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SYNTHESIS AND PROPERTIES OF BUTATRIENES CONTAINING A BISDEHYDRO[13]ANNULENE SYSTEM AS TERMINAL GROUPS

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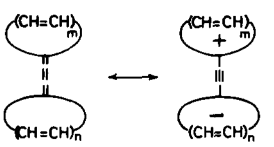
Summary: The compounds bearing a butatriene linkage between bisdehydro[13]annulene and electron donating and withdrawing systems have been synthesized. The contribution of a dipolar structure in these compounds is discussed on the basis of the spectral data.

A cyclic-conjugated system containing a butatriene linkage between two unsaturated odd-membered rings are generally described as the formula (1). In the case of m = n, there can be no contribution of the dipolar structure in these compounds. On the other hand, in the case of m ≠ n, the contribution of the dipolar structure (2) is expected in the ground state. It might be expected that the compound (1) shows the more contribution of the dipolar structure[1] than fulvalenes which are mostly typical polyenes with rather strongly localized carbon-carbon double bonds.[2] In this point of view, several compounds of the general formula (1) have been reported.[3] However, relatively little is known about the charge-separation or polarization of the cross-conjugated system having Csp^2-Csp-Csp-Csp^2 linkage.

The fulvalene-like system (3) containing a bisdehydro[13]annulene moiety is of interest because the [13]annulene moiety might behave like a negative or a positive end, *i.e.*, 4 ↔ 3 ↔ 5. When a cyclic system joined at opposite end in 3 tends to show a cationic form (*i.e.*, n = 2N+1), the contribution of the structure (4) might be expected. On the other hand, when a small or a medium ring in 3 tends to show an anionic form (*i.e.*, n = 2N), the contribution of 5 might be expected. It is known that ^{1}H NMR chemical shifts of inner and outer protons of a macrocyclic annulene reflect the tropicity,[4] and the ^{1}H NMR chemical shifts of the bisdehydro[13]annulenone (*i.e.*, a paratropic system) and the bisdehydro[13]annulenyl anion (*i.e.*, a diatropic system) have been reported.[5] Therefore, the contribution of the dipolar structure in 3 can be detected easily by comparison with the ^{1}H NMR chemical shifts of the paratropic or diatropic [13]annulene. We now wish to report the synthesis of the fulvalene-like butatrienes (6 ∿ 11) and the spectroscopic detection of the polar structure.



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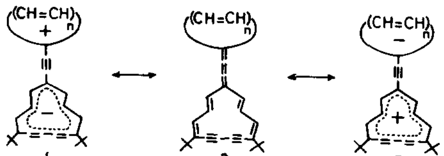

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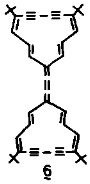

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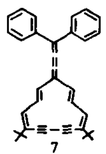

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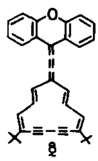

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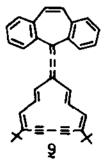

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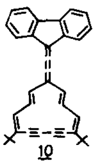

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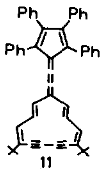

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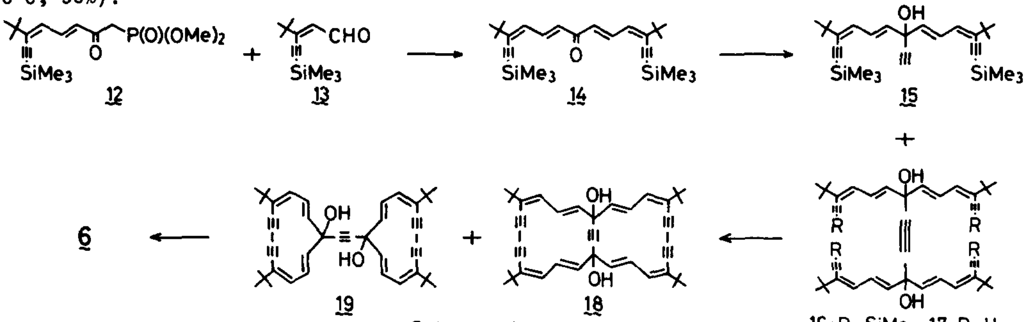
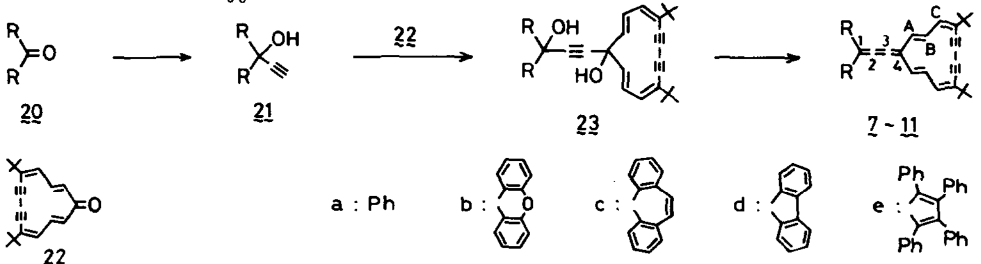
The synthesis of 6[6] was carried out by the reaction sequence shown in Scheme 1. The Wittig-Horner reaction of 13[7] with the carbanion derived from the ketophosphonate (12)[8] afforded the bis(trimethylsilyl)ketone (14, yellow cryst., mp 110.5∿112.0°C, 75%).[9] The reaction of 14 with an excess of acetylenedimagnesium bromide in THF gave a mixture of 15 and 16, which were separated by column chromatography on alumina (15, colorless cryst., mp 101.5∿103.0 °C, 45%; 16, pale yellow amorphous solid, 32%). Reaction of 16 with NaOH in aq. ethanol gave the diol (17, pale yellow amorphous solid, 90%), which was then oxidized with copper(II) acetate in pyridine-methanol-ether under high dilution conditions to give two bicyclic glycols (18, colorless solid, 5%; 19, colorless fine cryst., dp > 200°C, 15%). Treatment of 19 with tin(II) chloride-hydrogen chloride in ether afforded the butatriene (6, dark violet cryst., dp > 150°C, 56%).



