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9-METHYLENETRICYCLO[4.3.1.0]DECA-2,4,7-TRIENE DERIVATIVES

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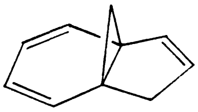
9-Methylenetricyclo[4.3.1.0]deca-2,4,7-triene (3a) and its derivatives possessing electron releasing group such as bis(dimethylamino)- and bis(methylthio)-groups at the exo-methylene carbon atom (3b and 3c) were synthesized from bicyclo[4.3.1]decatetraenyl anion (2). It has been shown that the closed norcaradiene tautomers (3a, 3b and 3c) are preferable to the opened nonafulvene tautomers (4a, 4b and 4c).

Tricyclo[4.3.1.0]deca-2,4,7-triene (1) has been shown to react with sodium methylsulfinyl anion in dimethyl sulfoxide to produce bicyclo[4.3.1]decatetraenyl anion (2).[1,2] This fact indicates that the incorporation of negative charge into 1 makes opened 10 pi-electron delocalized structure having C_9-perimeter favorable. The stability of the bridged 10-pi-electron carbanion raised out attention as to whether the exo-methylene derivatives (3) of 1 having the electron releasing substituents such as dimethylamino and methylthio groups might also be capable existence as the bridged nonafulvenes (4)[3] rather than the closed norcaradiene type tautomers (3). The following studies were carried out mainly for the purpose of exploring these possibilities.



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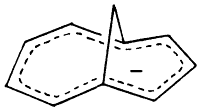

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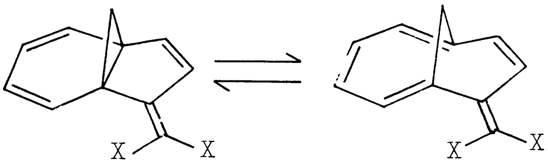


(3) (4)

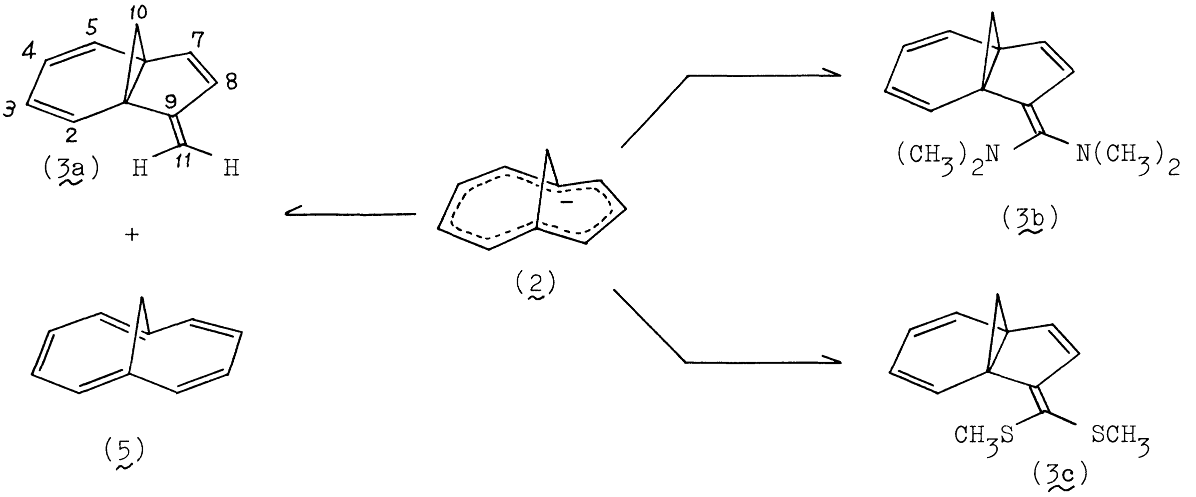
Bicyclo[4.3.1]decatetraenyl Anion (2)

Although the anion (2) could readily be prepared in dimethyl sulfoxide the solution is inadequate for the subsequent low tepemperature reaction due to the relatively high freezing point of the solvent. We were able to find a procedure for conveniently preparing the anion in tetrahydrofuran (THF)-tetramethylethylenediamine (TMEDA) solution. Thus, a solution of 130 mg of 1[4] in 5 ml of THF and 0.5 ml of TMEDA was stirred under nitrogen at 0°C, and a solution of an equivalent of n-butyllithium in n-hexane was added dropwise. After the mixture was stirred at 0°C for 30 min, 0.5 ml of deuterium oxide was added. Usual work-up gave pure hydrocarbon

(97% yield), the nmr spectrum of which indicated essentially complete deuterium incorporation at the methylene position.

9-Methylenetricyclo[4.3.1.0]deca-2,4,7-triene (**3a**).

