric aggregates are the predominant species since *t*-BuLi is known to exist as a tetramer in both hydrocarbon and diethyl ether solutions.[10] There is, however, no direct evidence that the chemistry discussed below involves only tetrameric *t*-BuLi and it is possible that highly reactive species of lower aggregation may be responsible for the reactions. For this reason, and for the sake of pictoral clarity, monomeric *t*-BuLi or species of unspecified aggregation [i.e., $(t\text{-BuLi})_n$] will be used in mechanistic formulations.

The outcome of reactions of *t*-BuLi with α,ω-diiodides and α-iodo-ω-haloalkanes are summarized in Table I. The most striking feature of these results is the total absence of product derived from Wurtz coupling of *t*-BuLi with the dihalides. The 1,3-, 1,4-, and 1,5-iodohaloalkanes (Table I, entries 1–10) react with *t*-BuLi to give, with the single exception of entry 5, essentially quantitative yields of cycloalkane. The 1,6- and 1,7-diiodoalkanes (Table I, entries 11–16) afford little cycloalkane but substantial amounts of *n*-alkane, produced by formal reduction of the diiodide, along with saturated hydrocarbons derived from intermolecular coupling of dihalide molecules.

The formation of three-, four-, and five-membered rings from the readily available diiodides upon treatment with *t*-BuLi provides a preparatively useful route to unfunc-

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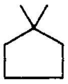
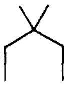
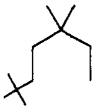
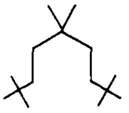
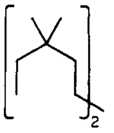
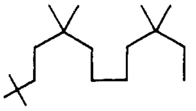
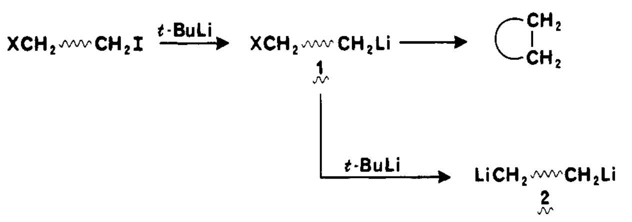
[34] *t*-BuLi (1 equiv) is consumed by formal reaction with the *tert*-butyl halide generated in the metal–halogen interchange. Although both isobutane and isobutylene have been identified as products of this reaction, the mechanism by which *t*-BuLi is consumed has not been established. Cf. Corey, E. J.; Beames, D. J. *J. Am. Chem. Soc.* **1972**, *94*, 7210 and Seebach, D.; Neumann, H. *Chem. Ber.* **1974**, *107*, 847.

Table II. Reaction of 1,5-Dibromo-3,3-dimethylpentane (5) with *tert*-Butyllithium[a]

entry	dibromide conc, M	products,[b] % yield[c]					
		 +	 +	 +	 +	 +	 + •••
1	0.1	22	24	19	3	5	4
2	1×10^{-2}	38	32	17	3	3	1
3	1×10^{-3}	44	32	15	~1	<1	

[a] Reactions performed at −23 °C by slow addition of *t*-BuLi to solutions of **5** in *n*-pentane–diethyl ether (3:2 by volume). [b] Other products also present but not identified. [c] Yields determined by GLC analysis of reaction mixtures using *n*-octane as internal standard and correction for detector response.

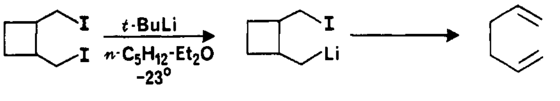
Scheme I



tionalized carbocycles.[32] While the cyclization of α,ω-dihalides has been attempted with mixed success using a variety of reducing agents,[35] the present method is notable for its simplicity and generality. Apparently, when the halogen atoms of the substrate are separated by five or fewer carbons, cyclization of the α-lithio-ω-haloalkane (**1**) produced via initial metal–halogen interchange (Scheme I) is a more favorable process than interchange at the remaining halogen to give a dilithio species (**2**). The proximity of the reactive centers in 1,3-, 1,4-, and 1,5-iodohaloalkanes is undoubtedly responsible for the facile cyclization as well as the reluctance of **1** to undergo a second interchange. The experimental conditions employed for the reactions reported in Table I (viz., slow addition of the alkyllithium to 0.1 M solutions of substrate) exploit the propensity for unimolecular cyclization of **1** by ensuring that the concentration of *t*-BuLi remains low during the experiment. Not surprisingly, reaction of **1** with *t*-BuLi to give **2** competes effectively with cyclization when the concentration of *t*-BuLi is high. Thus, exploratory experiments in which solutions of 1,4- or 1,5-diiodide were added to a large excess of *t*-BuLi afforded, after hydrolysis, quantities of *n*-alkane derived from protonation of **2** along with variable yields of carbocyclic product.

As the chain length of the α-iodo-ω-haloalkane is increased the production of α,ω-dilithio compounds by interchange at both ends of the substrate will cease to be excluded by cyclization of the initially formed **1** (Scheme I). As shown in Table I (entries 11–16), a dramatic decrease in the yield or cycloalkane occurs in the reactions of 1,6-diiodoalkanes with *t*-BuLi. The precipitous drop in cycloalkane production at a chain length of six carbon atoms is not without precedent. A similar observation has been made by Garst and Barbas in their study of the reactions of alkali naphthalenes with α,ω-dihalides.[36] The bulk of the product from reactions of 1,6- or 1,7-diiodides with *t*-BuLi is the parent alkane along with smaller amounts of saturated hydrocarbons derived from intermolecular coupling of diiodide molecules. Although the formation of dimers, trimers, etc. from coupling of 1,6- and 1,7-diiodides was not investigated in detail, it is of some interest to note that these reactions are visually different than analogous reactions employing 1,3-, 1,4-, or 1,5-diiodides. Thus, whereas addition of *t*-BuLi to solutions of the latter compounds in pentane–ether leads to formation of a white, crystalline precipitate (perhaps a LiI·(*t*-BuLi)$_n$ complex),[37] reactions of 1,6- or 1,7-diiodides afford a stringy, insoluble material. When the stringy precipitate produced in reaction of 1,6-diiodohexane with *t*-BuLi was isolated and treated with D_2O, the major product proved to be 1,12-dideuterio-*n*-dodecane. This result suggests that long chain α,ω-dilithioalkanes are produced when cyclization of **1** is an unfavorable process. Not surprisingly, the extent of such intermolecular coupling could be decreased by lowering the initial concentration of the diiodide. As shown in Table I (entries 11–13), metal–halogen interchange between 1,6-diiodohexane and *t*-BuLi leads cleanly to *n*-hexane and cyclohexane when sufficiently dilue solutions of substrate are employed.

The formation of 1,5-hexadiene upon treatment of *cis*-1,2-bis(iodomethyl)cyclobutane with *t*-BuLi deserves comment as it is the only example in Table I in which an unsaturated hydrocarbon is produced. The failure to observe reductive cyclization is not unexpected in view of the strain inherent in bicyclo[2.2.0]hexane. It should be noted, however, that were any bicyclo[2.2.0]hexane formed in the reaction, it would have been stable under the conditions employed for the analysis. Thus, 1,5-hexadiene is undoubtedly produced by fragmentation[38] of a monolithio intermediate generated via metal–halogen interchange. The surprising feature of this result is the very fact that it is unique. No such fragmentation is observed in reactions of apparently analogous 1,4-diiodides (Table I, entries 3 and 4). The failure to observe extensive fragmentation of 1-lithio-4-iodoalkanes may be a consequence of the highly covalent nature of the carbon–lithium bond in the solvent system used in the present study.[10]



Reaction of *t*-BuLi with α,ω-dibromides having structures similar to those of the iodohaloalkanes discussed above leads to complex mixtures of saturated hydrocarbons. The results of experiments using 1,5-dibromo-3,3-dimethylpentane (**5**) for which quantitative yield data are available (Table II) are illustrative of the general be-

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(35) The literature relating to cyclization of 1,3- and 1,4-dihalides has been reviewed in the Houben–Weyl series. For cyclopropanes, see: Wendisch, D. In "Methoden der Organischen Chemie"; Georg Thieme: Stuttgart, 1971; Vol. 4/3. For cyclobutanes, see: Seebach, D. *Ibid.* Vol. 4/4.

