Synthesis of Tri- and Disubstituted Fluorenols and Derivatives Thereof Using Catalytic [2+2+2] Cyclotrimerization

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Abstract: A method for regioselective synthesis of 2,4-disubstituted and more highly substituted fluorenols using catalytic [2+2+2] cyclotrimerization of mono- and disubstituted diynes with terminal alkynes was explored. In the former case, the preferential formation of the 2,4-regioisomers was achieved in the presence of Cp*Ru(cod)Cl, whereas Rh-based catalysts tended to provide 3,4-regioisomers as the major products. The 2,4-disubstituted fluorenols were converted into the corresponding 9,9′-spirobifluorene derivatives and their structural and photophysical properties were evaluated.

Keywords: catalysis; cyclotrimerization; spirobifluorene; fluorescence; regioselectivity

1. Introduction

Fluorenols are polycyclic aromatic compounds consisting of two benzene moieties bridged by a methylene group. Compounds with the fluorene scaffold can be found in natural products (e.g., dendroflorin, gramniphenols, vitrofolals, etc.), and many of these substances have interesting biological properties [1]. The unique fluorene moiety, because of its electron donating properties and their large steric hindrance due to its bulkiness, was also used to design effective phosphine ligands for organometallic reactions like Buchwald–Hartwig, Sonogashira, and Suzuki coupling [2]. The use of the Fmoc (9-fluorenylmethyloxycarbonyl) protective group in Merrifield peptide synthesis should also be mentioned [3]. Compounds with the fluorene, and especially spirobifluorene scaffolds, are also of interest in material sciences [4,5]. For example, it was shown as early as 2002 that a spirobifluorene-cored oligoaryl compound could act as an emitter or a host for blue organic light-emitting devices in thin-layer films [6]. As another example, a study showed that appropriate positioning of the donor–acceptor and chromophoric groups onto the fluorenone backbone made it possible to manipulate fluorenones to emit light in from green to blue range of the visible spectrum [7]. Further, copolymers of fluorene with fullerenes have been considered an interesting material for collecting solar light and are therefore promising materials for polymer photovoltaics [8]. One should also not forget the work in the area of spirobifluorenes by Poriel and others, who have devoted much effort to synthesis and property elucidation of various spirobifluorenes and their 2- [9–12] and 4-substituted congeners [12–16]. For example, comparison of photophysical properties of phenyl and pyrimidyl substituted spirobifluorenes in the C2 and C4 positions provided several observations [12].
First, the substitution by a phenyl unit at the C4 position results in weaker modification of the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) levels compared to substitution at the C2 position. This could be attributed to the potential extension of conjugation length and hence a decrease of the HOMO–LUMO gap. Second, the substitution by the electro-deficient pyrimidyl substituent compared to the phenyl one leads to a significant lowering of the LUMO level. However, to the best of our knowledge, there has not been a report on the study of multi-substituted spirobifluorenes, e.g. 2,4-disubstituted ones.

The lack of data is related to the problem of a simple and fast synthesis of a series of such compounds. Although the maternal spirobifluorene was prepared by Gomberg et al. in 1930 [17], this issue has not been addressed to date. All of the previous work used classic synthetic approaches for preparation of 2- or 4-substituted spirobifluorenes based on cross-coupling reactions, such as the Suzuki–Miyaura reaction [18]. Hence, a different and simple approach must be devised.

From a general point of view, the synthesis of compounds possessing specifically decorated benzene rings is an important task of organic synthesis. The most straightforward method for preparation of such compounds is catalytic [2+2+2] cyclotrimerization [19,20] of appropriately substituted alkynes. Since fluorenes belong to the class of compounds possessing benzene rings, we envisioned that their specifically decorated congeners could be prepared using such a methodology. Since our first endeavors in this respect rendered the synthesis of 1,2,3,4-tetrasubstituted fluorenols (precursors for spirobifluorenes) using catalytic cyclotrimerization reactions of suitably substituted diynes with alkynes [21,22], we expected that the same methodology could be applied in this instance as well. With these facts in mind, we set the following goals. First, we aimed to develop a method for the selective synthesis of variously substituted fluorenols (precursor for the respective spirofluorenes) based on catalytic [2+2+2] cyclotrimerization reaction. The main attention was focused on the scope of the selective preparation of 1,2,4- and 1,3,4-trisubstituted, and mainly 2,4-disubstituted fluorenols. Second, we aimed to assess effect of a catalyst on 1,2,4- and 1,3,4-, and 2,4- and 2,3-selectivity in the synthesis of the respective fluorenols. Third, we aimed to convert the fluorenols into the corresponding spirofluorenes. The attention was mainly focused on the preparation of 2,4-disubstituted spirobifluorenes. Fourth, we aimed to evaluate substituent effect in 2,4-disubstituted fluorenols on photophysical properties of the spirobifluorenes.