For the synthesis of 9-methylenetricyclo[4.3.1.0]deca-2,4,7-triene (**3a**), the lithium salt of **2** was prepared as described above and subsequently introduced by addition to a solution of methylene chloride/n-butyllithium complex$^{5)}$ in THF-ether-n-hexane maintained at below -90°C. After complete addition, the reaction mixture was gradually warmed up to room temperature. The product was purified by column chromatography on alumina (with 6% of water) using pet. ether (bp$<$50°C) eluent which gave a 46% yield of **3a** as an air sensitive colorless prisms of mp 34.0°C, m/e 142 (M^+), uv, λ_{max} (cyclohexane) 225 nm (log ε 4.15) and 280 (s, 3.51), along with a minute amount of the known ring enlargement product, 1,6-methano[10]annulene (**5**).$^{6)}$ The assignment of structure **3a** is based on its well-defined nmr spectrum [Fig. 1a]. Thus, **3a** exhibits nonaromatic resonance at δ 6.3-5.6 (m, 6H, H-2~5,7,8), 5.01 (bs, 1H, H-11), 5.08 (bs, 1H, H-11'), 1.65 (d, 1H, H-10, J=2.5 Hz) and 0.19 ppm (d, 1H, H-10', J=2.5 Hz). The AX-type absorption of J=2.5 Hz is attributable to the $-CH_2-$ protons of a norcaradiene structure (**3a**).



9-Bis(dimethylamino)methylenetricyclo[4.3.1.0]deca-2,4,7-triene (**3b**)

Introduction of the bis(dimethylamino)methylene group into **1** was effected by direct condensation of the anion (**2**) with bis(dimethylamino)ethoxycarbonium tetrafluoroborate$^{7)}$ in THF-TMEDA under nitrogen at -70°C. After stirring at room temperature for 30 min, the mixture was diluted with water. From the ether extract product (**3b**) was obtained in 45% yield as an air sensitive colorless liquid. Freshly prepared sample shows correct mass, m/e 228 (M^+); uv λ_{max} (cyclohexane) 213, 245, 272, 284 and 315 nm with tailing to 450 nm$^{8)}$ and nmr, δ 6.6-6.4 (m, 1H, H-2), 6.2-5.8 (m, 5H, H-3, 4,5,7,8), 2.92 and 2.71 (s, 6H, each, NMe_2), 1.71 (d, 1H, H-10, J=3.5 Hz) and 0.13 (d, 1H, H-10', J=3.5 Hz) [Fig. 1b]. Again the chemical shift of the olefinic protons and the most characteristic absorption of an AX-system at δ 1.77 and 0.25 with a geminal coupling constant of 3.5 Hz are suggestive of a norcaradiene structure (**3b**).