(36) Garst, J. F.; Barbas, J. T. *J. Am. Chem. Soc.* **1974**, *96*, 3239 and 3247. It is to be noted that, although 1,4- and 1,5-dihalides are reductively cyclized upon treatment with alkali naphthalenes, the yield of cycloalkane is moderate (ca. 40–60%) and significant amounts of alkylated naphthalenes are produced.

(37) Glaze, W.; West, R. *J. Am. Chem. Soc.* **1960**, *82*, 4437.

(38) (a) Grob, C. A.; Schiess, P. W. *Angew. Chem., Int. Ed. Engl.* **1967**, *1*, 6. (b) Grob, C. A. *Ibid* **1969**, *8*, 535.

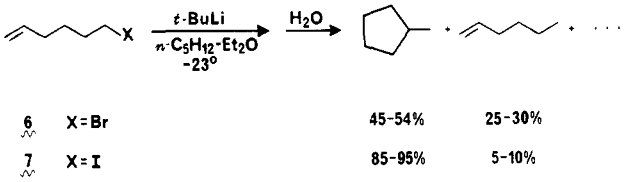
havior[1] of primary dibromides. As shown in Table II, the dibromide, in contrast to 1,3-, 1,4- and 1,5-iodohaloalkanes, does not undergo clean metal–halogen interchange as evidenced by the relatively low yield (ca. 20–45%) of cycloalkane produced in the reaction. Under conditions that provide an essentially quantitative yield of 1,1-dimethylcyclopentane from the corresponding diiodide **3** and bromoiodide **4** (Table 1, entries 9 and 10), dibromide **5** is coverted to a mixture of products composed of substantial amounts of *tert*-butyl-containing alkanes (ca. 15–25% of the product mixture) formed by Wurtz coupling with the alkyllithium as well as large quantities of 3,3-dimethylpentane and some saturated hydrocarbons derived from intermolecular coupling of substrate molecules. It should be noted that whereas the intermolecular dimerization of the dibromide is virtually eliminated by running the reaction at higher dilution (compare entries 1 and 3, Table II), the extent of "mixed" coupling with *t*-BuLi is unaffected by a 100-fold decrease in concentration of the reaction medium.

The formation of relatively large quantities of 3,3-dimethylpentane in the reaction of **5** with *t*-BuLi is notable. The mechanism depicted in Scheme I, which accounts for the formal reduction of 1,6-diiodohexane to *n*-hexane by consecutive interchange reactions leading to a dilithioalkane, can not be involked to explain the result. Clearly, the fate of a 1-bromo-5-lithio species generated in an initial metal–halogen exchange of **5** with *t*-BuLi is cyclization rather than subsequent conversion to a dilithio compound. Indeed, 1-bromo-5-iodo-3,3-dimethylpentane (**4**) affords the same 1-bromo-5-lithio intermediate upon metal–halogen interchange and 1,1-dimethylcyclopentane is the sole product of the reaction (Table I, entry 10). We shall return to this point below.

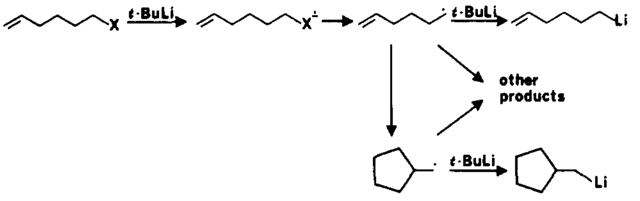
Comparison of the results presented in Table I with those contained in Table II (which are representative of the general behavior of dibromides in reactions with *t*-BuLi)[1] reveals that exclusive metal–halogen interchange is observed only when at least one halogen atom of the α,ω-dihalide is an iodine. An explanation of this finding requires knowledge of the mechanism(s) of metal–halogen interchange and Wurtz-type coupling.

It seems well established that Wurtz–coupling of alkyl halides with nonresonance stabilized alkyllithiums[39] occurs via a SET process.[22,31] Evidence for the intervention of alkyl radicals in such reactions has been accrued from product analyses,[13,40] trapping experiments,[31,40] observation of chemically induced nuclear polarization (CIDNP) in the coupling products,[23,41] and direct observations by EPR spectroscopy.[27] Unfortunately, as noted above, the evidence for a SET-mediated metal–halogen interchange is less compelling.[42] We have, therefore, begun to explore reactions of alkyl- and aryllithiums with various alkyl halides that are capable of producing rearranged products if radical intermediates are generated in the reaction.[44] The results of these studies will be presented in due course but data from preliminary experiments using 6-bromo- and 6-iodo-1-hexene are of interest in the present context since they establish that metal–halogen interchange between *t*-BuLi and primary bromides or iodides occurs predominantly (and perhaps exclusively) via SET.

Scheme II



Scheme III



Since the 5-hexenyl radical is known to cyclize cleanly to the cyclopentylmethyl radical in an essentially irreversibly reaction ($k \sim 10^5\ s^{-1}$),[45] the observation of products containing the cyclopentylmethyl moiety from reactions employing 6-substituted-1-hexene substrates has been taken as evidence for the intervention of radicals. As illustrated in Scheme II, treatment of either 6-bromo (**6**) or 6-iodo-1-hexene (**7**) with *t*-BuLi affords, after hydrolysis, high yields of methylcyclopentane. These results demonstrate that both the dibromide and the iodide undergo metal–halogen interchange via a SET mechanism. The quite high yield of cycloalkane from the iodide is indicative of an essentially quantitative interchange while the lower yield of methylcyclopentane from the bromide reaction is consistent with the lower proportion of metal–halogen interchange observed in reactions of *t*-BuLi with dibromoalkanes (Table II).

Similar results have been obtained from studies of the reaction of 6-halo-1-hexenes with aromatic radical anions[28,46] and organostannyl alkalis,[29,30] and the conventional explanation for the observation of rearranged products is depicted in Scheme III. Electron transfer from the (associated) alkyllithium gives a radical anion that is assumed[8,24,28–30,47] to rapidly loose halide generating a free 5-hexenyl radical. Competition between unimolecular cyclization and further reduction to 6-lithio-1-hexene (a topic treated quantitatively by Garst and Barton[46]) is responsible for the relative proportions of methylcyclopentane and 1-hexene in the product mixture. Obviously, other radical reactions (i.e., coupling, diproportionation,

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[39] Coupling of alkyl halides and charge-delocalized alkyllithiums seems to involve a polar, S_N2-like reaction. See, for example: (a) Sommer, L. H.; Korte, W. D. *J. Org. Chem.* **1970**, *35*, 22. (b) Zieger, H. E.; Mathisen, D. *J. Am. Chem. Soc.* **1979**, *101*, 2207.

[40] Bryce-Smith, D. *J. Chem. Soc.* **1956**, 1603 and references therein.

