multiplet resonances of H_3 of the 4 isomer and H_5 of the 3 isomer and H_3 of the 2 isomer. All these approaches yielded results that were in good agreement.

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Registry No.—$Tl(O_2CCF_3)_3$, 23586-53-0; $CH_3C_6H_5$, 108-88-3; C_6H_6, 71-43-2; 2-tolylthallium bis(trifluoroacetate), 42006-01-9; 3-tolylthallium bis(trifluoroacetate), 55288-00-1; 4-tolylthallium bis(trifluoroacetate), 23586-55-2.

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Lithium Vapor Synthesis for 1,5-Dilithiopentane and 1,6-Dilithiohexane and the Reaction of Lithium Vapor with Dihalopropanes

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Previously, the one direction taken in our work directed toward the development of general synthetic methods for polylithium organic compounds[1-5] was an investigation of the reaction of alkanes which were halogen substituted at several sites. We reported[3] that the products were completely lithium-substituted alkanes and lower molecular weight fragments. The principal product was found to be the completely lithium-substituted analogue of the parent alkane. For example, the reaction of 1-bromopropane gave a 20% yield of a solid polymeric lithium compound, octalithiopropane.[3]

$$Li_{(g)}(900\ ^\circ C) + BrCH_2CH_2CH_3 \rightarrow \underset{20\%}{CLi_3CLi_2CLi_3} + \text{completely lithium-substituted fragments}$$

The abstraction reaction of lithium vapor with the carbon–halogen bond is an extremely exothermic reaction, (i.e., ~110 kcal/mol), and the subsequent lithium atom reaction with the alkyl radical forms a 56 kcal/mol bond. The subsequent monolithium-substituted product is undoubtedly vibrationally excited, enabling the reaction to proceed toward more extensive lithium substitution for hydrogen.

We have found that alkanes will not react with lithium vapor until they are heated to temperatures on the order of 800 °C before being mixed with lithium vapor, and are thus vibrationally excited over a continuum of vibrational states. Based on our studies in this area,[3] the effect of vibrational excitation occurs only through approximately three carbon–carbon bonds, so that longer chain compounds are not completely substituted by lithium.

In the present study, milder reaction conditions have been sought and a modified reactor system (Figure 1) has been designed to facilitate more selective substitution of lithium at the carbon–chlorine bond and the synthesis of dilithio-substituted alkanes from dichloralkanes. 1,5-Dichloropentane, 1,6-dichlorohexane, 1,3-dichloropropane, and 1,3-dibromopropane were chosen for this study.

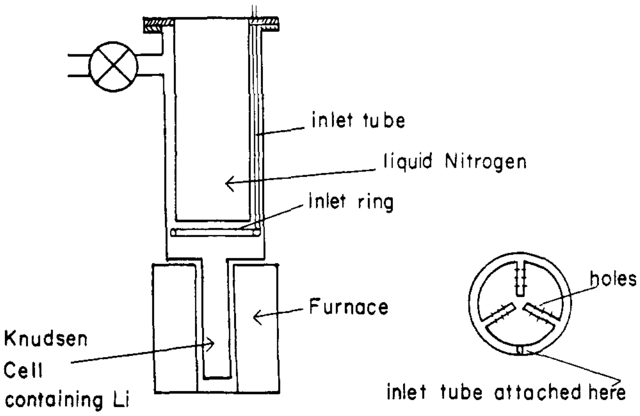

Figure 1. The improved reactor.

In a typical reaction, 1,5-dichloropentane was studied in a stainless steel reactor (Figure 1) with an Inconel Knudsen cell. One-quarter of a milliliter or 2×10^{-3} mol of 1,5-dichloropentane was admitted to the reactor over a 25-min period, a rate of 8×10^{-5} mol/min. The extremely reactive products were removed from the cold finger under argon and carefully hydrolyzed using D_2O on a vacuum line. Excess D_2O was removed using a −95 °C trap, and the products were then separated by gas chromatography. The same procedure was followed for 1,6-dichlorohexane, except that this reactant was admitted to the reactor at a rate of 8×10^{-5} mol/min for 25 min. The reactants 1,3-dihcloropropane and 1,3-dibromopropane were admitted over a 25-min period at a rate of 2×10^{-5} mol/min.

