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A SYNTHETIC APPROACH TO ANNULENOANNULENOANNULENE, AN ANTHRACENE-LIKE SYSTEM

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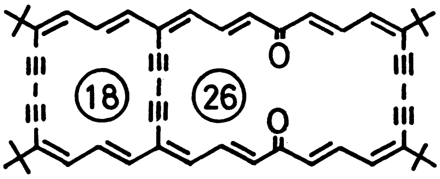
An improved synthesis of tetra-*t*-butylhexakisdehydro[18]annuleno[26]annulenedione, a key compound for the synthesis of the tricyclic annulenoannulenoannulene, was carried out. Two dideuterio derivatives of the [18]annuleno[26]annulenedione has been synthesized. An attempted synthesis of tetra-*t*-butyloctakisdehydro[18]annuleno[18]annuleno[18]annulene is described.

Recently we have reported the synthesis of tetra-*t*-butylhexakisdehydro[18]annuleno[26]annulenedione (**1**),1) a key substance for the synthesis of tetra-*t*-butyloctakisdehydro[18]annuleno[18]annuleno[18]annulene (**2**). The overall yield of **1** by this route was rather poor and only small amounts could be obtained conveniently. Therefore, an alternative synthesis of **1** was developed using the ketophosphonate (**6**) as chain-lengthening reagent (Scheme 1).



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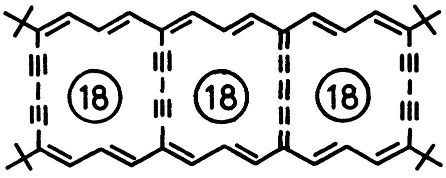

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Treatment of the aldehyde (**3**)2) with the carbanion derived from trimethyl phosphonoacetate gave the ester (**4**, colorless oil, bp 116 - 121 °C/ 2.5 Torr, 72%). The ketophosphonate (**6**, 77%)3) was prepared by the reaction of **4** with lithiomethyl(dimethoxy)phosphine (**5**) at -70 °C according to the procedure of Dauben et al. The reaction of the dialdehyde (**7**)1) with the carbanion derived from the ketophosphonate (**6**) at -10 °C for 1.5 h afforded the acyclic diketone (**8**, reddish orange cryst., decomp 133-136 °C, 62%).5) The diketone (**8**) was treated with copper(II) acetate in pyridine and methanol at room temperature (1 h) and then 80 °C (3 h). Oxidative coupling at room temperature initially yielded the monocyclic diketone which could be converted into the [18]annuleno[26]annulenedione (**1**) at 80 °C accompanied with the cleavage of the trimethylsilyl groups. The spectral data of **1** were identical with those of an authentic sample obtained by the previous route.1)

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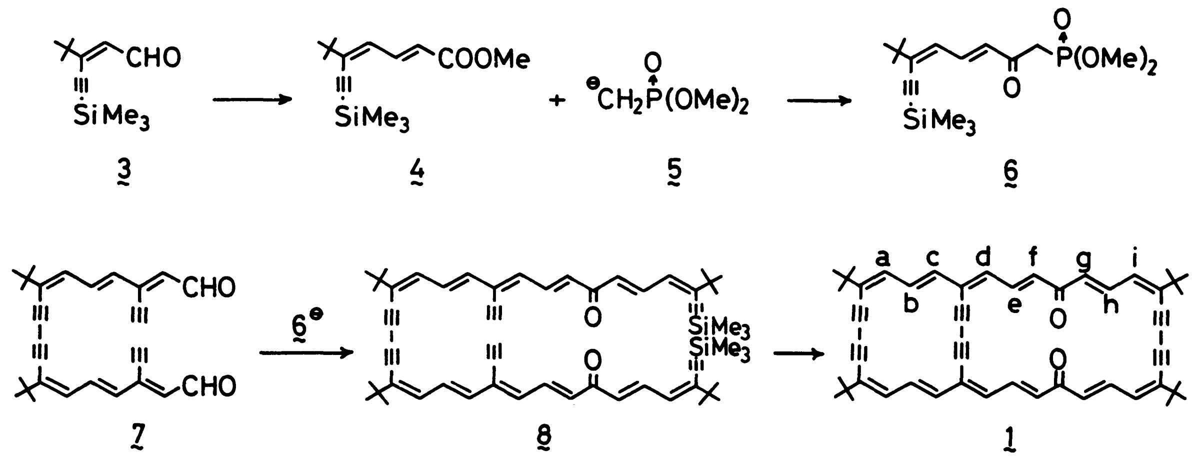


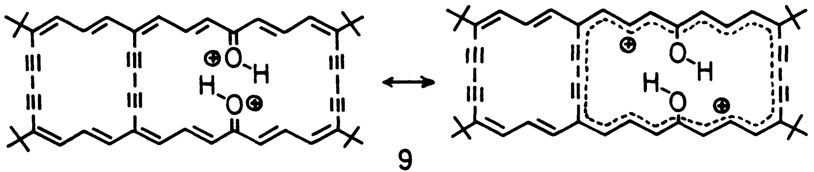
Scheme 1.

