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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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.

in heptane at 50°, in THF and dimethoxyethane (DME) the time for the evolution of half the calculated amount of ethane at the same temperature is 2 h 15 min and 3 h 10 min, respectively. If the reaction mixtures are boiling, the evolution of ethane takes about 1 h.

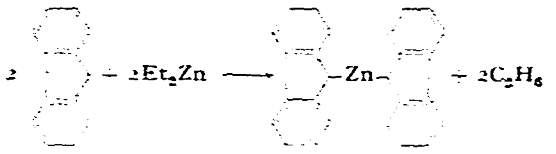
In dimethylformamide (DMFA) and dimethyl sulfoxide (DMSO) the reaction is exothermic and the times of "half-evolution" is 270 and 200 sec, respectively. The largest solvation effect was found in the case of HMTAF (< 8 sec):

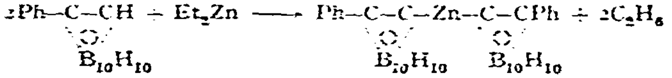
$$2\mathrm{PhC{\equiv}CH} + \mathrm{Et_2Zn} \longrightarrow \mathrm{PhC{\equiv}CZnC{\equiv}CPh} + 2\mathrm{C_2H_6}$$

Mixed organozinc compounds prepared in DMFA and DMSO[10] also react with phenylacetylene.

Bis(phenylethynyl)zinc which has previously been described[7] as a solid insoluble in organic solvents, is actually easily soluble in DMFA, DMSO, HMTAF and may be precipitated from its solutions by ethers. With $\mathrm{CuBr_2}$ it gives diphenylbutadiyne in good yields.

Fluorene and phenylbarene easily react with diethylzinc in HMTAF at raised temperatures to give solvated symmetrical derivatives:





$$2\,\mathrm{Ph{-}\underset{B_{10}H_{10}}{C{-}CH}} + \mathrm{Et_2Zn} \longrightarrow \mathrm{Ph{-}\underset{B_{10}H_{10}}{C{-}C}{-}Zn{-}\underset{B_{10}H_{10}}{C{-}C}Ph} + 2\mathrm{C_2H_6}$$

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