[41] Ward, H. R. *Acc. Chem. Res.* **1972**, *5*, 18 and references therein.

[42] CIDNP is not observed in reactions of alkyl halides with alkyllithiums under conditions known (ref 13) to give exclusive metal–halogen interchange (cf. ref 23 and 41). These negative results have been interpreted as being consistent with a polar or concerted mechanism for the interchange (ref 8, 23, and 41). When both coupling and interchange reactions occur, CIDNP spectra are observed for the coupling products, alkanes and alkenes formed via disproportionation and provided the halide is an iodide, the alkyl iodide reactant and product formed due to rapid, radical-mediated, iodide transfer (ref 43). No polarization is observed in the signals of either the reactant or product alkyllithium. It has, however, been suggested that polarization due to radical intermediates in the metal–halogen interchange may be suppressed by line broadening and/or other relaxation processes engendered by alkyllithium aggregates (cf. ref 23).

[43] Cooper, R. A.; Lawler, R. G.; Ward, H. R. *J. Am. Chem. Soc.* **1972**, *94*, 545 and 552.

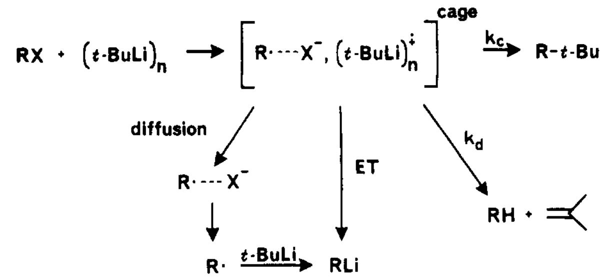
[44] We are aware of only one report dealing with reactions of an alkyllithium with a cyclizable alkyl halide radical probe. This study, involving reaction of *n*-butyllithium with 6-bromo-1-phenyl-1-hexyne, supports a radical mechanism for both Wurtz coupling and formal reduction of the halide via diproportionation but it provides no evidence for SET in metal–halogen interchange. See: Ward, H. R. *J. Am. Chem. Soc.* **1967**, *89*, 5517.

[45] Griller, D.; Ingold, K. U. *Acc. Chem. Res.* **1980**, *13*, 317.

[46] Garst, J. F.; Barton, F. E., III. *J. Am. Chem. Soc.* **1974**, *96*, 523.

[47] Bigot, B.; Roux, D.; Salem, L. *J. Am. Chem. Soc.* **1981**, *103*, 5271 and references therein.

Scheme IV



and scavenging by solvent) can lead to a variety of other products. Minor variations in reaction conditions can alter the product yields (hence the range of yields in Scheme II). Indeed, ongoing studies indicate that an unknown proportion of the methylcyclopentane produced in these reactions is apparently the result of slow but non-negligible cyclization of 6-lithio-1-hexene to cyclopentylmethyllithium.

The demonstration that metal–halogen interchange of primary bromides and iodides with *t*-BuLi occurs via SET, coupled with prior art establishing the presence of alkyl radicals in Wurtz coupling, suggests a common SET mechanism for these two reactions. However, the qualitatively different behavior of bromides and iodides when treated with *t*-BuLi (Tables I and II) is inconsistent with any mechanism that does not involve the departing halogen in the product-partitioning step. This situation is reminiscent of the more subtle halogen dependence observed in reactions of alkyl halides with sodium tetraphenylethylenide[48] and we believe it has a similar, but more general, explanation. The apparent mechanistic dilemma is resolved if the species formed via electron transfer to alkyl halides exist as intermediates with halogen dependent lifetimes. Although such intermediates in a formal sense correspond to alkyl halide radical anions, they are perhaps more correctly formulated as alkyl radical–halide ion complexes.

The much debated question of the existence of stable alkyl halide radical anions has recently been addressed by EPR observation of the species formed upon electron capture by various alkyl halides in rigid, aprotic media.[33,49] The results of these studies are consistent with the formation of alkyl radical–halide ion adducts (i.e., $R\cdot\text{---}X^-$) rather than true σ^* radical anions (i.e., $R\text{–}X^{-}\cdot$). The residual, albeit weak, association between alkyl radical and halide ion has been interpreted in terms of a charge-transfer interaction that is halogen dependent.[33] Thus, adducts produced from alkyl iodides should be more stable toward ultimate dissociation than those formed from alkyl bromides due to the lower electronegativity and higher polarizability of the iodide ion.[50]

Incorporation of these alkyl radical–halide ion complexes as intermediates following SET to alkyl halides is shown in Scheme IV. Electron transfer from the associated *t*-BuLi to RX gives a geminate pair involving the adduct ($R\cdot\text{---}X^-$) and a (presumably associated) radical cation. The disparate behavior of bromides and iodides in reactions with *t*-BuLi is understandable in terms of a competition between diffusive separation of the geminate pair prior to dissociation of the adduct and decomposition of the adduct with the cage. If the lifetime of the $R\cdot\text{---}X^-$ complex is long enough to allow for separation of the geminate pair (ca. $>10^{-8}$ to 10^{-9} s), dissociation of the adduct will produce a free alkyl radical whose fate, in the absence of scavenging by solvent, will be reduction by *t*-BuLi leading to overall metal–halogen interchange. This scenario provides an explanation for the exclusive interchange observed when iodine-containing substrates are treated with *t*-BuLi (Table I) and requires only that alkyl radical–iodide ion complexes have lifetimes sufficiently long to permit diffusion from the site at which they are produced prior to dissociation.

Scheme IV also provides a rationale for the qualitatively different behavior of bromides vis-a-vis iodides. The complex product mixtures found in reactions of α,ω-dibromides with *t*-BuLi (Table II) are consistent with the formation of alkyl radical–bromide ion adducts that are less stable toward dissociation than analogous iodide containing species. A radical–halide ion complex with a short lifetime (ca. $\leq 10^{-8}$ to 10^{-9} s) will dissociate to give a caged radical and a halide ion. The four most probable fates of the alkyl radical thus produced are as shown diagrammatically in Scheme IV: (i) geminate combination (k_c) with a *tert*-butyl radical (or radical cation) to afford a "mixed" coupling product; (ii) crossed disproportionation (k_d) with a neighboring *tert*-butyl radical (or radical cation) to give alkane and isobutylene; (iii) reduction by subsequent electron transfer affecting metal–halogen interchange; (iv) diffusive separation giving a free alkyl radical that suffers reduction upon encounter with alkyllithium. On this basis the relatively large amounts of 3,3-dimethylpentane and the lower, concentration independent yields of "mixed" Wurtz products formed in reactions of **5** with *t*-BuLi are attributable to the cage processes of disproportionation and combination, respectively.[51]

The results do not allow for detailed analysis of the fate of the *t*-BuLi following SET to the alkyl halide. Very little if any *tert*-butyl halide was found as a product of the reactions reported in Tables I and II. The bulk of the alkyllithium appears to be converted to isobutane, isobutylene and variable amounts of 2,2,3,3-tetramethylbutane. While these products are consistent with disproportionation and combination of *tert*-butyl radicals generated in the SET process, they might also have resulted from the rapid consumption of *tert*-butyl halide by its known reaction with *t*-BuLi.[34,52] A consistent if provisional extension of Scheme IV would attribute formation of *tert*-butyl halide to rapid and reversible halogen exchange: $t\text{-Bu}\cdot + R\text{–I(Br)} \rightleftarrows t\text{-Bu–I(Br)} + R\cdot$. Such radical mediated exchange of halogen is known to be much more rapid for iodides than for bromides.[43,53] These possibilities are being assessed in experiments using other alkyllithiums which, upon reaction with α,ω-dihalides, would provide alkyl halides that are stable under the reaction conditions.

