work-up, the ether was evaporated. The residue on standing, at room temperature for 2 days, crystallized as ethyl ethanetetracarboxylate and was collected by filtration. Recrystallization was from hexane. The filtrate was subjected to distillation and separated into the following fractions; starting material and a mixture of ethene- and ethanetricarboxylates. Ethyl ethanetetracarboxylate was identified with an authentic sample by infrared and nmr spectra; the sample was prepared by the condensation of 2 moles of ethyl malonate. The identity was confirmed by a mixture melting point determination (75°).

# The Pyrolysis of Unsolvated Alkyllithium Compounds

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The rates of thermal decomposition of unsolvated ethyl-, *n*-butyl-, isopropyl-, and *sec*-butyllithium have been investigated at several temperatures in the range 82–130°. The rate constants for olefin product formation, obtained manometrically, indicate the following order of stability: ethyl ~ *n*-butyl > isopropyl > *sec*-butyl. Activation parameters in each case are *ca.* 25 kcal ($\Delta H^*$) and −10 to −16 cal deg$^{-1}$ ($\Delta S^*$). The factors which distinguish the system from the decomposition in hydrocarbon solution are discussed.

Finnegan and Kutta[2] have reported recently on the thermal decomposition of *n*-butyllithium in decane solution in the temperature range 130–150°. The reaction is catalyzed by lithium *n*-butoxide and exhibits a hydrogen isotope effect consistent with the postulated *cis*-elimination mechanism. In this paper we would like to report the results of a similar study of the thermal decomposition of some alkyllithium compounds in the pure, liquid state. An unusual feature of the reaction under such conditions, reported earlier,[3] is the rather high percentage of *cis*-2-butene obtained from the pyrolysis of pure *sec*-butyllithium. This and other aspects of the pyrolysis in the undiluted state will be discussed in the following sections.

## Experimental Section

**Reagents.**—Alkyl halides were used as purchased or after distillation. In any case they were shown to be >99% pure by vapor–liquid partition chromatography. Lithium metal was enriched with 1% sodium (Lithium Corporation of America).

**Preparation, Purification, and Pyrolysis of Alkyllithiums.**—The same procedure was used as reported previously.[3] Alkyl chlorides were used for the preparations except for ethyl bromide. In most cases the alkyllithium solutions were filtered in the drybox and concentrated to thick syrupy liquids by removal of the pentane solvent. Ethyllithium was extracted from the reaction mixture with benzene and recrystallized by partial removal of the solvent in the drybox. The material was purified by distillation into U-tubes at *ca.* 90° and 50 μ as were each of the other alkyllithiums prior to decomposition.[3] The oil bath used for heating the pyrolysis tubes was regulated to ±0.05°. Decomposition rates were followed by observing the increase in vacuum-line pressure with a cathetometer to ±0.05 mm. Products were analyzed by vapor–liquid partition chromatography as before,[3] except for the pyrolysis products of ethyllithium, for which a silica gel column at 165° was employed. Infrared spectra confirmed the gas analyses.

The relative percentages of butene isomers from the decomposition of *sec*-butyllithium (neat) were invariant during a single run. This was established by sampling and analyzing the product gases in one run at several times after initiation of the decomposition.

## Results and Discussion

**Products.**—The pyrolytic elimination of lithium hydride from alkyllithium compounds such as *n*-butyl-, ethyl-, and isopropyllithium is apparently a nonfree-

radical process[2,4] in which the olefinic product is contaminated only if the reaction is carried out under conditions in which the partial pressure of olefin is large. In that case, metallation of the olefin may occur followed by other complicating reactions resulting in a variety of products.[4a] Under the conditions employed, we find that the gaseous product consists of no less than 98% of the olefin to be expected from simple β elimination of lithium hydride. In the case of *sec*-butyllithium, the three expected olefins are found, and the distributions are shown in Table I. Until recently,

## Table I

### Product Distributions from the Pyrolysis of *sec*-Butyllithium (Neat)[a]

| Temp, °C | 1-Butene | Distribution, %<br>*cis*-2-Butene | *trans*-2-Butene |
|---|---|---|---|
| 78.4 | 34 | 51 | 15 |
| 87.0 | 32 | 53 | 15 |
| 104.0 | 29 | 54 | 17 |

[a] <1% *n*-butane was observed in each case.

these data represented the only example of an elimination reaction in which the thermodynamically less favored *cis*-2-butene predominates. More recently, Brown and Klimisch[5] have reported that the E2 elimination of alkyl tosylates in *t*-butyl alcohol may yield predominately *cis*-2 olefin if the attacking base is sufficiently bulky, *e.g.*, potassium *t*-butoxide.

