desired rearrangement. Our efforts to find this and other "hetero" analogs of the neophyl rearrangement are therefore continuing.

### Experimental

Phenoxyacetaldehyde was prepared by the oxidation of glycerol α-phenyl ether (a gift from the Miner Laboratories, Chicago, Ill.) with lead tetraacetate according to Speer and Mahler[13] (48%, b.p. 82° at 4 mm., semicarbazone m.p. 144.5–145.5°, 2,4-dinitrophenylhydrazone m.p. 137.5–138°, in agreement with literature values[13]). The decarbonylations were performed as described in other work.[2] The reaction material was processed *via* gas chromatography (g.c.) on a Perkin-Elmer Model 154C instrument equipped with a column of Union Carbide X-525 silicone oil (15% on firebrick, 6 ft. × 0.25 in., 128°, helium carried gas pressure 20 p.s.i.g.) Assignment of structure to the products isolated by g.c. was *via* infrared and g.c. comparison with knowns. Mixing experiments indicated that about 3 mole % of benzyl alcohol and benzaldehyde each could readily be detected in the residues from decarbonylation. Carbon monoxide was collected over water and determined by absorption in cuprous sulfate–β-naphthol in a Fisher–Orsat apparatus. The molecular weights of the nonvolatile reaction residues from several runs were determined cryoscopically by the freezing point depression of benzene. Further details of the experiments performed may be found in Table I.

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[13] R. J. Speer and H. R. Mahler, *J. Am. Chem. Soc.*, **71**, 1133 (1949).

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# The Thermal Decomposition of *sec*-Butyllithium

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*Received October 6, 1964*

Although the thermal decomposition of ethyllithium and *n*-butyllithium have been reported by Ziegler[2] and Bryce-Smith,[3] no systematic investigation of the reaction has been made. In the course of such a study we have examined the products of the decomposition of *sec*-butyllithium in the pure, liquid state and in hydrocarbon solutions. The solid product has been identified as virtually pure lithium hydride. With the exception of a small amount (<1%) of *n*-butane, the organic product consists of the isomers of butene shown in Table I.

TABLE I

PRODUCT DISTRIBUTIONS FROM THE DECOMPOSITION OF *sec*-BUTYLLITHIUM

| | | Olefin products (%) | | |
|---|---|---|---|---|
| Temp., °C | Solvent | 1-Butene | *cis*-2-Butene | *trans*-2-Butene |
| 78 | Pure liquid | 34 | 51 | 15 |
| 80 | Octane (1.84 *M*) | 40 | 34 | 26 |

The unusual nature of this reaction is apparent when one examines other β-elimination reactions from *sec*-$C_4H_9X$ systems. DePuy and King[4] have tabulated the distribution of butene isomers for β-elimination reactions which have been identified as typical E1, E2, or *cis*-elimination processes. It is significant that in no case does the *cis*:*trans* ratio exceed unity, and in most cases does not deviate appreciably from the "equilibrium value" which favors the *trans* isomer by a factor of 3:1 at 25°.[4]

We are unable at this time to describe the exact mechanism of the elimination of lithium hydride from alkyllithium compounds. It is clear, however, that the preference for the *cis* isomer is indicative of unusual steric requirements in the activated complex. This may be due to the well-known association of alkyllithium compounds in both the pure state and in organic solvents. Thus the crystal structure of ethyllithium consists of tetramers,[5] while hexamers and tetramers are indicated in the vapor phase[6] and in benzene.[7] *t*-Butyllithium is tetrameric in benzene.[8]

It is conceivable, for example, that the orientation of a *sec*-butyllithium tetramer into the proper conformation for *cis* β-elimination results in the preference of *cis*-2-butene over the *trans* isomer. The increase in the percentage of the latter in octane may be accounted for by a rapid equilibrium between tetramers (or hexamers) and dimers in which the steric requirements are less rigid.

### Experimental

**Preparation and Purification of *sec*-Butyllium.**—The preparation was carried out under an argon atmosphere in a three-necked 1-l. reaction flask equipped with a Hirschberg stirrer, Friedrichs reflux condenser, and a dropping funnel. Lithium sand was prepared by rapidly shaking molten lithium metal (1.1 g.-atoms with 2% sodium,[9] Lithium Corporation of America) in mineral oil, with sodium oleate added to disperse the metal as it solidified. The metal was filtered after cooling and transferred to the flask along with 250 ml. of dry pentane (Phillip's Pure grade). *sec*-Butyl chloride (0.5 mole, Eastman Kodak, purified), mixed with 150 ml. of pentane, was placed in the dropping funnel. Approximately 10% of the chloride and a slight amount of heat were added to initiate the reaction, as evidenced by the formation of a purple-colored coating on the metal. The remainder of the halide was added dropwise over a period of 4–5 hr. After refluxing for 2 hr. longer, the reaction vessel was taken into a drybox and the mixture was filtered. The pentane solution of *sec*-butyllithium was concentrated by vacuum distillation.

