Vapour Synthesis of Polylithium Compounds: the Effect of Halogens in Activating the Carbon–Hydrogen Bond

By L. G. SNEDDON and R. J. LAGOW

(*Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts* 02139)

Summary Reaction of lithium vapour with partially halogenated propanes at 800—1000 °C followed by hydrolysis with D_2O in tetrahydrofuran indicates that saturated and unsaturated perlithiated C_2 and C_3 compounds and probably CLi_4 are formed.

RECENT studies[1] have demonstrated that the reaction of excess of lithium vapour at 800—1000 °C with perhalogenated organic compounds led to the first perlithiated alkanes: tetralithiomethane and hexalithioethane. We now report that perlithio products may also be obtained by reaction of lithium vapour with only partially halogenated hydrocarbons. Alkanes in their ground vibrational states do not react with lithium vapour.[2] Probably the very exothermic reaction of lithium at the halogenated sites produces vibrationally excited carbon–hydrogen bonds which react with lithium vapour.

The reaction of lithium vapour with various partially halogenated propanes was carried out as described previously.[2] In a typical reaction, *ca.* 5 g of lithium was vaporized during 30—35 min and allowed to react with 0·50 g of 1-bromopropane. The reaction vessel was then opened under argon and the brittle grey solid was removed. This solid was then hydrolysed in tetrahydrofuran solution at −10 °C with D_2O in a vacuum line.

The volatile products of the hydrolysis were then separated by vacuum line fractionation. The material passing a −128 °C trap and stopping in a −196 °C trap (the C_2–C_3 hydrocarbons) was then analysed by g.l.c. using a 10 m × $\frac{1}{4}$ in Durapak phenyl isocyanate on Porasil C column. The individual compounds were identified by comparison of their retention times with those of known samples. The mass and i.r. spectra of the C_2–C_3 fraction indicated that the products appear to be totally deuteriated with only a small

TABLE

	$CH_2ClCH_2CH_2Cl$	$CH_2ClCHClCH_2Cl$	$CH_3CH_2CH_2Br$	$CH_3CHBrCH_3$
CD_3CD_3	3·9%	4·5	10·3	6·9
$CD_2{=}CD_2$	0·2	0·6	2·6	0·9
$CD_3CD{=}CD_2$	12·7	23·6	7·9	1·4
$CD_3CD_2CD_3$	9·2	9·1	19·8	16·0
$CD_3C{\equiv}CD$	0·6	1·3	4·4	0·9
$CD_2{=}C{=}CD_2$ ..	11·9	0	0	2·8

amount of partially deuteriated species. The total yield of the C_2–C_3 fraction varied greatly, ranging from 45 to 11% in different runs with 1-bromopropane. The other products which were not identified were probably CD_4 (not trapped at −196 °C) and higher-molecular weight material resulting from polymerization of the perlithio-propanes. Yields of the C_2–C_3 fraction in other reactions were: from 2-bromopropane, 26 and 29%; 1,2,3-trichloropropane, 39 and 23%; and 1,3-dichloropropane, 38·6%.

Yields of the individual products in the C_2–C_3 fractions (based on the halogenated propanes consumed) are given in the Table. These data reveal that both fragmentations to give C_2Li_6, C_2Li_4, and presumably CLi_4 and eliminations to give C_3Li_6 and C_3Li_4 are competing against the reaction to give perlithiopropane C_3Li_8. It is significant that the highest yields of C_3Li_8 were obtained from those propanes containing only one halogen atom, while when more than one halogen atom was present, the major product was perlithiopropene. This result suggested that it might be possible to synthesize larger perlithiohydrocarbons by using only a few selectively placed halogens to activate the molecule.

As a test of this hypothesis we also studied the reaction of lithium vapour with several partially halogenated butanes. The reactions, hydrolysis with D_2O, and separation of the products were carried out as described above, but in contrast to the result with the partially halogenated propanes, no perlithiobutanes were obtained. For the reaction of 2-chlorobutane with lithium vapour, 16·2% C_4H_9D and no perdeuteriated butane were obtained, the remaining observed products being C_3D_4 and C_2D_4. Similar results were obtained from the reaction with 2-chloroisobutane and 1-chlorohexane. In each case only the monosubstituted derivative and fragmentation products were obtained. The reaction of 1,4-dichlorobutane with lithium vapour gave only fragmentation products and no disubstituted derivatives. This result is consistent with the higher yield of C_3Li_8 obtained from 1-bromopropane. The reaction of lithium with 1,5-dichloropentane or 1,6-dichlorohexane might be expected to produce complete lithium substitution on the alkane.

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