The ^{1}H-NMR spectrum of a solution of 1 in CF_3COOD indicated the formation of the rather paratropic species as shown in Table 1. The differences in chemical shifts between CF_3COOD- and CD_2Cl_2-solutions of 1 are also shown in brackets, *i.e.*, [$\tau(CF_3COOD)$ - $\tau(CD_2Cl_2)$]. The outer and inner protons moved to higher and lower fields, respectively, presumably due to the formation of the protonated molecule (9). The tendency is more pronounced in the [26]annulenedione moiety as compared with that in the [18]annulene moiety.

The electronic spectra of tetra-*t*-butyltetrakisdehydro[26]annulenedione (10)$^{4)}$ in THF and the [18]annuleno[26]annulenedione (1) in THF and CF_3COOH are shown in Fig. 1. The absorption curves of 1 in THF are closely related to those of the [26]annulenedione (10) except for a bathochromic shift. However, the curves of 1 in CF_3COOH shows a marked bathochromic shift along with tailing up to the long wavelength region.

Table 1. ^{1}H-NMR Parameters of 1 in CF_3COOD (100 MHz, 35 °C, τ-values). The Figures in Brackets are the Differences between $\tau(CF_3COOD)$ and $\tau(CD_2Cl_2)$.

Ha	3.49 (d, J=12.0) [0.17]	Hb	1.07 (dd, J=12.0, 14.5) [-1.51]	Hc	3.87 (d, J=14.5) [1.45]
Hd	3.87 (d, J=12.5) [0.55]	He	-1.54 (dd, J=12.5, 14.5) [-3.06]	Hf	4.36 (d, J=14.5) [0.79]
Hi	4.35 (d, J=11.5) [0.38]	Hh	-1.30 (dd, J=11.5, 15.0) [-2.97]	Hg	4.35 (d, J=15.0] [0.74]
t-Bu	8.80 (s) [0.02]	*t*-Bu	8,89 (s) [0.09]		



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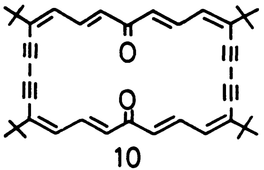

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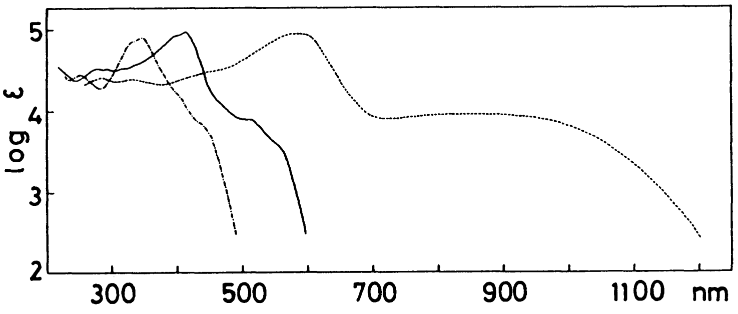
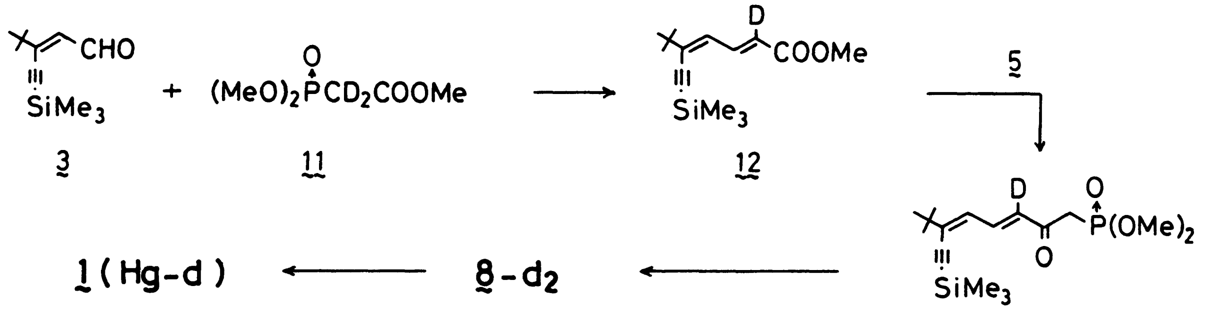


