Relative reactivities of organic Group IVB lithium compounds

I. Metalation of fluorene

Metalations of fluorene by Ph_3MLi ($M = Si, Ge, Sn, Pb$) reagents have been reported[1], and the reaction has served as a basis for estimating the relative basicities of the Ph_3M anions. An extension of that study has now included a wider variety of silyllithium reagents, which are shown in Table 1. It was expected that the reagents, methyldiphenylsilyllithium and dimethylphenylsilyllithium, would be more reactive than triphenylsilyllithium; therefore, reaction with the latter reagent was run under milder conditions than those previously used[1]. It was discovered in the first experiment that the metalation of fluorene by triphenylsilyllithium is a somewhat more facile reaction than had been indicated in the earlier study. Carbonation of the reaction mixture after 4 h at room temperature gave a 97 % yield of fluorene-9-carboxylic acid; whereas, the previously reported 18 h reaction period had given a 69 % yield[1]. Even milder conditions were employed for the comparative studies given in Table 1, and triphenylgermyllithium was included with the hope of differentiating its metalating ability from that of triphenylsilyllithium.

The results indicate the following series of decreasing reactivity: $MePh_2SiLi \geqq Me_2PhSiLi > Ph_3GeLi > Ph_3SiLi \approx Ph_3SiSiPh_2Li$. The order observed for methyldiphenylsilyllithium and dimethylphenylsilyllithium is not that which would be expected from a consideration of the electronic effects of methyl and phenyl groups. That the order is, in fact, real, is indicated in two other studies of the relative reactivities of the three reagents; namely, displacement of chloride from *n*-butyl chloride[2] and cleavage of tetrahydrofuran[3]. The slightly greater reactivity of triphenylgermyllithium over triphenylsilyllithium, seen in the present reactions, is not evident in the study of chloride displacement[2]; in fact, the opposite order is observed.

Difficulty was encountered in reproducing the yield from metalations with pentaphenyldisilanyllithium. Definitive results were not expected, since the reagent is prepared[4] by cleavage of decaphenylcyclopentasilane[5] with an excess of triphenylsilyllithium. A 75–79 % yield of pentaphenyldisilane was obtained[4] upon hydrolysis of the reaction mixture. In several attempts to repeat the preparation, the best yield of pentaphenyldisilane obtained upon hydrolysis was 63 %. It is likely that the solutions used for metalation of fluorene contained more than one silyllithium species. However, the yield of fluorene-9-carboxylic acid was not appreciably different from that obtained with triphenylsilyllithium. One might expect that *d*-orbitals on the silicon atom adjacent to the anion would participate in stabilization of the anion:

$$Ph_3Si{-}\overset{\ominus}{\ddot{S}}iPh_2 \longleftrightarrow Ph_3\overset{\ominus}{\ddot{S}}i{=}SiPh_2$$

Such an effect was not evident in the present reactions.

Experimental

Triphenylsilyllithium[6], methyldiphenylsilyllithium[6], dimethylphenylsilyllithium[6], and triphenylgermyllithium[7] were prepared according to published directions in tetrahydrofuran solution. The tetrahydrofuran was purified by refluxing over sodium wire, distillation into lithium aluminum hydride, and distillation from the hydride immediately before use. Analysis of the lithium reagents was carried out by double titration with allyl bromide[8].

Metalation of fluorene by triphenylsilyllithium. To 7.63 g (0.046 mole) of fluorene in 380 ml of tetrahydrofuran, cooled to 0° by a Dry Ice–acetone bath, was added at one time 77 ml of 0.596 *M* triphenylsilyllithium (0.046 mole). The solution was stirred for 1.5 h with the temperature maintained between 0° and 5°, then carbonated by pouring onto a Dry Ice–ether slurry. After allowing the mixture to warm to 0°, dilute hydrochloric acid was added, followed by several extractions with ether. The combined ether layers were extracted with 400 ml of 5 % sodium hydroxide in several portions. The basic extracts were boiled, then acidified with 10 % hydrochloric acid. Filtration afforded a solid product which was recrystallized from glacial acetic acid to obtain 4.7 g of crude fluorene-9-carboxylic acid, m.p. 225–230°. A second recrystallization from the same solvent raised the m.p. to 229–232° (mixed m.p.), 4.3 g (44.5 %).