The primary methods of characterization of each fraction were mass spectroscopy and GLC retention times. The characterization of the deuterium substitution sites was unambiguous using mass spectroscopy, but for the title compounds the deuterium substitution was also confirmed by ^1H NMR.

The hexane, pentane, butane, and propane, etc., fractions were collected separately for high-resolution mass spectra to positively identify each species. The entire product mixture was also analyzed by low-resolution mass spectroscopy. The product distributions shown in Table I are averages of at least three runs, each with a reproducibility of ±5%.

Table I. Distribution of Hydrolysis Products (%)

	1,5-dichloropentane	1,6-dichlorohexane
C_2D_6	11	23
C_2D_4	1	3
C_2D_2	28	19
C_3D_8	7	7
C_3D_6	2	4
C_3D_4	19	8
C_4D_{10}	1	5[a]
$DCH_2(CH_2)_3CH_2D$	31	trace
$DCH_2(CH_2)_4CH_2D$		31

	1,3-dibromopropane	1,3-dichloropropane
C_2D_6	24	29
C_2D_4	1	1
C_2D_2	6	8
C_3D_8	12	33
C_3D_6	47	13
C_3D_4	trace	trace
C_4D_{10}	9	6

[a] For 1,6-dichlorohexane, the butane produced in hydrolysis was composed of a mixture of butanes containing 1–10 deuteriums.

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This new reaction system was successful in controlling the reactions, such that 1,5-dichloropentane and 1,6-dichlorohexane were converted to the 1,5- and 1,6-dilithio compounds, which have been previously reported by West and Rochow,[6] in identical yields of 31%.

$$\mathrm{ClCH_2(CH_2)_3CH_2Cl + Li_{(g)}(800\ ^\circ C) \rightarrow \underset{31\%}{LiCH_2(CH_2)_3CH_2Li} + \underset{19\%}{C_3Li_4} + \underset{11\%}{C_2Li_6} + \underset{28\%}{C_2Li_2}}$$

$$\mathrm{ClCH_2(CH_2)_4CH_2Cl + Li_{(g)}(800\ ^\circ C) \rightarrow \underset{31\%}{LiCH_2(CH_2)_4CH_2Li} + \underset{23\%}{C_2Li_6} + \underset{19\%}{C_2Li_2}}$$

However, the reactions of 1,3-dibromopropane and 1,3-dichloropropane gave completely substituted lithium compounds with no remaining protons present after hydrolysis when examined by mass spectrometry or NMR. One would conclude that the energy of the chlorine abstraction reaction was too great to dissipate prior to reaction.

$$\mathrm{ClCH_2CH_3CH_2Cl + Li(800\ ^\circ C) \rightarrow \underset{33\%}{CLi_3CLi_2CLi_3} + \underset{29\%}{C_2Li_6} + \underset{13\%}{CLi_2{=}CLiCLi_3}}$$

The composition of the hydrolysis products which were removed from the cold finger is given in Table I. Because the only material worked up from the reaction were the products which were collected on the cold finger, the recovered material conversions in this experiment total from 25 to 35% of the theoretical and the yields are based on the material from the cold finger. The material collected on the sides of the reactor was not studied due to the difficulty of handling the entire reactor under argon.

1,5-Dichloropentane. The gas chromatographic analysis of the products from the 1,5-dichloropentane reaction showed that an *n*-pentane species was the major product, with some *n*-butane as well as several two- and three-carbon fragments (Table I). The mass spectrum of the pentane peak showed a parent ion at *m/e* 74, corresponding to $C_5H_{10}D_2^+$, and the next major peaks were at *m/e* 58 and 44, corresponding to $C_4H_8D^+$ and $C_3H_6D^+$. This pattern can arise only if the deuterium atoms are in the 1 and 5 positions, indicating that 1,5-dilithiopentane was formed. A mass spectral analysis of the remaining products showed that they were all predeuterated.