2. Results

2.1. Synthesis of 1,2,4- and 1,3,4-Trisubstituted Fluorenols

It has been well-established that cyclotrimerization of monosubstituted diynes with terminal alkynes catalyzed by various Rh-catalysts favor the preferential formation of 1,2-isomers (ortho-isomers) [23] at the expense of 1,3-isomers (meta-isomers). However, the selectivity, i.e., 1,2- and 1,3-isomer ratios, can be controlled by the ligand environment around the central rhodium atom—at least to a certain level—as shown recently by us and others [24–34]. This is the result of the reaction mechanism, although the true nature of such regioselectivity has not yet been exactly comprehended. A somewhat more complicated situation may arise when substituted diynes are cyclotrimerized with terminal alkynes. Such a situation was encountered during our study on synthesis of fluorenes using Rh-catalyzed catalytic cyclotrimerization [21]. In this instance, we carried out the cyclotrimerization of diynol 1 with ferrocenylethyne under catalysis of Wilkinson’s catalyst. The reaction provided mixture of 3 (ortho-isomer) and 3’ (meta-isomers) in a 3:1 and 2.5:1 ratio, respectively (Scheme 1).
In order to evaluate generality of this trend, i.e., 3 vs. 3′ selectivity, a series of cyclotrimerizations of 1c with various terminal alkynes 2 was carried out (Table 1). During the course of the experiments, we found that carrying out the reaction under microwave irradiation and in the presence of Ag₂CO₃ gave better yields of the cyclotrimerization products. After work-up, crude fluorenols were immediately oxidized to the corresponding fluorenones 4 with PCC, because they could be handled more easily than the maternal fluorenols 3. In general, the isolated yields of mixtures of fluorenones 4 and 4′ may seem mediocre, but they reflected isolated yields after two steps and purification. Immediately, after running the cyclotrimerizations, crude reaction mixtures were analyzed by proton nuclear magnetic resonance (¹H NMR). The starting compounds 1 were consumed and fluorenols 3 were formed in approximately 50–60% yields (because of overlap of product signals with residual phoshine and other unidentified signals, exact determination was not possible). Another problem constituted separation of the products from residual phosphines, which was very problematic, tedious, and provided rather low isolated yields of the products. As far as potential homocyclotrimerization of 1 is concerned, the respective homotrimer was detected in yields of 2–7% (¹H NMR). In summary, the reactions with 4-methoxyphenylethyne 2a, 4-methylphenylethyne 2b, 3-thienylethyne 2f, and trimethylsilyl ethyne 2g preferentially gave 1,3,4-regioisomer 4′ (Entries 1, 2, 6 and 8), whereas with 4-biphenylethyne 2c, phenylethyne 2d, and 1-pentyne 2g preferentially provided 1,2,4-regioisomer 4 (Entries 3, 4, and 7). Interestingly, the reaction with 4-trifluorophenylethyne 2e gave the equimolar mixture of 4 and 4′ (Entry 5). Concerning conclusions regarding the structural features of alkynes and the obtained regioisomer ratios, it was difficult to rationalize either on the basis of steric hindrance or electronic effects, e.g., polarization of the triple bond, at this point.

Table 1. Cyclotrimerization of 1c with 2 catalyzed by Wilkinson’s catalyst.

| Entry | R               | Yield (%)  | 4:4′  |
|-------|-----------------|------------|-------|
| 1     | 4-MeOC₆H₄       | 43         | 1:3.2 |
| 2     | 4-MeC₆H₄        | 31         | 1:1.6 |
| 3     | 4-PhC₆H₄        | 42         | 1:0.7 |
| 4     | Ph              | 23         | 1:0.8 |
| 5     | 4-CF₃C₆H₄       | 26         | 1:1   |
| 6     | 3-thienyl       | 18         | 1:1.3 |
| 7     | n-Pr            | 25         | 1:0.7 |
| 8     | Me₃Si           | 15         | 1:2.4 |

Isolated yields. Determined by proton nuclear magnetic resonance (¹H NMR).