The unified SET mechanism shown in Scheme IV for metal–halogen interchange and Wurtz coupling of *t*-BuLi with primary iodides and bromides is of some predictive value. It implies that the course of reactions between organolithiums and organohalides should be affected by changes in the oxidation and reduction potentials of the reactants[54] as well as the lifetime of the radical–ion ad-

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(48) Garst, J. F.; Roberts, R. D.; Pacifici, J. A. *J. Am. Chem. Soc.* **1977**, *99*, 3528.

(49) Symons, M. C. R. *Pure Appl. Chem.* **1981**, *53*, 223 and references therein.

(50) Indirect support for this supposition is found in the recent report that the radical anion generated from HI by electron capture in the gas phase has a much longer lifetime than that produced from HBr. See: Spence, D.; Chupka, W. A.; Stevens, C. M. *J. Chem. Phys.* **1982**, *76*, 2759.

(51) Sheldon, R. A.; Kochi, J. K. *J. Am. Chem. Soc.* **1970**, *92*, 4395.

(52) Formation of 2,2,3,3-tetramethylbutane in reactions of *tert*-butyl halide with *t*-BuLi could be attributed to protonation of 1-lithio-2,2,3,3-tetramethylbutane formed upon addition of *t*-BuLi to the isobutylene produced in the formal elimination reaction (ref 34).

(53) Evans, F. W.; Fox, R. J.; Szwarc, M. *J. Am. Chem. Soc.* **1960**, *82*, 6414.

ducts. These, in turn, are dependent on such factors as the structures of the compounds (i.e., primary, secondary, or tertiary aliphatic or aromatic), nature of the halogen, and degree of association of the organolithium. We are actively investigating the effect of changes in these factors on the outcome of reactions between organolithiums and halogen-containing substrates.

Experimental Section

Melting points and boiling points are uncorrected. Proton magnetic resonance spectra were recorded on Varian EM-360 or Bruker WH-90 instruments and shifts are referenced with respect to internal Me_4Si. Carbon-13 magnetic resonance spectra were obtained on a Bruker WH-90 spectrometer in the FT mode operating at 22.6 MHz; shifts are referenced with respect to Me_4Si and peak multiplicities are reported for off-resonance, proton-decoupled spectra. Infrared spectra were recorded on a Perkin-Elmer 283 grating spectrometer. Refractive indices were measured on a Bausch and Lomb Abbe-3L refractometer thermostated at 20.0 °C by means of a circulating water bath. Analytical gas–liquid chromatography (GLC) was effected with a Perkin-Elmer Model 3920-B instrument fitted with flame ionization detectors and matched, $^1/_{16}$ in. stainless-steel columns. Analytical GLC columns are coded as follows: (A) 10 ft, 20% SE-30 on Anakrom AB (60/80 mesh); (B) 5 ft, 20% SE-30 on Anakrom A (60/80 mesh); (C) 20 ft, 20% SE-30 on Anakrom A (60/80 mesh). Area ratios were determined using a Linear Instruments Model 282 recording integrator or, in those few cases where baseline separation of peaks was not achieved, by manual integration with a Keuffel and Esser compensating planimeter. Unless otherwise noted all yields determined by GLC analysis have been corrected for detector response under conditions of the analysis using weighed samples of pure product and standard. Preparative GLC was accomplished on a Varian Aerograph A-90P fitted with one of the following 0.25-in. aluminum columns: (A) 3 ft, 10% SE-30 on Anakrom U (60/80 mesh); (B) 4 ft, 20% SE-30 on Anakrom U (60/80 mesh); (C) 10 ft, 20% SE-30 on Anakrom U (60/80 mesh). High-resolution mass spectra (MS) were obtained on an AEI MS-902 instrument at 70 eV and GLC-MS was performed on a Hewlett-Packard 5985B system at 70 eV using a 50-m quartz capillary OV-101 column. Microanalyses were performed by either Baron Consulting Co., Orange, CT, or Galbraith Laboratories, Inc., Knoxville, TN.

All reactions involving alkyllithiums were conducted under an atmosphere of dry argon using standard syringe/cannula techniques.[55] Diethyl ether was freshly distilled under argon from either dark purple solutions of sodium/benzophenone or lithium aluminum hydride. Olefin-free *n*-pentane was distilled under argon from ether calcium hydride or lithium aluminum hydride. The concentration of commercial solutions of *t*-BuLi in pentane (Aldrich or Lithium Corp. of America) was determined prior to each reaction by the method of Watson and Eastham[56] and all alkyl halides were freshly distilled prior to use.

Literature procedures were followed for the preparation of *cis*-1,2-bis(iodomethyl)cyclohexane,[57] *exo,cis*-1,2-bis(iodomethyl)bicyclo[2.2.1]heptane,[58] 1,5-dibromo-3,3-dimethylpentane (5),[59] 1-chloro-5-iodopentane,[60] 1,6-diiodohexane,[61] 1,7-diiodoheptane,[61,62] and 6-bromo-1-hexene.[63]

1,3-Diiodo-2,2-diethylpropane. When the general procedure of Landauer and Rydon[64] was followed, a mixture of 68.3 g (0.22 mol) of triphenyl phosphite, 13.2 g (0.10 mol) of 2,2-diethyl-1,3-propanediol,[65] and 46.6 g (0.30 mol) of methyl iodide was heated at reflux for 43.5 h with the exclusion of moisture. After cooling to room temperature the mixture was diluted with 200 mL of ether and the organic extract was washed successively with ten 10-mL portions of 10% aqueous sodium hydroxide and one 200-mL portion of water. The ethereal layer was dried (K_2CO_3) and concentrated to afford a viscous oil containing the diiodide and diphenyl methylphosphonate. Distillation of the residue gave the diiodide, bp 82–83 °C (0.15 mm), as an impure solid which was purified by repeated sublimations to afford 6.8 g (19%) of an analytically pure sample: mp 57–57.5 °C; ^1H NMR ($CDCl_3$) δ 0.68–0.95 (m, 6 H), 1.30–1.67 (m, 4 H), 3.20 (s, 4 H); ^{13}C NMR ($CDCl_3$) δ 8.58 (q, CH_3), 17.84 (t, C(1,3)), 26.46 (t, CH_2), 37.74 (s, C(2)); mass spectroscopic molecular weight calcd for $C_8H_{14}I_2$, 351.9194; found, 351.9177. Anal. Calcd for $C_7H_{14}I_2$: C, 23.89; H, 4.01. Found: C, 24.03; H, 4.17.