Another run of the reaction was made with the same molar quantities of reagents in a total of 140 ml of tetrahydrofuran. The mixture was stirred at room temperature for 4 h before carbonation. The same work-up afforded 9.28 g (96.8 %) of fluorene-9-carboxylic acid, m.p. 226–230°. In addition, 6.7 g (62 %) of triphenylsilane, m.p. 40–41°, and 0.2 g (2.5 %) of fluorene, m.p. 111–113° (mixed m.p.), were isolated on alumina chromatography of the neutral fraction of the reaction mixture.

The remainder of the reactions reported in Table 1 were carried out as described in the first paragraph above under the same conditions of time, temperature and concentrations of reagents.

TABLE 1

METALATIONS OF FLUORENE

Organic Group IVB lithium compounds were allowed to metalate fluorene under identical conditions of time, temperature and concentrations of reagents, followed by carbonation to produce fluorene-9-carboxylic acid.

R_3MLi reagent	*Yield of fluorene-9-carboxylic acid, %*		
	Run 1	*Run 2*	*Average*
$Ph_2MeSiLi$	65.2	57.4	61.3
$PhMe_2SiLi$	61.6	54.7	58.1
Ph_3GeLi	46.1	53.2	49.6
Ph_3SiLi	44.5	37.7	41.1
$Ph_3SiSiPh_2Li$	44.6	39.8	42.2[a]

[a] A third run with this reagent gave a yield of 20.3 %, which was not included in the average.

Preparation of pentaphenyldisilanyllithium. To 10.50 g (0.0115 mole) of decaphenylcyclopentasilane in 150 ml of tetrahydrofuran was added 103 ml of 0.675 *M* triphenylsilyllithium (0.0695 mole), and the mixture was stirred at room temperature for 46 h. A 25 ml aliquot was removed by pipette and hydrolyzed in dilute hydrochloric acid. The ether layer was separated and filtered to give hexaphenyldisilane, 0.24 g, m.p. 360–364°. The filtrate was dried and evaporated, followed by alumina chromatography of the resulting solid. Petroleum ether (b.p. 60–70°) eluted traces of oil. Mixtures of petroleum ether (b.p. 60–70°) with benzene eluted pentaphenyldisilane, which was recrystallized from the same solvent system to obtain 0.76 g (*ca.* 40 %) of the product, m.p. 219–221° (mixed m.p.).

A second 25 ml aliquot was removed from the reaction mixture after 94 h. The same work-up afforded hexaphenyldisilane (0.27 g) and pentaphenyldisilane (1.12 g, *ca.* 63 %).

A repeated run gave *ca.* 35 % of pentaphenyldisilane after 48 h and *ca.* 57 % after 96 h. Solutions used for the metalation of fluorene were stirred for 96 h.

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Chemistry Department,
Iowa State University,
Ames, Iowa (U.S.A.)

HENRY GILMAN
FRANK K. CARTLEDGE

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Effect of solvents on reactions of organometallic compounds

V*. Effect of solvation on zinc alkyl capacity for metalation reactions

In the course of our investigations concerning the influence of solvation on the reactivity of organometallic compounds[1–5] we have investigated the metalation of mono-substituted acetylenes, fluorene and phenylbarene[6] by organozinc compounds in strongly solvating media.

Zinc alkyls (but not diphenylzinc[7]) are relatively weak metalating agents and do not react, in convenient conditions, either with fluorene or phenylbarene. The reaction with phenylacetylene is rather slow.

Since the predominant solvation of cations gives rise to an increase of nucleophilicity of organometallic compounds[8] and the metalation of hydrocarbons by Grignard reagents is much facilitated in the presence of tetrahydrofuran (THF)[8] or hexamethyltriamidophosphate (HMTAF)[9], it was reasonable to predict that metalation by zinc alkyls would be facilitated in strongly solvating solvents.

Indeed, although diethylzinc does not react to any extent with phenylacetylene

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* Part IV, see ref. 3.