Scheme 1

The synthesis of the butatrienes (7 ∿ 11) was accomplished by the reaction sequence shown in Scheme 2. The ethynyl alcohols (21a and 21b) obtained by the reaction of the ketones (20a and 20b) with lithium acetylide were treated with BuLi in THF to give the corresponding lithio derivatives. The reaction of the lithio derivatives with the bisdehydro[13]annulenone (22)[10] yielded the diols (23a, colorless cryst., mp 176.5∿178.0°C, 38%) and (23b, colorless fine cryst., mp 118.5∿123.0°C, 36%), respectively. Treatment of these diols (23a and 23b) with tin(II) chloride-hydrogen chloride in ether afforded the corresponding butatrienes (7, reddish brown cryst., dp > 200°C, 94%) and (8, deep bluish violet cryst., 80%), respectively.

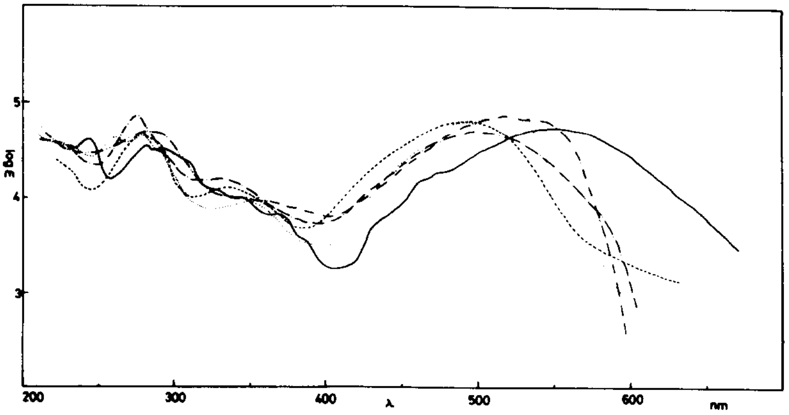
For the synthesis of the butatrienes (9, 10 and 11), the ethynyl alcohols (21c, 21d and 21e) derived from the ketones (20c, 20d and 20e) were firstly treated with EtMgBr to give the corresponding Grignard derivatives, which were then allowed to react with 22 to give the diols (23c, colorless cryst., dp > 210°C, 51%), (23d, colorless fine cryst., mp 134.5∿135.0°C, 24.5 %), and (23e, pale yellow fine cryst., mp 129.5∿131.5°C, 43%), respectively. The diols (23c, 23d and 23e) were converted into the butatrienes (9, 10 and 11) under similar reaction conditions used for 7 and 8 (9, deep reddish violet cryst., dp > 185°C, 74%; 10, deep reddish violet cryst., dp > 190°C, 81%; 11, reddish brown cryst., dp > 220°C, 58%).

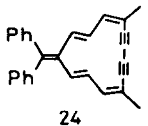


Scheme 2

The electronic spectra of the butatrienes (**6** ∿ **11**) are shown in Figure 1 and the ^{1}H NMR parameters (chemical shifts in τ-values) of **6** ∿ **11** are summarized in Table 1 together with those of the bisdehydro[13]annulenone (**22**). The electronic spectra of these butatrienes show two intense absorption maxima (*ca.* 280 and 490 ∿ 550 nm). The longer absorption bands are assignable to $\pi \rightarrow \pi^*$ transitions on the basis of the results of Runge.$^{11)}$ The shorter absorption bands may be associated with $\delta \rightarrow \delta^*$ transitions, because the positions of the bands are little affected by substitution.$^{11)}$

The difference in the chemical shifts between the outer and inner protons ($\tau_o - \tau_i$) can be regarded as an approximate measure of tropicity. As shown in Table 1, the Δτ-values increase in the order **8** < **9** < **7** < **6** ≤ **10** < **11** < **22**. The butatriene (**6**) should show no contribution of the dipolar structure, because **6** bears two equivalent bisdehydro[13]annulene parts as the terminal groups. Therefore, the [13]annulene moiety in **11** may be slightly positive and consequently paratropic, although the paratropicity is weaker than that of the [13]annulenone (**22**). On the contrary, the [13]annulene moiety in **8**, which shows smaller Δτ-values than that in **6**, may be slightly negative and seems diatropic (the inner protons in an atropic [13]annulene (*e.g.*, **24**)$^{12)}$ were observed at lower field relative to the outer protons, presumably owing to a superposition of the anisotropic effect and the steric compression between the inner protons). The paratropicity observed in **11** reflects the facility of the charge-separation in the butatriene linkage as compared with the ethylene linkage (*e.g.*, the outer and inner protons of **25**$^{13)}$ were observed at τ 3.15 and 2.08, respectively: Δτ = 1.07).