Approximately 15 ml. of concentrated *sec*-butyllithium solution was transferred to a flask while still in the drybox. The flask was connected through a U-tube trap to a vacuum stopcock. The apparatus was removed from the drybox and attached to a high-vacuum line. After pumping on the system to remove the last traces of solvent, the flask was heated in a mineral oil bath at approximately 90°. The *sec*-butyllithium distilled and collected in the U-tube which was cooled with liquid air. *sec*-Butyllithium distils easily under these conditions yielding a clear, viscous liquid at room temperature. The residual pressure in the system was approximately 50 μ. The distillation flask was then sealed off, leaving the U-tube containing the *sec*-butyllithium on the vacuum line.

**Thermal Decomposition of *sec*-Butyllithium.**—For the decomposition of the pure liquid a thermoregulated oil bath at the desired temperature (±0.05°) was raised around the U-tube, and decomposition was followed manometrically. When the decomposition was carried out in octane solution the alkyllithium compound was transferred after distillation to the drybox where the solution was prepared. After analysis by the Gilman double titration method,[10] an appropriate amount of the solution was placed in a boiling flask with condenser attached.[11] The flask was transferred to the vacuum line and the decomposition was carried

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[1] National Science Foundation Research Participant, 1963–1964.

[2] K. Ziegler and H. Gellert, *Ann.*, **567**, 179 (1960).

[3] D. Bryce-Smith, *J. Chem. Soc.*, 1712 (1955).

[4] C. H. DePuy and R. W. King, *Chem. Rev.*, **60**, 431 (1960).

[5] H. Dietrich, *Acta Cryst.*, **16**, 681 (1963).

[6] J. Berkowitz, D. A. Bafus, and T. L. Brown, *J. Phys. Chem.*, **65**, 1380 (1961).

[7] T. L. Brown and M. T. Rogers, *J. Am. Chem. Soc.*, **79**, 1859 (1957).

[8] M. Weiner, G. Vogel, and R. West, *Inorg. Chem.*, **1**, 654 (1962).

[9] C. W. Kamienski and D. L. Esmay, *J. Org. Chem.*, **25**, 1807 (1960).

[10] H. Gilman and A. H. Haubein, *J. Am. Chem. Soc.*, **66**, 1515 (1944).

[11] D. F. Detar, *ibid.*, **78**, 3911 (1956).

out as described above. Tap water was circulated through an ice bath and then through the condenser during the decomposition to prevent the distillation of the solvent.

**Analysis of Gaseous Decomposition Products.**—After completion of a decomposition run, the gaseous product was collected in a trap at −70° and subsequently transferred to a second vacuum line in series with a gas sample valve and a gas chromatograph. Analysis of the decomposition product was made on a 20 ft. × 0.25 in. column with 20% didecyl phthalate substrate on Chromasorb-P treated with hexamethyldisilazine. Peaks were identified by comparison of retention times with standards supplied by The Matheson Company. Quantitative analysis of the decomposition products was made by measuring the area under each peak, with appropriate thermal conductivity corrections. A synthetic mixture containing known partial pressures of the isomeric butenes was prepared and used to calibrate the detector. The temperature and the flow rate were 41° and 4.7 cc./min. The retention times of 1-butene, *cis*-2-butene, and *trans*-2-butene are 3.9, 5.7, and 5.1 min., respectively, under these conditions, which provided base-line separation. The percentages of products listed in Table I are within ±1% of all runs analyzed.

Infrared spectra from 2–16 μ of the decomposition products and a synthetic mixture prepared from the pure olefins in the appropriate amounts were essentially the same. The spectra were taken on a Perkin-Elmer 237 infrared spectrophotometer in a 10-cm. path-length cell.

**Acknowledgment.**—The present study was supported by a grant from the Robert A. Welch Foundation and by the National Science Foundation Research Participation Program for High School Teachers. We are grateful to Charles Ludeman for the chromatographic analyses.

