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SYNTHESES OF POSITION ISOMERS OF DI-t-BUTYL-DIPHENYLDIDEHYDRO[14]ANNULENE AND A DIMETHOXY DERIVATIVE

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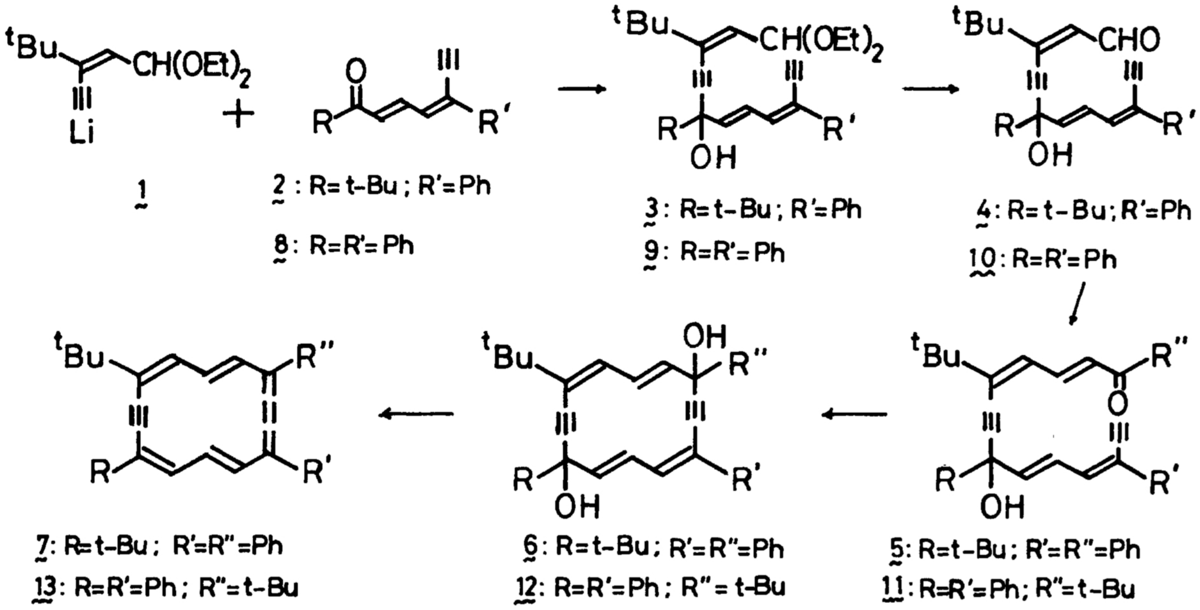
Two position isomers of di-t-butyl-diphenyldidehydro[14]annulene have been prepared according to a stepwise sequence of reactions and their physical properties were compared with those of another position isomer, 3,10-di-t-butyl-7,14-diphenyl-1,8-didehydro[14]-annulene. The synthesis of 3,10-di-t-butyl-6,13-dimethoxy-7,14-diphenyl-1,8-didehydro[14]annulene has been performed. The introduction of methoxy groups causes a hypsochromic shift with hypochromism and a bathochromic shift with strong hyperchromism of medium and longest wavelength bands of the electronic spectrum, respectively.

Properties of position isomers of annulene bearing substituents capable to conjugate with the annulene ring seem to be of considerable interest in comparison with those of the corresponding o-, m-, and p-isomers of benzenoid series. In this communication we wish to report the syntheses of "ortho"- and "meta"-isomers of di-t-butyl-diphenyl-1,8-didehydro[14]annulene and a dimethoxy derivative of "para"-isomer.[1)]

A pentenynal diethyl acetal[2)] was converted into lithio derivative (**1**) by means of ethereal phenyllithium and then mixed with a solution of a dienynyl ketone (**2**)[3)] in ether. Chromatography of the product on alumina afforded hydroxy acetal (3, pale yellow liquid, 64%) and hydroxy aldehyde (**4**, 23%). Hydrolysis of **3** with aqueous tartaric acid yielded **4** (mp 101.2-102.1°C from n-hexane, 91%).

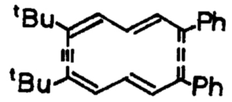
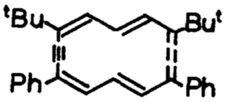
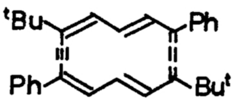


The ketone (5, mp 88.5-89.5°C from n-hexane, 69%) obtained by the aldol condensation of 4 with acetophenone was dissolved in tetrahydrofuran and the solution was added to a suspension of powdered potassium hydroxide in liquid ammonia.4) The cyclic glycol (6, pale yellow solid) obtained by working up the reaction mixture was treated with stannous chloride dihydrate in ether saturated with hydrogen chloride. Chromatographic purification of the product on alumina yielded "ortho"-isomer of di-t-butyl-diphenyldidehydro[14]annulene (7, 55% based on 5).

