# Reaction of Lithium Atoms at 800 °C with Chlorocarbons; A New Route to Polylithium Compounds

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*Summary* Reaction of excess of atomic lithium at 800—1000 °C with carbon tetrachloride and hexachloroethane produces tetralithiomethane and hexalithioethane, the first examples of perlithiated alkanes; the new compound tetralithioethylene is also produced in the first reaction.

THE preparation of polylithium compounds from chlorocarbons in solution has been precluded by formation of reactive intermediates, such as dichlorocarbene, which react with the solvent. We have used a large excess of lithium vapour under high vacuum conditions to prevent reaction of intermediates with species other than atomic lithium.

Lithium was vaporised in a stainless steel reactor with a stainless steel Knudsen cell heated resistively, and the chlorocarbon vapour, at room temperature, was admitted through a tube above the Knudsen cell orifice. Products were collected on liquid nitrogen-cooled coldfinger.

A large excess (9—11 g) of high-purity lithium metal was vaporized during 30—45 min and allowed to react with *ca.* 1·5 g of $CCl_4$. The product was a brittle grey-white solid which was extremely sensitive to air and moisture and, in contrast to lithium, exploded violently on contact with water. It was removed under argon and hydrolysed at 0 °C with $D_2O$ in a vacuum line. The products were collected, expanded into a gas-phase molecular weight apparatus for a mass balance measurement and then recondensed.

The total yield of products varied from 95 to 99% (based on $CCl_4$). The products were then separated, collected, and characterized with a high-resolution double-focussing C.E.C.-21-110B mass spectrometer and again on a Hitachi RMU-6 mass spectrometer, both at 70 eV. Strong parent ions were observed for $CD_4^+$ (20·05639), $C_2D_4^+$ (32·05640), and $C_2D_2^+$ (28·02819). The yield of $CD_4$ ranged from 10 to 18% based on $CCl_4$ [average *ca.* 14% (1 mmol)]. The average

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yield of $C_2D_4$ was 61% (*ca.* 3·4 mmol) and the average yield of $C_2D_2$ was 20% (*ca.* 1·1 mmol). A derivative of the reactive solid was formed with neat chlorotrimethylsilane, and a small amount of solid was recovered for spectroscopic work. Its n.m.r. spectrum showed a singlet at $\tau$ 9·80 ($CHCl_3$ internal standard), in agreement with the spectra reported for $C(SiMe_3)_4$.[1] The mass spectrum showed a parent peak at 304 and a $P-CH_3$ peak [$C(SiMe_3)_4$] with the appropriate isotope distribution for silicon. $C_2(SiMe_3)_4$ was also produced and was characterized by a parent peak at 316 with a silicon isotope pattern and a singlet in its n.m.r. spectrum.

Under similar experimental conditions, *ca.* 1·5 g of hexachloroethane was allowed to react with excess of lithium vapour. The very reactive solid was then hydrolysed with $D_2O$ and handled similarly to the $CCl_4$ product. In several experiments the hydrolysis product was entirely $C_2D_6$, and the mass spectra contained the parent ion $C_2D_6^+$ (36·08444), and ions for $C_2D_5^+$ (34·07010), $CD_3^+$ (18·02294), and $CD_2^+$ (16·02842). The yields averaged 80% based on $C_2Cl_6$ (*ca.* 5·1 mmol of $C_2D_6$). In other experiments where it appears that the lithium vapour concentration was less, 10—20% of $C_2D_4^+$ and $C_2D_2^+$ were observed and the total yield of deuteriated products was still *ca.* 80%. The solid was also treated with neat $ClSiMe_3$ and a small amount of solid product was recovered. It showed a strong mass spectral peak at *m/e* 231 [$C(SiMe_3)_3^+$] with the appropriate silicon isotopic pattern and a singlet in the SiMe region in its n.m.r. spectrum. It is not surprising that no parent ion was observed for $C_2(SiMe_3)_6$ owing to the high degree of steric interference of the trimethylsilyl groups.

If the lithium concentration is reduced by a factor of two during the reaction with $CCl_4$ or $C_2Cl_6$, the products are more complex and a number of high molecular weight products are observed after deuteriation. Most are unsaturated species such as $C_3D_4$ and some contain as many as six carbon atoms. Presumably these result from recombination of reactive species such as dilithiocarbene instead of further reaction with lithium.

The reaction of lithium vapour with chlorocarbons at high temperatures appears to provide a general route to the little known polylithiocarbons. Present work is directed toward finding satisfactory solvents for these interesting species.

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[1] R. L. Merker and M. T. Scott, *J. Organometallic Chem.*, 1965, **4**, 98.