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Preliminary communication

PREPARATION AND ISOLATION OF ALKYLIODOSTRONTIUM AND ALKYLIODOBARIUM COMPOUNDS

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Summary

Alkyliodo-strontium and -barium compounds solvated by tetrahydrofuran $RMI \cdot (C_4H_8O)_m$, analogous to Grignard reagents, have been isolated and some of their properties and reactions are discussed.

Calcium will form organometallic compounds that are analogous to Grignard reagents [1] and studies of the reactions of these species with a variety of organic compounds have been carried out [2]. Reactions of alkyl halides with metallic strontium or barium have been reported not to give organometallic products [3]. Recent work, however, has indicated that alkyliodobarium species can be prepared in solution in low yields [4] and that aryl compounds of strontium can also be isolated [5].

We have prepared and isolated in good yields alkyl derivatives of both strontium and barium of the general formula $RMI(THF)_n$ (M = Sr, Ba; n = 1-3; THF = tetrahydrofuran). The compounds in Table 1 are colourless microcrystalline solids formed by reaction of the finely divided metal (purity Ba > 99.5%, Sr > 99%) with the appropriate alkyl halide, RI, in tetrahydrofuran at −78°C in vacuum. The compounds are very reactive, decomposing slowly in vacuum at room temperature and rapidly in a moist atmosphere. They are soluble in tetrahydrofuran (from which they are recrystallisable) and in 1,2-dimethoxyethane.

^1H NMR studies of the species in 1,2-dimethoxyethane or diglyme (60 or 100 MHz; room temp.) show resonances assignable to THF but no resonances due to H atoms of the alkyl groups could be identified. This may be a consequence of a chemical exchange process, but further studies have been hampered by the low solubilities, especially at low temperatures. IR spectra of the solids, though difficult to obtain without some decomposition, show bands arising from alkyl C—H, coordinated THF (e.g. $1033 \pm 1\ cm^{-1}$) and low frequency

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TABLE 1

ANALYTICAL DATA OF THE $RMI(THF)_n$ COMPOUNDS PREPARED

Compound	Reaction time (h)	Yield[a]	Analyses found (calcd.) (%)		Hydrolysis	
			M[b]	I	Hydrocarbons liberated[c]	Mol (%) volatile[d]
$MeSrI(THF)_3$	8	80	19.6 (19.65)	28.0 (28.5)	CH_4(100), C_2H_6(16)	77
$EtSrI(THF)_2$	7	87	22.8 (22.6)	33.7 (32.7)	CH_4(2), C_2H_6(100), C_2H_4(1), C_2H_2(2), C_3H_6(1), C_4H_{10}(<1)	66-76
n-$PrSrI(THF)_2$	9	68	21.9 (21.8)	31.8 (31.6)	CH_4(16), C_2H_6(1), C_3H_8(100), 1-C_3H_6(24), C_6H_{14}[e]	67
n-$BuSrI(THF)_3$	9	78	18.0 (18.0)	26.2 (26.0)	CH_4(trace), C_2H_6 (trace), C_4H_{10}(100), 1-C_4H_8(20), C_8H_{18}[e]	60
$EtBaI(THF)$[f]	8	86	37.2 (37.6)	34.5 (34.7)	CH_4(5), C_2H_6(100)	71

[a] % yield based on RI used. [b] M = Sr or Ba. [c] Relative molar amounts in parentheses (GLC). H_2 negligible. [d] (Moles of volatile product (above −78°C trap)/moles of $RMI(THF)_m$ hydrolysed) × 100. [e] Determined separately. [f] THF 18.7% (determined by GLC). Theoretical 19.6%.

vibrations (e.g. RSrI(THF)$_n$ 372-385 cm^{-1}) which may arise from ν(M—C) or ν(M—O) (cf. Grignard reagents [6]). The structures of these complexes are probably analogous to the related Grignard reagents [7].

Solvolysis of the freshly prepared compounds by water or methanol gives hydrocarbon, RH, as the main product. Some alkene, R(—H), and coupled product, R—R, are also produced and relatively small amounts of other hydrocarbons are formed (see Table 1). After standing in vacuo at room temperature decomposition of the solids takes place, so that subsequent hydrolyses yield differing relative amounts of hydrocarbons. Thus, from EtSrI(THF)$_2$ the relative amount of ethane with respect to all other hydrocarbons, especially acetylene, and, to a lesser extent, methane, decreases with time. The mechanism of the decomposition and the production of the variety of hydrocarbons is being studied. Carbide formation is one probable process.

Only low yields of tertiary alcohols are formed by reaction of MeSrI(THF)$_3$ with alkyl ketones. With acetone in stoichiometric proportions in THF between −78 and −30°C (20 h) 2-methyl-2-propanol (8%) is produced after hydrolysis and the only major isolable product is unreacted ketone. Most of the organometallic compound is consumed during the reaction and hydrocarbon gas (CH_4 and C_2H_6) is liberated so that enolisation and reaction with the solvent may also be taking place. With aryl ketones tertiary alcohols may be produced. Thus with diphenylketone under similar reaction conditions 1,1-diphenylethanol (up to 69% (24 h)) is formed on hydrolysis. Unreacted diphenylketone or, with prolonged reaction at room temperature, the secondary alcohol, diphenylmethanol, are isolable as minor products. During the reaction some radical anion is formed so that radical processes must be taking place to some extent.

Reactions of all the organometallic compounds with a variety of organic functional groups are being investigated and will be reported later.

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References

1 M.A. Zemlyanichenko, N.I. Sheverdina, I.M. Viktorova, N.P. Barminova and K.A. Kocheshkov, Dokl. Akad. Nauk. SSSR, 194 (1970) 95; N. Kawabata, A. Matsumura and S. Yamashita, Tetrahedron, 29 (1973) 1069; and earlier references.
2 N. Kawabata, H. Nakamura and S. Yamashita, J. Org. Chem., 38 (1973) 3403; M. Chastrette and R. Gauthier; J. Organometal. Chem., 66 (1974) 219.
3 F. Schulze, Iowa State J. Sci., 8 (1933) 225; B.J. Wakefield, Advan. Inorg. Chem. Radiochem., 11 (1968) 390.
4 I.I. Lapkin, M.N. Rybakova, M.I. Belonovich and L.M. Novoselitskaya, Zh. Obshch. Khim., 42 (1972) 2681.
5 K.A. Kocheshkov, L.F. Kozhemyakina and N.I. Sheverdina, Izv. Akad. Nauk, SSSR, Ser. Khim. (1973) 2400; L.F. Kozhemyakina, N.I. Sheverdina and K.A. Kocheshkov, Dokl. Akad. Nauk. SSSR, 220 (1975) 99.
6 J. Kress and A. Novak, J. Organometal. Chem., 86 (1975) 281.
7 M. Vallino, J. Organometal. Chem., 20 (1969) 1; G.D. Stucky and R.E. Rundle, J. Amer. Chem. Soc., 86 (1964) 4825.