The unusually high yield of *cis*-2-butene from the pyrolysis of *sec*-butyllithium may also be explained by a consideration of the steric factors associated with alkyllithium compounds. It is now well known that these species are found only in aggregates, usually tetramers or hexamers. The structures of ethyllithium[6] and methyllithium[7] have recently been determined by X-ray diffraction, and both consist of tetramers. Other workers have shown that *t*-butyllithium is tetrameric,[8] while ethyllithium[9] and *n*-butyllithium[10]

(1) National Science Foundation Research Participant, 1963–1964.

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(4) (a) K. Ziegler and H. Gellert, *Ann.*, **567**, 179 (1960); (b) D. Bryce-Smith, *J. Chem. Soc.*, 1712 (1955).

(5) H. C. Brown and R. L. Llimisch, *J. Am. Chem. Soc.*, **87**, 5512 (1965).

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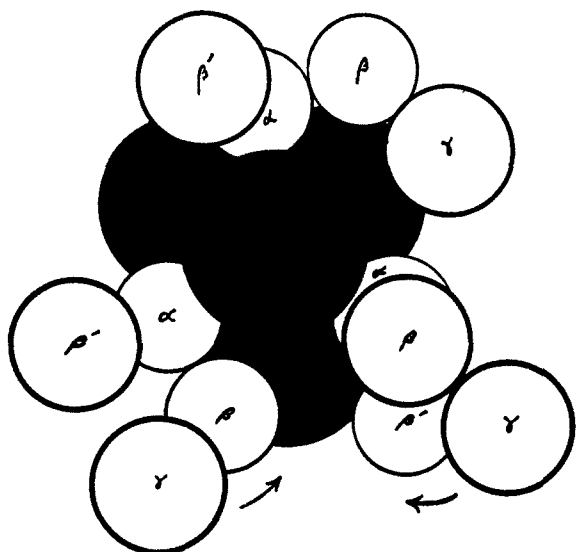(10) D. Margerison and J. P. Newport, *Trans. Faraday Soc.*, **59**, 2058 (1963).

Figure 1.—A model of the tetramer of *sec*-butyllithium showing two alkyl groups in the *cis* orientation and one in the *trans* orientation: $\alpha$ = CH, $\beta$ = CH$_2$, $\beta'$ = CH$_3$, $\gamma$ = CH$_3$. Shaded atoms represent lithium.

are hexameric in benzene. Although no data are available concerning the degree of association of alkyl-lithium compounds in the vicinity of 100°, it seems reasonable to assume that oligomers persist at such temperatures.

Using the bond angles and distances obtained from the X-ray diffraction studies,[6,7] a model of the *sec*-butyl-lithium tetramer was constructed. A view of one conformation of such a model is shown in Figure 1. The molecule may be thought of as a tetrahedron of lithium atoms (probably distorted as Dietrich observed in ethyllithium[7]) with *sec*-butyl groups coordinated to each face of the tetrahedron by four-center electron-deficient bonds. Although *trans* conformations of the *sec*-butyl groups are by no means precluded, it does appear that *cis* orientations are favored. As Figure 1 indicates, the two *sec*-butyl groups in the foreground do not interfere with each other until they are rotated into *trans* conformation. Obviously, one of the two may be rotated away from the other in a direction opposite to that of the arrows. Rotation in this sense into a *trans* conformation cannot be accomplished for each *sec*-butyl group, however, since interactions with the other alkyl groups on adjacent faces will become severe. In fact, we note that a true *trans* orientation is never allowed in a tetrameric unit of this type, since the alkyl groups are forced away from the tetrahedron of lithium atoms. Thus, an aggregate of this type appears to consist of a nucleus of metal atoms with hydrocarbon chains extending out from the nucleus. It is apparently this "micellular" nature which accounts for the solubility of alkyllithium compounds in hydrocarbon solvents.

