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SYNTHESIS AND PROPERTIES OF BISDEHYDRO[4n+2]ANNULENEDIONES†

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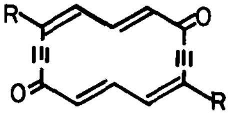
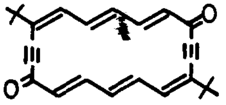
Summary: Bisdehydro[14]- and [18]annulenediones have been synthesized by cyclic dimerization of corresponding ω-ethynyl acid chlorides in the presence of palladium-copper catalyst in triethylamine-benzene and fully characterized by analyses and their ^{1}H-NMR, mass, electronic and IR spectroscopic evidences.

Whether a [4n+2]annulenedione shows some quinonoid character or not is a very interesting, but not fully explored problem. Recently some tetrakisdehydro[18]annulenediones1),2), 15,16-dimethyl-15,16-dihydropyrenedione3) and 1,6-methano[10]annulenediones4) have been synthesized and their chemical and electrochemical behavior2) have been reported. We have interested in the preparation and properties of bisdehydro[4n+2]annulenediones considering the highly aromatic nature of our bisdehydro[4n+2]annulenes5).

An interesting coupling reaction of terminal alkynes with acyl chlorides by palladium-copper catalyst to give ethynyl ketones has been reported by Tohda, Sonogashira, and Hagihara6). The efficient dimerization reaction of ethynylpolyene ketones to form cyclic glycols5) seemed to suggest that the coupling reaction of alkyne with acid chloride can be adapted for the cyclic dimerization of ω-ethynyl acid chlorides to form bisdehydro[4n+2]annulenediones. This paper is concerned with the realized anticipation, *i.e.*, the preparation and some properties of bisdehydro[4n+2]annulenediones (1, 2, 3, and 4).



1: R=t-Bu
2: R=Ph



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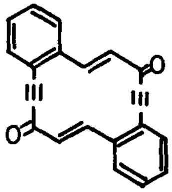

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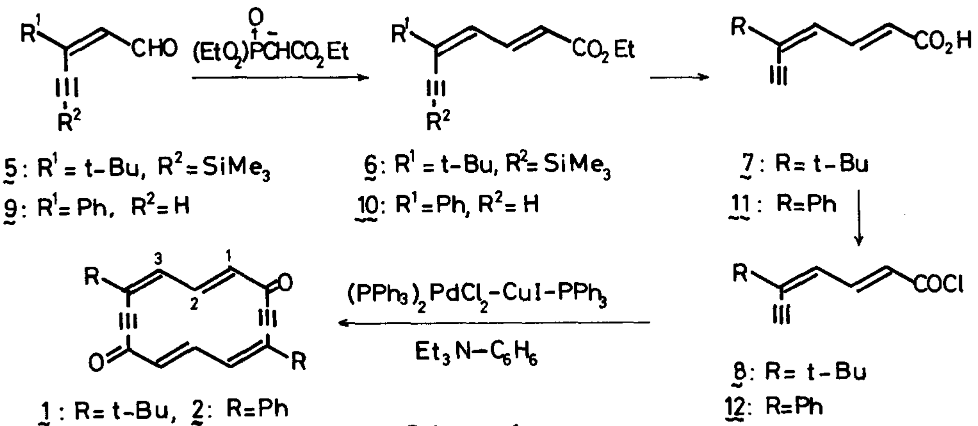
The synthesis of di-*t*-butyl- and diphenylbisdehydro[14]annulenediones (1 and 2) were carried out by the reaction sequence outlined in Scheme 1. The Wittig-Horner-Emmons reaction of trimethylsilylethynyl aldehyde (5)7) with the carbanion derived from triethyl phosphonoacetate gave dienyne ester (6, colorless oil, bp 103-105°C/ 2mmHg, 90%)8). Hydrolysis of 6 with KOH in aq. methanol yielded dienyne carboxylic acid (7, colorless needles, mp 132.0-136.8°C (dec.), 89%). Treatment of 7 with thionyl chloride in methylene chloride gave acid chloride (8, yellow oil, bp 69-75°C/ 9×10^{-4}mmHg, 49%). The reaction of 8 in degassed triethylamine-benzene (1:1) at room

