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POLYHALO-ORGANOMETALLIC AND -ORGANOMETALLOIDAL COMPOUNDS XXIX*. LITHIATION OF 1,2,3-TRICHLORO- AND 1,2,3,4-TETRACHLORO-BENZENES. ORGANOSILICON DERIVATIVES

IONEL HAIDUC** and HENRY GILMAN
Department of Chemistry, Iowa State University, Ames, Iowa 50010 (U.S.A.)

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Recently, several polychlorosubstituted benzenes were metalated with n-butyllithium, to give haloaromatic organolithium derivatives. Thus, pentachlorobenzene[2] and 1,2,4,5-tetrachlorobenzene[2] gave pentachlorophenyllithium, 1,2,4,5-tetrachloro-3,6-dilithio- and 1,2,4,5-tetrachloro-3-lithiobenzene[2]. Also, 1,3,5-trichlorobenzene can be metalated with n-butyllithium[3] to give mono-, di-, and tri-substituted lithio derivatives. In all cases, the replacement of the aromatic hydrogen (metalation) is the predominant reaction and halogen–metal exchange was observed only to a very limited extent with pentachlorobenzene[2].

We have found that in the reaction of 1,2,3-trichlorobenzene and 1,2,3,4-tetrachlorobenzene with n-butyllithium in tetrahydrofuran (THF) at low temperature, both halogen–metal exchange and hydrogen replacement take place concurrently, the former being predominant. The organolithium compounds thus formed were derivatized *in situ* with chlorotrimethylsilane and other chlorosilanes***; the proton magnetic resonance afforded very ready identification of the compounds.

In the reaction of 1,2,3-trichlorobenzene with n-butyllithium (in 1:1 molar ratio), followed by derivatization with chlorotrimethyl silane, two organosilicon compounds were isolated and identified: 1,3-dichloro-2-trimethylsilylbenzene (I) (b.p. 52°/0.25 mm, n_D^{20} 1.5427) and 1,2,3-trichloro-5-trimethylsilylbenzene (II) (b.p. 68°/0.25 mm, n_D^{20} 1.5530), which were formed according to the following scheme:

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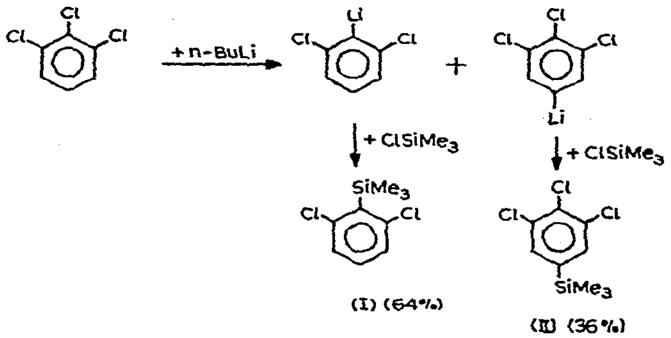
* For Part XXVIII see ref. 1.

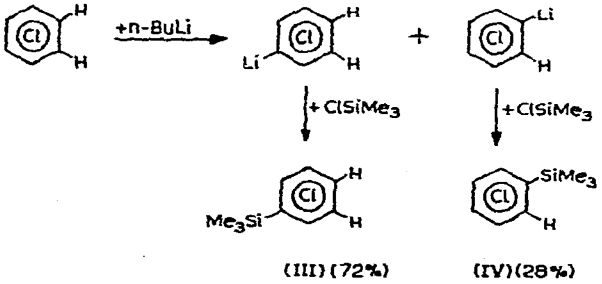
** On leave of absence (February–September, 1968) from the permanent address: Babes-Bolyai University, Chemistry Department, Cluj (Romania).

