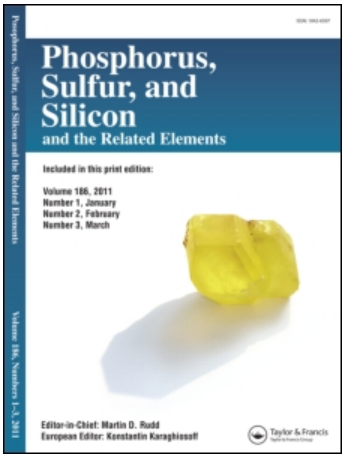

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Simple Syntheses of Polysubstituted Arenes Via Acyclic Precursors

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

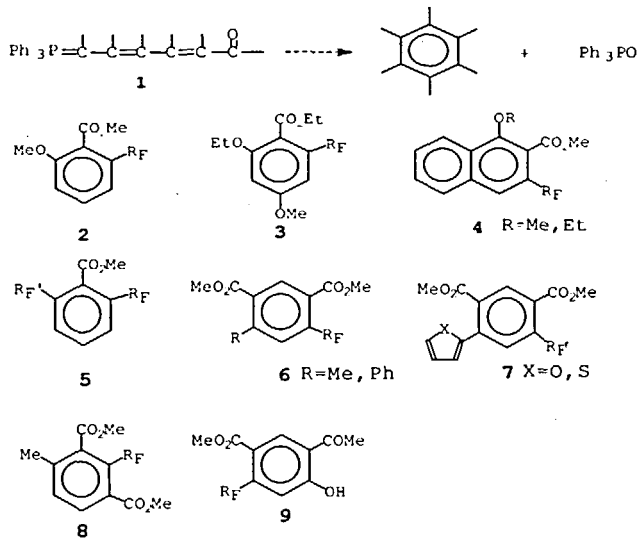
Keywords: phosphorane; polysubstituted arene; perfluoroalkynoate; acyclic precursor

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[1,2]. 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[3]. 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_3PO to afford polysubstituted aromatic compound. Several types of tri- and tetra-substituted aromatic compounds(**2-9**) were synthesized by using this method[4-10]. It is a facile and

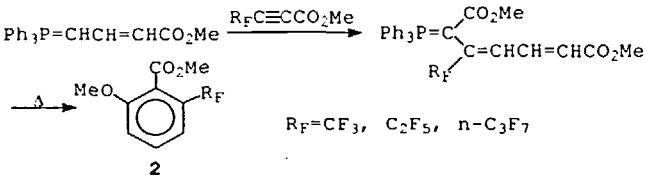
efficient method attributing to its simplicity and the production of only a sole product with functional groups at definite positions.

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.

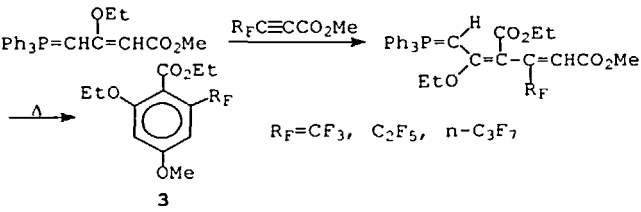


[4+2] MODE

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

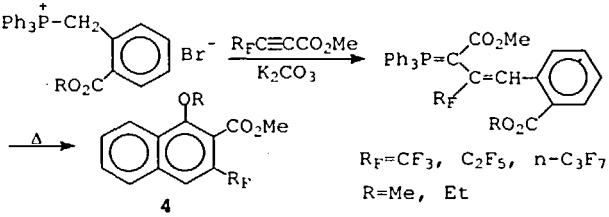


2. Synthesis of Ethyl 2-Ethoxy-4-methoxy-6-perfluoroalkyl-benzoates



3

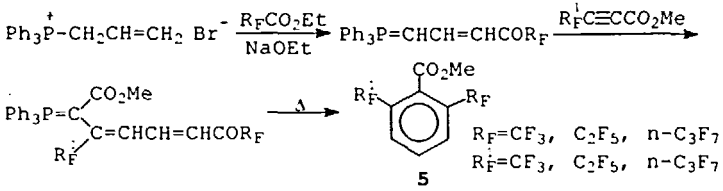
3. Synthesis of Methyl 1-Alkoxy-3-perfluoroalkyl-2-naphthoates



4

[3+1+2]MODE

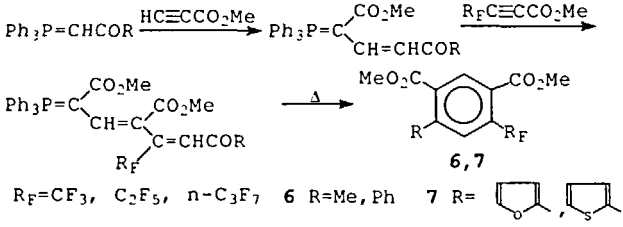
1. Synthesis of Methyl 2,6-Bisperfluoroalkylbenzoates



5

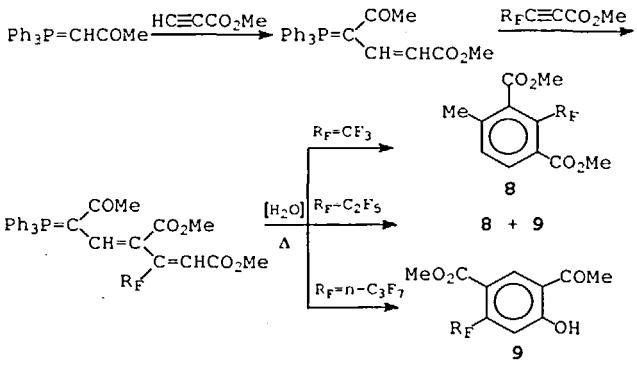
[2+2+2]MODE

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



6,7

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



Acknowledgements

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