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Synthesis, properties and application of electronically-tuned tetraarylarsonium salts as phase transfer catalysts (PTC) for the synthesis of *gem*-difluorocyclopropanes

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ABSTRACT

Preparation of *gem*-difluorocyclopropane from α-methylstyrene and chlorodifluoromethane was investigated under basic two-phase conditions. Although simple tetraalkylammonium salts appeared uneffective as phase-transfer catalysts (PTC) for this purpose, tetraphenylarsonium chloride displayed moderate activity, and inspired studies of the phenomena. To improve its efficiency we synthesized set of electronically-tuned tetraarylarsonium analogues. Their preparation revealed interesting exchange process of aryl substituents on the arsonium center, whereas activity studies demonstrated a correlation of catalytic efficiency with electronic effects of the substituents. Two of the tetraarylarsonium catalysts were characterized by X-ray studies.

1. Introduction

Synthesis of *gem*-dihalocyclopropanes [1] and their transformations [2,3] gained a widespread interest in chemical literature, and method of choice of their preparation is two-phase catalytic system utilizing trihalomethanes and solution of inorganic base. According to the mechanism proposed by Mąkosza [4–6] deprotonation of trihalomethane at the interfacial region generates an alkali metal salt, which remains trapped until it exchanges with lipophilic organic cation of the catalyst, usually a quaternary ammonium salt (Q^+X^-). Then, the newly formed lipophilic pair enters the organic phase, where trihalomethyl anion spontaneously dissociates into the dihalocarbene and halide anion. Then, dihalocarbene adds to the double bond of the olefin, while Q^+X^- migrates back to the interface and exchanges anion in a following turnover of the catalytic cycle (Fig. 1).

Although the presented protocol is very efficient, and does not require application of strictly anhydrous conditions as other homogeneous systems [7], preparation of analogous *gem*-difluorocyclopropanes [8–15] from chlorodifluoromethane (**1**, freon 22) appeared to be virtually impossible. As soon as in 1971 Weyerstahl reported that 1-bromo-1-fluoro- and 1-chloro-1-fluorocyclopropanes can be synthesized under basic two-phase conditions, in contrast to 1,1-difluoroanalogues [16]. Soon thereafter Buddrus proposed an alternative procedure, utilizing chlorodifluoromethane, ethylene oxide, and tetraalkylammonium bromide, as a catalyst [17]. Under homogeneous conditions bromide anion opened oxirane ring giving bromoethoxide, which acted as a base. Despite high efficiency of this protocol in the synthesis of *gem*-difluorocyclopropanes, its application was limited by harsh reaction conditions: heating in autoclave to 100–140 °C. Another approach was demonstrated by Jończyk, et al. [18] Under basic PTC conditions mixture of bromoform and dibromodifluoromethane generated difluorocarbene, which added to alkenes. Important mechanistic difference was based on the presence of bromoform, which deprotonated at the interface, and so-formed tribromomethyl anion, after transportation to the organic phase, induced halophilic reaction with CF_2Br_2. Then, difluorocarbene, generated in the absence of hydroxide, efficiently added to alkenes.

The presented data suggest that limitations of efficient generation of difluorocarbene and its addition to alkenes under basic two-phase conditions most likely arise from unfavorable position of the $CX_3^- \leftrightarrows CX_2 + X^-$ equilibrium that results in decomposition of halodifluoromethyl anion at the interface, prior to the migration to the bulk organic phase. In this context

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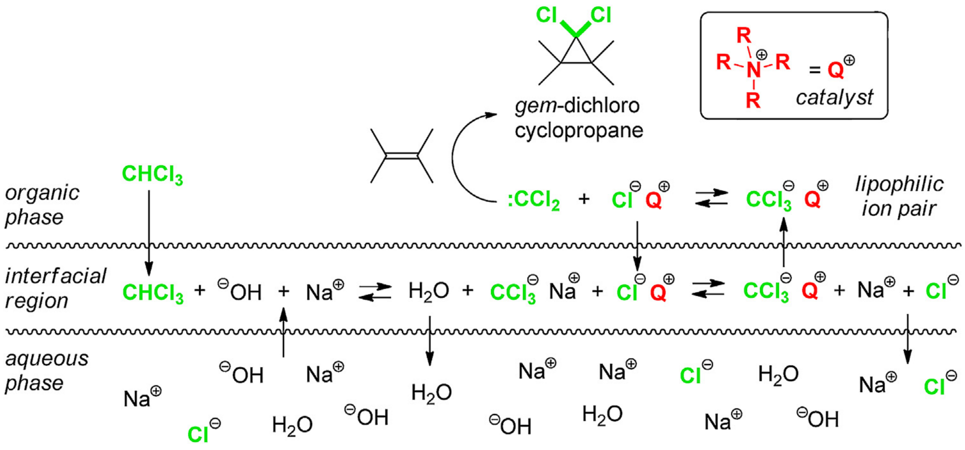


