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> SHORT COMMUNICATIONS

Formation of Polyaromatic Compounds by Coupling of Aryl Iodides with Arylacetylenes in the Presence of Palladium-Based Ligand-Free Catalytic Systems

E. V. Larina, A. A. Kurokhtina, E. V. Yarosh, N. A. Lagoda, and A. F. Schmidt*

Irkutsk State University, ul. K. Marksa 1, Irkutsk, 664003 Russia *e-mail: aschmidt@chem.isu.ru

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Cross-coupling of aryl, hetaryl, and vinyl halides with acetylenes with formation of substituted alkynes (Sonogashira reaction) is catalyzed by Pd(II) complexes in the presence of a base, copper(I) compound, and organic ligand [1]. Many examples have been reported for the formation of analogous products in high yield in the absence of copper(I) compound but in the presence of organic ligands (see, e.g., pioneering publication [2]). If neither copper compound nor organic ligand is added, the yield of the Sonogashira reaction sharply decreases. For example, the yield of diphenylacetylene in the reaction of equimolar amounts of iodobenzene and phenylacetylene catalyzed by $Pd(OAc)_2 - 2 PPh_3$ was quantitative, but it decreased to less than 3% in the absence of triphenylphosphine. Nevertheless, the conversion of both phenylacetylene and iodobenzene was complete. At first glance, this result may be rationalized by the fact that in the absence of Cu(I) and ligand the major reaction pathway is carbopalladation of acetylene (c) rather than nucleophilic substitution of halogen (b) in the product of oxidative addition (a) of organic halide to

Pd(0) by acetylide ion (Scheme 1). Carbopalladation of acetylene gives σ -alkenyl palladium complex analogous to products of oxidative addition of vinyl halides to Pd(0). It is known that the stability of such complexes (even when β -hydrogen atoms are present therein) allows catalytic coupling of vinyl halides with various nucleophiles to be accomplished (e.g., Heck [3], Suzuki [4], Kumada [5], and Buchwald–Hartwig reactions [6]). Thus, in the absence of Cu(I) and strong ligands it becomes possible to efficiently generate arylated σ -alkenyl palladium complexes from aryl halides and acetylenes, and these complexes are capable of reacting with various nucleophiles. However, this approach has not been implemented so far in cross-coupling reactions (Scheme 1).

In fact, the only example of such transformations is the three-component reaction of aryl halides with acetylene and arylboronic acid [7, 8]. This reaction conforms to the following path: oxidative addition (a), carbopalladation (c), and transmetalation (e)(Scheme 1). The feasibility of the above approach was indirectly confirmed by the formation of enynes as





 $1, Ar = Ar' = Ph; 2, Ar = Ph, Ar' = 4-MeC_6H_4; 3, Ar = Ph, Ar' = 4-MeOC_6H_4; 4, Ar = Ph, Ar' = 4-MeC(O)C_6H_4; 5, Ar = 4-MeC_6H_4, Ar' = Ph; 6, Ar = 4-MeOC_6H_4, Ar' = Ph; 7, Ar = 4-MeC(O)C_6H_4, Ar' = Ph; 8, Ar = 4-MeC_6H_4, Ar' = 4-MeOC_6H_4.$

Sonogashira by-products in the two-component system aryl halide–acetylene in the absence of Cu(I) [9], as well as by studying model stoichiometric reactions [10]. In this case, enynes were formed according to the following reaction sequence: oxidative addition (a), carbopalladation (c), and nucleophilic substitution (f), where acetylide ion acted as nucleophile in the final step (Scheme 1).

We were the first to obtain experimental evidences for the third path including successive carbopalladation of the second and third acetylene molecules (Scheme 1, d). In the reactions of aryl iodides with excess arylacetylenes (Scheme 2; 8 examples), apart from small amounts of the corresponding diarylacetylene 1 (Sonogashira product) and enyne 2 (observed previously), we detected tetraarylbenzenes 3-5 and tetraarylfulvenes 6-8. Tetraarylfulvenes 6-8 were formed via Markovnikov carbopalladation of the first arylacetylene molecule, so that the product possessed no β -hydrogen atom necessary for elimination of palladium and closure of benzene ring after successive carbopalladation of two more arylacetylene molecules. The cyclization to six-membered ring with formation of tetraarylbenzenes is possible only in the case of anti-Markovnikov carbopalladation of the first arylacetylene molecule. The presence of three regioisomeric tetraarylbenzenes 3-5 and three regioisomeric tetraarylfulvenes 6–8 in the reaction mixture indicates different regioselectivities in the carbopalladation of the second and third arylacetylene molecules. Thus, two-component reactions of organic halides with acetylenes may form the basis of a new family of two- and three-component couplings with various nucleophiles.

Coupling of aryl iodides with arylacetylenes (general procedure). The reactions were carried out at 80° C in a reactor equipped with a rubber septum and magnetic stirrer (477.5 rpm) by mixing 5 mL DMF, 5 mmol of aryl iodide, 10 mmol of arylacetylene, 0.08 mmol of Pd(OAc)₂, 1 mmol of naphthalene (internal standard), and 6.5 mmol of tributylamine (base). Samples were withdrawn intermittently and analyzed by GC/MS; the yields were determined by the internal standard technique.

Gas chromatographic–mass spectrometric analysis was performed on a Shimadzu QP 2010 Ultra instrument equipped with a GsBP-5MS column (0.25 mm× 30 m, film thickness 0.25 μ m); carrier gas helium, oven temperature programming from 100 to 250°C; total ion monitoring in the a.m.u. range 15–900 (integer values) at a rate of 5000 a.m.u./s. The products were identified by comparing their mass spectra with those included in Wiley, NIST, and NIST05 MS libraries and of authentic samples (Aldrich).

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