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# Nonmetallic Wurtz coupling reaction of perfluorohexyl iodide

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ABSTRACT

It is shown for the first time that the Wurtz reaction can be realized by the action of an organic substance (triphenylphosphine) on an alkyl halide (perfluoroalkyl iodide) without the use of metals. It was found that when trying to prepare the bis (3,3'-aminophenyl) (fluoroalkyl) phosphine oxide by four-step synthesis, in the first stage of the reaction of perfluoro-1-iodohexane with triphenylphosphine does not proceed towards the formation of an intermediate quaternary phosphonium salt. Instead, the carbon chain of perfluoroalkyl iodide dimerizes to form perfluorododecane - Wurtz reaction product. We have proposed a new pathway for homocoupling of perfluoroalkylhalides into even-numbered perfluoroalkanes.

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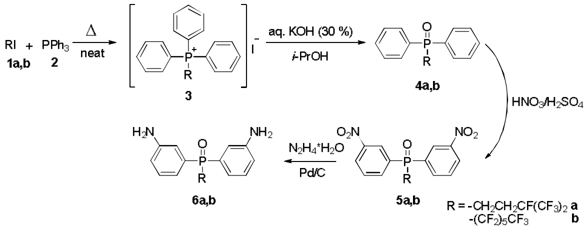
Is known that diarylphosphine oxide derivatives containing fluorinated alkyl substituents are useful as a monomer in preparation of polymers with improved properties such as chemical resistance and electrical insulating property as well as adhesiveness and flame retardancy.[1] The introduction of fluoroalkyl side chain has several advantages such as low dielectric constants, optical clarity, high permeability and high selectivity for gas separation, hydrophobicity and oleophobicity, besides the increased solubility.[2-4] Polymers with phosphorus moieties have several advantages,[5-7] such as good adhesion to various substrates, excellent solubility in organic solvents, high thermal oxidative stability and radiation resistance and resistant to atomic oxygen exposure.[8,9] This study reports a four-stage synthesis about four-step synthesis of bis(3,3'-aminophenyl)fluoroalkylphosphine oxides **6** according to a modified method.[10] The supposed synthetic route is illustrated in scheme 1 and the details are as follows. As a fluoro-containing alkylators are chosen having an ethyl spacer group which separate perfluoroalkyl group from the phosphine oxide group 1,1,1,2-tetrafluoro-4-iodo-2-(trifluoromethyl)butane (**1a**) and 1-iodoperfluorohexane (**1b**).



**Scheme 1.** The supposed synthetic route for synthesis of bis(3,3'-aminophenyl)fluoroalkylphosphine oxides **6**

## 1. Reaction of perfluoroalkyl substituted ethyl iodide *1a* with triphenylphosphine. Synthesis of phosphine oxide *6a*

When 1,1,1,2-tetrafluoro-4-iodo-2-(trifluoromethyl)-butane (**1a**) is used, intermediate phosphonium iodide **3a** is first obtained with a high yield according to known procedure (see supporting information).[1] Should be noted that the using of solvents (toluene) significantly reduces the reaction rate and yield.[1]

Next, obtained phosphonium salt **3a** is undergone Michaelis-Arbuzov rearrangement using 30 % alkali gives two products: target diphenyl(3,4,4,4-tetrafluoro-3-(trifluoromethyl)butyl) phosphine oxide (**4a**) and impurity triphenylphosphine oxide (**4c**) in ratio 9:1. This ratio is constant varying reaction conditions and can be explained on the electron withdrawing nature of the perfluoroalkyl group attached to phosphorus via ethyl spacer group. In the third step phosphine oxide **4a** is converted to bis(3-nitrophenyl)(3,4,4,4-tetrafluoro-3-(trifluoromethyl)-butyl)phosphine oxide (**5a**) via a typical procedure of nitration by a mixture of concentrated nitric acid (4.4 eq.) in concentrated sulfuric acid. In the final step phosphine oxide **5a** is reduced to bis(3-aminophenyl)(3,4,4,4-tetrafluoro-3-(trifluoromethyl)-butyl)phosphine oxide (**6a**) with Pd/C and $NH_2NH_2$. The procedure of preparation of amine with required purity has been optimized to goal the least losses at the purification stage. The best total yield (65 %) and purity (≥98 %) are obtained with only one column purification after nitration stage and no further purification after reduction of phosphine oxide **5a**.