Fig. 1. Mechanism of synthesis of *gem*-dichlorocyclopropanes under PTC conditions with quaternary ammonium salt [4–6].

important observations were described by Dehmlow, who studied effect of PT-catalysts on product distribution in reaction of bromoform with allyl bromide under basic conditions [19]. In the process two competitive reactions may simultaneously occur: addition of dibromocarbene to the C=C bond, and S_N2 substitution of Br^- with CBr_3^- ($CH_2=CHCH_2Br + CBr_3^- \rightarrow CH_2=CHCH_2CBr_3 + Br^-$). As both species CBr_2 and CBr_3^- remain in equilibrium ($CBr_2 + Br^- \leftrightarrows CBr_3^-$), catalysts, which favor reaction of the latter form, are expected to shift the equilibrium toward anionic form. Interestingly, in this role tetraphenyl arsonium chloride appeared to be very efficient catalyst [20], strongly favoring formation of the substitution product. Although exact nature of the effect remained unclear, we believed that similar approach may help to stabilize the short-living chlorodifluoromethyl anion, generated by deprotonation of **1**, by shifting unfavorable equilibrium of decomposition to difluorocarbene [21].

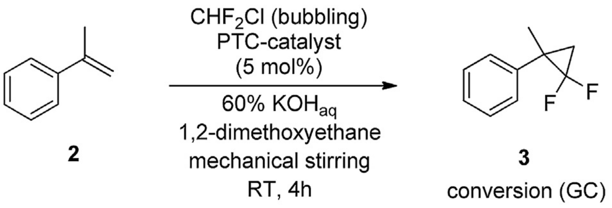
In our report we present studies of two-phase reaction of **1** with model α-methylstyrene under basic conditions catalyzed with tetraarylarsonium salts. We demonstrate also our attempts on synthesis of electronically-tuned tetraarylarsonium salts, novel catalysts for the PTC processes.

2. Results and discussion

2.1. Preliminary experiments with chlorodifluoromethane (1) under PTC conditions

Our studies started from preliminary experiments, to define initial reaction conditions and parameters. As one of the reagents is a gas at RT (**1**; b.p. = –41 °C) we decided to bubble it through the reaction mixture (see Scheme 1), and use ethereal solvent, which display high solubility of **1** at RT.

To reduce blowing away of the solvent by the bubbled gas we used 1,2-dimethoxyethane, which has relatively high boiling point (b.p. = 85 °C). Other parameters were inspired by protocol published recently for other PTC process (concd aqueous solution of KOH with mechanical stirring of the mixture) [22]. As a model olefin we applied α-methylstyrene (2-phenylpropene), alkene of moderate nucleophilicity. Samples of upper organic phase were taken and analyzed with GC. Original sample of 1-methyl-1-phenyl-2,2-difluorocyclopropane **3** was synthesized according to the literature method [18].

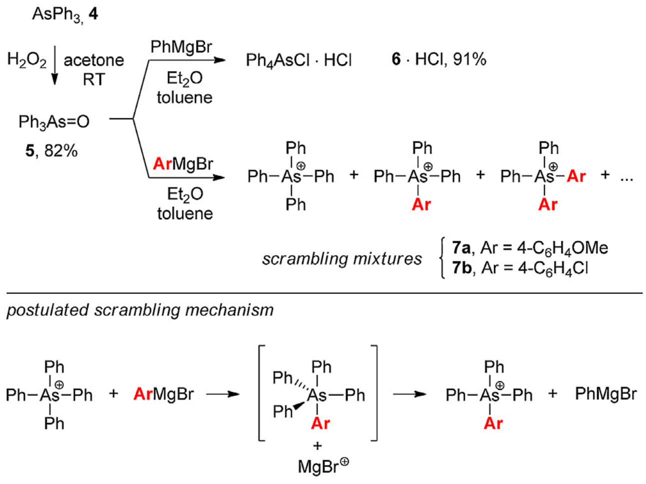


Scheme 1. Studies of model synthesis of *gem*-difluorocyclopropane **3**.