***cis*-1,2-Bis(2-iodoethyl)cyclohexane.** Dry pyridine (105 mL) was cooled to −23 °C and 39.1 g (0.34 mol) of freshly distilled methanesulfonyl chloride was added dropwise at such a rate that the temperature never exceeded −10 °C. The stirred mixture was recooled to −23 °C and a solution of 24.38 g (0.14 mol) of *cis*-1,2-bis(2-hydroxyethyl)cyclohexane[66] in 94 mL of dry pyridine was slowly added such that the temperature of the reaction mixture remained below −10 °C. Following complete addition, the mixture was stirred for 4 h at −23 °C and then allowed to stand at 0 °C overnight. The mixture was poured onto 750 mL of ice-cold 0.45 M aqueous HCl and the resulting oil was taken up in 30 mL of chloroform. The aqueous phase was extracted with 200 mL of chloroform and the combined organic extracts were washed successively with 200 mL of water, 100 mL of saturated aqueous $NaHCO_3$ and 200 mL of water. After drying ($MgSO_4$), volatile components were removed by rotary evaporation and the crude, oily dimesylate was added to a solution of 48.4 g (0.32 mol) of sodium iodide in 245 mL of dry acetone. The stirred mixture was heated at reflux for 2 h under an atmosphere of dry argon and stirring was continued at room temmperature overnight. The mixture was filtered and the filtrate was concentrated at reduced pressure to give an oil which was partitioned between 200 mL of ether and 200 mL of water. The organic phase was washed with 100 mL of 10% aqueous sodium thiosulfate and three 100-mL portions of water, dried ($MgSO_4$), and concentrated by rotary evaporation to give an oil which was chromatographed over neutral, activity 1 alumina with pentane elution. Fractions containing the diiodide were combined and concentrated at reduced pressure. Distillation of the residue afforded 13.80 g (25% from diol) of the title compound: by 120–125 °C (0.01 mm). An analytical sample was prepared by preparative GLC on column A at 200 °C: ^{13}C NMR ($CDCl_3$) δ 5.46 (t, $-CH_2I$), 23.24 (t, C(4,5)), 27.59 (t, C(3,6)), 33.33 (t, CH_2CH_2I), 39.13 (d, C(1,2)); mass spectroscopic molecular weight calcd for $C_{10}H_{18}I_2$, 391.9499; found, 391.9504. Anal. Calcd for $C_{10}H_{18}I_2$: C, 30.64; H, 4.63. Found: C, 30.88; H, 4.73.

***cis*-1,2-Bis(iodomethyl)cyclobutane.** Using the procedure described above, the dimesylate was prepared from 11.09 g (96 mmol) of *cis*-1,2-bis(hydroxymethyl)cyclobutane.[67,68] The crude dimesylate was added to 36.42 g (243 mmol) of sodium iodide in 180 mL of dry acetone and the mixture was stirred overnight at ambient temperature under an atmosphere of argon. Inorganic salts were removed by filtration and the filtrate was concentrated by rotary evaporation to give an oily residue that was partioned between 200 mL of ether and 200 mL of water. The ethereal extract was washed with 50 mL of 10% aqueous sodium thiosulfate and three 10-mL portions of water. After drying ($MgSO_4$), the

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(54) It is worth noting that mechanistic information on the metal-halogen interchange of aryl bromides with aryllithium (ref 18) or *n*-BuLi (ref 19) does not exclude the possibility of a SET process involving aromatic radical anions. Indeed, although the possibility was apparently not considered in either investigation, the slopes of the Hammett correlations observed in these studies are similar in sign and magnitude to those found in other reactions of aromatic halides that have been interpreted in terms of SET (for example, see: Tsou, T. T.; Kochi, J. K. *J. Am. Chem. Soc.* **1979**, *101*, 6319).

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organic extract was concentrated by rotary evaporation and the residue was distilled to give 14.9 g of a yellow oil, bp 85–88 °C (0.1 mm). Passage of the distillate through a short column of neutral, activity 1 alumina with pentane elution afforded 14.0 g (44%) of white, crystalline diiodide, mp 30–31 °C [lit.[67] bp 110–111 °C (2 mm), mp 34–35 °C].

1,4-Diiodo-2-phenylbutane. Dry pyridine (37 mL) was cooled to −12 °C and 13.8 g (0.12 mol) of freshly distilled methanesulfonyl chloride was added dropwise such that the temperature remained below 0 °C. The stirred mixture was recooled to −12 °C and a solution of 8.3 g (0.05 mol) 2-phenyl-1,4-butanediol[69] in 33 mL of dry pyridine was slowly added at rate such that the temperature did not exceed 0 °C. After the addition was complete, the mixture was stirred for 4 h at −12 °C and at 0 °C overnight. The reaction mixture was poured onto 260 mL of 0.45 M aqueous HCl, the resulting oil taken up in 200 mL of chloroform and washed with two 200-mL portions of water. After drying ($MgSO_4$), volatile components were removed by rotary evaporation and the residual oil was added to 17.4 g (0.12 mol) of sodium iodide in 100 mL of dry acetone. The mixture was heated with stirring at reflux under an atmosphere of argon for 17 h and then allowed to cool to room temperature. Inorganic salts were removed by filtration, the filtrate was concentrated at reduced pressure, and the residue was purified by pentane elution from a column of neutral, activity 1 alumina. Concentration of the fractions containing the diiodide afforded 7.2 g (37%) of analytically pure material: IR (neat) 3085, 3060, 2955, 1600, 1580, 1495, 1450 and 1235 cm^{-1}; ^{13}C NMR ($CDCl_3$) δ 4.15 (t, C(4)), 12.12 (t, C(1)), 38.75 (t, C(3)), 48.03 (d, C(2)), 126.99 (d), 127.09 (d), 128.47 (d), 140.59 (s); mass spectroscopic molecular weight calcd for $C_{10}H_{12}I_2$, 385.9029; found, 385.9043. The diiodide should be stored in a freezer since it decomposes when kept at room temperature for any length of time.

1,5-Diiodo-3,3-dimethylpentane (3). A mixture of 22.0 g (49 mmol) of 3,3-dimethyl-1,5-pentanediol ditosylate (mp 57–59 °C, lit.[70] mp 56–57 °C), 37.5 g (250 mmol) of sodium iodide, and 400 mL of dry acetone was heated at reflux for 2 h under argon and then stirred an additional 18 h at room temperature. The inorganic salts were removed by filtration, the filtrate was concentrated by rotary evaporation, and the residue was partitioned between 300 mL of chloroform and 250 mL of water. The organic phase was washed with 100 mL of 10% aqueous sodium thiosulfate and 100 mL of water, dried ($MgSO_4$), and concentrated under reduced pressure to give a mobile oil. Distillation of the residue through a 10-cm Vigreux column afforded 14.8 g (84%) of the diiodide: bp 84–85 °C (0.08 mm); IR (neat) 2950, 2920, 2860, 1463, 1382 and 1362 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.90 (s, 6 H), 1.74–2.03 (m, 4 H), 2.98–3.26 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ −0.19 (t, C(1,5)), 25.79 (q, CH_3), 38.41 (s, C(3)), 46.76 (t, C(2,4)); mass spectroscopic molecular weight calcd for $C_7H_{14}I_2$, 351.9194; found, 351.9175. Anal. Calcd for $C_7H_{14}I_2$: C, 23.89; H, 4.01; I, 72.11. Found: C, 23.63; H, 3.83; I, 71.67.

1-Bromo-5-iodo-3,3-dimethylpentane (4). A mixture of 12.9 g (0.05 mol) of 1,5-dibromo-3,3-dimethylpentane (5), 7.5 g (0.05 mol) of sodium iodide, and 400 mL of dry acetone was heated at reflux overnight under an atmosphere of argon. The mixture was allowed to cool to room temperature, volatile components were removed by rotary evaporation at water aspirator pressure, and the residue was partitioned between 100 mL of ether and 100 mL of water. The organic phase was separated, the aqueous phase extracted with an additional 100 mL of ether, and the combined organic extracts were washed successively with 100 mL of water, 50 mL of 10% aqueous sodium thiosulfate, 100 mL of water, and 100 mL of brine. After drying ($MgSO_4$), the extract was concentrated by rotary evaporation. GLC analysis of the residue on column B at 150 °C revealed that the reaction mixture consisted of three components. The two fractions having the shortest and longest retention times were identified as 1,5-dibromo-(5) and 1,5-diiodo-3,3-dimethylpentane (3), respectively. The intermediate retention time component was isolated most conveniently by preparative GLC on column B at 200 °C followed by pentane elution from a short column of neutral, activity 1 alumina. Concentration of the pentane eluent afforded pure 4: mass spectroscopic molecular weight calcd for $C_7H_{14}BrI$, 303.9324; found, 303.9312.