1,6-Dichlorohexane. The gas chromatographic analysis of the 1,6-dichlorohexane products gave an *n*-hexane species as the major product, with a trace of *n*-pentane, some *n*-butane, and the usual two- and three-carbon fragments. The mass spectrum of the hexane fraction was interpreted (by the same process used on pentane) as indicating that this material was 1,6-dideuteriohexane. The pentane was found to be 1,5-dideuteriopentane, and the butane was found to be a mixture of species with 2–10 deuteriums present. The other products were predeuterated and, therefore, likely to be produced by a fragmentation process.

1,3-Dichloro- and 1,3-Dibromopropanes. The 1,3-dibromopropane reaction gave a propene species as the major product with a propane to propene ratio of 1:3.4; the 1,3-dichloropropane reaction gave a propane species as the major product with a propane to propene ratio of 2.7:1. A mass spectrum of the propane products showed, in both cases, that the propane was predeuterated, with no trace of the desired 1,3-dideuteriopropane.

As previously mentioned in the manuscript, West and Rochow have studied the reactions of dibromoalkanes with lithium metal in ethyl ether and have previously prepared the compounds 1,5-dilithiopentane and 1,6-dilithiohexane.[6] Very interestingly, in a series of six α,ζ-dibromoalkanes, only $Br(CH_2)_2Br$ and $Br(CH_2)_3Br$ have been reported to yield no dilithio products. In this study the lithium compound was quenched in situ with chlorotrimethylsilane. While the reaction was reported to work well for the methylene analogue and higher analogues with yields as high as 71% of the trimethylsilyl derivative obtained, West and Rochow reported that absolutely none of the trimethysilyl compounds were obtained for the ethyl and propyl analogues and that only a small amount of a rather involatile oil was left after distillation.

Registry No.—1,5-Dichloropentane, 628-76-2; 1,6-dichlorohexane, 2163-00-0; 1,3-dichloropropane, 142-28-9; 1,3-dibromopropane, 109-64-8; $LiCH_2(CH_2)_3CH_2Li$, 2223-58-7; C_3Li_4, 69815-14-1; C_2Li_6, 38827-80-4; C_2Li_2, 1070-75-3; $LiCH_2(CH_2)_4CH_2Li$, 2223-57-6; $CLi_3CLi_2CLi_3$, 69815-15-2; $CLi_2{=}CLiCLi_3$, 69815-16-3.

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Absolute Configuration of Chalcone Epoxide. Chemical Correlation

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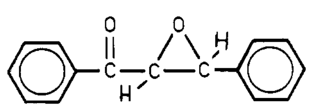
The chiral epoxychalcone 1 is one of a series of optically active epoxy ketones recently prepared via asymmetric catalysis.[1a–c] Crucial in an understanding of the mechanism of this asymmetric synthesis is the knowledge of the absolute configuration of the chiral product. Assignment of absolute configuration using the sign of the Cotton effect is unreliable in the case of 1 and its homologues since the absolute conformation is unknown. Determination of the absolute configuration by X-ray structure determination of a series of epoxy ketones has obvious inherent difficulties. The correlation of the absolute configuration of 1 described in this paper can without undue difficulty be applied to other epoxychalcones carrying like or unlike substituents in either ring.



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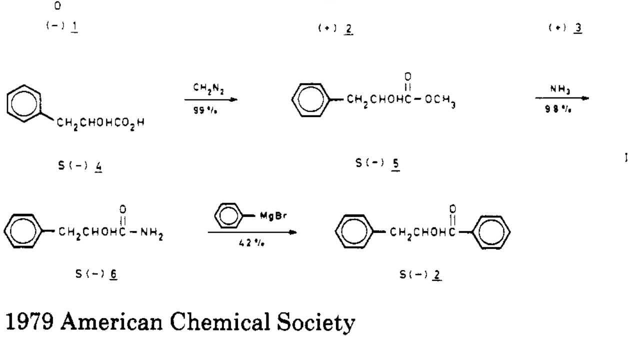
Scheme I shows the chemical correlation used. Reduction

Scheme I



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