A hydroxy acetal (9, amorphous solid) obtained by the reaction of 1 with a ketone (8)5) was hydrolyzed with aqueous tartaric acid to give a hydroxy aldehyde (10, pale yellow plates, mp 84.3-85.7°C from CCl_4 and cyclohexane) in almost quantitative yield; Mass (m/e) 394 (M^+). Condensation of 10 with pinacolone followed by chromatography on alumina yielded a hydroxy ketone (11, yellow powder, 80%) which could not be crystallized. Intramolecular cyclization of crude 11 by means of potassium hydroxide in liquid ammonia afforded crude cyclic glycol (12, yellow solid). Black crystalline solid obtained on treatment of crude 12 with stannous chloride-hydrogen chloride in ether was chromatographed on alumina to give "meta"-isomer (13, Mass (m/e) 442 (M^+), 20.5% based on 11).

The physical properties of "ortho"- and "meta"-isomers (7 and 13) are summarized in Table 1 together with those of "para"-isomer (14).3) The position

Table 1. Physical Properties of Position Isomers of Didehydro[14]annulene

	 "ortho"- **7**	 "meta"- **13**	 "para"- **14**
Crystals	deep green plates	reddish green needles	brownish violet needles
Mp (°C)	248.0-249.0	200.8-202.0	>200
NMR(τ)			
Inner-H	13.51, t J=13.5 Hz	13.54, t 13.65, t J=13.5 Hz J=13.5 Hz	13.54, t J=13.5 Hz
t-Bu	8.10, s	8.07, s	8.06, s
Ph-H(m,p)$^+$	2.38, m	2.40, m	2.43, m
Ph-H(o)$^+$	1.37, m	1.41, m	1.42, m
Outer-H adjacent to t-Bu	0.58, d J=13.5 Hz	0.64, d J=13.5 Hz	0.56, d J=13.5 Hz
Outer-H adjacent to Ph	0.26, d J=13.5 Hz	0.17, d J=13.5 Hz	0.26, d J=13.5 Hz
UV**			
I	624 (1800)	624 (1270)	623 (1640)
II	507 (37200)	499 (37100)	508 (52600)
III	361 (215000)	368 (187000)	357 (195000)

* 100 MHz in $CDCl_3$. + τ-Values of center of multiplets.

** Main absorption maxima (nm) in THF and ε-values (in parentheses).

isomers (**7**, **13** and **14**) exhibit closely related NMR spectra. On the other hand, the absorption intensity of medium wavelength band (II) in the electronic spectrum of "para"-isomer (**14**) was found appreciably larger than those of other isomers (**7** and **13**). However, as illustrated in Fig. 1, entire absorption curves showed striking similarity in contrast with the marked difference observed between m- and p-terphenyls. This fact seemed to relate with the direction of polarization in the dehydroannulene. Taking this into consideration, we have

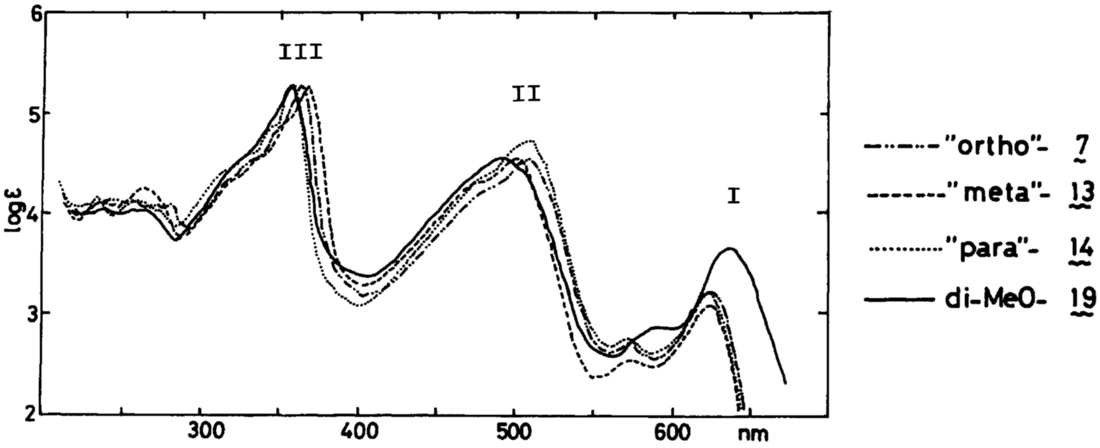
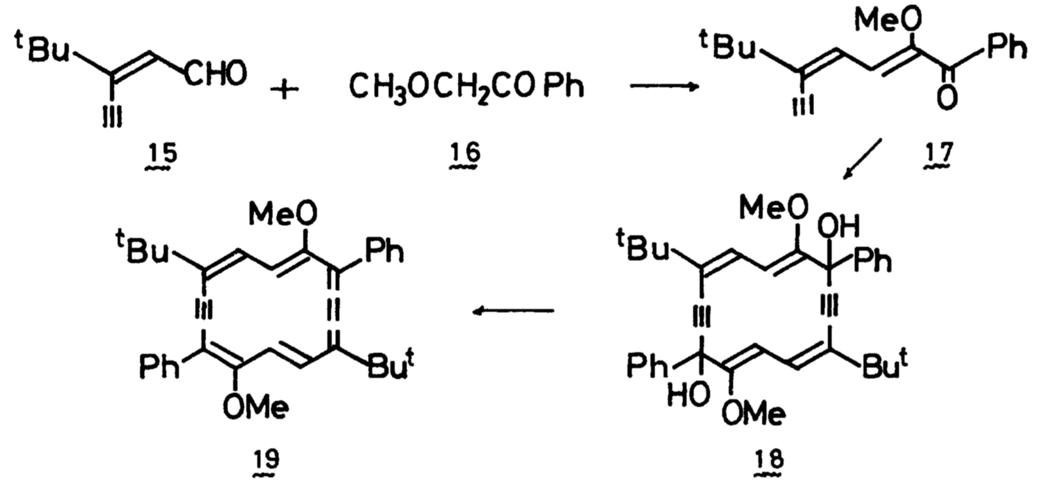


