Notizen / Notes

A Novel Route to the Triphenylene Ring System by a Triple Intramolecular Acyloin Condensation

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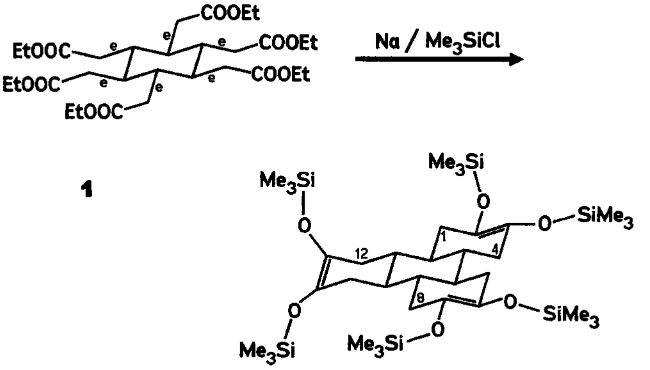
A one-pot synthesis of a sixfold functionalized dodecahydrotriphenylene **2** with D_3 symmetry starting from 1,2,3,4,5,6-hexakis(eq)(ethoxycarbonylmethyl)cyclohexane (**1**) is described. The new and straightforward approach to this tetracyclic ring system is based on a triple intramolecularly occurring acyloin condensation by using sodium in the presence of chlorotrimethylsilane.

The interest in triphenylene, hydrotriphenylenes, or substitution products thereof has been rekindled in recent years mainly due to studies on inclusion compounds[1] and plate-shaped liquid crystals[2] or the search for organic ferromagnetic materials[3]. For the latter two topics sixfold symmetrically hetero(chalcogen[2,4], halogen[3], or nitrogen[3])-substituted derivatives are desired, but not yet known, of *hydro*triphenylenes.

The first synthesis of such a hydrotriphenylene derivative **2**, containing six oxygen functions, starting from the known hexakis(eq)(ethoxycarbonylmethyl)cyclohexane[5] (**1**) is decribed here. When **1** is subjected to the conditions of the acyloin condensation by using sodium in the presence of chlorotrimethylsilane[6] **2** is obtained in 53% yield.



1

2

The discoid, symmetric structure of this new D_3-symmetric trisenediol compound **2** is clearly derived from its mass and ^{13}C-NMR spectra showing first the molecular ion with an intensity of 100% and second only four ^{13}C signals (see Experimental) in a ratio of 1:1:1:3.

In conclusion, our results can be summarized as follows: firstly, the synthesis of **2** constitutes a novel route in the relatively small number of synthetic methods leading to this type of tetracarbocyclic ring system[7]; secondly, the threefold cyclization reaction of **1** yields a racemic mixture of the product **2** having D_3 symmetry; thirdly, as far as we know, a *triple*[8,9] intramolecular acyloin condensation has not previously been reported; fourthly, the *sixfold* functionalization of the dodecahydrotriphenylene skeleton of **2** automatically occurring in this novel tetracyclic ring formation is of great value for future work, e.g. on larger saturated, plate-shaped liquid crystals[5,10].

The notable yield of the trisenediol hexasilyl ether **2** is presumably due to the fact that six-membered rings are formed in each case.

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Experimental

(4aα,4bβ,8aα,8bβ,12aα,12bβ)-1,4,4a,4b,5,8,8a,8b,9,12,12a,12b-Dodecahydro-2,3,6,7,10,11-hexakis(trimethylsilyloxy)triphenylene (**2**): According to the typical procedure[6] the hexaester **1** (600 mg, 1 mmol) was added under argon to a suspension of an excess of carefully powdered sodium (280 mg, 12 mmol) in toluene (10 ml) and chlorotrimethylsilane (1.3 g, 12 mmol). After subsequent heating of the reaction mixture at 120°C for 20 h and usual workup, **2** was purified by flash chromatography [alumina, neutral, 80 ml; petroleum ether/ethyl acetate (30:1)]. Yield: 400 mg (53%) **2** as a yellowish viscous liquid. — ^{13}C NMR (Bruker AM 270, $CDCl_3$): $\delta = 130.72$ (s, C=C), 42.81 (d, central ring carbon atoms), 34.95 (t, CH_2), 0.82 (q, $SiCH_3$), signal ratio 1:1:1:3. — MS [Varian MAT 711, 70 eV (150°C)]: m/z (%) = 768 (100) [M^+], 753 (8) [$M^+ - CH_3$], 384 (10) [$M^+/2$], 73 (94) [$Si(CH_3)_3^+$].

$C_{36}H_{72}O_6Si_6$ Calcd. 768.3945 Found 768.3945 (MS)

CAS Registry Numbers

1: 135191-18-3 / **2**: 137670-02-1

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