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SYNTHESES OF TETRA-*t*-BUTYLHEXAKISDEHYDRO[18]ANNULENO[26]ANNULENEDIONE AND DI-*t*-BUTYLDIFUROTRISDEHYDRO[18]ANNULENE

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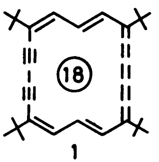
Tetra-*t*-butylhexakisdehydro[18]annuleno[26]annulenedione, a key substance for the synthesis of tetra-*t*-butyloctakisdehydro[18]annuleno-[18]annuleno[18]annulene has been synthesized. Formation of di-*t*-butyldifurotrisdehydro[18]annulene was observed on heating a solution of diformylmethylene derivative of the tetrakisdehydro[18]annulene.

In spite of fascinating developments in the chemistry of nonbenzenoid aromatic compounds, condensed systems of aromatic annulenes corresponding to anthracene still remain unknown. Because tetra-*t*-butylhexakisdehydro[18]annuleno[18]annulene (2)[1)] corresponding to naphthalene was found to be highly delocalized system consisting of two aromatic tetra-*t*-butyltetrakisdehydro[18]annulenes (1),[2)] we have interested in the properties of tetra-*t*-butyloctakisdehydro[18]annuleno[18]annuleno-[18]annulene (3), a anthracene-like system.

We now wish to report the synthesis of tetra-*t*-butylhexakisdehydro[18]annuleno-[26]annulenedione (4) as a key substance for the annulenoannulenoannulene (3) together with the formation of di-*t*-butyldifurotrisdehydro[18]annulene (5) by the thermal reaction of the intermediary dialdehyde (12).



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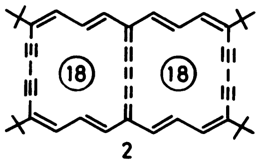

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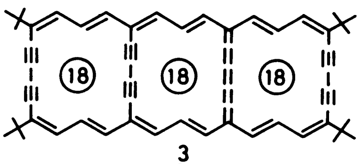

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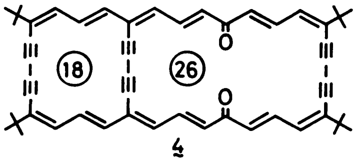

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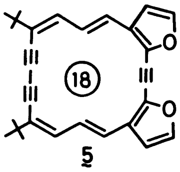

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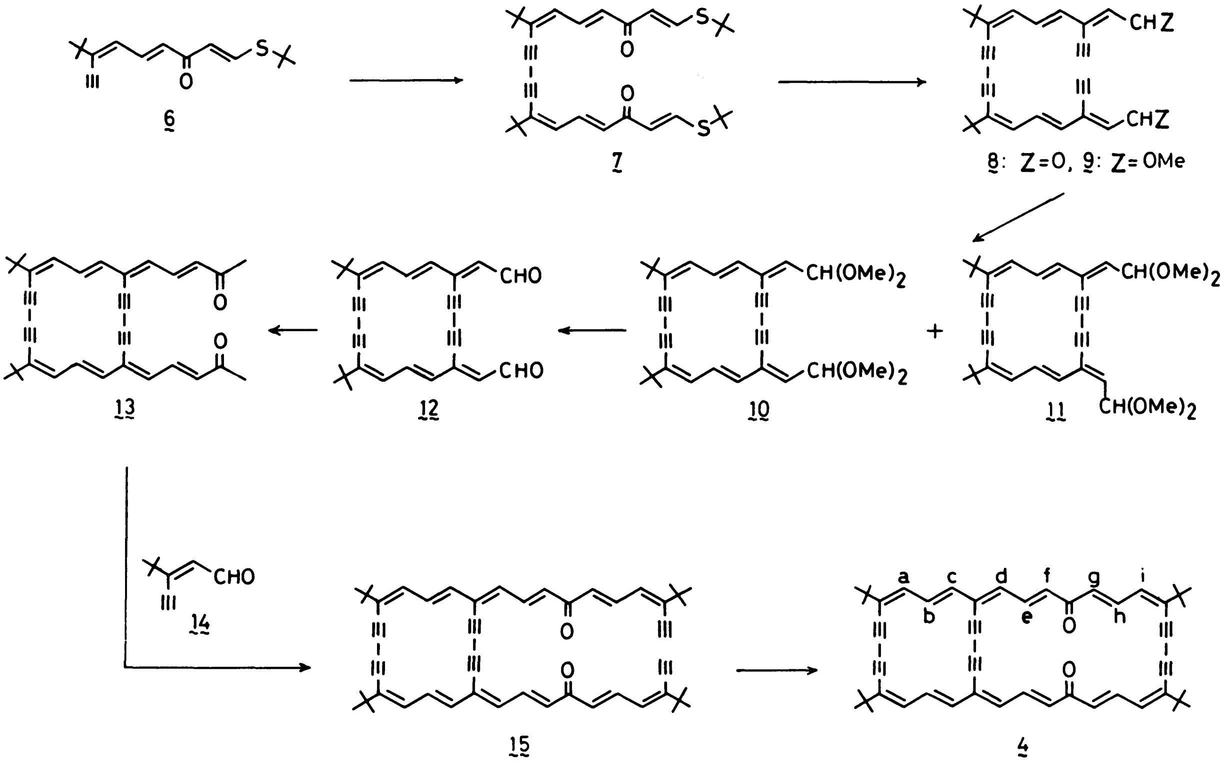
The synthesis of the [18]annuleno[26]annulenedione (4) was carried out by the reaction sequence outlined in Scheme 1. Oxidative coupling of the thiovinyl ketone (6)3) with copper(II) acetate in pyridine-methanol afforded the diketone (7, bright yellow plates, mp 116 ∿ 118°C, 76%).4) Reaction of 7 with lithium acetylide in THF3) followed by rearrangement and hydrolysis with a dilute sulfuric acid yielded the unstable dialdehyde (8, orange solid, 63%). Treatment of 8 with *p*-TsOH and $CH(OMe)_3$ gave the acetal (9), which was oxidized with copper(II) acetate in pyridine-methanol-ether under high dilution conditions to give the *syn*- and *anti*-cyclic compounds (10 and 11). Irradiation of the *anti*-product (11) in ether gave the *syn*-acetal (10). The combined *syn*-acetal (10) was hydrolyzed with 1M H_2SO_4 in THF to afford the cyclic dialdehyde (12, orange plates, decomp. 130 ∿ 140°C, 39% based on 7). The cyclic dialdehyde (12) was unstable under alkaline conditions. However, 12 was considerably stable to light, atmospheric oxygen and acids, although 12 contains the macrocyclic quinodimethane structure, *i.e.*, 18π-electronic counterpart of xylylene derivative. Treatment of 12 with the carbanion derived from $(EtO)_2P(O)CH_2COCH_3$ gave the diketone (13, dark red prisms, decomp. 215°C) in 45% yield. The aldol condensation of 13 with excess 14 under mild alkaline conditions afforded the monocyclic diketone (15, reddish violet crystals, decomp. > 160°C, ∿ 10%). Oxidative coupling of 15 with copper(II) acetate in pyridine-methanol afforded the desired [18]annuleno[26]annulenedione (4, dark reddish violet crystals, decomp. > 200°C).5)