Fig. 1. Electronic spectra of position isomers of didehydro[14]annulene

carried out the synthesis of a dimethoxy derivative of "para"-isomer, 3,10-di-t-butyl-6,13-dimethoxy-7,14-diphenyl-1,8-didehydro[14]annulene (19).

The product of the aldol condensation of a pentenynal (15)[6] with ω-methoxyacetophenone (16)[7] was chromatographed on alumina to give a methoxy ketone (17, bp 110-120°C/0.67 Pa, Mass (m/e) 268 (M^+), 80%) as a rather unstable liquid.



A tetrahydrofuran solution of 17 was added to a suspension of potassium hydroxide in liquid ammonia. Chromatography of the reaction product on alumina resulted in crude separation of diastereomers of cyclic glycol (18, mp 247.9-249.1°C (dec.), 17% and mp 265.2-266.1°C (dec.), 30%). These diastereomers were found to be difficult to purify, but both of the crude isomers gave dimethoxyannulene (19) on treatment with stannous chloride-hydrogen chloride. More conveniently, the product of cyclic dimerization, without purification, could be converted into the dimethoxyannulene (19, deep green plates, mp 281.5-282.7°C (dec.) from n-hexane-benzene (5:1), Mass (m/e) 502 (M^+), 33% based on 17).

The data of NMR and electronic spectra of 19 are tabulated in Table 2.

Table 2. NMR and Electronic Spectra of Dimethoxyannulene (19)

NMR*	Inner-H	t-Bu	OMe	m,p-H of Ph$^+$	o-H of Ph$^+$	Outer-H
(τ)	13.76, d J=13.5 Hz	8.15, s	6.09, s	2.43, m	1.51, m	0.49, d J=13.5 Hz

UV**	I	II	III
λ(ε)	637 (4540)	492 (35000)	356 (177000)

* 100 MHz in $CDCl_3$. + τ-Values of center of multiplets.

** Main absorption maxima (nm) in tetrahydrofuran.

The electronic spectrum of 19 (Table 2 and Fig. 1) clearly shows hypsochromic shift of medium wavelength band (II) with hypochromism and bathochromic shift of the longest wavelength band (I) with strong hyperchromism as compared with the electronic spectrum of "para"-isomer (14). This results suggest that the direction of polarization of the longest wavelength band (I) is perpendicular and that of medium and short wavelength bands (II and III) is parallel to the long axis of the dehydroannulene molecule as shown in Fig. 2.

Bathochromic shifts of the medium and short wavelength bands (II and III) observed in 3,10-di-t-butyl-di-p-methoxyphenyl-1,8-didehydro[14]annulene (I: 625 ; II: 524 ; III: 367 nm)$^{8)}$ as compared with 14 are consistent with this view.

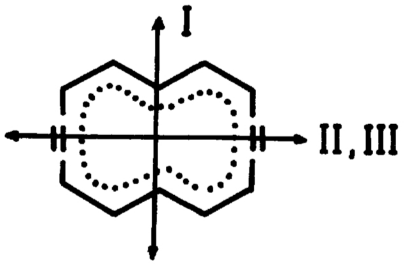


Fig. 2. Possible direction of polarization of 1,8-didehydro[14]annulene

REFERENCES AND NOTES

1) The "ortho"-, "meta"-, and "para"-annulenes formally correspond to o-, m-, and p-terphenyls, respectively, i.e., dipolar quinoid structures can be drawn in the cases of "ortho"- and "para"-annulenes, but not in "meta"-isomer.

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