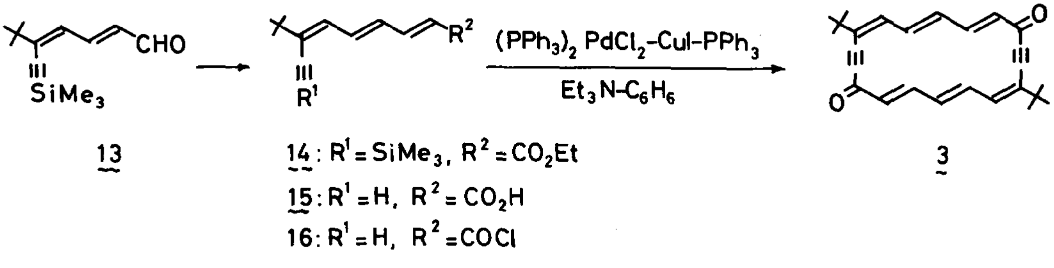
† Dedicated to the memory of Professor Franz Sondheimer.

temperature in the presence of $(PPh_3)_2PdCl_2$(0.06 eq.), CuI(1.2 eq.) and PPh_3(0.28 eq.) under nitrogen atmosphere gave desired di-*t*-butylbisdehydro[14]annulenedione (1, yellow crystals, mp > 120°C (dec.), 12%, Mass(m/e): 320 (M^+), 305, 249; IR(KBr-disk): 2195s, 1628vs, 1613s cm^{-1}). The reaction also proceeded in triethylamine-THF or triethylamine-1,2-dimethoxyethane with palladium-copper catalyst to afford 1. However, treatment of 8 with CuI(1 eq.) in triethylamine-benzene gave no cyclic dimer (*i.e.*, 1), and polymerization of 8 was observed.

For the synthesis of diphenylbisdehydro[14]annulenedione (2), enyne aldehyde (9)$^{9)}$ was firstly converted into dienyne ester (10, pale yellow needles, mp 53.2-55.6°C, 78%) with triethyl phosphonoacetate. Hydrolysis of 10 with KOH in aq. methanol gave acid (11, pale yellow crystals, mp > 170°C (dec.), 76%). Acid chloride (12, yellow oil) was obtained on treatment of 11 with thionyl chloride in benzene. The reaction of 12 with $(PPh_3)_2PdCl_2$-CuI-PPh_3 in triethylamine-benzene at room temperature gave the diphenylbisdehydro[14]annulenedione (2, orange crystals, mp > 150°C (dec.), 6% based on 11, Mass (m/e): 360 (M^+); IR(KBr-disk): 2175m, 1610vs, 1582s cm^{-1}).



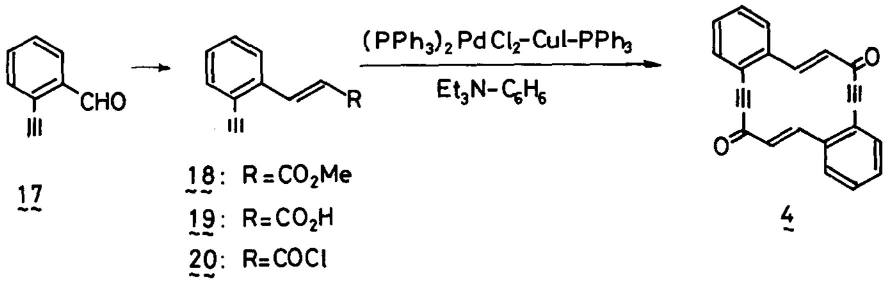
Scheme 1



Scheme 2

The synthetic route of di-*t*-butylbisdehydro[18]annulenedione (3) was shown on Scheme 2. Ester of ethynyldienic acid (14, pale yellow viscous oil, 80%) obtained by the reaction of trimethylsilylethynyl aldehyde (13)$^{10)}$ with triethyl phosphonoacetate was hydrolyzed to give acid (15, pale yellow crystals, mp 123.8-126.2°C (dec.), 93%). The reaction of 15 with thionyl chloride in benzene yielded acid chloride (16, pale yellow viscous oil), which was treated with $(PPh_3)_2PdCl_2$-CuI-PPh_3 in triethylamine-benzene at room temperature to give the di-*t*-butylbisdehydro[18]annulenedione (3, orange yellow crystals, mp > 150°C, 6% based on 15, Mass(m/e): 372 (M^+); IR(KBr-disk): 2175m, 1619vs, 1594s cm^{-1}).

