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ALKYLATION OF SCHLEYER'S LITHIOCARBON C_4Li_4 BY METHYL IODIDE

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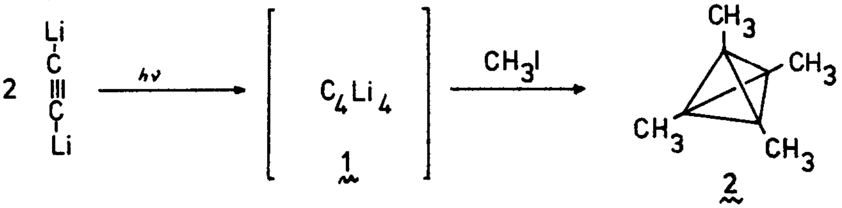
Summary - Alkylation of lithiocarbon C_4Li_4 gives the hydrocarbon C_8H_{12} to which the structure of tetramethyltetrahedrane has been ascribed.

The problem of tetrahedrane has fundamental importance from the theoretical point of view. Inspite of fairly extensive literature (see reviews [1]) the attempts at synthesis of this unique structure remains unsuccesful until recent times. In 1978 there appeared two preliminary communications claiming success with this long pursued goal [2,3]. G.Maier and co-workers [2] described the synthesis of tetra-tert-butyltetrahedrane starting from the corresponding homotetrahedranone. P.von R.Schleyer and co-workers described the synthesis of tetralithium derivative of tetrahedrane (1, C_4Li_4) by photolysis of LiC≡CLi [3]. The idea for that synthesis came as the result of the extensive theoretical investigation of polylithiocarbons and related compounds by the group of P.von R.Schleyer and J.Pople [4].

In the course of our study of cage compounds [5], it occured to us that compound 1 could, in principle, be used as a starting material for the synthesis of tetrahedrane derivatives. To prove this idea, we investigated the alkylation of 1 by methyl iodide, using the folowing procedure : 10 ml of CH_3I was added dropwise (20 min) to a stirred suspension of solid 1 (prepared from 0.25 mol of Li in accordance with Ref.3) in 100 ml of NH_3. The mixture was kept at room temperature to evaporate the NH_3, diluted with 250 ml of water and extracted with pentane. After the careful evaporation of pentane, 0.2-0.5g of colourless residue was obtained, representing the mixture of pentane and new compound (2:1).

The IR spectrum of the mixture contained the bands 1380, 1465, 2863 and 2935 cm^{-1}. The ^1H NMR spectrum of the mixture showed a new signal at δ 1.26 ppm, which is absent in a pure pentane.

The ^{13}C NMR spectra of the mixture showed two new peaks at 29.51 ppm(quaternary carbon atom) and at 29.46 ppm (CH_3 group); the assignment has been made by off-resonance. The mass-spectra (both electron and field ionization) of this mixture has shown peaks with m/e 108(M), 107(M-1) and 92($M-CH_3-H$). These data forced us to conclude that alkylation of **1** by methyl iodide leads to the formation of tetramethyltetrahedrane **2**[6]. This work demonstrate,in principle,a promising synthetic way to obtain the tetrahedrane structure via tetralithium derivative **1**; this investigation is now actively underway.



References and notes

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[6] Electron diffraction experiments as well as attempts to obtain low temperature X-ray diffraction data are in progress.

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