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# CHEMISTRY

T. V. TALALAEVA, A. N. RODIONOV,

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## Abstract

## Full Text

### CHEMISTRY

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## SYNTHESIS OF ISOTOPICALLY SUBSTITUTED ORGANOLITHIUM COMPOUNDS

In connection with the study of the structure of organolithium compounds, we were interested in the synthesis of isotopically substituted compounds of ethyllithium and phenyllithium. The synthesis of samples of isotopically substituted ethyllithium was carried out starting from the corresponding deuterated derivatives of ethyl chloride:  $\alpha$ -dideuteroethyl chloride,  $\beta$ -trideuteroethyl chloride, and pentadeuteroethyl chloride, with a deuterium content of 93-99% relative to the calculated amount (<sup>1</sup>, <sup>2</sup>). Ethyllithium with the isotope lithium-6 is obtained from ethyl chloride and lithium containing 92.5% lithium-6.

**Table 1**

Starting compounds	Amount of D, or Li-6 in starting compound, %	Compound RLi obtained	Yield of cryst. compound RLi, %	Li or Li-6, % calculated	Li or Li-6, % found	Valence vibrations of C-H or C-D groups according to IR spectra, cm <sup>-1</sup>
C <sub>2</sub> H <sub>5</sub> Cl + Li	—	C <sub>2</sub> H <sub>5</sub> Li	45	19.31	19.18; 19.25	2952, 2920, 2880, 2846, 2786, 2760
C <sub>2</sub> H <sub>5</sub> Cl + Li-6	92.5	C <sub>2</sub> H <sub>5</sub> Li-6	40	17.14	16.83; 16.89	2955, 2930, 2875, 2840, 2795, 2750

Starting compounds	Amount of D, or Li-6 in starting compound, %	Compound RLi obtained	Yield of cryst. compound RLi, %	Li or Li-6, % calculated	Li or Li-6, % found	Valence vibrations of C-H or C-D groups according to IR spectra, $\text{cm}^{-1}$
$\text{CH}_3\text{CD}_2\text{Cl}$ + Li	99	$\text{CH}_3\text{CD}_2\text{Li}$	30	18.29	18.30; 18.35	2950, 2930, 2870, 2138, 2092, 2040
$\text{CD}_3\text{CH}_2\text{Cl}$ + Li	95	$\text{CD}_3\text{CH}_2\text{Li}$	35	17.82	17.56; 17.53	2811, 2781, 2760, 2215, 2164, 2040
$\text{C}_2\text{D}_5\text{Cl}$ + Li	93	$\text{C}_2\text{D}_5\text{Li}$	40	16.95	16.66; 16.68	2186, 2150, 2120, 2095, 2025
$\text{C}_6\text{H}_5\text{Br}$ + $\text{C}_4\text{H}_9\text{Li}$	—	$\text{C}_6\text{H}_5\text{Li}$	85	8.27	8.15; 8.04 *	3065, 3055, 3040, 2960 (C -H); 1600, 1478, 1008 (ring vibra- tions)

Starting compounds	Amount of D, or Li-6 in starting compound, %	Compound RLi obtained	Yield of cryst. compound RLi, %	Li or Li-6, % calculated	Li or Li-6, % found	Valence vibrations of C-H or C-D groups according to IR spectra, $\text{cm}^{-1}$
$\text{C}_6\text{H}_5\text{Br}$ + $\text{C}_4\text{H}_9\text{Li-6}$	92.5	$\text{C}_6\text{H}_5\text{Li-6}$	70	7.23	7.36; 7.47 *	3050, 3035, 2955 (C-H); 1595, 1478, 1008 (ring vibrations)
$\text{C}_6\text{D}_5\text{Br}$ + $\text{C}_4\text{H}_9\text{Li}$	94	$\text{C}_6\text{D}_5\text{Li}$	70	7.80	7.92; 7.87 *	2276, 2256, 2205, 2175 (C-D); 1590, 1014 (ring vibrations)
$\text{C}_6\text{D}_5\text{Br}$ + $\text{C}_4\text{H}_9\text{Li-6}$	94-D	$\text{C}_6\text{D}_5\text{Li-6}$	69	6.82	6.64; 6.65 *	2278, 2254, 2204, 2179 (C-D); 1590, 1014 (ring vibrations)

Starting compounds	Amount of D, or Li-6 in starting compound, %	Compound RLi obtained	Yield of cryst. compound RLi, %	Li or Li-6, % calculated	Li or Li-6, % found	Valence vibrations of C-H or C-D groups according to IR spectra, $\text{cm}^{-1}$
$n\text{-CH}_3\text{C}_6\text{H}_4\text{BLi-6}$ + $\text{C}_5\text{H}_{11}\text{Li-6}$	92.5 – 92.5	$n\text{-CH}_3\text{C}_6\text{H}_4\text{Li-6}$	75	6.19	6.07; 6.22 *	–

\* Lithium analysis with allowance for the impurity of lithium bromide.

All reactions are carried out in an atmosphere of pure argon. Benzene for cryoscopy is used after being kept over sodium under argon. Solutions and solvents are either siphoned under argon pressure or transferred with pipettes filled with argon (2). From transparent and colorless benzene solutions of isotopically substituted ethyllithium, obtained in 75-90% yield, crystals of ethyllithium are isolated (yield 42-30%). For analysis, a weighed portion of ethyllithium sealed under argon in an ampoule is decomposed with alcohol in an atmosphere of argon, under an inert solvent; water is then added, and the solution is titrated with 0.1 *N* sulfuric acid with phenolphthalein, without interrupting the flow of argon (3). The procedure for the analysis of samples of deuterated ethyllithium was preliminarily

has been repeatedly checked on samples of ordinary crystalline ethyllithium. It was found that, with careful work under argon and with the most complete possible exclusion of access by moisture and air, reliable analytical results can be obtained. The same results can be obtained by using the method of double titration with benzyl chloride, observing the precautions indicated for the analysis of solutions of *n*-butyllithium (3,4); otherwise erroneous results may be obtained, or the sample under investigation may decompose and become contaminated during the analysis (3,4). Samples of aromatic lithium compounds with the lithium-6 isotope are isolated in hexane or benzene by an exchange reaction (5) with a solution of *n*-butyllithium or *n*-amyllithium containing the lithium-6 isotope (92.5% isotope). Starting from pentadeuterobenzene, under the same conditions, completely deuterated phenyllithium is obtained. The deuterium content in the starting bromobenzene is 94.5%. The crystalline aromatic compounds obtained contain 5-10% lithium bromide. Table 1 gives the analytical

results after subtracting the lithium bromide content. Additional data characterizing the synthesized isotope-substituted organolithium compounds by the valence vibrations C–H and C–D were obtained from IR spectra (<sup>6</sup>); for the aromatic compounds, ring vibrations are also given.

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*Note: Figure translations are in progress. See original paper for figures.*

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