The loss of steroselectivity upon dilution with hydrocarbon solvent is apparently due to the incipience of alkoxide catalysis.[2,11] Although the effect of alkoxides on the structure and pyrolysis of *sec*-butyllithium will be the subject of a later paper, it is appropriate to report

at this time that lithium *sec*-butoxide apparently cleaves the tetrameric structure of *sec*-butyllithium (in freezing cyclohexane) according to eq 1.[12,14] The steric

$$(RLi)_4 + 2LiOR = 2[(RLi)_2(LiOR)] \tag{1}$$

requirements of the alkoxide base apparently are less than that of a second dimer, resulting in an increase of *trans*-2 olefin upon pyrolysis.[3,11]

The rather small percentage of 1-butene observed in this work is consistent with a transition state such as I in which some carbon–carbon double-bond character is present.[2] The increase in 1-butene observed when the

$$
\begin{array}{c}
\text{H} \quad \text{H} \\
| \quad | \\
\text{CH}_3{}^{\delta-}\text{—}\overset{..}{\text{C}}\overset{..}{\text{:..}}\overset{..}{\text{C}}{}^{\delta+}\text{—CH}_3 \\
\overset{\delta+}{\text{Li}} \quad \overset{..}{\text{H}}{}^{\delta-} \\
\text{I}
\end{array}
$$

reaction is alkoxide catalyzed may be due to the over-all stabilization of I by the base. With the partial charges shown in I partially neutralized by the presence of the alkoxide, the percentage of 1-butene increases owing to the statistical factor. A study of the pyrolysis of other secondary and tertiary alkyllithiums, currently in progress, should yield more information concerning the factors which are responsible for product control in these systems.

**Kinetic Results.**—Rate constants for pyrolysis runs were evaluated from first-order Guggenheim plots which were linear in all cases.[16] Most of the runs were analyzed by the Guggenheim method in order to avoid errors due to the inaccuracies involved in measuring $P_\infty$. In cases where $P_\infty$ was carefully measured, however, both treatments gave identical results. The rate constants for product formation shown in Table II fit the following equations, obtained by a least-square analysis of the data.

$$\text{C}_2\text{H}_5\text{Li:} \quad \ln k/T = 18.85 - 1.30 \times 10^4/T \tag{2}$$

$$n\text{-C}_4\text{H}_9\text{Li:} \quad \ln k/T = 18.74 - 1.30 + 10^4/T \tag{3}$$

$$i\text{-C}_3\text{H}_7\text{Li:} \quad \ln k/T = 15.58 - 1.14 \times 10^4/T \tag{4}$$

$$s\text{-C}_4\text{H}_9\text{Li:} \quad \ln k/T = 16.49 - 1.15 \times 10^4/T \tag{5}$$

It is interesting to note that, whereas the pyrolysis of alkyllithium compounds in hydrocarbon solutions is accelerated by lithium alkoxides,[2] it is also accelerated by the removal of both solvent and alkoxides. The value of the rate constant for *n*-butyllithium decomposition obtained by Finnegan and Kutta is $7.5 \times 10^{-5}$ sec$^{-1}$ at 130° in the presence of 22% oxygen-bound lithium,[2] a factor of approximately 7 slower than that obtained at the same temperature for liquid *n*-butyllithium (Table II). The activation parameters obtained by Finnegan and Kutta appear to vary from
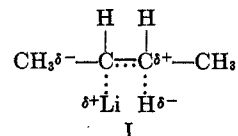
(11) H. W. Kutta, M.S. Thesis, The Ohio State University, Columbus, Ohio, June 1964. A typical olefin distribution from base-catalyzed pyrolysis of *sec*-butyllithium consists of 51% 1-butene, 22% *cis*-2-butene, and 27% *trans*-2-butene.

(12) Models of the tetramer of *sec*-butyllithium suggest that strain exists owing to the interaction of *sec*-butyl groups about the close-packed lithium atoms, as discussed above. The addition of alkoxide is evidently sufficient to destroy the tetramer rather than to replace alkyl groups with alkoxide ions, or to coordinate with the tetramer. The latter is unlikely, since no "open faces" are available in the tetrameric structure such as those in the hexamers of ethyllithium to which bases may attach.[13]

(13) T. L. Brown, J. A. Ladd, and G. N. Newman, *J. Organometal. Chem.* (Amsterdam), **3**, 1 (1965).

(14) A structure has recently been proposed[15] for the dimer–base complex which appears to be reasonable.

(15) Z. K. Cheema, G. W. Gibson, and J. F. Eastham, *J. Am. Chem. Soc.*, **85**, 3517 (1963).

(16) A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," 2nd ed, John Wiley and Sons, Inc., New York, N. Y., 1961, p 49.