1-Bromo-5-iodopentane. Following the general procedure of Kabalka and Gooch,[60] a solution of 4.47 g (30 mmol) of 5-bromo-1-pentene[71] in 5 mL of dry tetrahydrofuran was cooled to 0 °C under an atmosphere of argon and 12.2 mL of a 0.84 M solution of borane in tetrahydrofuran (10.25 mmol BH_3) was added over a 3-min period. The resulting solution was heated for 1 h at 50 °C and allowed to cool to room temperature. Anhydrous methanol (4 mL) was added to the reaction mixture followed 5 min later by sequential addition of 30 mL of a 4.0 M solution of sodium acetate in anhydrous methanol and 3.85 g (20 mmol) of iodine monochloride. The resulting mixture was stirred at room temperature for 45 min and poured into 100 mL of water and sufficient 1.0 M aqueous sodium thiosulfate solution was added (ca. 20 mL) to produce two clear, colorless layers. The mixture was extracted with three 50-mL portions of ether, and extracts were dried ($MgSO_4$) and concentrated to give a pale yellow oil. Chromatography of the residue over neutral, activity 1 alumina with pentane elution afforded, after concentration, a mobile liquid which was distilled to give 2.24 g (40%) of the bromoiodide: bp 115–118 °C (12mm); IR (neat) 3000, 2950, 2930, 2850, 1450, 1425 and 1205 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.05–2.22 (m, 6 H), 3.20 (t, J = 6.5 Hz, 2 H), 3.42 (t, J = 6.0 Hz, 2 H); mass spectroscopic molecular weight calcd for $C_5H_{10}BrI$, 275.9011; found, 275.9016. Anal. Calcd for $C_5H_{10}BrI$: C, 21.69; H, 3.64. Found: C, 21.82; H, 3.64.

3-*tert*-Butyl-1,6-hexanediol. A 500-mL, three-necked, round-bottomed flask with nonground glass joints was fitted with a low temperature thermometer and gas inlet and outlet tubes using drilled corks. A solution of 13.8 g (0.10 mol) of 4-*tert*-butylcyclohexene[72] in a mixture of 150 mL of methylene chloride and 50 mL of absolute methanol was placed in the reaction flask and cooled to −78 °C (dry ice/acetone bath). The reaction mixture was oxidized at −78 °C using an ozone stream (2% by weight of O_2) generated with a Welsbach T-23 Laboratory Ozonator until the characteristic blue color of ozone persisted for several min (total reaction time, ca. 1.5 h). The cold reaction mixture was poured into a 1-L, three-necked, round-bottomed flask equipped with a Friedrich condenser, magnetic stirrer, and thermometer. The ozonide was reduced by cautious addition, over a 1-h period, of an ice-cold solution of 30.5 g (0.80 mol) of sodium borohydride in 200 mL of 50% aqueous ethanol to the stirred, cold reaction mixture. During the reduction of the temperature of the mixture was not allowed to rise above 10 °C. After the addition was complete, the mixture was stirred for 1 h at room temperature then heated at 50 °C for 1 h, and finally stirred at room temperature overnight. Excess sodium borohydride was hydrolyzed by dropwise addition of 180 mL of 10% aqueous sulfuric acid to the stirred mixture, volatile components were removed by rotary evaporation, the residue was diluted with a small amount of water, and the mixture was made slightly basic with 10% aqueous sodium hydroxide. The organic phase was separated, the aqueous phase washed with three 200-mL portions of ether and the combined organic extracts were dried ($MgSO_4$) and concentrated at reduced pressure. This oxidation was repeated five times and the combined residue from the five 0.1-mol scale reactions was distilled to give 61.9 g (72%) of the diol: bp 99–100 °C (0.08 mm); $n^{20}{}_D$ 1.4467; IR (neat) 3320, 2940, 2865, 1472, 1390, 1362 and 1045 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.87 (s, 9 H), 0.88–1.96 (m, 7 H), 2.12 (concentration-dependent singlets, 2 H), 3.63 (distorted t, 4 H); ^{13}C NMR ($CDCl_3$) δ 27.49 (t, C(4)), 27.66 (q, CH_3), 32.58 (t, (C(5)), 33.83 (s, $C(CH_3)_3$), 34.48 (t, C(2)), 44.71 (d, C(3)), 62.92 (t, C(1)), 63.09 (t, C(6)). Anal. Calcd for $C_{10}H_{22}O_2$: C, 68.92; H, 12.72. Found: C, 69.26; H, 12.77.

3-*tert*-Butyl-1,6-hexanediol Ditosylate. A solution of 1.7 g (0.01 mol) of 3-*tert*-butyl-1,6-hexanediol in 21.4 mL of dry pyridine was cooled to 0 °C and 7.64 g (0.04 mol) of freshly purified *p*-toluenesulfonyl chloride was added in portions over a 2-h period. The reaction mixture was allowed to stand at 0 °C for 20 h before being poured onto a mixture of 40 mL of water and 70 g of ice.

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After stirring for 1 h, 200 mL of ether was added, the ethereal layer was removed, and the aqueous layer was extracted with three 50-mL portions of ether. The combined ethereal extracts were washed successively with 50 mL of cold aqueous hydrochloric acid (1:1:v/v) and 100 mL of water, dried over a mixture of K_2CO_3 and Na_2SO_4, and concentrated under reduced pressure to give an oil that solidified on standing at 0 °C overnight. Recrystallization from ethanol yielded 4.2 g (87%) of the ditosylate: mp 68.5–69.5 °C; mass spectroscopic molecular weight calcd for $C_{24}H_{34}O_6S_2$, 482.1794; found, 482.1814.

3-*tert*-Butyl-1,6-diiodohexane. A mixture of 82.1 g (0.17 mol) of 3-*tert*-butyl-1,6-hexanediol ditosylate, 127.4 g (0.85 mol) of sodium iodide, and 1360 mL of dry acetone was stirred for 18 h at room temperature under an atmosphere of argon. The precipitate was removed by filtration and the filtrate was concentrated at reduced pressure to give an oil which was partitioned between 500 mL of chloroform and 500 mL of water. The organic phase was washed with two 200-mL portions of 10% aqueous sodium thiosulfate and two 200-mL portions of water, dried (Na_2SO_4), and concentrated by rotary evaporation. The residual oil was fractionated through a 10-cm Vigreux column to give 56.1 g (82%) of the diiodide: bp 100–102 °C (0.08 mm); IR (neat) 2950, 2860, 1470, 1420, 1390, 1360, 1300, 1270, 1220, 1190 and 1170 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.63–2.39 [overlapping pattern, 16 H, i.e., 0.88 (s, 9 H)], 2.86–3.55 (m, 4 H). Anal. Calcd for $C_{10}H_{20}I_2$: C, 30.48; H, 5.12. Found: C, 30.89; H, 5.22.

General Procedure for the Reactions of α-Iodo-ω-haloalkanes with *t*-BuLi. A stirred solution of 10 mmol of the diiodide or iodohaloalkane and an accurately weighed quantity of the hydrocarbon internal standard (typically 10 mmol) in 100 mL of dry *n*-pentane–diethyl ether (3:2 by volume) was cooled to −23 °C (CCl_4/dry ice bath) under a blanket of argon and 2.0–2.2 molar equiv of *t*-BuLi in pentane was added via syringe over a 5-min period. The reaction mixture was stirred for 30 min at −23 °C (during which time a precipitate forms), the cooling bath was removed, and 10 mL of water was **cautiously** added. After warming to room temperature the organic phases was separated, dried ($MgSO_4$), and analyzed by GLC to give the results presented in Table I. Reactions at higher dilution were conducted similarly.