Dibenzobisdehydro[14]annulenedione (4) was synthesized by Misumi *et al.* using the Castro reaction of cuprous salt of *o*-iodocinnamoylacetylene in 1.2% yield[11]. We applied the palladium-copper catalyzed dimerization for the synthesis of 4 (Scheme 3). 2-Ethynylbenzaldehyde[12] was converted into ester (18, pale yellow oil, 98%) on treatment with the carbanion derived from trimethyl phosphonoacetate. Hydrolysis of 18 with KOH in aq. methanol afforded acid (19, colorless crystals, mp 190.3-191.3°C, 98%). The reaction of 19 with thionyl chloride in benzene followed by treatment with $(PPh_3)_2PdCl_2$-CuI-PPh_3 in triethylamine-benzene yielded the dibenzobisdehydro[14]annulenedione (4, lemon yellow needles, mp > 500°C, 5% based on 19, Mass(m/e): 308(M^+); IR (KBr-disk): 2220s, 2195m, 1615s, 1590s cm^{-1}).



Scheme 3

Table 1. ^1H NMR Parameters of Annulenediones (1, 2, 3, and 4, τ-values)

1	(CD_2Cl_2)	H^1	3.82	dd, J=15.5, 0.5	H^2	0.46	dd, J=15.5, 11.0
		H^3	3.35	dd, J=11.0, 0.5	*t*-Bu	8.80	s
1	(CF_3COOH)	H^1	3.64	d, J=15.5	H^2	-0.62	dd, J=15.5, 11.5
		H^3	3.21	d, J=11.5	*t*-Bu	8.74	s
2	(CD_2Cl_2)[11]	H^1	3.59	d, J=15.5	H^2	0.23	dd, J=15.5, 11.5
		H^3	3.59	d, J=11.5	Ph	2.20 ∿ 2.59	m
3	(CD_2Cl_2)	H^1	3.86	d, J=15.5	H^2	1.35	dd, J=15.5, 11.5
		H^3	3.52	dd, J=15.0, 11.5	H^4	1.69	dd, J=15.0, 11.5
		H^5	3.40	d, J=11.5	*t*-Bu	8.81	s
3	(CF_3COOH)	H^1	3.70	d, J=15.5	H^2	0.16	dd, J=15.5, 12.0
		H^3	3.56	dd, J=14.5, 12.0	H^4	0.66	dd, J=14.5, 11.5
		H^5	3.32	d, J=11.5	*t*-Bu	8.78	s
4	(CD_2Cl_2)	H^1	3.14	d, J=16.5	H^2	0.83	d, J=16.5
		aromatic protons	2.13 ∿ 2.54	m			
4	(CF_3COOH)	H^1	2.87	d, J=16.0	H^2	0.24	d, J=16.0
		aromatic protons	2.03 ∿ 2.43	m			

The ^{1}H NMR parameters of annulenediones (**1**, **2**, **3**, and **4**) are summarized in Table 1 and the electronic absorption spectral data of **1**, **2**, and **3** are given in Table 2. The ^{1}H NMR parameters show no indication of any appreciable ring current like *p*-quinones. The inner protons (H^2, H^4) moved to lower field in CF_3COOD presumably owing to the partial protonation on carbonyl groups of annulenediones. The absorption curves of annulenediones in CF_3COOH were similar to those in THF, and showed a marked bathochromic shift along with tailing up to the long wavelength region.

The chemical and electrochemical reduction of annulenediones (**1** and **3**) has been investigated and evidence for the quinonoid nature of **1** and **3** has been obtained$^{14)}$.

Table 2. Electronic Spectra of Annulenediones (**1**, **2**, and **3**). λmax (ε) nm.

1 (THF)	260(36700), 277sh(26800), 290(26300), 323(25700), 338(22600), 382(1200).
1 (CF_3COOH)	268(37300), 307(32700), 341(23800), 444(8140). Tailing up to 600 nm.
2 (THF)	233(20200), 274(24600), 322(42200), 336(39800), 367(29100), 382(27800).
2 (CF_3COOH)	282(22500), 343(31300), 408(20100). Tailing up to 900 nm.
3 (THF)	295sh(57500), 306(60800), 319(63000), 345sh(34400), 357sh(30800), 424(2310).
3 (CF_3COOH)	306(55500), 343(55000). Tailing up to 800 nm.

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