Journal of Fluorine Chemistry 185 (2016) 213–223

Contents lists available at ScienceDirect

Journal of Fluorine Chemistry

journal homepage: www.elsevier.com/locate/fluor

Unusual photocyclization of perfluoro *cis*-1,2-dimethyl-1,3-butadienyl benzenes as a means to synthesize partially fluorinated naphthalenes

Michiharu Yamamoto, Dale C. Swenson, Donald J. Burton *

Department of Chemistry, The University of Iowa, Iowa City, IA 52242, USA

ARTICLE INFO

Article history:
Received 27 July 2015
Received in revised form 21 September 2015
Accepted 22 September 2015
Available online 9 October 2015

Keywords:
Photocyclization
Perfluoro-*cis*-1,2-dimethyl-butadienylbenzene
1,2-Difluoro-3,4-bis(trifluoromethyl)naphthalene
Photoelimination of HF
1,1,2-Trifluoro-3,4-bis(trifluoromethyl)-1,4-dihydronaphthalene

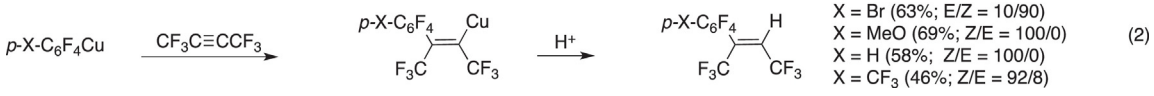
ABSTRACT

Photoirradiation of the titled compounds perfluoro-*cis*-1,2-dimethyl-butadienyl benzenes (**1**), which were prepared in several steps from perfluorovinyl bromide, results in the formation of the corresponding novel naphthalene derivatives and 1,4-dihydronaphthalenes. Isolated 1,1,2-trifluoro-3,4-bis(trifluoromethyl)-1,4-dihydronaphthalene (**3a**) could be converted into 1,2-bistrifluoromethyl-3,4-difluoronaphthalene (**2a**) by base treatment (DABCO); however, **3a** did not lead to **2a** by photoreaction, suggesting **3a** was not a possible photochemical precursor. Competitive photoreaction studies suggest that varying the substituent on benzene ring (e.g. methyl or trifluoromethyl) does not significantly affect the reaction rate. Presently, this reaction mechanism is not yet clearly understood.

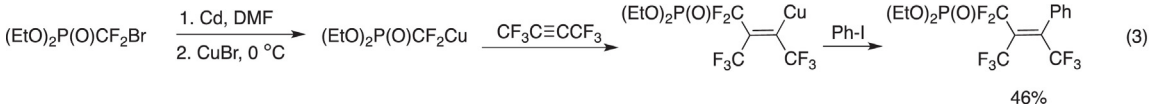
1. Introduction

We have reported that trifluoromethylcopper [1,2], F-vinyl copper [3,4], and F-acetylenic copper [5] reagents could be readily obtained via copper(I) halide metathesis reaction of the corresponding cadmium or zinc reagent (Eq. (1)). These reagents have found extensive utility in preparative organofluorine chemistry [6]. Terminal F-vinyl copper reagents added to perfluoroalkynes can give extended dienyl copper reagents, which could be functionalized via coupling reactions (Eq. (2)) [7,8]. The reaction of F-dienyl copper reagents with aryl halides generates coupled products (Eq. (3)) [7–10]. We focused on perfluoro *cis*-1,2-dimethyl butadienyl benzenes (1) which could be readily prepared from perfluoro-1,3-butadienyl copper (6) reagents (Scheme 1).

$$R_FCF=CFX + M \xrightarrow[RT-60^\circ C]{DMF} R_FCF=CFMX + (R_FCF=CF)_2M + MX_2 \xrightarrow[RT]{Cu(I)X} R_FCF=CF=CFCu \quad X=Br,I \quad M=Cd,Zn \quad 68-99\% \tag{1}$$