With simple benzyltriethylammonium chloride as a catalyst (TEBACl, 5 mol%) we observed ≤3% of conversion of **2** according to GC. However, with commercially available tetraphenylarsonium chloride (5 mol%), the process run much better, giving 35% of conversion to **3**. It is worth to stress that hydrodynamic conditions substantially affect the process – mechanical stirring is crucial to reproduce the results. In routine experiments at the beginning (usually first 3–4 h) we observed a moderately exothermic hydrolysis of **1** (temperature was kept at 25–35 °C with cold water-bath), and gradual conversion of alkene. Then the reaction stopped, and further stirring and bubbling of the chlorodifluoromethane resulted in no changes of the mixture. Besides at lower temperatures (e.g. ice-water bath) viscosity of the mixture, after partial hydrolysis of **1**, made the stirring difficult (at least at scale 19 mmol of **2**, applied in our studies). Unfortunately all attempts to further improve the conversion have failed.

2.2. Attempts of synthesis of unsymmetrical aryltriphenylarsonium salts

Therefore we decided to synthesize modified arsonium catalysts to increase efficiency of the process. Inspiration of this work was a possibility of stabilization and transportation of the unstable $CClF_2^-$ anion in the form of hypervalent complex with the catalyst, instead of simple electrostatic interaction, typical for the ion pairs. Promising candidates for the specific task seemed to be arsonium salts, which may act as simple PTC catalysts [19], and also extend coordination sphere with ancilary ligands to give neutral 5-coordinated arsanes [23]. Interestingly this kind of hypervalent catalysis was demonstrated on organostannanes, applied in synthesis of alkyl fluorides [24]. Both electron-donors and electron-acceptors were selected as substituents in *para* position of the aromatic rings, namely methoxy and chlorine groups. We assumed that hypothetical equilibrium of formation of arsene derivative $Ph_4As^+ + CClF_2^- \leftrightarrows Ph_4AsCF_2Cl$ can be controlled by electronic properties of the arsenium center, modulated with substituents. Optimally, the equilibrium should be established at similar concentrations of the reacting species (K ≈ 1), to favor both: association of the anion at the interface, and its release in the bulk organic phase.



Scheme 2. Reactions of triphenylarsine oxide (**5**) with arylmagnesium bromides (top), and postulated scrambling mechanism (bottom).

Initially, to make the preparation of modified arsonium salts simple, we tried to introduce substituents to one aromatic ring of the cation. For this purpose commercially-available triphenylarsine **4** was oxidized with hydrogen peroxide in acetone to triphenylarsine oxide **5** in 82% of yield, and then transformed into tetraphenylarsonium chloride-hydrochloride in reaction with phenyl magnesium bromide [25]. After crystallization from aqueous solution of HCl product **6** · HCl was obtained in 91%, based on arsine oxide **5** (Scheme 2, top).

Then, we generated 4-methoxyphenyl magnesium bromide, and 4-chlorophenyl magnesium bromide and treated with Ph_3AsO (**5**) under the same conditions. In both cases after quench and aqueous work-up we obtained solid products, but attempts of further crystallization were unsuccessful. Surprisingly ^1H and ^{13}C NMR analysis of product **7a** revealed a complex mixture. Although aromatic region (6–8 ppm) was poorly diagnostic at ^1H NMR, close examination of signals around 3.8 ppm revealed presence of 4 singlets, characteristic for the OMe groups, with very close chemical shift values (±0.01 ppm; Fig. 2, left).

