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Preliminary communication

Reaction of haloarenetricarbonylchromium with trimethylphosphite: palladium-catalyzed Arbuzov reaction versus arene displacement by trimethylphosphite

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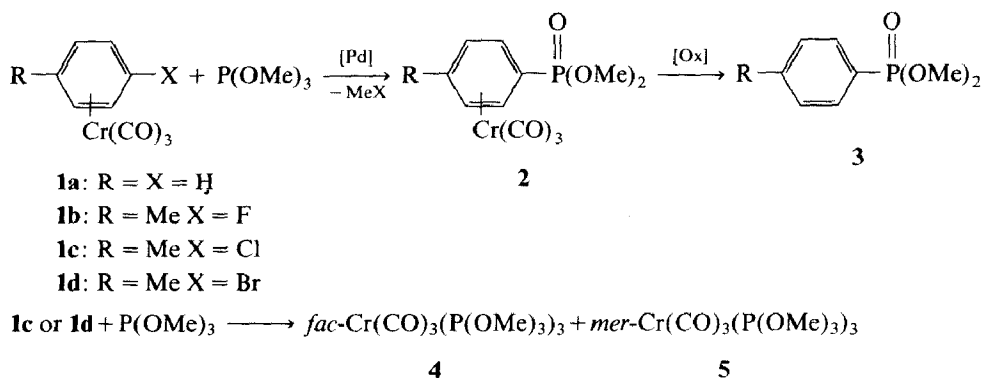
Abstract

The Arbuzov reaction of trimethylphosphite with *p*-bromo-, and also with *p*-chloro-toluenetricarbonylchromium is achieved at 80–120 °C, in the presence of a Pd⁰ or Pd^{II} complex, which acts as a catalyst. A competitive displacement of the haloarene by trimethylphosphite occurs, and the resulting diastereoisomeric complexes are obtained.

The Arbuzov reaction of compounds containing a P^{III}–O bond with alkyl halides is one method for P^V–C bond formation [1]. It has been used to prepare phosphine oxides (and then phosphines) having a chiral phosphorus atom [2] with at least one alkyl substituent. Nevertheless, it would be interesting to prepare analogous chiral trisarylphosphines, since this type of ligand has not been studied in asymmetric transition metal catalysis [3]. The literature provides examples of Arbuzov reactions with vinyl [4] and aryl [5] halides, but they require not only catalysis, but also high temperatures (160–190 °C), except with very special substrates such as perfluoro-cyclobutenes [6] or picryl halides [7]. The activation of aryl halides by the Cr(CO)₃ group (equivalent to that of a nitro group) has been used in some formal S_N Ar reactions [8]. We report here preliminary results on the Cr(CO)₃-activation method in the case of the Arbuzov reaction.

The compounds **1a** to **1d**, prepared according to published methods [9], were allowed to react with trimethylphosphite in the presence of a substoichiometric amount of a palladium complex (Pd(dba)₂ or PdCl₂, dba = dibenzylideneacetone) (Scheme 1).

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Scheme 1

Starting from **1a** at 80 °C or from **1b** at 116 °C, in the presence of PdCl₂, no reaction is observed. In the absence of a palladium complex at 100–120 °C (in a mixture of cyclohexane and “free” chloride), or in the presence of a palladium complex at 80 °C, the chloride **1c** does not give the phosphonate **3**, but a mixture of the isomeric tricarbonyltris(trimethylphosphite)chromium complexes **4** (minor, 10%) and **5** (major, 90%). These complexes were previously prepared by displacement reactions from other arenetricarbonylchromium [10–12], and the same major stereoisomer (*mer*, **5**) was obtained [12].

Starting from the chloride **1c**, the phosphonate **2** is isolated in 27% yield if the reaction is carried out in the presence of 20% PdCl₂ and at a temperature of at least 120 °C. Starting from the bromide **1d** and 20% Pd(dba)₂, the phosphonate **2** is obtained in 32% yield from as low a temperature as 80 °C. These yields correspond to much more than 100% reaction of the palladium complexes, showing that the latter act as catalysts. In both cases, the substrate totally disappears and the complexes **4** and **5** are still formed, resulting from the displacement of the haloarene from the Cr(CO)₃ group (relatively little displaced *p*-tolylphosphonate **3** (~ 5%) is directly produced).