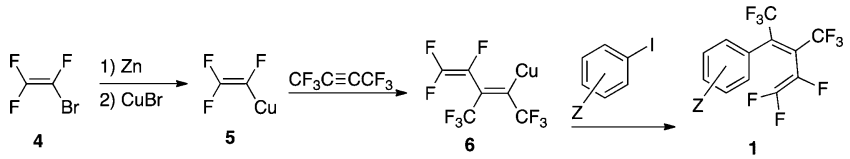
(2)



(3)

* Corresponding author.
E-mail address: mburton105@gmail.com (D.J. Burton).

http://dx.doi.org/10.1016/j.jfluchem.2015.09.016
0022-1139/

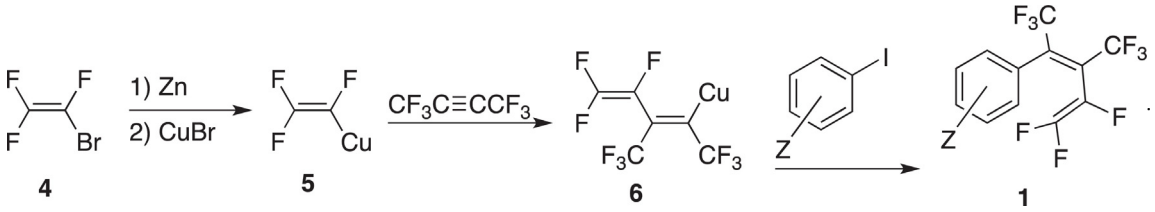


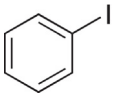
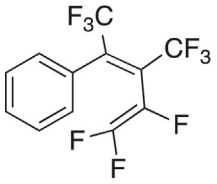
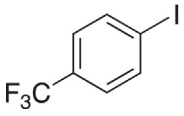
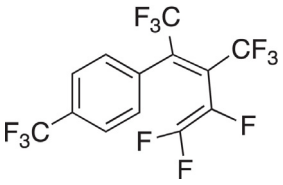
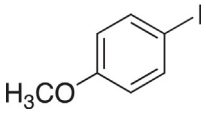
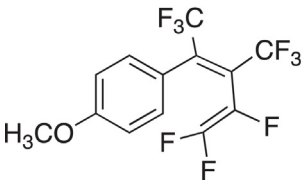
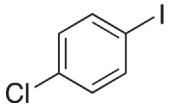
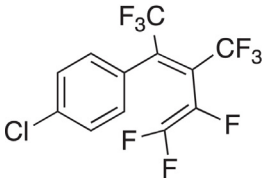
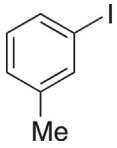
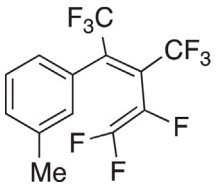
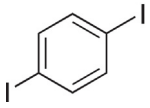
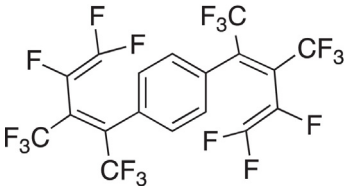
Scheme 1. Synthesis of perfluoro *cis*-1,2-dimethyl butadienyl benzenes (**1**).

2. Results and discussion

Preparation of **1** was carried out by the method [7] shown in Table 1. These transformations were carried out by the one-pot reaction under N_2 atmosphere. Conversion of **5** to **6** was done at room temperature and the yield was calculated by ^{19}F NMR spectroscopy using an internal trifluoromethyl benzene standard. In the conversion of **6** to **1**, a variety of functionalized aryl iodides

Table 1
Preparation of perfluoro-*cis*-1,2-dimethyl-butadienyl benzenes **1**.



Entry	Aryl iodide	1	Yield (%)[a]
1a			76
1b			83
1c			87
1d			86
1e			91
1f			52

[a] Isolated yields based on aryl-iodide.