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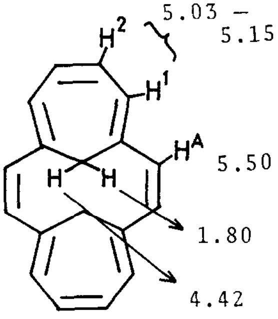
A SYNTHESIS OF A DOUBLY-BRIDGED [24]ANNULENE

Koji Yamamoto,*[a] Mitsuo Shibutani,[b] Shigeyasu Kuroda,[b] Emiko Ejiri,[c] and Jūro Ojima*[c]

[a]*Dept. of Chemistry, Faculty of Engineering Science, Osaka University, Toyonaka 560,* [b]*Dept. of Industrial Chemistry, Faculty of Engineering, Toyama University, and* [c]*Dept. of Chemistry, Faculty of Science, Toyama University, Gofuku, Toyama 930, Japan*

Summary: Reductive coupling of 1,6-bis(2-formylvinyl)cyclohepta-1,3,5-triene with a low-valent titanium reagent afforded a paratropic bismethano[24]annulene.

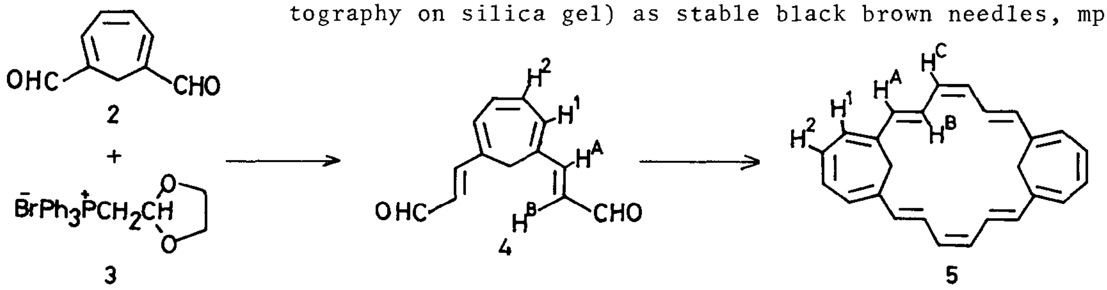
The reductive coupling of carbonyl compounds with low-valent titanium salt[1)] seems to serve a new tool for the synthesis of large-membered conjugated polyenes (annulenes), since the synthesis of annulenes had so far involved lengthy reaction sequence. Recently, in practice, Tanner *et al.* reported a synthesis of bismethano[16]annulene (1) from cycloheptatriene-1,6-dialdehyde (2) with titanium tetrachloride and zinc, and showed 1 to be paratropic.[2)] In view of this and no precedents of bridged [24]annulene,[3)] synthesis of the higher analogue of 1, bismethano[24]annulene (5) carrying inner protons, seemed to be of considerable interest for the purpose comparing the properties.



1

τ values in $CDCl_3$

Cycloheptatriene-1,6-dialdehyde (2) was converted to the bis-vinylogue 4 by the method of Cresp *et al.*[4)] Reaction of 2 and the salt 3 in DMF with ethanolic LiOEt at 75°C, followed by hydrolysis with dilute hydrochloric acid in THF at room temperature, gave 71% of 4[5)] (isolated by chromatography on Al_2O_3) as yellow needles, mp 163–164°C; ^1H NMR (90 MHz) τ 0.39 (d, J=7.2 Hz, 2H, -C$\underline{H}$O), 2.81 (d, 15.6, 2H, H^A), 3.24–3.44 (m, 4H, H^1 and H^2), 3.58 (dd, 15.6, 7.2, 2H, H^B), and 7.22 (s, 2H, -C$\underline{H}_2$-). Reductive coupling of 4 with titanium trichloride and $LiAlH_4$ in refluxing dimethoxyethane[6)] gave 4.8% of 5[5)] (isolated by chromatography on silica gel) as stable black brown needles, mp



200°C (dec); ^{1}H NMR (270 MHz) τ 1.01 (dd, J=15.1, 8.8, 4H, H^B), 3.73 (dd, 4.2, 2.7, 4H, H^2), 4.05 (d, 4, 4H, H^1), 4.07 (d, 14.9, 4H, H^A), 4.25 (d, 8.5, 4H, H^C), and 5.89 (s, 4H, $-CH_2-$).

The ^{1}H NMR spectrum of **5** is illustrated in Fig. 1. As we see from Fig. 1, the molecule **5** is paratropic, as might be expected of 24π-system, since the inner H^B proton resonates in a low field, while the outer H^A, H^C, H^1, and H^2 protons do in rather high field. Also, the bridged methylene protons of **5** resonate in lower field (Δ -1.2 ppm), as compared with those of the dialdehyde **4** (*vide ante*).

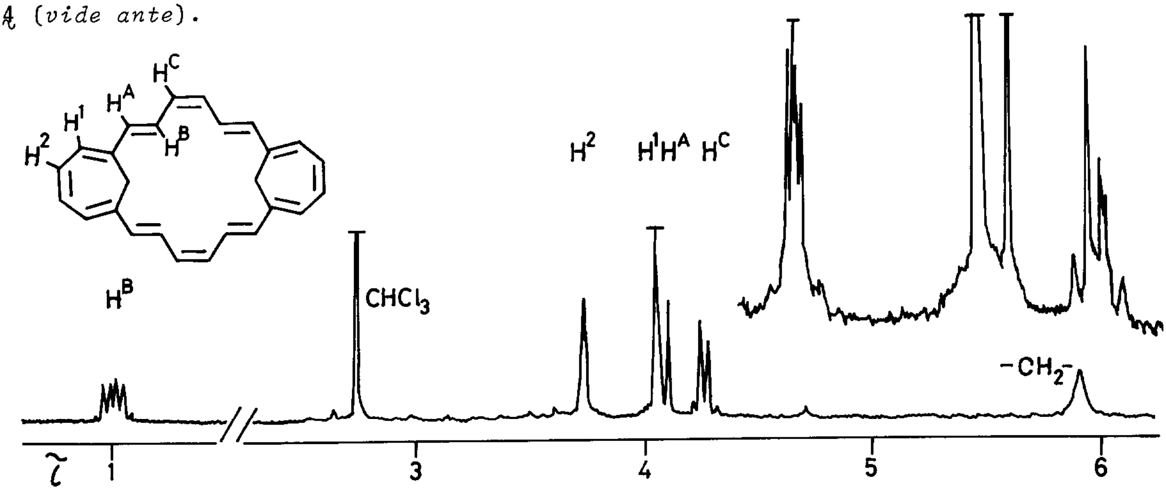


Fig. 1. The 270 MHz ^{1}H NMR spectrum of **5** in CDCl$_3$

An inspection of Dreiding molecular model reveals that the conjugated system in **5** is more disadvantageous than in **1** with respect to spatial orbital overlap of π-electrons. This is reflected in degree of paratropicity, *i.e.*, planarity of the molecular skeleton between **1** and **5**; **5** being much less paratropic than **1**.

The additional thermal stability of the bismethano[24]annulene **5** when compared with the [24]annulene$^{7a)}$ and the trisdehydro[24]annulene$^{7b)}$ might come from rigidity of the ring skeleton due to two methylene bridges.

Further studies on doubly-bridged [4n]-membered annulenes are now in progress.

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