With respect to our previous work on ligand effect on regioselectivity [34], we were curious whether it was possible to control, or to alter, the regioisomer ratio by changing the ligand environment around the central metal atom. Namely, we asked whether it would be possible to shift the selectivity for formation of 1,2,4-trisubstituted fluorenols. In order to test ligand effect, a brief screening of four
bidentate ligands, namely BINAP, dppp, dpbb, and dppf, was undertaken [35,36]. As a model reaction, the cyclotrimerization of diyne 1c with phenylacetylene 2d was chosen. The catalytic systems were formed by mixing of [Rh(cod)]BF$_4$ with an appropriate ligand at 60 °C for 16 h (Table 2). In all cases, the full conversion of the starting material was observed. Because of the overlap of the phosphine signals with those of internal standards, $^1$H NMR yields could not be determined accurately. However, a gross estimate of conversion to 4d and 4d’ was ~40–50%. The use of dppp and dppf had a positive effect on regioselectivity, preferentially giving rise to regiosomer 4d’. The respective mixture of 4d:4d’ were obtained in ratios of 1:3.2 and 1:2.4, respectively (Entries 1 and 5). Interestingly, the use of BINAPs provided mixtures containing a higher proportion of regioisomer 4d (Entries 3–4). The partial separation of 4d and 4d’ during column chromatography allowed isolation of a sufficient amount of 4d’, which yielded a suitable material for single crystal X-ray diffraction analysis after recrystallization (Figure 1). The isolation and characterization of 4d and 4d’ allowed us to unequivocally interpret the recorded NMR data and determine the respective regioisomer ratios. Since it was next to impossible to separate other regioisomer mixtures into isomerically pure substances, the fluorenones were not converted into the corresponding spirobifluorenes.

Table 2. Cyclotrimerization of 1c with 2d catalyzed by Wilkinson’s catalyst.

| Entry | Ligand   | $\beta$ (°) $^1$ | 4d:4d’ $^2$ |
|-------|----------|-----------------|-------------|
| 1     | dppp     | 91              | 1:3.2       |
| 2     | dpbb     | 94              | 1:1.6       |
| 3     | (R)-BINAP| 93              | 1:0.7       |
| 4     | (S)-BINAP| 93              | 1:0.8       |
| 5     | dppf     | 99              | 1:2.4       |

$^1$ Bite angle. $^2$ Determined by $^1$H NMR.

Figure 1. ORTEP drawing of 4d’ with 50% probability.
2.2. Synthesis of 2,4-Disubstituted Fluorenols

In the next step, we focused on synthesis of disubstituted fluorenols with the main goal of synthesizing selectively 2,4-disubstituted fluorenols as precursors of the corresponding spirobifluorenes. Since only one example of a synthesis and application of a 2,4-disubstituted spirobifluorene has been reported [37] and there is a lack of data regarding their photophysical properties, we decided to develop a strategy for their preparation and to apply it for synthesis of a larger library of such compounds bearing aryl and other substituents with various electron-withdrawing or -donating substituents.

At the outset, we screened several catalytic systems to assess selectivity for the formation of 2,4-substituted fluorenols 6 (meta-isomer). A model reaction was chosen for the cyclotrimerization of diaryln 5a with alkyne 2b (Table 3). As expected, the use of Wilkinson’s catalyst (Entry 1) provided a preferential ortho-isomer 6h’. An attempt to modulate regioselectivity using the [Rh(cod)2]BF4/dppp system was not met with success, and 6h’ was obtained as the major product (Entry 2). In the next step, we decided to use Cp*Ru(cod)Cl, which is known to preferentially give rise to “meta-isomers”. The preferential formation of the “meta-isomer” is the result of different reaction mechanism [38]. As expected, its use resulted in the preferential formation of 6h (a mixture of 6h and 6h’) was obtained in a 10:1 ratio) in a 46% combined isolated yield. A rather low yield of products was the consequence of undesirable homocyclotrimerization of 5 to 7. In order to minimize the side reaction, cyclotrimerization of 5a with various amounts of 2b (1–10 eq) were carried out (Table 4). However, when an excess of seven-fold or higher of 2b was used, the ratio remained almost constant at ~5/1 (Entries 5–7).

