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SOME COMPETITIVE REACTIONS INVOLVING POLYHALOARYL–METALLIC REAGENTS

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SUMMARY

The competition between chlorotrimethylsilane and benzophenone for a polyhaloaryl–metallic (Li or MgX) reagent demonstrates a reactivity preference and the effect of solvent on this preference.

INTRODUCTION

Since little is known of the reactivity of polyhaloaryl–metallic reagents towards various substrates, despite their extensive use in syntheses, some competitive reactions involving these reagents were examined. Competing reactions of mixtures of chlorotrimethylsilane with styrene or fluorene for an organolithium reagent have been reported[1], but the formation of a more reactive organolithium reagent can be a complicating factor. To avoid such problems the polyhaloaryl–metallic reagents were reacted with a mixture of chlorotrimethylsilane and benzophenone. The results illustrate a reactivity preference and the effect of solvent on this preference.

RESULTS AND DISCUSSION

In THF, the aryllithiums; *viz.*, phenyl-, pentafluorophenyl-, pentachlorophenyl-, and 2,3,5,6-tetrachloro-4-pyridyllithium, reacted exclusively with chlorotrimethylsilane. The findings were essentially the reverse when the solvent was ether; the carbinol being the major product. Similar preferences were observed for some polyhaloaryl-Grignard reagents in THF or ether. Phenylmagnesium bromide behaved anomalously in that it reacted preferentially with benzophenone, in both THF and ether. Solvent effects were observed in many reactions involving pentafluorophenyl–metallic reagents[2–5]. For the Grignard, lithium and copper reagents the successful accomplishment in THF or DMAC* of reactions which failed in a less polar solvent such as ether was ascribed to the increased nucleophilicity of the pentafluorophenyl anion in such solvents. Thus, pentafluorophenyllithium in hexane at −70° was found[6] to hardly react with chlorotrimethylsilane.

Pentafluorophenyl-Grignard reagents are not typical of aryl-Grignard re-

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* DMAC = dimethylacetamide.

agents. For non-polyhalogenated Grignard reagents the rate of reaction with a variety of substrates decreased with increasing basicity of the solvent. Electrophilic attack by the metal is more important than the nucleophilic character of the organic radical[7], and electron withdrawing substituents are found to hinder their reactions. Typical aryl-Grignard reagents in ether exist mainly as the species RMgX, whereas in THF they contain considerable quantities of diarylmagnesium complexes, as do pentafluorophenyl-Grignards in both ether and THF[8,9]. Thus the position of the Schlenk equilibrium appears to be of little consequence in explaining the different behaviour of the polyhaloaryl-Grignard reagents and phenylmagnesium bromide. It has been proposed[10] that the reactivity of organolithiums increases with a decreasing aggregation number. However, little is known concerning the degree of association of polyhaloaryl–metallic reagents.

Two mechanisms were proposed for the reaction of organometallic reagents with a chlorosilane; *viz.* a four-centre process, or a backside nucleophilic attack on silicon which, for organolithiums, probably also involves electrophilic assistance by the metal[11]. Four-centre transition states are not susceptible to solvent and steric effects. Addition of Grignards to ketones is best explained in terms of a termolecular reaction involving initial complex formation and a six-centre transition state[9]. Such complexes have not been detected in the addition of the more reactive organolithiums to ketones[12].

The results may indicate that different mechanisms are probably operative for the reactions of polyhaloaryl–metallic reagents, phenyllithium, and phenylmagnesium bromide with chlorotrimethylsilane and benzophenone. Furthermore, the cited solvent effects for the reactions of pentafluorophenyl–metallic reagents[2–5], the observed decreasing rate of reaction with increasing electronegativity of the organic group for the reaction of some hydrocarbon Grignards with benzophenone[13], and the greater ease of coupling of Grignards with chlorosilanes in more polar solvents, may partly explain the preference of phenyllithium and polyhaloaryl–metallic reagents for chlorotrimethylsilane in THF. The reaction probably proceeds via nucleophilic attack by the polyhaloaryl anion.

Related reactivity studies in which pairs of perhaloarylmetallic compounds (where M is −MgX, Li, Cu) complete for a substrate, and where trichloro-2-thienylmetallic compounds were included, will be reported soon.