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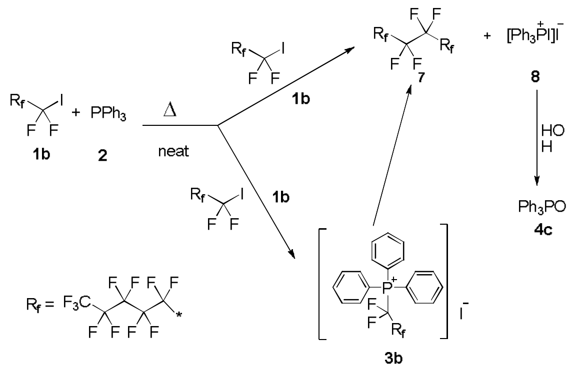
### 2. Unexpected reaction of perfluoroalkyl iodide *1b* with triphenylphosphine

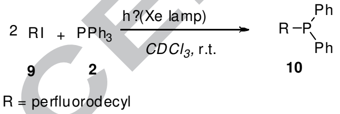
While attempting to prepare the bis (3,3'-aminophenyl)-(fluoroalkyl) phosphine oxide (**6b**) using perfluorinated alkyl iodide **1b** in the first stage of the synthesis, the expected phosphonium salt **3b** isn't detected by ESI-MS (Scheme **2**).



**Scheme 2.** Reaction of perfluoroalkyl iodide **1b** with triphenylphosphine

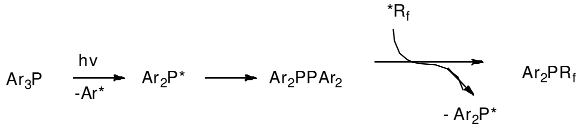
A thorough study of compounds in reaction mixture by ESI-MS has shown a presence of perfluorododecane (**7**) – a product of carbon chain doubling of 1-iodoperfluorohexane **1b** with m/z ratio 661.78 $(M+Na)^{1+}$. Also signals 279.20 $(M+H)^{1+}$ and 557.27 $(2M+H)^{2+}$ are detected which could confirm formation of triphenylphosphine oxide **4c**. However expected signal at 27.9 p.p.m. ($^{31}P$ NMR, $CDCl_3$) produced by triphenylphosphine oxide **4c** is absent, the $^{31}P$ NMR spectrum is contained only signal at 47.5 p.p.m. ($CDCl_3$) which confirms the presence of only triphenyliodophosphonium iodide **8**.[11-12] The absent of the signals of this compound in the conditions of ESI-MS can be explained by the hydrolysis of $[Ph_3P^+I]I^-$ adduct to triphenylphosphine oxide **4c**. The coupling product perfluorododecane (**7**) was obtained with excellent yield (89%).

It was also found that prolonged boiling (100 °C) of iodide **1b** in the dark in the absence of triphenyl phosphine did not lead to dimer 7. Along with this, on the other hand,[13] the literature describes the interaction of perfluorodecyl iodide with triphenylphosphine under the irradiation of the Xe lamp light resulting in the formation of compound **10** by substitution of the phenyl group with a perfluoroalkyl group (Scheme **3**).



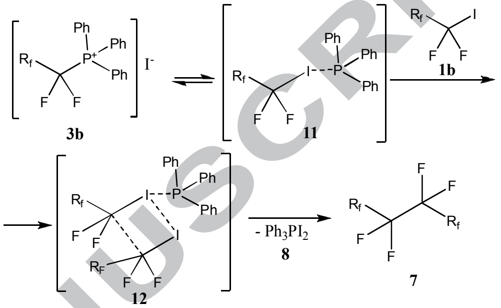
**Scheme 3**. The supposed synthetic route for synthesis of bis(3,3'-aminophenyl)fluoroalkylphosphine oxides 6

Authors[14] based on experimental results (formation of intermediate perfluoroalkyl and diarylphosphonium radicals) proposed a radical mechanism for the formation of compound **10** according to the following scheme **4**.



**Scheme 4**. Proposed pathway of formation compound **10**

The absence of the analog of compound **10** - (HPLC-ESI-MS/MS) in the products of our reaction gives grounds to assume that the dimerization of the perfluoroalkyl group does not occur by the radical pathway and the ion pathway is not even considered because of the presence of strong electrostatic repulsion between like charges. On the other hand, in work[14] by NMR spectroscopy, the study of the behavior of triphenylphosphine in the reaction with electrophiles revealed the existence of an equilibrium between the ionic ($P^{IV}$) and covalent ($P^{V}$) forms of the phosphorus compounds (e.g., $[Ph_3P^+I]\ I^- = Ph_3PI_2$). According to the X-ray structural analysis compound **8** exists in the ionic[15] ($P^{IV}$) form. We performed quantum-chemical calculations with Gaussian 09W program using the Semi-empirical method PM3, and found that covalent ($P^{V}$) form **3b** is unlikely. A comparison of the enthalpies of the transition state (TS) **11** (65.79 kcal/mol) and form **3b** (83.42 kcal/mol) shows a greater possibility of TS **11**.