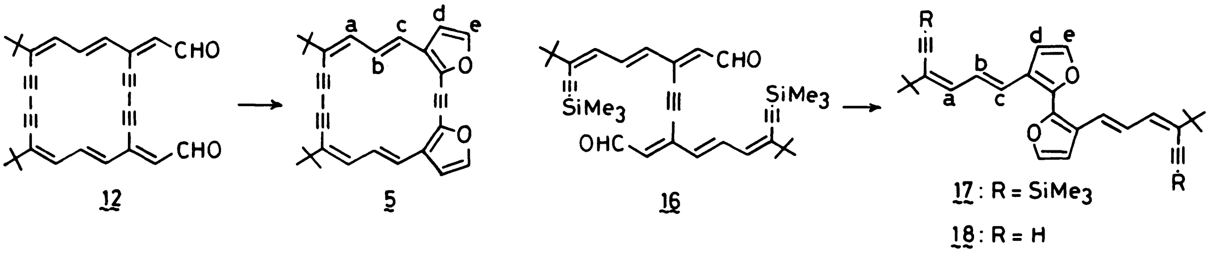
Scheme 1

The ^{1}H NMR parameters of **4** are summarized in Table 1. Assignment of the olefinic protons of **4** could be achieved by the double resonance and Eu(fod)$_3$ techniques. The molecular weight of the [18]annuleno[26]annulenedione (**4**) could not be determined by the mass spectrum (EI- and FD-methods) owing to its involatility and thermal instability. The structure was however confirmed by compararison with the spectral data of tetra-*t*-butyltetrakisdehydro[26]annulenedione.$^{1)}$

The thermal cyclization of the dialdehyde (**12**) was carried out on heating a solution of **12** in toluene under reflux for 1 hr (Scheme 2).$^{6)}$ The difurotrisdehydro[18]annulene (**5**) was obtained as bright yellow fine needles (mp 130.0 ∿ 131.0 °C, 83%).$^{7)}$ The similar cyclization of the acyclic dialdehyde (**16**)$^{3)}$ in benzene under reflux for 2 hrs afforded the 2,2'-bifuran derivative (**17**, bright yellow needles, mp 171 ∿ 173°C, 67%).$^{8)}$ Removal of the trimethylsilyl groups of **17** with NaOH in aq. ethanol gave the diethynyl bifuran (**18**, yellow leaflets, mp 146.0 ∿ 147.5°C (decomp.), 97%). The thermal cyclization of **12** and **16** proceeds readily to give new type of annelated annulene (*i.e.*, **5**) and the precursor (*i.e.*, **18**). Therefore, macrocyclic system containing difuranylacetylene or 2,2'-bifuran units can be prepared by this methods. The ^{1}H NMR parameters of **5**, **17** and **18** are summarized in Table 2.