*** For references to the reactions of organolithium reagents with chlorosilanes, see ref.4.



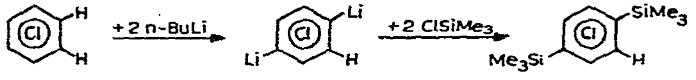
The compound, formed via halogen–metal exchange was the predominant component (about 64%) of the reaction product. The compound II, formed via metalation represented about 36% of the reaction product isolated. The proton magnetic resonance spectrum (PMR) of (I) shows a singlet at $\tau = 9.51$ ppm (Si–CH_3 protons) and a multiplet centered at $\tau = 3.0$ ppm (aromatic protons), with an integrated peak area ratio of 9:3 (3:1). The PMR spectrum of (II) consists of a singlet at $\tau = 9.66$ ppm (Si–CH_3 protons) and a singlet at $\tau = 2.85$ ppm (aromatic protons), with an integrated area ratio of 9:2 (4.5:1). Further structural evidence was obtained by alkaline cleavage of $SiMe_3$ groups (with a 5% aqueous solution of NaOH in refluxing THF) to give 1,3-dichlorobenzene (from I) and 1,2,3-trichlorobenzene (from II).

In a similar reaction of 1,2,3,4-tetrachlorobenzene with n-butyllithium (in 1:1 molar ratio), followed by *in situ* derivatization with chlorotrimethylsilane, two compounds were isolated: 1,2,4-trichloro-3-trimethylsilylbenzene (III) (b.p. 83–85°/0.4 mm) and 1,2,3,4-tetrachloro-5-trimethylsilylbenzene (IV) (b.p. 97°/0.4 mm, m.p. 47–48°), in accordance with the following scheme (only substituents other than chlorine are indicated):



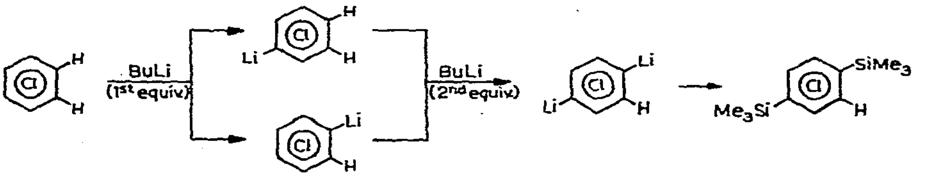
The PMR spectrum of (III) is of AB type in the region characteristic for aromatic protons, showing two doublets centered at $\tau = 2.70$ ppm and $\tau = 2.92$ ppm (from spin–spin coupling of two *ortho* hydrogens, with $J(HH) = 8$ cps) and a singlet at $\tau = 9.50$ ppm (Si–CH_3 protons). The integrated peak area ratio is 9:2 (4.5:1). Compound IV exhibits a simple PMR spectrum, consisting of a singlet at $\tau = 9.62$ ppm (Si–CH_3 protons) and a singlet at $\tau = 2.63$ ppm (aromatic proton) with an integrated area ratio of 9:1. The relative proportions of the two products are those indicated in the scheme, again showing that the halogen–metal exchange is predominant over the metalation. Alkaline cleavage gives 1,2,4-trichlorobenzene (from III) and 1,2,3,4-tetrachlorobenzene (from IV), respectively.

When 1,2,3,4-tetrachlorobenzene was treated with two moles of n-butyllithium, the main product isolated was 1,2,4-trichloro-3,6-bis(trimethylsilyl)benzene (V) (78% of the reaction product, b.p. 102–103°/0.25 mm, n_D^{20} 1.5490), along with some (III) (13%) and a minor amount of (IV) (2%). The PMR spectrum of (V) shows peaks at $\tau = 9.50$ ppm and $\tau = 9.63$ ppm (Si–CH_3 in two different environments) and a peak at $\tau = 2.73$ ppm (aromatic proton), with an integrated area ratio of 18:1. Compound V is interesting because it is the result of halogen–metal and hydrogen–metal exchange in the same molecule:



(V)

while in the first two reactions described above the halogen–metal and hydrogen–metal exchange occurred in two different molecules. It appears that the dilithiation which finally gives (V) is a stepwise process, with both monolithium derivatives formed in the first step giving the same dilithio compound:



No evidence was obtained for any replacement of a second aromatic hydrogen by lithium.

Compound V was alternatively prepared in good yield by metalation of (III) with n-butyllithium in THF at low temperature, followed by derivatization with chlorotrimethylsilane.

It seems worth mentioning that in all halogen–metal exchanges observed here, a middle chlorine (having two Cl neighbors) rather than a marginal one (having an H neighbor) in the parent polyhalobenzene undergoes the exchange. with the insertion of the lithium between two chlorine atoms.

The experimental details and the products obtained by derivatizing the organolithium compounds reported here with other chlorosilanes will be described in the full paper to be published at a later date.

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