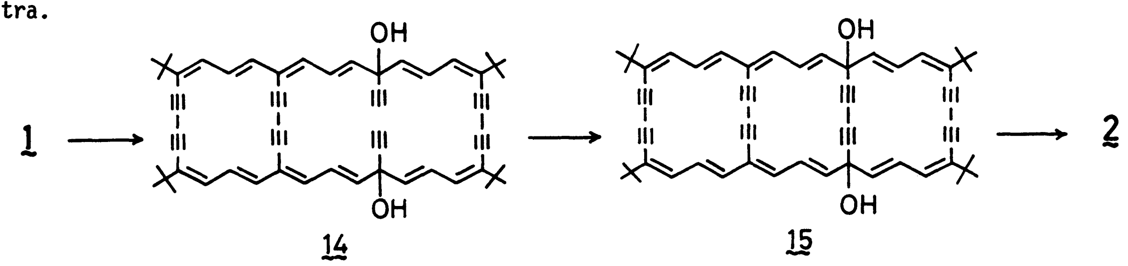
Fig. 1. Electronic spectra of 1 in THF (——), 1 in CF_3COOH (------), and 10 in THF (–·–·–).

It was found that the incorporation of deuterium occurred at the Hf-positions, when a solution of **1** in CF_3COOD was allowed to stand for 3 d at room temperature. Under these conditions **1** was stable enough and the Hf-deuterated derivative was recovered quantitatively. In order to confirm the deuterated positions, we have carried out the synthesis of the Hg-deuterated derivative of **1**, because it is difficult to make unambiguous assignment of Hf and Hg only on the basis of spectroscopic analysis. Trimethyl phosphonoacetate was treated with sodium methoxide in methanol-*d*, and the reaction mixture was neutralized with acetic acid-*d* to give **11** (bp 110-115 °C/ 3 Torr, 64%, deuterium conversion 77%). The reaction of **3** with the carbanion derived from **11** (NaH was used) gave the ester (**12**, 93%, deuterium conversion 71%), which was converted into the ketophosphonate (**13**, 70%). The reaction of **7** with the carbanion obtained from **13** gave **8**-d_2 (62%). which could be converted into **1** (Hg-*d*) in 24% by analogous reaction sequence. The ^1H-NMR spectra of two deuterated [18]annuleno[26]annulenediones [**1** (Hf-*d*) and **1** (Hg-*d*)] show disappearance of Hf and Hg protons, respectively.



Scheme 2.

For the synthesis of the annulenoannulenoannulene (**2**), **1** was treated with lithium acetylide-ethylene diamine complex in THF to give the diol (**14**, dark red solid, 94%), which was found to be an inseparable mixture of the *cis*- and *trans*-isomers. Oxidative coupling of **14** with copper(II) acetate in pyridine-methanol-ether under high dilution conditions afforded the tricyclic glycol (**15**, dark violet cryst., decomp > 220 °C, 23%),$^{5)}$ which may be the *cis*-isomer.$^{4)}$ Treatment of **15** with tin(II) chloride-hydrogen chloride in THF under argon atmosphere gave a dark red solution which rapidly changed into a orange solution at 0 °C. The substance was very air-sensitive and could not be isolated from the dark red soultion. Therefore, a solution obtained by $SnCl_2$ and DCl (HCl) in THF-d_8 (THF) was directly subjected to the measurements of the ^1H-NMR and electronic spectra.



Scheme 3.

The electronic spectrum of the dark red solution is illustrated in Fig. 2 together with those of tetra-*t*-butyltetrakisdehydro[18]annulene (**16**)$^{6)}$ and tetra-*t*-butylhexakisdehydro[18]-annuleno[18]annulene (**17**).$^{4)}$ The spectrum of the solution shows two intense absorption maxima at 521 and 778 nm (the ε-values could not be measured) and the absorption curves indicates the formation of an annulene with very long conjugated system like **2**.