Table 1. ^{1}H NMR Parameters of Tetra-*t*-butylhexakisdehydro[18]annuleno-[26]annulenedione (**4**) (CD_2Cl_2, 35°C, τ-values).

3.32 d (J=11.5) H_a	2.58 dd (J=11.5, 15.0) H_b	3.51 d (J=15.0) H_c
3.32 d (J=12.0) H_d	1.52 dd (J=12.0, 14.5) H_e	3.57 d (J=14.5) H_f
3.61 d (J=15.0) H_g	1.67 dd (J=11.5, 15.0) H_h	3.40 d (J=11.5) Hi
8.78 s *t*-Bu	8.80 s *t*-Bu	



Scheme 2

Although **5**, **17** and **18** gave no first-order 100 MHz ^{1}H NMR spectra, *i.e.*, the protons (H_a, H_b and H_c) appeared as an ABC multiplet, the chemical shifts and coupling constants of H_a, H_b and H_c of **5**, **17** and **18** could be obtained by simulation. The difurotrisdehydro[18]annulene (**5**) seems to be potentially aromatic system. However, ^{1}H NMR chemical shifts of the inner and outer protons of **5** showed no induction of any appreciable ring current as compared with those of acyclic **17** and **18**. Examination of molecular model suggests that **5** cannot be planar. The annelation of two furan rings onto the trisdehydro[18]annulene system should cause the marked decrease of diatropicity of the annulene ring.$^{9)}$ Therefore, the atropic nature of **5** could be ascribed to the combined effect of annelation and low planarity of the molecule.

Further transformations of the [18]annuleno[26]annulenedione (**4**) into the [18]annuleno[18]annuleno[18]annulene (**3**) are now in progress.

Table 2. ^{1}H NMR Parameters of **5**, **17** and **18** (100MHz, 35°C, τ-values).

5	3.42 H_a	3.11 H_b	3.17 H_c	(J_{ab}=7.0, J_{bc}=14.0, J_{ac}=1.5 Hz)	
($CDCl_3$)	3.46 d(J=2.0) H_d		2.60 d(J=2.0) H_e	8.78 s *t*-Bu	
17	3.50 H_a	2.91 H_b	2.90 H_c	(J_{ab}=9.0, J_{bc}=15.0, J_{ac}=1.5 Hz)	
($CDCl_3$)	3.34 d(J=2.0) H_d		2.59 d(J=2.0) H_e	8.82 s *t*-Bu	9.73 s $SiMe_3$
18	3.38 H_a	2.85 H_b	2.82 H_c	(J_{ab}=9.0, J_{bc}=15.0, J_{ac}=1.5 Hz)	
(CD_3COCD_3)	3.15 d(J=2.0) H_d		2.35 d(J=2.0) H_e	6.05 s ≡CH	8.80 s *t*-Bu

References

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2) S. Tomita and M. Nakagawa, *Bull. Chem. Soc. Jpn.*, 49, 302 (1976).
3) S. Akiyama, M. Iyoda, and M. Nakagawa, *J. Am. Chem. Soc.*, 98, 6410 (1976).
4) All new compounds described in this communication gave IR, NMR, and mass spectral data consistent with the assigned structures and satisfactory elemental analyses were obtained.
5) The electronic spectral maxima of **4** are as follows: λ_{max}^{THF} (ε) 277.5 (34,200), 291.5 (33,500), 315 sh (33,400), 395 sh (82,100), 415.5 (92,300), 513 sh (8,060), 555 sh (3,840) nm.
6) For the thermal cyclization of decadienyndials see, R. Muneyuki, M. Morimoto, M. Tanaka, T. Katakami, T. Kashitani, M. Iyoda, and M. Nakagawa, *Bull. Chem. Soc. Jpn.*, 46, 2565 (1973).
7) **5**: ^{13}C NMR ($CDCl_3$) δ 144.6, 133.7, 133.4, 132.9, 129.4, 128.9, 123.0, 110.3, 88.4, 83.1, 82.5, 36.4, 29.6; UV $\lambda_{max}^{cyclohexane}$ (ε) 263.5 (51,800), 339 (32,700), 400 sh (5,410) nm.
8) **17**: UV $\lambda_{max}^{cyclohexane}$ (ε) 214 (20,200), 229 (19,700), 250 sh (11,300), 258 sh (15,500), 269 sh (20,800), 278 (23,100), 305.5 (10,600), 317 (12,200), 380 sh (49,600), 401.5 (68,200), 425.5 (50,100) nm.
9) R. R. Jones, J. M. Brown, and F. Sondheimer, *Tetrahedron Lett.*, 1975, 4183.

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