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Preparation of Polychlorinated 2-Phenylthiophenes

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Two novel polychlorinated unsymmetrical biaryls viz., 2-(1,2,4,5-tetrachlorophenyl)-3,4,5-trichlorothiophene and 2-(1,2,4,5-tetrachlorophenyl)-3,4-dichlorothiophene have been prepared in 56-58% yields by reacting 1,2,4,5-tetrachloro-3-iodobenzene respectively with trichloro- and 3,4-dichloro-2-thienylcopper. The ir, nmr and mass spectra of these new compounds are reported.

(Keywords: Copperorganic compounds; Polychloro-2-thienylcopper; 1,2,4,5-Tetrachloro-3-iodobenzene)

Synthese von polychlorierten 2-Phenylthiophenen

Zwei neue unsymmetrische Polychloro-biaryle, 2-(1,2,4,5-Tetrachlorophenyl)-3,4,5-trichlor- und 3,4-dichlor-thiophen wurden mit Ausbeuten von 56-58%, durch Reaktion von 1,2,4,5-Tetrachlor-3-jod-benzol mit Trichlor- bzw. 3,4-Dichlor-2-thienylkupfer dargestellt. Die IR-, NMR- und Massenspektren der neuen Verbindungen werden beschrieben.

Introduction

Recently we reported the preparation of some perhalogenated unsymmetrical biaryls by reacting perhaloarylcoppers with perhaloiodoarenes in refluxing dioxan or tetramethyltetrahydrofuran[1] (Scheme 1). The organocoppers in Scheme 1 are prepared by the following metathesis and are probably polymeric

$$R\mathrm{Mg}X + \mathrm{CuI} \xrightarrow{THF} R\mathrm{Cu} + \mathrm{Mg}X_2$$

cluster compounds as are their lithium counterparts[2]. Furthermore these may have solvent molecules and metal salts incorporated as ligands[3].

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Scheme 1

$$R\text{Cu} + R'\text{I} \xrightarrow[100\,^{\circ}\text{C}\quad 40\,\text{h}]{\text{Dioxan}} R\text{—}R' \quad (28\text{—}56\%)$$

$$R = R' = \text{C}_6\text{Cl}_5,\ \text{C}_6\text{F}_5,\ (4\text{-C}_5\text{Cl}_4\text{N}),\ (2\text{-C}_4\text{Cl}_3\text{S}),\ R \neq R' \text{ in } R\text{—}R'$$

We report now an extension of the above work to include the application of Scheme 1 in the preparation of two new polychlorinated unsymmetrical biaryls.

Materials and Methods

All reactions were conducted under a positive pressure of dry, oxygen-free nitrogen in ethereal solvents which were dried over sodium wire and then distilled from sodium-benzophenone ketyl before use. Ir spectra were recorded on a Perkin-Elmer Model 21 Spectrometer. Nmr spectra were recorded using a Varian A 60 Spectrometer and *TMS* as the internal standard. The yields are based on the starting pentachloroiodobenzene. The temperatures quoted are uncorrected.

Trichloro-2-thienylcopper[4]: This reagent was prepared by reacting trichloro-2-thienylmagnesium halide[5] (x mol) with copper(I) chloride (x mol) at room temperature in *THF* for 6 h.

3,4-Dichloro-2-thienylcopper:[6] This was prepared by metathesizing 3,4-dichloro-2-thienyllithium (x mol) with copper(I) chloride (x mol) in *THF* as reported previously[6].

1,2,4,5-tetrachloro-3-iodobenzene[7]: This was synthesized by iodinating 2,3,5,6-tetrachlorophenylmagnesium chloride[7] in benzene—*THF* solution at 0 °C.

Reaction of 1,2,4,5-tetrachloro-3-iodobenzene with trichloro-2-thienylcopper: Synthesis of 2-(1,2,4,5-tetrachlorophenyl)-3,4,5-trichlorothiophene

To trichloro-2-thienylcopper [prepared from trichloro-2-thienylmagnesium halide (0.04 mol) and copper(I) chloride (0.04 mol) in *THF* (150 ml)] was added 1,2,4,5-tetrachloro-3-iodobenzene (0.04 mol) in dioxan (100 ml). *THF* was then distilled off under nitrogen and the mixture (which still contained approximately 50 ml of dioxan) was heated at 100 °C for 40 h[1]. The mixture was then cooled to room temperature and hydrolysed with a saturated solution of ammonium chloride in acqueous ammonia and the organic material was extracted with benzene. The benzene extract was washed with ammonium chloride/aq. ammonia solution until copper halide was completely removed, then it was washed with water and dried over anhydrous sodium sulphate. Upon removal of benzene there was obtained a pale brown solid. This was chromatographed on a silica gel column using petroleum ether (b.p. 60-80 °C) as an eluant. This gave a white solid which was further purified by recrystallisation from benzene-petrol ether (1:1 *v*/*v*) and then pure trichloro-2-(1,2,4,5-tetrachlorophenyl)thiophene (56%) was obtained, m.p. 165-167 °C. Analysis: found Cl 61.54%; calc. for $C_{10}H_1Cl_7S_1$, Cl 61.83%. The ir spectrum (nujol mull) showed the following absorption frequencies at cm^{-1}: 3 050 w, 1 550 w, 1 527 w, 1 350 w, 1 314 s, 1 275 w, 1 225 m br, 1 158 s, 1 110 w, 1 007 s sh, 906 m, 878 s, 821 m br sh, 753 w br, 710 m and 704 s. The ^{1}H-nmr spectrum of this compound showed a singlet at $\delta = 7.7$ ppm in $CDCl_3$.