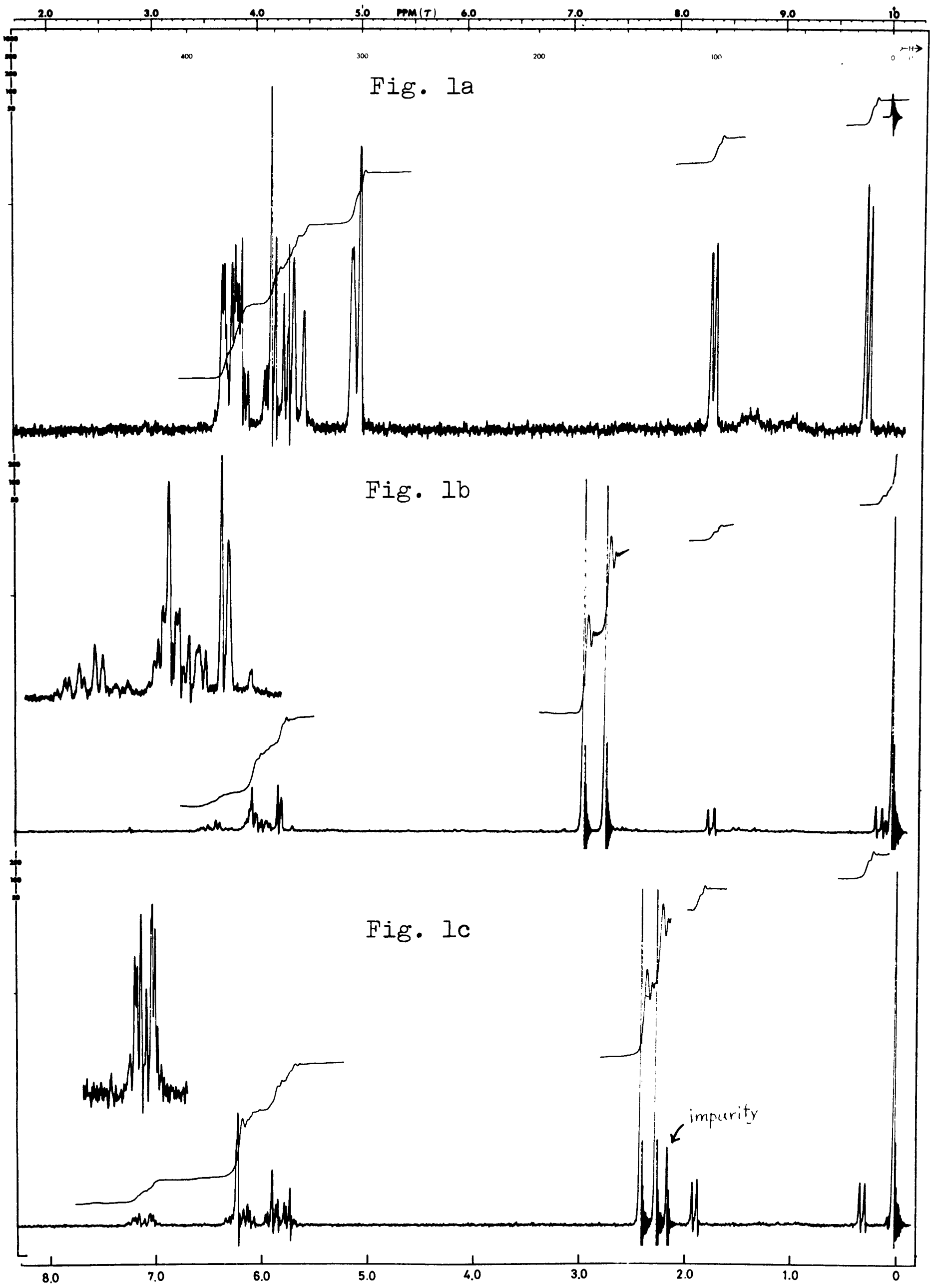


Fig. 1.
60 MHz nmr spectra of (3a), (3b) and (3c) in $CDCl_3$.

9-Bis(methylthio)methylenetricyclo[4.3.1.0]deca-2,4,7-triene (3c)

For preparation of the corresponding bis(methylthio)methylene derivative, a solution of 2 in THF-TMEDA was treated with dimethyltrithiocarbonate[9] under nitrogen at -70°C followed by the addition of methyl iodide. Purification of the product by the repeated alumina (with 5% of water) column chromatography to yield 20% of 3c as a labile yellow liquid, m/e 234 (M^+), uv λ_{max} (cyclohexane) 226, 264 (s) and 316 nm.[8] Structure assignment to the norcaradiene tautomer (3c) was again borne out by the nmr examination [Fig. 1c]. Thus, besides olefinic absorptions at δ 7.3-7.0 (m, 1H, H-2), 6.4-5.7 (m, 5H, H-3,4,5,7,8) and two SCH_3 groups at δ 2.43 and 2.26 (s, 3H each), the spectrum exhibited an AX-type signals at δ 1.89 and 0.30 with a coupling constant of 2.9 Hz, pointing to the presence of a cyclopropane moiety.

Even though the electron releasing groups are attached to the exo-methylene carbon atom of 3a, the position of the equilibrium between the closed norcaradiene and the opened nonafulvene tautomer [(3)$\rightleftharpoons$(4)] is shifted to the former. To conclude, it is noting that although the results presented here are mainly qualitative, the geometrical factor may play a much more significant role than the electronic effect in the valence tautomeric equilibrium between the methylenetricyclo[4.3.1.0]-deca-2,4,7-triene (3) and the methano-bridged nonafulvene (4).

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REFERENCES AND NOTES

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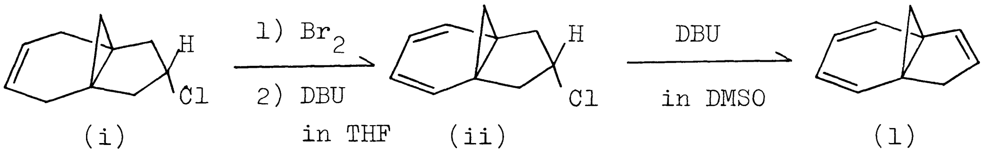
3) For simple nonafulvenes, see K. Hafner and T. Tappe, Angew. Chem., 81, 564 (1969); K. Hafner in "Aromaticity, Pseudo-aromaticity, Anti-aromaticity", ed. by E. D. Bergman and B. Pullman, Academic Press, Inc. 1971, p. 256.

4) Prepared according primarily to the prodecure of Radlick and Rosen[2] with slight modifications described below: Treatment of the chloride (i) with equimolar amount of bromine in dichloromethane at -78°C and bisdehydrobromination of the resulting dibromide with two molar amount of 1,8-diazabicyclo[5.4.0]undecene-7 (DBU) in refluxing THF under nitrogen gave the diene (ii) in 94% yield. The final dechlorination was also effected by using the three-fold excess of DBU in dimethyl sulfoxide at 120°C for 1 hr and afforded the triene (1) in 72% yield. This improved procedure provides 26.5% over-all yield of the triene (1) from 2-indanol.



(i) (ii) (1)

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8) Exact ε-values could not be obtained due to instability of the compound.

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