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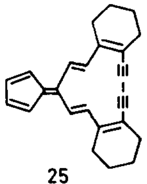

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Figure 1. The Electronic Spectra of the Butatrienes (**7** ∿ **11**) in Cyclohexane.
(**7**: ------ **8**: ——— **9**: —·—·— **10**: ··········· **11**: —··—··—)

Table 1. The ^{1}H NMR Parameters of the Butatrienes (**6** ∿ **11**) and the Bisdehydro[13]annulenone (**22**).
(100 MHz, $CDCl_3$, τ-values, rt)

	H_A	H_B	H_C	*t*-Bu	Δτ (H_A - H_B)	Δτ (H_C - H_B)
6	3.62 d (J=16.5)	1.95 dd (J=10.5, 16.5)	3.42 d (J=10.5)	8.85 s	1.69	1.49
7	3.51 d (J=16.5)	2.41 dd (J=10.5, 16.5)	3.31 d (J=10.5)	8.82 s	1.10	0.90
8	3.34 d (J=16.0)	2.83 dd (J=10.0, 16.0)	3.22 d (J=10.0)	8.78 s	0.51	0.39
9	3.56 d (J=16.5)	2.50 dd (J=10.5, 16.5)	3.33 d (J=10.5)	8.84 s	1.06	0.83
10	3.46 d (J=16.5)	1.78 dd (J=10.5, 16.5)	3.34 d (J=10.5)	8.81 s	1.68	1.56
11	3.81 d (J=16.5)	1.42 dd (J=10.5, 16.5)	3.63 d (J=10.5)	8.88 s	2.49	2.21
22	4.03 d (J=17.0)	0.41 dd (J=9.5, 17.0)	3.74 d (J=9.5)	8.80 s	3.62	3.33

In order to investigate in detail the contribution of the dipolar structure, the IR and ^{13}C NMR spectra have been examined (Table 2). The IR absorption band of butatriene portion is very useful for identifying and detecting the butatriene functional group. This absorption band in 7 ∿ 11 appears around 2020 cm^{-1} so that the contribution of acetylene form (IR, 2190 ∿ 2260 cm^{-1}) cannot be detected in the IR spectra. The ^{13}C NMR chemical shifts of the butatriene parts in 6 ∿ 11 may suggest a slight charge-separation, because the chemical shifts of the sp^2-carbon (C_4) are shifted to lower field in the order 8 < 9 = 7 < 6 < 10 < 11. This order corresponds to that of the $\Delta\tau$-values and reveals the increase of negative charge. The chemical shifts of the sp-carbons (C_2 and C_3) in 7 ∿ 11, however, were observed in the region of about 126 to 157 ppm, suggesting hardly detectable contribution of the acetylenic dipolar structure (27) (^{13}C NMR chemical shifts of acetylenes are δ 65 ∿ 90 ppm). The slight charge-separation may be also due to the contribution of the dipolar structure (28 and 29), because the chemical shifts of C_2 in 7 ∿ 11 are distinct from those of C_3. Consequently, the slight charge-separation observed in the butatrienes (7 ∿ 11) may be attributable to some participation of the dipolar structure (30).

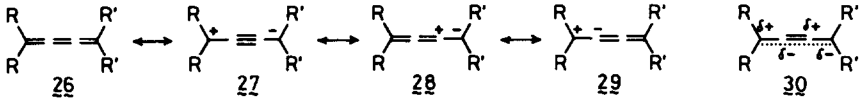

Table 2. The IR and ^{13}C NMR Parameters of 6 ∿ 11.

		6	7	8	9	10	11
IR (KBr-disk) cm^{-1}		2009$^{a)}$	2013	2024	2013	2025	2025
^{13}C NMR$^{b)}$	C_1	121.9	125.7	113.8	126.4	121.3	130.1
	C_2	143.6	141.6	125.3	145.9	135.1	148.7
($CDCl_3$)	C_3	143.6	156.8	153.8	155.6	155.9	156.1
	C_4	121.9	118.8	115.2	118.8	122.9	129.5

a) Laser Raman spectrum. b) TMS as the internal standard.

References and Notes

1) Experimental evidence and theoretical treatments have suggested that rotational barriers of butatrienes are much smaller than those of ethylenes. Therefore, the transition state of the rotation, *i.e.*, diradical or dipolar structure, is more stabilized in butatrienes than in ethylenes. *Cf.*, W. Runge, Chapter 2 in "The Chemistry of Ketenes, Allenes, and Related Compounds, Part 1", ed. by S. Patai, John Wiley (1980).

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