Interestingly, a similar pattern was observed also at ^{13}C NMR for signals around 164 and 56 ppm, attributable to C_{arom}-OCH_3, and C_{arom}-OCH_3, respectively (Fig. 2, center). Corresponding components of the mixture differed very slightly in structure, giving a gradual change of chemical shifts of the resonances. Therefore, we assumed that individual components of the mixture are arsonium salts, which differ in a number of aromatic rings substituted with methoxy groups, and the observed differences in chemical shifts arise from electronic effects of the substituents transmitted by the tetracoordinated arsonium center. Indeed, when the mixture was analyzed with mass spectrometry, we observed a similar set of peaks at 383, 413, 443, 473, attributable to $AsPh_4$, $AsPh_3Ar$, $AsPh_2Ar_2$, and $AsPhAr_3$ cations, respectively (confirmed with HRMS, $Ar = 4\text{-}C_6H_4OMe$; Fig. 2, right) [26]. The obtained data clearly suggested that during the reaction aromatic ligands equilibrate on the arsonium center, leading to inseparable mixture of tetraarylarsonium salts. Interestingly, a similar pattern was observed on MS spectrum of mixture **7b** with 4-chlorophenyl magnesium bromide, but in this case NMR spectra were more difficult to interpret. On the base of literature data [23] this kind of exchange most likely proceeds by the formation of intermediate pentavalent arsanes (Scheme 2, bottom). It is worth to remind, that formation of such hypervalent species (namely $Ar_4AsCClF_2$) was inspiration for our studies.

2.3. Modified synthetic plan – synthesis of tetraarylarsonium salts

The unsuccessful attempts of synthesis of unsymmetrically substituted salts led us to new synthetic targets. We focused on symmetrical tetrasubstituted arsonium salts, which after scrambling of the aromatic rings should lead to the same, well-defined products. Indeed, reaction of Grignard reagents derived from 4-bromoanisole, 1-bromo-4-chlorobenzene, 1-bromo-3,5-dichlorobenzene, and 1-bromo-3,5-bis(trifluoromethyl)benzene with $AsCl_3$ gave arsines **8a**-**d**, which were oxidized to arsine oxides **9a**-**d**, and subjected to next reaction with arenemagnesium bromides, to obtain 4 new tetraarylarsonium bromides **10a**-**d** of excellent purity, according to ^1H and ^{13}C NMR (see the Supporting information for details; Scheme 3, top).

Tetra(4-methoxyphenyl)- (**10a**), tetra(4-chlorophenyl)- (**10b**), tetrakis(3,5-dichlorophenyl)- (**10c**) and tetrakis[3,5-bis(trifluoromethyl)phenyl]arsonium bromide (**10d**) were characterized with MS, which confirmed identity of the cations. Unfortunately, attempt of synthesis of analog tetrakis(3,4,5-trimethoxyphenyl) arsonium catalyst appeared to be unsuccessful (Scheme 3, bottom). First we observed that generation of Grignard reagent from 1-bromo-3,4,5-trimethoxybenzene in diethyl ether is extremely slow [27], so we metallated the aryl halide with *n*-BuLi in THF at −78 °C, and treated with $AsCl_3$ to obtain methoxysubstituted arsine **8e** in 79% of yield. Then, the arsine was oxidized

