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REACTIONS OF AROMATIC RADICAL ANIONS VIII.
ORGANOMETALLIC SYNTHESIS USING SODIUM NAPHTHALENE

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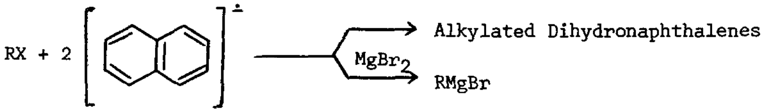
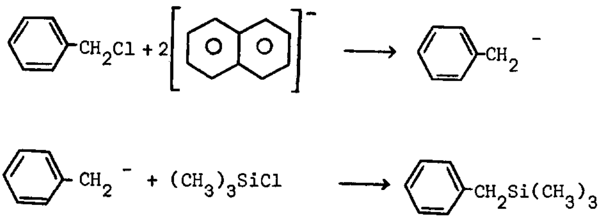
In previous work we have reported that Grignard reagents are readily prepared by magnesium bromide capture of the anion produced from the sodium naphthalene reduction of organic halides.[1] The resultant Grignard can be reacted by conventional reagents including organometallic halides to give other organometallic derivatives



$$RMgBr + R'_{N}MX \rightarrow R\text{-}M\text{-}R'_{N} + MgX$$

The radical anion route offers a convenient and rapid alternative when the usual Grignard methods are unsuccessful.[2] We have now found it possible to prepare other organometallics directly by sodium naphthalene reduction of the mixed organo and metal halides.

When sodium naphthalene in tetrahydrofuran (THF) was added to a premixed solution of benzyl chloride and trimethylsilyl chloride, a 90% yield of benzyltrimethyl silane was obtained. Benzyl chloride alone is reduced by sodium naphthalene to give mainly bibenzyl, benzylated dihydronaphthalenes and a trace of toluene.[3] In the absence of benzyl chloride, trimethylsilyl chloride reacts with sodium naphthalene to form disylated dihydronaphthalenes.[4] These results suggest a mechanism analogous to Grignard formation which involves electron transfer to the organic halide to form the anion.



In contrast, Sakurai[5] obtained bibenzyl as the major product in the reaction of trimethylsilyl sodium and benzyl chloride. The lower yield of benzyltrimethylsilane is evidently a result of the predominance of electron transfer from the silyl anion.

A variety of organic halides were reacted under similar conditions. The sodium naphthalene solution (1M) was added rapidly with mixing and cooling to the solution of organic halide and freshly distilled organometallic halide under an atmosphere of dry nitrogen until the intense green color of the radical anion persisted. The mixture was quenched in a small amount of water and the organic layer was analyzed quantitatively using gas chromatography with internal standards. The products were isolated by trapping techniques and identified by spectroscopic methods. The results are listed in Table 1.

Table 1. Yields for Reactions of Organic Halides and Trimethylsilyl Chloride with Sodium Naphthalene.

Halide	Molar Ratio of Me_3SiCl/RX	Yield (%) of $RSiMe_3$
ϕCH_2Cl	2	90
ϕ-Cl	2	60
ϕ-Br	2	40[a]
CH_2=CH-CH_2Cl	3	60
CH_2=CH-CH_2Br	3	23[a]
$CH_3(CH_2)_4CH_2Cl$	2	20[b]
CH_3CH=CHBr	3	10

[a] The corresponding bromides give lower yields than the chlorides because of the competing reaction with the more reactive unreacted halide.

[b] The other products are alkyldihydronaphthalenes and hexane arising from proton abstraction from solvent.

Dialkylation of dimethylsilyl dichloride proceeded readily to form dibenzyldimethylsilane (85%) when a 1:1 molar ratio of benzyl chloride was used. This method appears to be of little use for phenyl substituted silanes which react preferentially with sodium naphthalene to give mainly hexaphenyldisilane.[6] However, for phenyl substituted phosphines this method appears preferential. Benzyldiphenylphosphine is prepared in 53% yield by the sodium reduction of benzyltriphenylphosphonium chloride in refluxing xylene.[7] In contrast, an 85% yield of the same material was obtained in a few minutes at room temperature from benzyl chloride and diphenylchlorophosphine.

In summary, the reaction would seem to be useful and sometimes the method of choice when electron transfer is to the organic halide rather than the organometallic halide and when the resultant anion is reasonably stable.

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