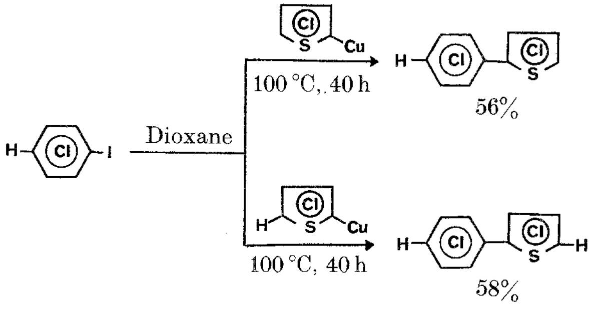
Reaction of 1,2,4,5-tetrachloro-3-iodobenzene with 3,4-dichloro-2-thienylcopper: Synthesis of 2-(1,2,4,5-tetrachloro-phenyl)-3,4-dichlorothiophene

1,2,4,5-Tetrachloro-3-iodobenzene (0.01 mol) was reacted with 3,4-dichloro-2-thienylcopper [prepared as described above from 3,4-dichloro-2-thienyllithium (0.01 mol) and copper(I) chloride (0.01 mol) in *THF* (100 ml)] in dioxan as before at 100 °C for 40 h[1]. The reaction was worked up as above and then there was obtained (2,3,5,6-tetrachlorophenyl)-3,4-dichlorothiophene (58%), m.p. 107-108 °C [from benzene-petrol ether (b.p. 60-80 °C)]. Analysis: found C 32.75%, Cl 58.23%; calc. for $C_{10}H_2Cl_6S$, C 32.73%, Cl 57.98%. The ir (KBr pellet) spectrum had the following chracteristic absorption frequencies at cm^{-1}: 3 100 m, 3 043 w, 1 540 m, 1 519 w, 1 446 s, 1 389 vs sh, 1 347 m sh, 1 332 vs, 1 322 s sh, 1 227 s sh, 1 168 s, 1 149 m, 1 138 w, 1 117 m sh, 1 029 s sh, 934 m sh, 872 vs, 861 m, 828 s sh, 726 vs, 720 m, 708 s, 687 s sh, 635 w sh, 573 s, 552 s, 540 s, 479 m sh and 450 w sh. The ^{1}H nmr spectrum (in $CDCl_3$, $(CH_3)_6Si_2O$ as internal standard] of the compound shows two singlets at $\delta = 7.72$ (polychlorinated benzene hydrogen) and 7.39 (polychlorinated thiophene hydrogen). The mass spectrum of the compound had the following important clusters centered around *m*/e, 370 (M^+), 333 $(M—Cl)^+$ and 298 $(M—2Cl)^-$.

Results and Discussion

Trichloro-2-thienylcopper reacts with 1,2,4,5-tetrachloro-3-iodobenzene in refluxing dioxan to give 2-(1,2,4,5-tetrachlorophenyl)-3,4,5-trichlorothiophene in 56% yield. Similarly, 3,4-dichloro-2-thienylcopper reacts with 1,2,4,5-tetrachloro-3-iodobenzene to give a 58% yield of 2-(1,2,4,5-tetrachlorophenyl)-3,4-dichlorothiophene (Scheme 2).

Scheme 2



Earlier, we reported the preparation of 2-(pentachlorophenyl)- 3,4-dichlorothiopene by a similar procedure[6].

Thus the coupling reaction described in Scheme 1 for the preparation of perhalogenated unsymmetrical biaryls is also applicable in the synthesis of polychlorinated unsymmetrical biaryls. The synthesis of unsymmetrical biaryls by coupling an organocopper with an iodoarene is very convenient since the preparation of the organocopper reagents is easy and the successive steps of the reaction can all be conducted in one reaction vessel. Furthermore because of the low[3,8,9] reactivity of organocoppers with such functional groups as keto, ester, nitro, isolated double bonds and internal acetylenes, this procedure is potentially applicable in the synthesis of unsymmetrical biaryls containing such functions.

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