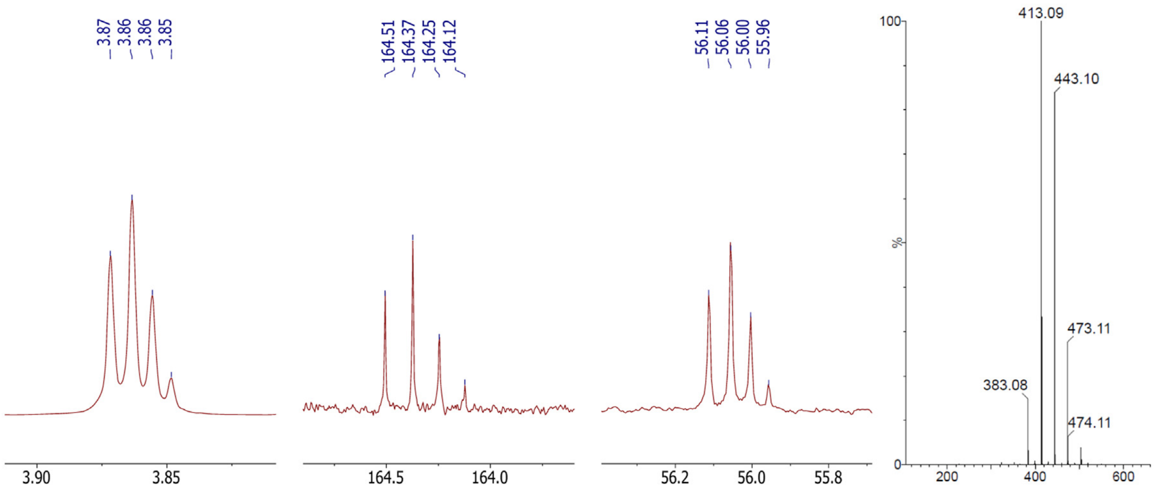
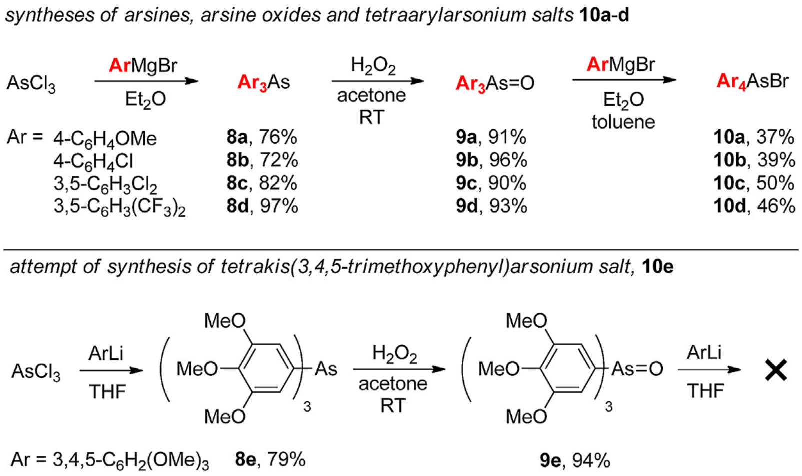


Fig. 2. Selected fragments of ^1H and ^{13}C NMR spectra and mass spectrum of mixture **7a** [26].



Scheme 3. Syntheses of arsines **8a-d**, arsine oxides **9a-d**, and arsonium salts **10a-d** (top), and attempt on synthesis of arsonium salt **10e** (bottom).

with H_2O_2/acetone system, but so-formed arsine oxide **9e**, failed to react further with ArLi. Most likely, presence of nine electron-donor methoxy groups electronically enriched the arsonium center, so the corresponding salt was not formed, or decomposed on attempts of isolation.

To confirm structure of the synthesized arsonium salts, two of them were characterized with X-ray studies. In both cases arsonium center displayed a tetrahedral geometry, and other parameters similar to structure of the parent tetraphenylarsonium cation (Fig. 3) [28,29].

2.4. Studies of catalytic activity of the synthesized tetraarylarsonium salts under PTC conditions

With the synthesized salts in hand we tested model reaction of α-methylstyrene with KOH, **1** and 1,2-dimethoxyethane, catalyzed by **10a**, **10c** and **10d**, and compared with activity of the parent catalyst **6** [31]. The results are presented in Table 1.

In consistency with our expectations we observed an intensive trend of conversions as a function of electronic properties of the arsonium salts. Those substituted with electron-acceptors displayed smaller catalytic activity, whereas donor substituted salt **10a** appeared superior to the parent salt **6**. Unfortunately, the obtained conversion reached maximum 53% that was still unsatisfactory for preparative purposes (analysis of the mixture with ^1H NMR confirmed presence of approximately equimolar mixture of **2** and **3**, as only detectable compounds). As pairs of alkenes and their 1,1-difluorocarbene adducts usually display very similar properties (boiling point, polarity, etc.), they are poorly separable by routine methods. Therefore, we did not attempted isolation of the synthesized product, although our experience in preparation of dihalocyclopropanes and literature data[18] suggest that both alkene **2** and its CF_2 adduct **3** remain stable under the reaction conditions.