Quantities of cyclized product from these reactions (or identically conducted experiments run without internal standard) were isolated by preparative GLC. The structures of the following compounds indicated in Table I were established by comparison of the spectroscopic properties of isolated material with those of commercially available samples (preparative GLC column and oven temperature given in parenthesis): 1,5-hexadiene (entry 5, column C, 50 °C), cyclopentane (entries 6–8, column C, 45 °C), cyclohexane (entries 11–13, column C, 50 °C), *n*-C_6H_{12} (entries 11–13, column C, 50 °C), *n*-$C_{12}H_{26}$ (entries 11 and 12, column A, 135 °C), *n*-$C_{18}H_{38}$ (entry 11, column A, 135 °C), *t*-butylcyclohexane (entry 14, column C, 190 °C), *cis*-decalin (entry 15, column C, 190 °C), cycloheptane (entry 16, column C, 100 °C). Structures of the remaining hydrocarbons were established on the basis of the following physical and spectroscopic properties exhibited by isolated samples.

1,1-Diethylcyclopropane. An analytical sample was obtained by preparative GLC on column C at 85 °C: $n^{20}{}_D$ 1.4041 (lit.[73] $n^{20}{}_D$ 1.4042); IR (neat) 3070, 2965, 2875, 2860, 1375 and 1008 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.11 (s, 4 H), 0.69–1.36 (complex pattern, 10 H); ^{13}C NMR ($CDCl_3$) δ 10.62 (q, CH_3), 11.41 (t, C(2,3)), 21.41 (s, C(1)), 28.25 (t, CH_2CH_3)).

***cis*-Bicyclo[4.2.0]octane.** An analytical sample of this known[74] material was obtained by preparative GLC on column C at 135 °C: IR (neat) 2970, 2930, 2880, 1465 and 1450 cm^{-1}; ^{13}C NMR ($CDCl_3$) δ 22.89 (t, C(7,8)), 24.63 (t, C(3,4)), 28.12 (t, C(2,5)), 33.23 (d, C(1,2)); mass spectroscopic molecular weight calcd for C_8H_{14}, 110.1096; found, 110.1094.

***exo,cis*-Tricyclo[4.2.1.0^{2,5}]nonane.** The known[75] hydrocarbon was isolated in 52% yield by fractionation of the reaction mixture: bp 62–70 °C (14 mm); IR (neat) 2050, 1475, 1455, 1430 and 1290 cm^{-1}; ^{13}C NMR ($CDCl_3$) δ 23.06 (t, C(9)), 27.67 (t, C(3,4)), 31.79 (t, C(7,8)), 39.39 (d, C(2,5)), 41.82 (d, C(1,6)); mass spectroscopic molecular weight calcd for C_9H_{14}, 122.1096; found, 122.1097.

Phenylcyclobutane. Distillation of the reaction mixture afforded 78% yield of product: bp 79–82 °C (17 mm); $n^{20}{}_D$ 1.5269 (lit.[76] bp 89–91 °C (25 mm); $n^{20}{}_D$ 1.5267).

1,1-Dimethylcyclopentane. An analytical sample was obtained by preparative GLC on column C at 90 °C: ^1H NMR ($CDCl_3$) δ 0.96 (s, 6 H), 1.33–1.62 (m, 8 H); ^{13}C NMR ($CDCl_3$) δ 24.56 (t, C(3,4)), 28.97 (q, CH_3), 38.96 (s, C(1)), 41.06 (t, C(2,5)). The ^{13}C shifts agree well with those reported[77] for this compound.

Reaction of 1,5-Dibromo-3,3-dimethylpentane (5) with *t*-BuLi. A stirred solution of 2.578 g (9.93 mmol) of **5** in 100 mL of dry *n*-pentane–diethyl ether (3:2 by volume) containing 1.139 g (9.98 mmol) of *n*-octane as internal standard was cooled to −23 °C under an atmosphere of argon and 12.0 mL of a 1.87 M solution of *t*-BuLi in pentane (22.4 mmol of *t*-BuLi) was added over a 5-min period. The reaction mixture was stirred for 30 min at −23 °C, the cooling bath was removed, and 10 mL of water was **cautiously** added. The organic phase was separated, dried ($MgSO_4$), and analyzed by GLC. Inspection of the mixture on column A at 37 °C revealed that the reaction afforded (in order of elution) 22% of 1,1-dimethylcyclopentane and 24% of 3,3-dimethylpentane. Less volatile components of the reaction mixture were analyzed by GLC on column B using linear temperature programming from an initial temperature of 50 °C to 200 °C at a rate of 16 °C/min. Yields of the various products are listed in Table II. A sample of each compound was isolated from the reaction mixture by preparative GLC on column B at 170 °C and structures were assigned on the basis of the following MS and ^{13}C NMR data. The assigned ^{13}C shifts agree within ca. ±1 ppm with values calculated using standard alkane parameters.[78]

2,2,5,5-Tetramethylheptane: mass spectrum, *m/e* 85 (55%, $(CH_3)_3CCH_2CH_2$), 71 (100%, $(CH_3)_2CCH_2CH_3$), 57 (89%, $(CH_3)_3C$); mass spectroscopic molecular weight calcd for $C_{11}H_{24}$, 156.1879; found, 156.1876.

2,2,5,5,8,8-Hexamethylnonane: ^{13}C NMR ($CDCl_3$) δ 27.40 (q, 5-CH_3), 29.44 (q, C(1,9)), 30.05 (s, C(2,8)), 31.96 (s, C(5)), 35.74 (t, C(4,6)), 37.73 (t, C(3,7)); mass spectroscopic molecular weight calcd for $C_{15}H_{32}$, 212.2505; found, 212.2495.

3,3,8,8-Tetramethyldecane: ^{13}C NMR ($CDCl_3$) δ 8.42 (q, C(1,10)), 25.04 (t, C(5,6)), 26.74 (q, 3,8-CH_3), 32.64 (s, C(3,8)), 34.11 (t, C(2,9)), 41.63 (t, C(4,7)); mass spectroscopic molecular weight calcd for $C_{14}H_{30}$, 198.2349; found, 198.2344.

2,2,5,5,10,10-Hexamethyldodecane: ^{13}C NMR ($CDCl_3$) δ 8.41 (q, C(12)), 25.03 (t, C(7) and C(8)), 26.72 (q, 10-CH_3), 27.31 (q, 5-CH_3), 29.40 (q, C(1)), 30.05 (s, C(2)), 32.27 (s, C(10)), 32.63 (s, C(5)), 34.11 (t, C(11)), 36.02 (t, C(4)), 37.75 (t, C(3)), 41.62 (t, C(6)), 41.97 (t, C(9)).

