

A One-Step Synthesis of Dehydro[12]annulenes Using Palladium-Catalyzed Reaction of *o*-Diiodoarenes with Acetylene Gas

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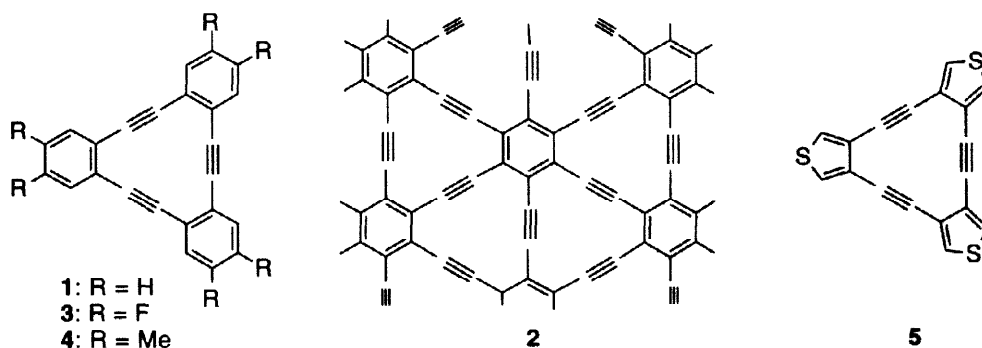
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Abstract:

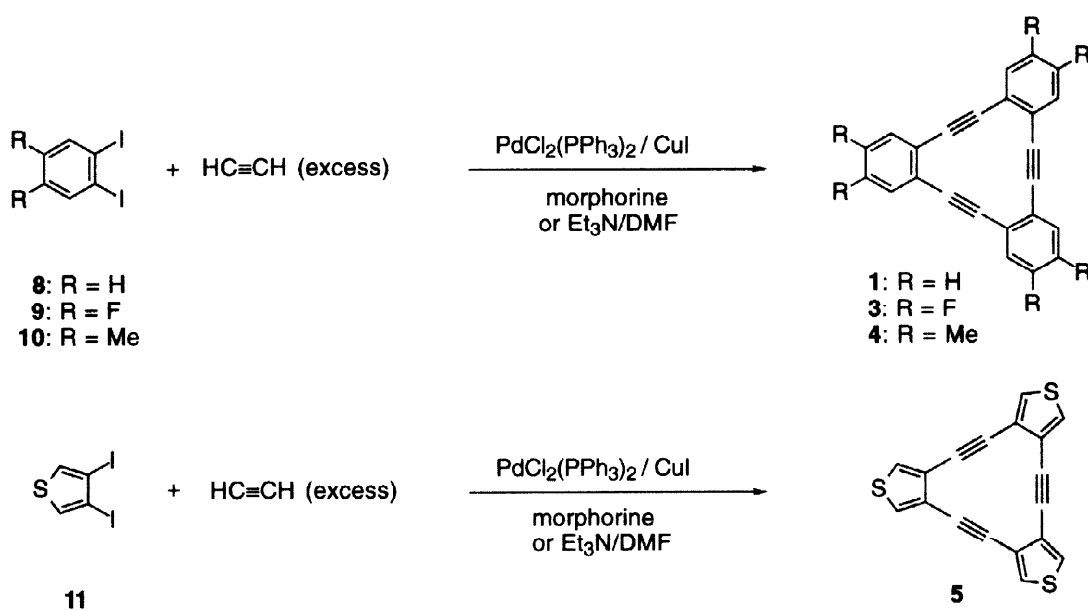
Hexadehydrotribenzo[12]annulene and its analogues were synthesized in a one-pot procedure by the palladium-catalyzed cross-coupling of *o*-diiodobenzene and its analogues with acetylene. The reaction proceeded smoothly to give the desired dehydro[12]annulenes in moderate yields. © 1998 Elsevier Science Ltd. All rights reserved.

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There is a considerable current interest in the chemistry of tribenzo[*a,e,i*]hexadehydro[12]annulene **1** [1-4], because the graphite-like carbon network **2** with a planar cyclic π -electron unit can be formally constructed from **1** [5,6], and because the interesting structural and conducting properties of the transition metal complexes derived from **1** have been recently explored [7,8]. During the course of our studies on the tribenzo[12]annulenes [9,10], we needed to synthesize tribenzohexadehydro[12]annulene **1** and its derivatives **3-5** using a short step procedure. We now report here a simple and efficient synthesis of **1** and **3-5** using the palladium-catalyzed cyclo-cotrimerization of *o*-diiodoarenes and acetylene.