**Scheme 5**. Proposed pathway of formation compound **7**

From all the above, we assume that the Wurtz dimerization of perfluoroalkyl iodide under the action of triphenylphosphine can proceed through a "push-pull" pathway. In case a three-molecular act, which is statistically unlikely, or stepwise, through the formation of a quaternary phosphonium salt **3b**, by interaction of the transition form (intermediate **11**) with perfluoroalkyl iodide (**1b**) by synchronous 4-centered intermediate **12** (see Scheme **5**).

*Conclusion*

Thus, we managed to get the product in quantitative yield. The found method opens the way to a simple and effective synthesis of perfluorinated hydrocarbons, excluding the use of metals and flammable explosive techniques for carrying out the reactions of Wurtz, Grignard. We have proposed a probable pathway for the formation of compound **7** by homocoupling of compound **1b**, but the establishment of a reaction mechanism requires further investigation.

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## Supplementary Material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/

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**Graphical Abstract**

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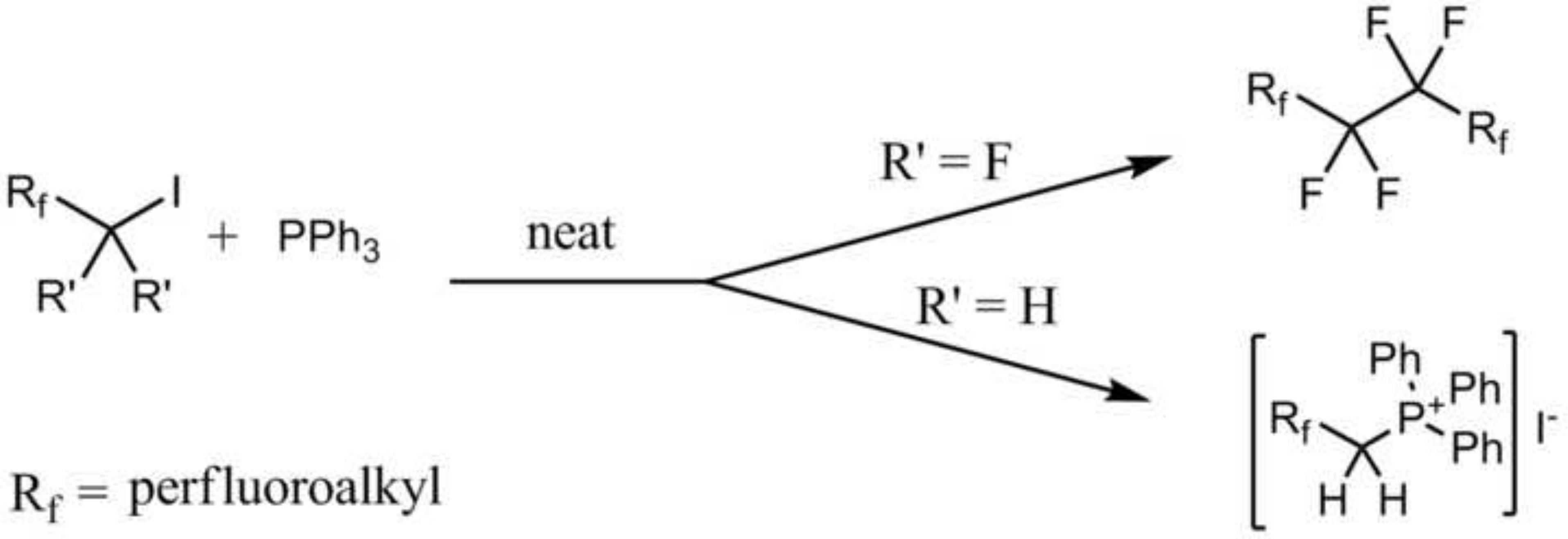

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A new pathway of dimerization of perfluoroalkyl halides to perfluoroalkanes was found. Perfluoroalkyl halides under the action of triphenylphosphine undergo homocoupling. Not of forming of the intermediate quaternary phosphonium salt.

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