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REDUCTIVE COUPLING OF BENZYLIC HALIDES BY CHLOROTRIS(TRIPHENYLPHOSPHINE)COBALT(I)

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Chlorotris(triphenylphosphine)cobalt(I) is an effective agent for the reductive coupling of benzylic halides under mild and neutral conditions.

Coupling of organic halides is an important synthetic reaction forming C-C bonds$^{1)}$. Low-valent transition metal reagents$^{2)}$ were recently used for the reductive coupling. In many such cases, a higher-valent transition metal compound coupled with a reducing agent was employed for this purpose. In the course of our investigation on the reaction of a mono-valent cobalt compound, chlorotris(triphenylphosphine)cobalt(I)$^{3)}$, we have found that $CoCl(Ph_3P)_3$ promotes the coupling of benzylic halides. The use of the complex in organic synthesis has so far been limited to the dimerization of olefins$^{4)}$. Here we wish to describe the reductive coupling of benzylic halides including benzal bromide and 1,2-dibromostilbene by means of $CoCl(Ph_3P)_3$, and also describe the reaction of a homobenzyl bromide. The advantages of the present reaction are as follows: 1) $CoCl(Ph_3P)_3$ is a rather stable complex to manipulate and can be easily prepared; 2) the reaction can be carried out under mild, non-basic conditions and can be accomplished in various organic solvents.

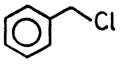
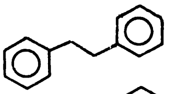
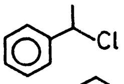
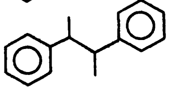
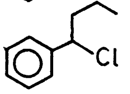
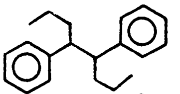
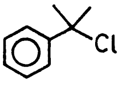
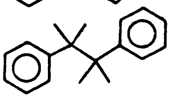
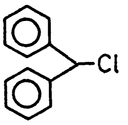
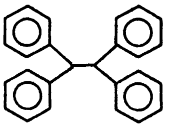
In a typical experiment, benzyl chloride (3 mmol) was treated with $CoCl(Ph_3P)_3$ (3.6 mmol) in 30 ml of degassed benzene at room temperature for 1.5 h under argon. The reaction mixture was filtered and the filtrate was washed with water, and concentrated to dryness. The residue was chromatographed on a silica gel column to give bibenzyl in 70 % yield.

Several examples of the coupling of the chlorides are summarized in the Table. Racemic α-chloroethylbenzene gave 2,3-diphenylbutane consisting of meso and dl isomers in a ratio of 1:1. A pair of isomers was also formed in the coupling of racemic α-chlorobutylbenzene. In the case of benzyl bromide the reaction was completed, within 5 minutes, faster than the reaction of the corresponding chloride under the same conditions to give bibenzyl in a similar yield.

The reaction was effected in various organic solvents: benzyl chloride was treated with $CoCl(Ph_3P)_3$ in organic solvents such as toluene, 1,2-dimethoxyethane, ethyl acetate, acetone, acetonitrile and N,N-dimethylformamide at room temperature to give rise to bibenzyl in 60-70 % yields.

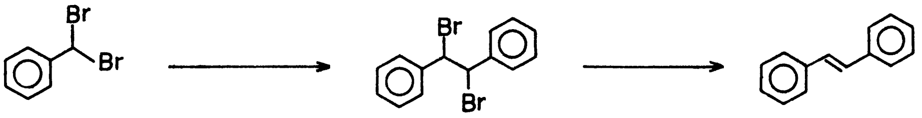
A reaction of a benzylic geminal dibromide, benzal bromide, with $CoCl(Ph_3P)_3$ (1.2 equiv.) in benzene at 50°C gave exclusively E-stilbene in 68 % yield. The formation of E-stilbene was assumed to proceed through the intramolecular reductive

Table Reductive coupling of benzylic halides[a]

Benzylic chloride	Reaction condition	Product	Yield(%)[b]
	r.t. 1.5 h		70
	r.t. 1 h		69[c]
	r.t. 2 h		75[d]
	r.t. 2 h		83
	r.t. 17 h		67

[a] Carried out in benzene by the use of 1.2 equiv. of the reagent. [b] Isolated yield. [c] Both meso (mp 124-125°C)[5)] and dl (oil)[5)] isomers were yielded in a ratio of 1:1 and were separated by silica gel column chromatography. [d] Both meso (mp 96-97°C)[6)] and dl (oil) isomers were formed in a ratio of 2:3 and were separated by silica gel column chromatography.

coupling of initially formed 1,2-dibromostilbene from the observation that 1,2-dibromostilbene was detected as a minor product on treatment of benzal bromide with 0.5 equiv. of $CoCl(Ph_3P)_3$ at room temperature. This was supported by the reaction of both meso and dl 1,2-dibromostilbene with $CoCl(Ph_3P)_3$ at 40°C for 3 h giving E-stilbene in 94 and 91 % yields, respectively.



A reaction of a homobenzyl halide, phenethyl bromide (benzene, 40°C, 8 h) afforded 2,3-diphenylbutane in 40 % yield as a mixture of meso and dl isomers (3:2). The reaction probably involves a 1,2-shift of hydrogen from the benzylic to homobenzylic position in the initially formed homobenzyl radical intermediate[7)].

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