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## Trimerization of Isocyanates by Trialkylantimony and -arsenic Oxides

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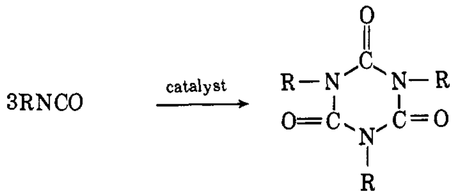
*Received October 5, 1964*

While investigating the properties of the group Va organometallics, it was noted that tri-*n*-butylantimony and triisobutylarsenic oxides, among others, were highly efficient catalysts for the trimerization of isocyanates to trialkyl and triaryl isocyanurates. With 2 mole % of either oxide, for example, *m*-chlorophenyl and phenyl isocyanates could be trimerized in bulk in 94–100% yields at room temperature over periods of time ranging from 15 min. to 1 hr.[1]



Trimers of the less reactive *o*-methoxyphenyl and ethyl isocyanates were obtained in 95 and 77% yields, respectively, by heating at 80° in the presence of tri-*n*-butylantimony oxide. The products obtained from both toluene and hexamethylene diisocyanates at room temperature were infusible, cross-linked resins with varying amounts of unreacted isocyanate. With dimethyl sulfoxide as a solvent, no unreacted isocyanate was noted in the latter. Trimers of *m*-nitrophenyl, *m*-chlorophenyl, and phenyl isocyanates were obtained in 71, 97, and 96% yields, respectively, at room temperature in heptane or benzene.

A variety of group Va oxides and esters were evaluated as trimerizing agents (Table I). Along with the oxides, tri-*n*-butylantimony diethoxide (expt. 1) and triisobutylantimony diacetate (expt. 2) were also found to be effective trimerizing agents. Noteworthy is the ability of triphenylarsenic oxide to trimerize methyl isocyanate and to catalyze both trimer (~30%) and carbodiimide formation with *m*-chlorophenyl isocyanate (expt. 3). This oxide had previously been reported to catalyze carbodiimide formation with phenyl and *sec*-octyl isocyanates.[2] The more basic trialkylantimony and -arsenic oxides, as well as isocyanates more susceptible toward nucleophilic attack, appear to enhance trimer formation.

Table I

Activity of Trimerizing Agents

| Expt. no. | Catalyst[a] | Results |
|---|---|---|
| 1 | $(n\text{-Bu})_3\text{Sb(OEt)}_2$ | Phenyl and *m*-chlorophenyl isocyanates trim. in 1 hr. at 28° |
| 2 | $(i\text{-Bu})_3\text{Sb(OAc)}_2$ | *m*-Chlorophenyl isocyanate trim. in 4 days at 28° |
| 3 | $(\text{Ph})_3\text{AsO}$ | Methyl isocyanate trim. in 15 min. at 28°; *m*-chlorophenyl isocyanate yielded trimer (~30%) and carbodiimide (~70%) |
| 4–5 | $(n\text{-Bu})_3\text{Sb}$,<br>$(n\text{-Bu})_3\text{SbCl}_2$ | No trim. of *m*-chlorophenyl isocyanate noted in 10 days at 28° |

[a] 2 mole %.

Addition of a slight excess of phenyl isocyanate to tri-*n*-butylantimony oxide under anhydrous conditions yielded some triphenyl isocyanurate along with a nondistillable oil believed to be a stoichiometric complex of the oxide and isocyanate. This suggests that an "isocyanate–oxide" complex originally formed in the trimerization reacts with excess isocyanate to generate the trimer.

### Experimental

**Materials.**—Isocyanates were purchased from either Eastman Chemical Co. or Matheson Coleman and Bell and were used as received. Hexamethylene diisocyanate was obtained from Ott Chemical Co. and was used as received. Triphenylarsenic oxide (Eastman) was recrystallized from heptane (m.p. 195–196°). Tri-*n*-butyl- and triisobutylantimony, as well as triisobutylarsenic, were prepared in this laboratory by a previously described procedure.[3] Their dichlorides were also prepared by a previously described procedure.[4]

**Tri-*n*-butylantimony Oxide.**—Tri-*n*-butylantimony oxide was prepared in 92% yield by the method of Dyke and Jones.[4]

**Triisobutylarsenic Oxide.**—This oxide was obtained in 94% yield by the caustic hydrolysis of triisobutylarsenic dichloride. After recrystallization from heptane, the product was obtained as white crystals with m.p. 158–160°.

*Anal.* Calcd. for $C_{12}H_{27}AsO$: C, 54.8; H, 10.6; As, 28.5. Found: C, 54.4; H, 10.0; As, 27.7.

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(1) By contrast, triphenyl isocyanurate is conventionally prepared by heating phenyl isocyanate for 25 hr. at 125° in the presence of ethanol and N-methylmorpholine: see I. C. Kogon, *J. Am. Chem. Soc.*, **78**, 4911 (1956).

(2) J. J. Monagle, *J. Org. Chem.*, **27**, 3851 (1962).

(3) W. Stamm and A. Breindel, *Angew. Chem.*, **76**, 99 (1964); *Angew. Chem. Intern. Ed. Engl.*, **3**, 66 (1964).

(4) W. J. C. Dyke and W. J. Jones, *J. Chem. Soc.* (London), 1921 (1930).