With working reaction conditions in hand, we decided to proceed with synthesis of a library of 2,4-disubstituted fluorenols using Ru-catalysis (Scheme 2). All reactions were carried out with 5 and 2 (1:2 molar ratios) catalyzed by Cp*Ru(cod)Cl (10 mol%) in dichloromethane at 20 °C for 5 h. The low molar ratio of 5:2 was kept for the sake of simplicity and to avoid high loads of alkynes 2. The cyclotrimerization of 5 with various alkynes 2 provided a set of 15 differently substituted fluorenols 6a-6o. Thirteen cyclotrimerization were performed with 5a (fluorenols 6a–6m) and two reactions were carried out with 5b (fluorenols 6n and 6o). All products were obtained in isolated yields in the range of 14–62%. Lower isolated yields of products reflected considerable homocyclotrimerization of 5 at the expense of the desirable cross-cyclotrimerization. Interestingly, regioisomer ratios of 6 and 6’ varied from 3:1 to 25:1. There seemed to be a rough general trend, as phenylethylenes bearing electron-withdrawing groups gave rather lower regioisomer ratios (e.g., 6a–6d), whereas those bearing electron-donating group gave higher ratios (6h–6k). Moreover, in some cases, it was possible to isolate the desired 2,4-disubstituted fluorenols (6a–6g, 6k, 6m, and 6n), whereas, in other cases, the respective regioisomer mixtures were inseparable (6h–6j, and 6l,6o). As far as 1H NMR analysis of the regioisomer ratio was concerned, the “meta-regioisomers” were identified by the characteristic doublet in the range of 7.89–8.01 ppm ($J_{meta} = 1.6 \text{ Hz}$). On the other hand, the “ortho-isomers” had characteristic doublets in the range of 6.22–6.45 ppm ($J_{ortho} = 7.6 \text{ Hz}$). The ortho-isomer was isolated in the case of 6’n.

| Table 3. Catalytic cyclotrimerization of 5a with 2b using different catalytic systems. |

| Entry | Catalytic system | Conditions | 6h:6h’ Yield (%) |
|-------|-----------------|------------|-----------------|
| 1     | [RhCl(PPh3)2] (3 mol%), Ag2CO3 (6 mol%) | 180 °C, MW, 1h | 1:2 62 |
| 2     | [Rh(cod)2]BF4 (10 mol%), dppp | THF, 60 °C, 16 h | 1:1.25 40 |
| 3     | Cp*Ru(cod)Cl (10 mol%), | CH2Cl2, 20 °C, 5 h | 10:1 46 |

1. Determined by 1H NMR. 2. Combined isolated yields.
Table 4. Catalytic cyclotrimerization of 5a with various amounts of 2b.

| Entry | 2b (eq) | 6h + 6h', Yield (%) | 7, Yield (%) |
|-------|---------|---------------------|-------------|
| 1     | 2       | 46                  | 40          |
| 2     | 3       | 47                  | 40          |
| 3     | 4       | 66                  | 19          |
| 4     | 5       | 66                  | 18          |
| 5     | 7       | 75                  | 14          |
| 6     | 9       | 76                  | 14          |
| 7     | 10      | 77                  | 15          |

1 Isolated yields. 2 $^1$H NMR yields (1,2,4,5-tetramethylbenzene was used as the internal standard).

Scheme 2. Cyclotrimerization of 5 with 2 to 6 and 6'.
The fluorenols were converted in three steps to the corresponding spirobifluorenes 9 (Scheme 3) [17,39]. The first step involved the oxidations of 6 with PCC and proceeded uneventfully to yield the corresponding fluorenones 8 in generally high isolated yields (73–98%). Their subsequent reactions with 2-biphenyllithium, followed by treatment with a mixture of AcOH/HCl under reflux, resulted in good yields as well. In most cases, the corresponding spirobifluorenes 9 were obtained in a broad range of isolated yields (36–89%). Again, in instances where lower isolated yields of 9 were obtained, considerable problems with purification were met, reducing the amount of obtained material. In two cases, the formation of spirobifluorenes was not successful. Conversion of 8a and 8k (obtained by oxidation of the respective fluorenols by PCC or MnO2, respectively) resulted in formation of complex reaction mixtures, in which the expected products were not detected.

Scheme 3. Formation of spirobifluorenes 9.
2.3. Structural Analysis

Attempts to crystals of some of the spirobifluorenes were provided in case of 9c, 9g, 9h, 9h', 9i, and 9n suitable crystals for X-ray analysis. A typical example is displayed the structure of 9g (Figure 2).

Figure 2. ORTEP drawing of 9g with 50% probability.