TABLE II

KINETIC RESULTS FOR THE PYROLYSIS OF SOME
ALKYLLITHIUM COMPOUNDS (NEAT)

| RLi | Temp, °C | $k \times 10^5$, sec$^{-1}$ | $\Delta H^*$,[a] kcal mole$^{-1}$ | $\Delta S^*$,[a] eu |
|---|---|---|---|---|
| $C_2H_5Li$ | 98.0 | 3.5 | $26 \pm 0.6$ | $-10 \pm 1$ |
| | 107.5 | 7.7 | | |
| | 117.9 | 17.8 | | |
| | 130.2 | 58 | | |
| $n\text{-}C_4H_9Li$ | 98.9 | 3.3 | $26 \pm 0.2$ | $-10 \pm 1$ |
| | 117.8 | 18.6 | | |
| | 129.9 | 53 | | |
| $i\text{-}C_3H_7Li$ | 82.0 | 2.5 | $23 \pm 0.4$ | $-16 \pm 1$ |
| | 88.6 | 4.8 | | |
| | 98.2 | 11.0 | | |
| | 106.3 | 20.8 | | |
| $s\text{-}C_4H_9Li$ | 78.4 | 2.8 | $23 \pm 0.9$ | $-14 \pm 2$ |
| | 87.0 | 5.8 | | |
| | 104.0 | 27 | | |

[a] Tolerances on $\Delta H^*$ and $\Delta S^*$ reflect deviations of the observed rate constants from values calculated from eq 2-5.

34 to 32 kcal/mole for $\Delta H^*$ and $+5$ to $-1$ eu for $\Delta S^*$.[2] Thus, the enthalpy of the elimination process is *lowered* in the absence of alkoxide and solvent, while the entropy of activation becomes *more negative*. Although the differences in $\Delta H^*$ and $\Delta S^*$ are rather small when experimental errors are considered, the factors contributing to each seem worthy of comment.

Solvation of alkyllithium compounds by hydrocarbon solvents is not usually attended by gains or losses of large quantities of heat. Fowell and Mortimer have measured the heat of solution of *n*-butyllithium in excess petroleum ether, and report a value of only $-0.7$ kcal/mole.[17] It is obvious, therefore, that $\Delta H^*$ values for reactions in solution and in the undiluted state will differ substantially only if the enthalpies of the transition states are different. One might predict that an ionic transition state, such as I, would be of higher energy in hydrocarbon solution than in a medium consisting of liquid alkyllithium, resulting in increased stability upon dilution with inert solvents.[18]

It seems likely that pyrolysis in the presence of alkoxides involves entirely different species and perhaps a modified mechanism. Whatever the exact stoichiom-

etry of the alkyllithium–base complex,[13,15] the reactive species would be considerably more ionic in character than an uncomplexed alkyllithium oligomer, and the energy of the ground state would appear to be lower after complexation.

The observed values of $\Delta H^*$ for neat and alkoxide-complexed alkyllithium pyrolyses (26 and 32 kcal/mole, respectively) are consistent with a stabilization of the ground state upon complexation. Although no thermochemical data are available, it does appear that reaction 1 should be exothermic. However, it is also true that the energy of the transition state will be lowered by complexation, especially in a nonpolar solvent. It seems reasonable that the alkyllithium medium, being more polar, is more condusive than a hydrocarbon solvent to the formation of the polar transition state (I), resulting in a lower $\Delta H^*$ for the neat pyrolyses.

The value of $\Delta S^*$ also should be expected to change when the pyrolysis is carried out in the presence of solvent and alkoxides. Although we expect a negative value for a *cis*-elimination process, the loss of rotational freedom may not be sufficient in the transition state to account for a large decrease in entropy. In fact, the values of $\Delta S^*$ for pyrolytic *cis* eliminations of alkyl halides ($-0.3$ to $-3.5$ eu) suggest that the values obtained in this work are rather large for such processes, and that other factors may contribute.[19] A reasonable explanation may be obtained by a consideration of the ordering of the solvent during the activation process. With or without added alkoxide, the transition state should be a rather polar species, such as I, and it is expected that its formation will result in considerable ordering of the solvent. However, the alkoxide-complexed species will already be considerably polar, and the value of $\Delta S^*$ for neat pyrolyses ($-10$ to $-16$ eu) is consistent with considerable loss of freedom of the medium owing to the formation of the proposed cyclic, polar transition state.

Further investigations into the nature of alkyllithium compounds in the presence of bases and the effect of the latter on the rates and stereochemistry of organometallic reactions are in progress.

(17) P. A. Fowell and C. T. Mortimer, *J. Chem. Soc.*, 3793 (1961).

(18) After reading this manuscript, C. W. Kamienski of the Lithium Corporation of America communicated to us that the stability of *n*-butyllithium in fact is enhanced by the addition of as little as 10% hydrocarbon.

(19) C. H. Depuy and R. W. King, *Chem. Rev.*, **60**, 454 (1960).