Although, the obtained data do not give a definite conclusion about origin of activities of the tetraarylarsonium catalysts (simple electrostatic interaction vs. hypervalent mechanism) best results were obtained with catalyst **10a**, in which positive charge of the arsonium center is delocalized into entire molecule, by the presence of electron-donor methoxy substituents. According to Dehmlow rationale [19], this can be explained by 'soft' character of the large cation, which favors in equilibrium 'softer' trihalomethyl anion, instead of more 'hard' halide anion, stabilizing this form in the organic phase. Alternatively, in terms of the postulated hypervalent mechanism, less electrophilic arsonium center in **10a**, as compared with **6** and more electrophilic salts, tends to release the CF_2Cl^- anion ($Ph_4AsCF_2Cl \leftrightarrows Ph_4As^+ + CClF_2^-$), when the process is rate-determining in the catalytic cycle. Unfortunately,

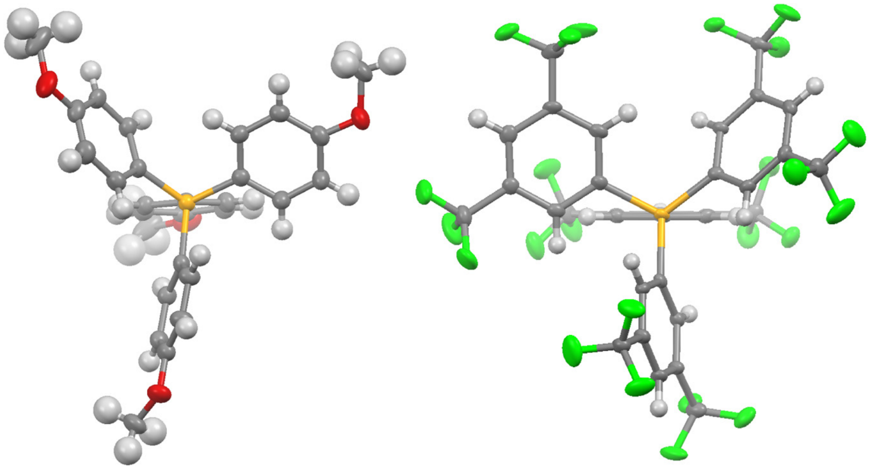


Fig. 3. ORTEP [30] representations of tetraarylarsonium cations (**10a**, left; **10d** right; counterions were omitted for clarity), shown as displacement ellipsoids drawn at the 50% probability level.

Table 1
Conversions of alkene **2** to difluorocyclopropane **3** catalyzed with tetraarylarsonium salts.

Catalyst	Structure	Conversion of **2** to **3** (GC)
10a	As(4-$C_6H_4OMe)_4$ Br	53%
6	$AsPh_4$ Cl	35%
10c	As(3,5-$C_6H_3Cl_2)_4$ Br	25%
10d	As[3,5-$C_6H_3(CF_3)_2]_4$ Br	13%

synthesis of (expectedly) more active catalyst **10e**, bearing four trimethoxyphenyl substituents, was unsuccessful, as described in section 2.3.

3. Conclusions

Pioneered more than 50 years ago phase-transfer catalysis remains a method of choice for the synthesis of *gem*-dihalocyclopropanes, except for difluoroderivatives. Preparation of the latter is still challenging, and justify search of other methods of generation and addition of difluorocarbene to alkenes, as demonstrated by recent achievements in the field [8–15]. We presented exploration of idea of hypervalent stabilization of chlorodifluoromethyl anion generated at the interphase in basic two-phase system by deprotonation of chlorodifluoromethane. Despite promising results (conversion of alkene to difluorocyclopropane adduct exceeded 50%) further improvement seems to be difficult to achieve, due to problems with preparation of electron-rich tetraarylarsonium salts.

4. Experimental section

Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC 1530413 (**10a**) and 1530544 (**10d**). Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, (fax: +44 1223 336033 or e mail: deposit@ccdc.cam.ac.uk).

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jfluchem.2017.03.014.

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[30] The ORTEP projections were generated using Mercury 2.4 program..

[31] Under similar conditions we tested also reaction of **2** with fluoroform (CHF_3), bubbled through the mixture, catalyzed with TEBACl, and **6**. In both cases we did not detected **3** in the reaction mixture according to GC. For similar conclusions about reaction of CHF_3/KOH/dioxane system with **2**, see: C.S. Thomoson, W.R. Dolbier Jr., Use of fluoroform as a source of difluorocarbene in the synthesis of difluoromethoxy- and difluorothiomethoxyarenes, J. Org. Chem., 78 (2013), 8904–8908.