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A new synthetic route to symmetrical photochromic diarylperfluorocyclopentenes

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Abstract: Symmetrical and photochromic diarylperfluorocyclopentene has been prepared by reaction of 3-lithio-5-chloro-2-methylthiophene with the ethyl ester of hexafluoroglutaric acid, followed by ring closure *via* a McMurry coupling. Compound **7** is a versatile intermediate for the development of photochromic materials. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: photochromism, diarylethenes, McMurry coupling

Diarylethenes constitute an important class of photochromic molecules. The switching process is thermally irreversible and the compounds show high fatigue resistance,¹ which are promising features for application in optical data storage,² molecular wires³ and as molecular switches.^{4,5} The most commonly used diarylethenes are the diarylperfluorocyclopentenes⁶ followed by the bisarylmaleic anhydrides,⁷ bisarylmaleimides,⁸ and bisarylcyclopentenes.⁹ Many functionalized diarylperfluorocyclopentenes have been synthesized.¹ They exhibit excellent photochromic behaviour and they are stable in the presence of air during cyclization at up to 80°C. Despite these attractive photochromic properties, the synthesis of these compounds is not trivial. The commonly used starting compound, octafluorocyclopentene, which is very volatile and expensive, has to undergo a double substitution reaction with a lithiated thiophene derivative. The yields are usually moderate at best, it is not easy to scale up the procedure, and a considerable amount of mono substituted perfluorocyclopentene product is formed.

Herewith we would like to present a new synthesis of symmetric diarylperfluorocyclopentenes based on the acylation of a thiophene derivative, followed by a McMurry coupling. *Via* this route a new diarylperfluorocyclopentene derivative has been

synthesized, which can easily be functionalized at the 5'-positions, and thus can be used as a building block for other functionalized diarylperfluorocyclopentenenes.

In the synthetic route presented here the relatively cheap hexafluoroglutaric acid **1** was used as a fluorine source, which was converted to its ethyl ester **2** (scheme 1). For the thiophene moieties 2-methylthiophene was used as the starting material, which was converted to 3-bromo-5-chloro-2-methylthiophene **5** by (i) chlorination at the 5-position with NCS in acetic acid and benzene and (ii) bromination at the 4-position with bromine in chloroform.

Scheme 1. Reagents and conditions: i, ethanol, reflux, H^+ , 99%; ii, NCS, acetic acid, benzene, reflux, 80%; iii, Br_2 , $CHCl_3$, 93%; iv, *n*-butyl lithium, $-78^\circ C$, **2**, 70%; v, $TiCl_3(THF)_3$, Zn, THF, $40^\circ C$, 55%.

Compound **5** then was lithiated at $-78^\circ C$ in ether using *n*-butyl lithium and subsequently a solution of **2** in ether was added at the same temperature.^{10,11}

After acidic work-up diketone **6** was obtained in a good yield. Finally ring closure was achieved through a titanium mediated coupling using $TiCl_3(THF)_3$ and Zn in THF at $40^\circ C$, to provide **7**, which was purified by column chromatography.¹²

It is, of course, in principle possible to use thiophene derivatives other than **5** in this route provided that they can be lithiated exclusively at the 3-position. However, it was found that 3-bromo-5-chloro-2-methylthiophene **5** is an extremely versatile intermediate

for the introduction of reactive groups at the 5'-positions of the diarylperfluorocyclopentenenes. Compound **5** undergoes exclusive lithium-halogen exchange with the bromine at the 3-position at -78°C , whereas the chlorine substituent is not affected under these conditions. Compound **7** can easily undergo a lithium-chlorine exchange at *ambient temperature* thus providing a handle to introduce functionality. For example dialdehyde **8** is readily synthesized by double lithiation of **7** with *n*-butyl lithium followed by quenching with DMF.

Scheme 2. Reagents and conditions: i, *n*-butyl lithium, r.t., DMF, 66%.

In conclusion, we have accomplished an efficient synthesis of versatile intermediate **7**, which can be readily converted to other photochromic derivatives, and the synthesis can be performed on a relatively large scale with good yields.

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- [11] **1,5-Bis(5'-chloro-2'-methylthien-3'-yl)hexafluoropentadione (6)**: n-Butyl lithium (1.6M in hexane, 5.4 ml, 8.64 mmol) was added to a stirred solution of **5** (1.75 g, 8.29 mmol) in anhydrous diethyl ether (25 ml) under nitrogen at -70°C. After 15 min. of stirring at the same temperature, the ethylester of hexafluoroglutaric acid (0.91 ml, 4.15 mmol) in anhydrous diethyl ether (2 ml) was added slowly at -80°C. The reaction mixture was quenched with hydrochloric acid (2N, 10 ml), extracted with ether (3 x 25 ml), washed with saturated sodium bicarbonate solution (1 x 25 ml) and H₂O (1 x 25 ml), dried (Na₂SO₄), filtered and the solvent evaporated under vacuum to yield a brown/reddish oil (1.36 g, 70%). ¹H NMR (200 MHz, 20°C, CDCl₃): δ_H 2.70 (s, 6H, CH₃), 7.31 (s, 2H, CH); ¹³C NMR (500 MHz, 20°C, CDCl₃): δ_C 17.05 (q, CH₃), 110.37 (t, CF₂), 111.08 (t, CF₂), 125.80 (d, CH), 126.19 (s, C-Cl), 128.92 (s, C-CO), 155.37 (s, C-CH₃), 177.85 (s, C=O); ¹⁹F NMR (500 MHz, 20°C, CDCl₃): δ_F -116.18 (t, 4F, CF₂), -122.73 (t, 2F, CF₂); MS (EI): 467 [M⁺]; IR (Nujol): 1696 cm⁻¹ (C=O).
- [12] **1,2-Bis(5'-chloro-2'-methylthien-3'-yl)perfluorocyclopentene(7)**: Compound **6** (0.96 g, 2.06 mmol), TiCl₃(THF)₃ (1.50 g, 4.12 mmol), Zn dust (0.53 g, 8.24 mmol) and THF (25 ml) were stirred under nitrogen at 40°C for 1 h. The mixture was cooled, poured over a filter filled with silica gel and eluted with petroleum ether 40/60. A white solid (0.49 g, 55%) was obtained after purification by chromatography over silica gel (petroleum ether 40/60). ¹H NMR (200 MHz, 20°C, CDCl₃): δ_H 1.88 (s, 6H, CH₃), 6.88 (s, 2H, CH); ¹³C NMR (500 MHz, 20°C, CDCl₃): δ_C 14.29 (q, CH₃), 110.67 (t, CF₂), 117.73 (t, CF₂), 123.92 (d, CH), 125.36 (s, C-Cl), 127.88 (s, C-CH₃), 140.37 (s, C=C); ¹⁹F NMR (500 MHz, 20°C, CDCl₃): δ_F -114.78 (t, J=5.5 Hz, J=5.0 Hz, 4F, CF₂), -136.37 (t, J=6.2 Hz, J=5.0 Hz, 2F, CF₂); MS (EI): 436 [M⁺], mp.; 132°C.