Although the palladium-catalyzed reaction of aryl halides with acetylenes is well known to produce the corresponding arylacetylenes in good yields [11,12], the palladium-catalyzed cyclotrimerization of *o*-iodophenyl-acetylene **7** produced tribenzo[12]annulene **1** only in a very low yield [13]. Interestingly, the direct reaction of *o*-diiodobenzene **8** with acetylene gas in the presence of PdCl₂(PPh₃)₂ and CuI in morpholine at 60 or 40 °C for 22 h proceeded smoothly to produce **1** in 38 or 36% yields, respectively, under the standard conditions [11] (Table 1, entries 1 and 2). A similar palladium-catalyzed cyclo-cotrimerization produced **1** in DMF in the presence of triethylamine [14,15] at 60 (37%) or 40 °C (38%) for 22 h or in the presence of piperidine at 60 °C for 48 h (39%) (entries 3-5). Since the cyclo-cotrimerization of **8** and acetylene gas was found to be an efficient method for the synthesis of **1**, we applied this new method for the synthesis of **3-5**.¹ Thus, similar reactions of the diiodides (**9**² and **11**) with acetylene in the presence of PdCl₂(PPh₃)₂ and CuI in morpholine afforded the tribenzo[12]annulene derivatives (**3** and **5**³) in 32 and 37% yields, respectively (entries 6 and 9). In the case of 4,5-diiodo-1,2-dimethylbenzene **10**, the palladium-catalyzed reaction with acetylene in morpholine gave the product **4** only in a very low yield, but the reaction in DMF in the presence of Et₃N produced **4** in 11% yield (entry 8).



Scheme 1

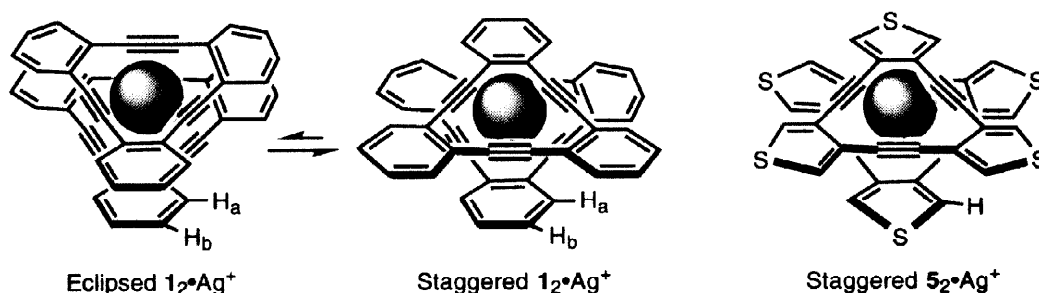
- All new compounds described in this communication were fully characterized by spectroscopic analyses. Selected data were as follows. **3**: pale yellow cryst., mp ca. 315 °C (decomp.), MS (*m/z*) 408 (*M*⁺); ¹H NMR (CDCl₃) δ 7.121 (m); ¹³C NMR (CDCl₃) δ 150.55 (d, *J*_{CF} = 255 Hz), 123.31, 120.90, 91.32; UV (THF) λ_{max} (ε) 258.5 (14,300), 265.5sh (19,000), 273.5 (46,200), 280 (40,400), 289 (109,000), 328 (1,500) nm. **4**: pale yellow cryst., mp ca. 340 °C (decomp.), MS (*m/z*) 384 (*M*⁺). **5**: pale yellow cryst., mp ca. 250 °C (decomp.), MS (*m/z*) 318 (*M*⁺); UV (THF) λ_{max} (ε) 250sh (16,700), 256sh (22,600), 265 (40,700), 271 (45,400), 280.5 (76,300), 289sh (23,000), 299 (12,600), 311.5 (10,700), 323 (8,860) nm.
- The compound **9** was prepared in 83% yield from 1,2-dibromo-4,5-difluorobenzene by treatment with KI and CuI in HMPA [16].
- Trithienocyclyne **5** was synthesized independently in 35% yield using the Castro reaction of the copper salt derived from 3-ethynyl-4-iodothiophene. All spectral data of **5** prepared by the Castro reaction are identical with those obtained from the palladium-catalyzed cross-coupling of 3,4-diiodothiophene with acetylene.

Table 1. Palladium-catalyzed cyclo-cooligomerization of **8-11** with acetylene.^a

Entry	Compound	Method ^b	Temp. (°C)	Time (h)	Product	Yield (%) ^c
1	8	A	60	22	1	38
2	8	A	40	22	1	36
3	8	B	60	22	1	37
4	8	B	40	22	1	38
5	8	C	60	48	1	39
6	9	A	60	22	3	32
7	9	B	60	48	3	24
8	10	B	60	22	4	11
9	11	A	60	22	5	37

^aThe diiodide (**8-11**), PdCl₂(PPh₃)₂ and CuI in morpholine or in DMF containing Et₃N or piperidine are heated under an atmosphere of acetylene. ^bConditions. A = **8-11** (3 mmol), PdCl₂(PPh₃)₂ (0.21 mmol), CuI (1.6 mmol) in morpholine (15 ml). B = **8-10** (3 mmol), PdCl₂(PPh₃)₂ (0.21 mmol), CuI (1.6 mmol), Et₃N (30 mmol) in DMF (15 ml). C = **8** (3 mmol), PdCl₂(PPh₃)₂ (0.21 mmol), CuI (1.6 mmol), piperidine (30 mmol) in DMF (15 ml). ^cIsolated yields.