6-Iodo-1-hexene (7). Following the general procedure of Crossland and Servis,[79] 5.00 g (0.05 mol) of 5-hexene-1-ol[80] was converted to its mesylate. The crude mesylate was added to a solution of 15.0 g (0.10 mol) of sodium iodide in 100 mL of dry acetone and the mixture was stirred under argon for 17 h at room temperature. Inorganic salts were removed by filtration and the filtrate was concentrated at reduced pressure. The resulting oil was dissolved in 100 mL of ether and washed with three 100-mL portions of water, two 50-mL portions of 10% aqueous sodium thiosulfate, and 100 mL of brine. After drying ($MgSO_4$), solvent was removed by rotary evaporation and the residue was distilled to give 9.15 g (87% from the alcohol) of the hexenyl iodide (**7**): bp 48–49 °C (1.0 mm); IR (neat) 3065, 2980, 2960, 1635, 1450, 1435, 1420, 1210 and 1165 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.1–2.4 (m, 6 H), 3.23 (t, J = 6.0 Hz, 2 H), 4.57–5.20 (m, 2 H), 5.25–6.05 (m, 1 H); mass spectroscopic molecular weight calcd for $C_6H_{11}I$, 209.9911; found, 209.9907.

Reactions of 6-Bromo- (6) and 6-Iodo-1-hexene (7) with *t*-BuLi. A solution of 2.0 mmol of the appropriate halide in 20

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mL of dry *n*-pentane–diethyl ether (3:2 by volume) containing 2.0 mmol of *n*-heptane as internal standard was cooled to −23 °C under a blanket of argon and 4.0 mmol of *t*-BuLi as a solution in pentane was added via syringe over a 5-min period. The reaction mixture was stirred for 30 min −23 °C, the cooling bath was removed, and 10 mL of water was cautiously added. After warming to room temperature, the organic phase was separated, dried ($MgSO_4$), and analyzed by GLC on column A at 35 °C. The results are presented in Scheme II. Methylcyclopentane and 1-hexene were identified by comparison of their retention times and mass spectra obtained by GC/MS with those of authentic samples.

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Registry No. **3**, 85807-81-4; **4**, 89891-12-3; **5**, 37746-17-1; **6**, 2695-47-8; **7**, 18922-04-8; *t*-BuLi, 594-19-4; $I(CH_2)_5I$, 628-77-3; $I(CH_2)_5Br$, 88962-86-1; $I(CH_2)_5Cl$, 60274-60-4; $I(CH_2)_6I$, 629-09-4; *n*-C_6H_{14}, 110-54-3; *n*-$C_{12}H_{26}$, 112-40-3; *n*-$C_{18}H_{38}$, 593-45-3; *n*-C_7H_{16}, 142-82-5; *n*-$C_{14}H_{30}$, 629-59-4; 1,3-diiodo-2,2-diethylpropane, 85807-77-8; 1,4-diiodo-2-phenylbutane, 85807-78-9; *cis*-1,2-bis(2-iodoethyl)cyclohexane, 85807-79-0; *exo,cis*-1,2-bis(iodomethyl)bicyclo[2.2.1]heptane, 85807-80-3; *cis*-1,2-bis(iodomethyl)cyclobutane, 77774-05-1; *cis*-1,2-bis(2-iodoethyl)cyclohexane, 85807-82-5; 1,7-diiodoheptane, 51526-03-5; 1,1-diethylcyclopropane, 1003-19-6; phenylcyclobutane, 4392-30-7; *cis*-bicyclo[4.2.0]octane, 28282-35-1; *exo,cis*-tricyclo[4.2.1.$0^{2,5}$]nonane, 16526-27-5; cyclopentane, 287-92-3; 1,1-dimethylcyclopentane, 1638-26-2; 1,5-hexadiene, 592-42-7; cyclohexane, 110-82-7; *tert*-butylcyclohexane, 3178-22-1; *cis*-decahydronaphthalene, 493-01-6; cycloheptane, 291-64-5; 3,3-dimethylpentane, 562-49-2; 2,2,5,5-tetramethylheptane, 61868-47-1; 2,2,5,5,8,8-hexamethylnonane, 89891-14-5; 3,3,8,8-tetramethyldecane, 85807-83-6; 2,2,5,5,10,10-hexamethyldodecane, 89891-15-6; methylcyclopentane, 96-37-7; 1-hexene, 592-41-6; 2,2-diethyl-1,3-propanediol, 115-76-4; *cis*-1,2-bis(2-hydroxyethyl)cyclohexane, 59434-70-7; *cis*-1,2-bis(hydroxymethyl)cyclobutane, 54445-64-6; 2-phenyl-1,4-butanediol, 6837-05-4; 3,3-dimethyl-1,5-pentanediol ditosylate, 53120-76-6; 5-bromo-1-pentene, 1119-51-3; 3-*tert*-butyl-1,6-hexanediol, 82111-97-5; 4-*tert*-butylcyclohexene, 2228-98-0; 3-*tert*-butyl-1,6-hexanediol ditosylate, 89891-16-7; 5-hexene-1-ol mesylate, 64818-36-6; 3-*tert*-butyl-1,6-diiodohexane, 89891-13-4.

Kinetics and Mechanism of Acetone Cyclic Diperoxide (3,3,6,6-Tetramethyl-1,2,4,5-tetraoxane) Thermal Decomposition in Benzene Solution

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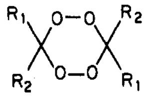
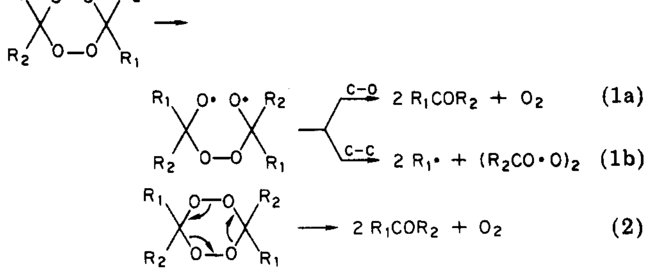
In the temperature range of 135.5 to 165.0 °C the main products of acetone cyclic diperoxide (ACDP) thermolysis in benzene solution are oxygen, acetone, and toluene, with minor yields of methyl isopropyl ether, methyl acetate, bibenzyl, methyl alcohol, methane, ethane, and carbon dioxide. The overall reaction follows a first-order kinetic law up to 60% ACDP conversion. At temperatures ranging between 135.5 and 145.0 °C the observed rate constant values are independent of the initial ACDP concentration, but at 150.5 and 165.0 °C, with concentrations higher than 0.1 and 0.06 mol kg^{-1}, respectively, a nearly linear dependence between the rate constant and concentration can be established. The activation parameters for the ACDP unimolecular decomposition reaction are $\Delta H^{\neq} = 35.7 \pm 1.1$ kcal mol^{-1} and $\Delta S^{\neq} = 0.0 \pm 0.3$ eu. Support for a stepwise mechanism instead of a concerted process is given by comparison of these parameters with those corresponding to alkyl peroxides and with the theoretically calculated activation energy for the ACDP homolysis. It is concluded that an induced decomposition of ACDP molecules by methyl radicals must be postulated in the thermolysis mechanism. That process, which gives oxygen, acetone, and methyl isopropyl ether as its products, has an estimated overall activation energy of 10 kcal mol^{-1}. In toluene solution at 165.0 °C this reaction is suppressed at ACDP initial concentration lower than 0.1 mol kg^{-1}.

It has been reported[1] that the thermal decomposition of diperoxides of the type illustrated, where R_1 and R_2 can



be the same or different groups (Me, Et, *t*-Bu, $-(CH_2)_5-$, Ph, and $PhCH_2$), give different products with yields dependent on the characteristics of the respective molecule substituents. For the decomposition of those peroxides, two main types of processes have been suggested: a stepwise mechanism with a biradical as intermediate, which further decomposes by C–O or C–C ruptures (Eq 1) and a concerted type decomposition (eq 2). The few



kinetic data for their reactions[2] and the scarce product

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