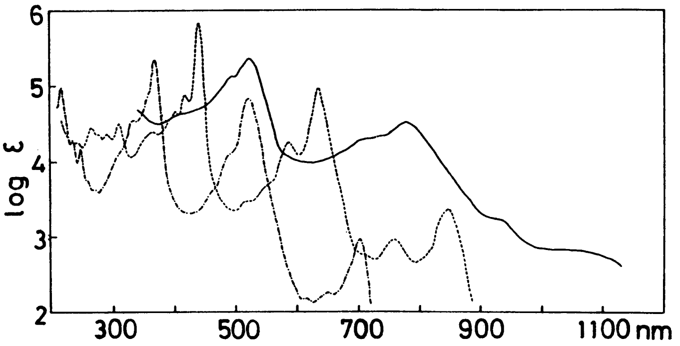
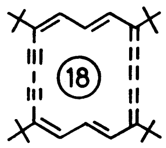


Fig. 2. Electronic spectra of **16** (-·-·-), **17**(--------), and the dark red solution obtained from **15** (———).



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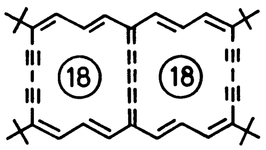

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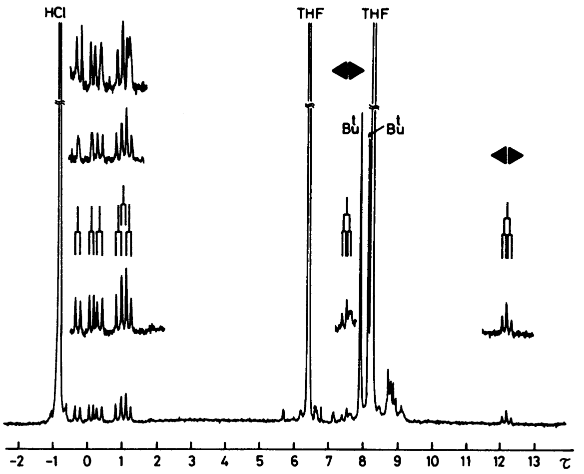

Fig. 3. 100 MHz ^{1}H-NMR spectrum of the solution (THF-d_8, -40 °C, τ-values).

The ^{1}H-NMR spectrum of the dark red solution obtained from **15** is shown in Fig. 3. In spite of the presence of signals of the solvent, hydrogen chloride and decomposition products, the spectrum exhibits characteristic signals of "acetylene-cumulene" dehydroannulene system. At the highest field the signal of the inner protons appears as the X part of a simple ABX pattern [τ 12.18 (dd, J=14.5, 12.0 Hz)]. The AB part (*i.e.*, the outer protons) of the ABX system appears as two doublet at τ -0.28 (d, J=14.5) and 0.12 (d, J=12.0). The assignment of the ABX system could be made with the decoupling experiment. Another simple ABX system of the inner and outer protons could be assigned in a similar manner [the inner protons, τ 7.52 (dd, J=14.5, 13.5); the outer protons, τ 0.36 (d, J=14.5) and 1.19 (d, J=13.5)]. Taking into account the structure of **15**, an additional ABX system should be present in the ^{1}H-NMR spectrum. The low field signals [τ 0.90 (d, J=14.5) and 1.05 (d, J=13.5)] may correspond to the AB part (*i.e.*, the outer protons) of the ABX system, however, the remaining X part could not be observed in the spectrum, presumably owing to overlap of the signals of the solvent or decomposition products.

The ^{1}H-NMR spectrum (Fig. 3) clearly shows the induction of diamagnetic ring current and the observed two signals of the *t*-butyl protons also indicate the fairly large diatropicity [τ 7.92 (s) and 8.15 (s)]. The above-mentioned results suggest the formation of the annulenoannulenoannulene (**2**) or a tricyclic annulene containing three diamagnetic [18]annulene rings. Unfortunately further studies on the structure of the product could not be feasible owing to the instability. Even though the diamagnetic product may hold an anthracene-like molecular framework as **2**, the π-electrons in the annulenoannulenoannulene do not seem to delocalize completely, because the ^{1}H-NMR spectrum indicates the molecular framework with C_{2v}-symmetry (anthracene bears D_{2h}-symmetry). The formation of a diamagnetic species with C_{2v}-symmetry cannot be excluded on the basis of the observed ^{1}H-NMR spectrum, because an unexpected reaction may occurs during the course of reductive dehydroxylation. It is therefore evident that further studies are required to clarify the properties of anthracene-like annulenoannulenoannulenes.

References

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