EXPERIMENTAL

All reactions were performed under an atmosphere of dry oxygen-free nitrogen. Ethereal solvents were dried over sodium, and THF was further dried by distillation from sodium benzophenone ketyl. n-Butyllithium in hexane (1.6 *M*) from the Foote Mineral Company was used to prepare the polyhaloaryllithium compounds. The organometallic reagents were prepared by reported procedures[14–20]. The physical constants of the products as isolated were: $C_6F_5SiMe_3$, b.p. 71–73°/25 mm (lit.[21]: 60°/14 mm); $C_6Cl_5SiMe_3$, m.p. 116–117° (lit.[22]: 116–117°); 4-$Me_3Si(C_5Cl_4N)$, m.p. 61–63° (lit.[16]: 62–63°); $C_6H_5SiMe_3$, b.p. 61–63°/20 mm, n_D^{20} 1.4913 (lit.[23]: 65°/20 mm., n_D^{20} 1.4908); $(C_6Cl_5)(C_6H_5)_2COH$, m.p. 152–153° (lit.[14]: 152.5°); $(C_6F_5)(C_6H_5)_2$-COH, b.p. 156–159°/1.5 mm, m.p. 54–56° (lit.[24]: b.p. 168°/2 mm, m.p. 59.5°); all identical to authentic samples prepared by the reported procedures, and $(C_6H_5)_3$-COH, m.p. 164°, identical to a commercial sample.

TABLE 1

COMPETITIVE REACTIONS OF ORGANOMETALLIC REAGENTS WITH BENZOPHENONE AND CHLOROTRIMETHYLSILANE

Organometallic reagent	Temp. (°C)	Solvent	Products (%)		
			Silane $RSiMe_3$	Carbinol RPh_2COH	Ph_2CO recovered
C_6H_5Li	0	THF	68	0	84
C_6F_5Li	−70	THF	60	0	85
	−70	THF	66	0	84
C_6Cl_5Li	−70	THF	59	0	89
	−70	THF	69	0	69
C_5NCl_4Li	−70	THF	53	0	77
C_6H_5Li	0	Et_2O^b	2	77	61^c
C_6F_5Li	−70	Et_2O	17	66	12
	−70	Et_2O	11	63	16
C_6Cl_5Li	−70	Et_2O	4	58	24
C_5NCl_4Li	−70	Et_2O^a	8	49	37
C_6H_5MgBr	0	THF	8	72	16
	0	THF	1	84	11
C_6F_5MgBr	0	THF	85	0	86^c
C_6Cl_5MgCl	0	THF	70	0	87
C_5Cl_4NMgCl	0	THF	70	0	78
C_6H_5MgBr	0	Et_2O	1	74	59^c
	0	Et_2O^b	0	97	49^c
C_6F_5MgBr	0	Et_2O	0	64	61^c

[a] Tetrachloropyridyllithium prepared in ether/hexane contains the 2-pyridyllithium as well as the 4-pyridyllithium (ref. 16). [b] Titrated before use, 0.10 mole exactly. [c] 0.20 mole of each substrate used.

General procedure

All reactions were carried out at the temperature given in Table 1. The organometallic reagent (from 0.10 mole of the arene) was added dropwise to a rapidly stirred mixture of benzophenone (0.1 mole) and chlorotrimethylsilane (0.1 mole) in the appropriate solvent and stirred for 30 min after completion of the addition, when Color Test 1[25] was negative. After hydrolysis with dilute acid and extraction with ether, the dried ether solution was fractionally distilled to remove solvent and collect the silanes $C_6H_5SiMe_3$ and $C_6F_5SiMe_3$. The residue was treated with petroleum ether (b.p. 60–70°) and filtered to remove $(C_6H_5)_3COH$, $(C_6Cl_5)(C_6H_5)_2COH$, and $(C_5Cl_4N)(C_6H_5)_2COH$. The filtrate was then chromatographed on a column of silica gel (3.5 × 75 cm), first eluting with petroleum ether (b.p. 60–70°), then CCl_4, and then C_6H_6 to separate the (polychloroaryl)trimethylsilanes, benzophenone, and any soluble carbinols.

Preparation of (2,3,5,6-tetrachloro-4-pyridyl)diphenylmethanol

Benzophenone (14 g, 0.076 mole) in THF (50 ml) was added slowly to 2,3,5,6-tetrachloro-4-pyridylmagnesium chloride (0.08 mole) in THF (110 ml) at 0°. The mixture was stirred for 16 h at room temperature before hydrolysis with 2 *N* HCl (200 ml). After extraction with ether and drying, the solvent was removed under reduced pressure. The residue was dissolved in hot benzene, "Norit" was added and the solution boiled for 5 min, before filtration and the evaporation of solvent. Crystallisation from petroleum ether (b.p. 60–70°) gave white crystals of (2,3,5,6-tetrachloro-4-pyridyl)diphenylmethanol (nc) (12.6 g, 42%), m.p. 161–162°. (Found: C, 54.36; H, 2.88; mol.wt. mass spectrometric, 399. $C_{18}H_{11}Cl_4NO$ calcd.: C, 54.14; H, 2.76%; mol.wt., 399.) The ^1H NMR spectrum in carbon tetrachloride revealed a singlet at τ 5.93 (OH) and a multiplet at τ 2.73 (C_6H_5). The infrared spectrum in nujol showed characteristic absorption bands at 2.81 (w), 6.90 (s), 7.76 (s) and 14.20 (s) μ.

This compound has also been made from 4-lithiotetrachloropyridine and benzophenone. A mixed melting point showed no depression. The yield was 65%.

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