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# Simple Syntheses of Polysubstituted Arenes Via Acyclic Precursors

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Summarizes the syntheses of polysubstituted arenes containing perfluoroalkyl group(s) via acyclic precursors.

Keywords: phosphorane; polysubstituted arene; perfluoroalkynoate; acyclic precursor

#### INTRODUCTION

Polysubstituted arenes are important intermediates in industry of synthetic medicines and dyestuffs, their fluoroalkylated analogues are more attractive as a result of the lipophilicity, electronegativity and the relatively small size of the fluoroalkyl group<sup>[1,2]</sup>. However, their preparations using the classical aromatic substitution reaction suffered from long synthetic routes, difficult to separate the positional isomers and hard to introduce the fluoroalkyl group<sup>[3]</sup>. Therefore, to study the convenient and efficient syntheses of fluorinated polysubstituted arenes is valuable in organic synthetic methodology. Recently, we had reported the syntheses of fluoroalkylated polysubstituted arenes through the addition of a phosphorane to a perfluoroalkynoate producing an acyclic precursor(1) possessing a conjugated six-carbon main chain with a terminal carbonyl group, when undergo intramolecular elimination of Ph<sub>3</sub>PO to afford polysubstituted aromatic compounds. Several types of tri- and tetra-substituted aromatic compounds(2-9) were synthesized by using this method<sup>[4-10]</sup>. It is a facile and

efficient method attributing to its simplicity and the production of only a sole product with functional groups at definite positions.

To synthesize polysubstituted arenes, the key step is to prepare the acyclic precursor—a phosphorane with a conjugate six-carbon main chain and a terminal carbonyl group. We have designed [4+2], [3+1+2] and [2+2+2] modes to get the precursor. Polysubstituted arenes were obtained by heating the precursor in certain solvent.

#### [4+2] MODE

#### 1. Synthesis of Methyl 2-Perfluoroalkyl-6-methoxybenzoates

#### 2. Synthesis of Ethyl 2-Ethoxy-4-methoxy-6-perfluoroalkyl-benzoates

3. Synthesis of Methyl 1-Alkoxy-3-perfluoroalkyl-2-naphthoates

#### [3+1+2]MODE

1. Synthesis of Methyl 2.6-Bisperfluoroalkylbenzoates

#### [2+2+2]MODE

1. Synthesis of Dimethyl 5-Perfluoroalkylbiphenyl-2,4-dicaboxylates and Dimethyl 4-Methyl-,  $4-(\alpha-Furyl)$ - and  $4-(\alpha-Thienyl)$ -6-perfluoroalkylisophthalates

# 2. Synthesis of Dimethyl 3-Perfluoroalkyl-4-(3-oxo-2-triphenylphosphoranylidene)-pent-2-enedioate and Its Cyclization

$$\begin{array}{c} \text{Ph}_{3}\text{P}=\text{CHCOMe} \xrightarrow{\text{HC}\equiv\text{CCO}_{2}\text{Me}} \\ \text{Ph}_{3}\text{P}=\text{C} \xrightarrow{\text{COMe}} \\ \text{Ph}_{3}\text{P}=\text{C} \xrightarrow{\text{COMe}} \\ \text{Ph}_{3}\text{P}=\text{C} \xrightarrow{\text{COMe}} \\ \text{CH}=\text{C} \xrightarrow{\text{CO}_{2}\text{Me}} \\ \text{CH}=\text{C} \xrightarrow{\text{CO}_{2}\text{Me}} \\ \text{C}=\text{CHCO}_{2}\text{Me} \\ \text{R}_{F} \xrightarrow{\text{C}_{2}\text{F}_{5}} \\ \text{R}_{F} \xrightarrow{\text{C}_{3}\text{F}_{7}} \\ \text{MeO}_{2}\text{C} \xrightarrow{\text{COMe}} \\ \text{R}_{F} \xrightarrow{\text{COMe}} \\ \text{CO}_{2}\text{Me} \\ \text{R}_{F} \xrightarrow{\text{CO}_{3}\text{F}_{7}} \\ \text{R}_{F} \xrightarrow{\text{COMe}} \\ \text{CO}_{2}\text{Me} \xrightarrow{\text{CO}_{2}\text{Me}} \\ \text{CO}_{2}\text{Me} \xrightarrow{\text{CO}_{2}\text{Me}} \\ \text{CO}_{2}\text{Me} \xrightarrow{\text{CO}_{2}\text{Me}} \\ \text{CO}_{2}\text{Me} \xrightarrow{\text{CO}_{2}\text{Me}} \\ \text{CO}_{3}\text{MeO}_{2}\text{C} \xrightarrow{\text{COMe}} \\ \text{CO}_{4}\text{MeO}_{2}\text{C} \xrightarrow{\text{COMe}} \\ \text{CO}_{5}\text{MeO}_{2}\text{C} \xrightarrow{\text{CO}_{4}\text{MeO}_{2}\text{C}} \\ \text{CO}_{5}\text{MeO}_{2}\text{C} \xrightarrow{\text{CO}_{4}\text{MeO}_{2}\text{C}} \\ \text{CO}_{6}\text{MeO}_{2}\text{C} \\ \text{CO}_{6}\text{$$

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