For the palladium-catalyzed cyclo-cooligomerization of dihalogenoarenes with acetylene, only diiodoarenes (**8-11**) can be employed successfully, and the reaction of the corresponding dibromoarenes afforded **1** and **3-5** in very low yields with large amounts of the recovered starting materials. The electron-withdrawing fluorine substituents in **9** slow down the rate of the reaction, whereas the thiophene ring in **11** apparently accelerates the reaction. In the case of 4,5-diiodo-1,2-dimethylbenzene **10**, the reaction proceeds in the presence of Et₃N in DMF to produce **4** in 11% yield, whereas the use of morpholine as the solvent diminishes the yield of **4**, presumably due to the low solubility of the intermediate and product in morpholine. Although the starting diiodoarenes (**8-11**) disappeared very rapidly in all reactions, the formation of [12]annulenes (**1** and **3-5**) seemed to be slow, and all reactions were carried out for 1-2 days.

**Fig. 1.** Sandwich structures of **12•Ag⁺** and **52•Ag⁺** in solution

Although the [12]annulene **1** has been shown to react with AgSO₃CF₃ to form the sandwich complex, **12•AgSO₃CF₃**, it has been dissociated to **1** and AgSO₃CF₃ in solution [17]. However, the sandwich complex derived from **1** and AgBF₄ in CD₂Cl₂ was found to be stable enough at room temperature to be characterized by ¹H- and ¹³C-NMR analyses. Thus, **1** and 0.5-2.0 equiv. of AgBF₄ were mixed in CD₂Cl₂ to form **12•AgBF₄** in solution. As shown in Table 2, ¹H and ¹³C-NMR spectra of the solutions of **1** and 1.0-2.0 equiv. of AgBF₄ in CD₂Cl₂ show almost the same chemical shifts obtained from **12•AgBF₄**. The H_a proton in **12•AgBF₄** shows an upper field shift in the ¹H-NMR spectrum due to the shielding effect of

the parallel benzene ring, whereas the H_b proton remains unchanged. Although the prismatic (eclipsed) and antiprismatic (staggered) conformations in the crystal have been reported for 12•AgSO₃CF₃, we propose that the staggered 12•AgBF₄ is more stable than the eclipsed 12•AgBF₄ on the basis of its ¹H-NMR data. In a similar manner, the silver complex 42•AgBF₄ was formed in solution. In the case of 52•AgBF₄, the ¹H-NMR data show almost no change in the chemical shift, whereas the ¹³C-NMR data clearly indicate the complex formation. The thiophene-ring of 52•AgBF₄ may be located in the staggered conformation so that the thiophene proton shows no shielding effect of the parallel thiophene ring as shown in Fig. 1.

Table 2. ¹H- and ¹³C-NMR data of **1** and **5** and their silver complexes.^a

	¹ H-NMR (δ ppm in CD ₂ Cl ₂)	¹³ C-NMR (δ ppm in CD ₂ Cl ₂)
1	7.35-7.38 (m, H _a), 7.21-7.24 (m, H _b)	132.38, 129.09, 126.83, 93.02
1 + 0.5 eq. AgBF ₄	7.13-7.17 (m, H _a), 7.22-7.26 (m, H _b)	132.26, 130.64, 124.29, 94.38
1 + 1.0 eq. AgBF ₄	7.17-7.21 (m, H _a), 7.23-7.26 (m, H _b)	132.29, 130.48, 124.61, 94.24
1 + 2.0 eq. AgBF ₄	7.14-7.18 (m, H _a), 7.22-7.26 (m, H _b)	132.27, 130.27, 124.30, 94.40
4	7.10 (s), 2.21 (s, CH ₃)	138.22, 133.15, 124.29, 92.42, 19.70
4 + 0.5 eq. AgBF ₄	6.94 (s), 2.19 (s, CH ₃)	139.59, 132.73, 121.97, 94.09, 19.89
5	7.473 (s)	128.32, 125.22, 86.25
5 + 0.5 eq. AgBF ₄	7.460 (s)	129.37, 123.82, 86.97

^aThe ¹H- and ¹³C-NMR spectra were measured in CD₂Cl₂ at room temperature.

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