Either a Pd^{II} or a Pd⁰ precursor can be used. In the catalytic cycle which has been proposed for the nickel-catalyzed Arbuzov reaction [5a], the first step is an oxidative addition of the bromide on a Ni⁰ complex.

The same step is encountered in the palladium-catalyzed analogous reaction of compounds containing a P(O)–H bond with aryl bromides and triethylamine [13], and in the Heck reaction as well [14]. Within the scope of this hypothesis, the Pd^{II} precursor (PdCl₂) can here be first reduced by the excess trimethylphosphite.

In a typical experiment, 1 mmol of haloarenetricarbonylchromium and 0.2 mmol of palladium complex are mixed in a 5/2 mixture of cyclohexane and free halide under argon. 0.50 ml (4 mmol) of trimethylphosphite is added. After heating (see Table 1), the solvent is removed and the residue is extracted with dichloromethane. The products **2**, **4** and **5** are separated on a silica gel column eluted with cyclohexane/ethyl acetate 80/20:

2 (*R_f* = 0.05): IR (KBr): ν(CO) 1909, 1974 cm⁻¹. ³¹P NMR: +23.08 ppm. ¹H NMR: 2.27 ppm (3H, s; CH₃ (*p*-tolyl)); 3.85 ppm (6H, d, ³*J*(POCH) 11 Hz: P(O)(OCH₃)₂); 5.04 ppm (2H, d, ³*J*(HC=CH) 5 Hz: *m*-H (tolyl)); 5.61 ppm (2H, m:

Table 1
Reactions of trimethylphosphite with haloarenetricarbonylchromium **1a–1d**

Halide	Solvent	Catalyst	<i>T</i> (°C)	Time (h)	Result
1a or 1b	4-MeC ₆ H ₄ F or C ₆ H ₆	PdCl ₂	b.p. (80 or 116)	24	No reaction
1c	Cyclohexane/ 4-MeC ₆ H ₄ Cl	none	120 ^a	9	10% 4 + 90% 5
1c	Cyclohexane/ 4-MeC ₆ H ₄ Cl	PdCl ₂	120 ^a	9	27% 2 (+ 4 + 5)
1d	Cyclohexane/ 4-MeC ₆ H ₄ Br	Pd(dba) ₂	80 ^a	5	32% 2 (+ 4 + 5)

^a Temperature of the oil bath.

o-H (tolyl)). The yellow solid **2** slowly decomposes in the air. After oxidation, *p*-tolylidimethylphosphonate **3** is obtained.

5 (*R_f* = 0.34): white solid: m.p. 182° C. IR (KBr): $\nu(\text{CO})$ 1958, 1972 cm⁻¹. ³¹P NMR: +140.76 ppm (1P, t, ²*J*(PCrP) 60 Hz: Cr–P(OMe)₃); +132.00 ppm (2P, t, ²*J*(PCrP) 60 Hz: Cr–P(OMe)₃). ¹H NMR: 3.65 ppm (m: Cr–P(OCH₃)₃).

4 (*R_f* = 0.52): ³¹P NMR: +144.06 ppm (in mixture with **5**). **4** and **5** decompose in the air to give trimethylphosphite and green chromium oxide [10]. NMR spectra were recorded in CDCl₃.

The *p*-chorotoluenetricarbonylchromium (air-stable and prepared in good yield, contrary to the corresponding *p*-bromo compound), can undergo the Arbuzov reaction at the same temperatures as those used in the stereoselective Arbuzov reaction of alkyl halides [2]. Focussing on the selectivity in the Arbuzov reaction (by reducing the excess of trimethylphosphite), chiral phosphinates synthesis (from chiral oxazaphospholidine or with a chiral palladium catalyst) will be investigated latter on the basis of these results.

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