In case of 9c, the structure determination was complicated by disorder of one –CF₃, described by two positions of each fluorine atom with a ratio of occupancy factors of 0.62:0.38. The unit cell of 9g contained two symmetrically independent molecules, from which one exhibited a disorder of –CF₃ moiety, hampering the overall precision of results. In case of 9h, the –CF₃ moieties were ordered. However, the position of one of the symmetrical molecules appeared to be occupied by two isomers with a ratio of 0.65:0.35. There were two symmetrically independent molecules in the unit cell of 9h' with disordered –CF₃ moieties. The most difficult structure from the whole series was that of 9n. It was composed of six symmetrically independent molecules in the unit cell, which included one more disordered molecule than others, with overall large displacement parameters of most of the atoms. Therefore, the ability of the crystal to diffract was significantly low. The poor quality of the crystal was triggered on several alerts during validation. However, we decided to include this structure in the paper to complete the series of synthesized compounds.

Concerning the sum of the dihedral angle derived from three C–C bonds (the inner rim C5-C12-C11-C4), which should reflect the degree of molecular twist, it took the following values: 8.1° (4d'), 1.8°(9c), 7.9 and 4.0° (9g), 2.8 and 4.1° (9h), 2.1 and 2.6 (9h'), 1.3 and 2.2 (9i), and 2.4–7.4° (9n). This indicates only a slight deformation of the fluorenyl core.
2.4. Photophysical Properties of Spirobifluorenes 9

We investigated the photophysical properties of the prepared spirobifluorenes 9. All the 2,4-disubstituted spirobifluorenes exhibited a very similar absorption spectra (Figure 3) and presented two thin bands at ~297 and ~309 nm (typical for all known unsubstituted and substituted SBFs) accompanied by a more or less intensive large band of lowest energy absorption centered in the range of 323–331 nm. This band was caused by the elongation of the π-electron system conjugation from the fluorene core to the phenyl ring of the substituents. At this low-energy wavelength, 2-n-Propyl-substituted 9m presented just a low intensity tail and interpreted only a limited degree of conjugation between the SBF core and aromatic C4-substituent. Other SBFs bearing an aromatic substituent at position C2 were slightly more red-shifted and showed significantly larger bands corresponding to more effective conjugation.

![Absorption spectra of 9 (10^{-5} M) in cyclohexane.](image)

The fluorescence spectra of SBFs 9 recorded in cyclohexane are presented in Figure 4. All the emission spectra evinced unresolved (9b, 9c, 9i, 9j, 9n, and 9o) or only partially resolved (9d–9h, 9l, and 9m) character peculiar to other 4-aryl substituted SBFs [13,21,22,39–44]. The obtained emission maxima ranged from 365 nm to 391 nm, whereas the emission spectra and maxima of C4-methoxyphenyl-substituted SBFs 9n and 9o were almost unnoticeably changed by the alteration of the C2 substituent (365 vs. 367 nm, SI-Figure S10, see SI). The emission characteristics of C4-trifluoromethylphenyl-substituted SBFs 9b–9m can be modulated by the electron density on C2-aryl substituent (e.g., 9c 369 nm vs. 9i 387 nm or 9j 391 nm, SI-Figure S11, see SI). The Stokes shifts (up to 66 nm, ~5200 cm^{-1}) and large and structureless emission fluorescence spectra of the prepared SBFs can be rationalized by high flexibility via the strong reorganization between geometries of S0 (ground state) and S1 (first singlet excited state), which were typical for the majority of the C4-aryl-substituted SBFs [45]. The absolute quantum yields (Φs) were determined in cyclohexane and were in the range of Φs = 0.14–1 (Table 5). Thus, with the exception of a few, the SBFs 9 represented efficient UVA emitters.
In summary, this work presented a simple method for the regioselective synthesis of 2,4-disubstituted fluorenols and the respective 9,9′-spirobifluorenes using a Ru-complex catalytic [2+2+2]-cyclotrimerization of diynes with terminal alkynes. Unlike the use of Rh-based catalytic systems that provide preferentially ortho-isomers, application of Cp*Ru(cod)Cl as the catalyst provided predominantly the meta-isomers. The reaction proceeded under mild reaction conditions and a high functional group tolerance. The observed meta/ortho selectivity was usually >9:1, and in some cases, only the meta-isomers were detected and isolated. The cyclotrimerizations yielded substituted fluorenols that were converted into the corresponding 9,9′-spirobifluorenes. A study of the photophysical properties of the corresponding 9,9′-spirobifluorenes showed that the presence of various substituents (based on aromatic systems) in positions 2 and 4 resulted in emission bands in the narrow region of \( \lambda_{\text{em}} = 330–391 \text{ nm} \) (in cyclohexane) and absolute quantum yields of emission \( \Phi_s \) = 0.14–1.00.

Supplementary Materials: Experimental details, diffraction analysis data, and copies of spectra are available online at http://www.mdpi.com/2073-4344/9/11/942/s1.
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