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Synthesis of 4,8-Dimethyl-5,7-nonamethyleneazulene

Shinji KUROKAWA* and Arthur G. ANDERSON, Jr.†

Department of Chemistry, Faculty of Education, Saga University, Honjo-machi, Saga 840

† *Department of Chemistry, University of Washington, Seattle, Washington, 98195, U. S. A.*

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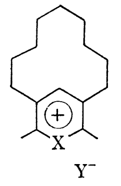
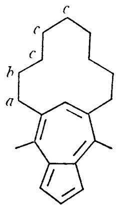
Synopsis. The title compound has been prepared from 2,6-dimethyl-3,5-nonamethylenepyrylium perchlorate and from 1,2,6-trimethyl-3,5-nonamethylenepyridinium iodide in low yield by reaction with sodium cyclopentadienide. The UV, visible and PMR spectra of the title compound are correlated with the structure.

Electrophilic substitution was used to prepare the intermediate for cyclization to a 1,3-meta-bridged azulene, 1,3-(5-cyano-6-oxoundecamethylene)azulene.[1)] This route was not possible for the formation of a 5,7-bridge. The later synthesis of 3,5-bridged pyrylium perchlorate (**1**) and pyrydinium iodide (**2**)[2)] made available compounds needed for a 5,7-bridged azulene by the Hafner route.



1: X=O, Y=ClO_4
2: X=NMe, Y=I



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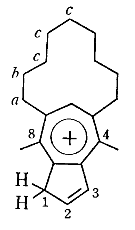

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Reaction of sodium cyclopentadienide with **1** or **2** gave a low ($\leq 0.3\%$) yield of the title compound (**3**) as violet crystals. The PMR spectrum of **3** in trifluoroacetic acid corresponded well to the structure of the conjugate acid (**4**).

A molecular model of **3** did not show steric strain such that appreciable distortion of the azulene ring would occur. Distortion of the ring should cause a larger bathochromic shift of the ultraviolet absorption than is caused by the tetraalkyl substitution, and ring distortion would also probably cause lower intensity of absorption and loss of fine structure.[3)] Comparison of the ultraviolet spectrum with those of the best model compounds in the literature (4,8-,[4)] 4,5-,[5)] and 4,7-dimethylazulenes[6)]) showed a shift to longer wavelengths for **3**, but the principal maximum at 581 nm agreed well with 578 nm calculated by Plattner's rule.[6)] The absence of ring distortion was also indicated by the high intensities (log ε 3.87 to 4.87) and the retention of fine structure.

The model of **3** showed the *c* methylenes over the pi-electron cloud of the aromatic ring in the sterically favoured conformations. The model also showed significant steric restrictions to rotational conversions from the many unsymmetric to the two symmetric conformations of the bridge. In agreement with the model, the PMR signal for the *c* methylenes (δ 1.25) is at higher field[7)] than that for the *b* methylenes (δ 1.78) which are nearer to the plane of the azulene ring. Comparison with the spectrum of 5,7-dimethylazulene[8)] showed a shift inversion for the 2- and 6-hydrogens: δ 7.48 and 7.61, respectively, for **3**, *vs.* δ 7.81 and 7.42. This may be explained by two factors: the very small concentration of **3** in the PMR solution would cause the 6-H signal to shift downfield, but would have little effect on the 2-H signal,[9)] and the effective shielding of the 6-H would be decreased by the asymmetrical interaction with the bridge hydrogens.[10)] The observed nonequivalence of 1-H and 3-H (δ 7.19 and 7.28) seems due to the asymmetrical magnetic anisotropy effect of the bridge. The small amount of material obtained did not permit experiments concerned with this point.

Experimental

PMR spectra (δ) were taken on a Hitachi R-22 spectrometer with TMS as internal standard, for **3**, with a Hitachi A-1600 signal averaging analyzer. MS were obtained at 70 eV on a Hitachi RMS-4 instrument. UV and visible spectra were recorded on a Hitachi 624 digital spectrometer with a Hitachi 056 recorder. IR spectra were taken on a JASCO A-3 spectrometer. Mps are uncorrected.

*2,6-Dimethyl-3,5-nonamethylenepyrylium Perchlorate (**1**).* This compound was prepared from cyclododecene [166 g (1 mol) purified by distillation; bp 111—116 °C/12 Torr] and acetic anhydride (511 g, 5 mol) in the presence of 70% perchloric acid[2)] except that stirring was continued for 2 h at room temperature after addition of the acid. Recrystallization of the product from 1% perchloric acid gave 41.3 g (12.4%) of **1** as pale yellow crystals, mp 181—182 °C (lit,[2)] 170 °C). IR (KBr) 3020, 2890—2940, 2855, and 1606 cm^{-1}. PMR (CF_3COOH) δ=2.94 (6H, s, CH_3), 3.02 (4H, t, J=6.0 Hz, *a*), 2.00 (4H, symmetrical m, *b*), 1.28 (10H, unsymmetrical m, *c*), and 8.80 (1H, s, pyrylium H).

*1,2,6-Trimethyl-3,5-nonamethylenepyridinium Iodide (**2**).* Dry ammonia gas was bubbled into a suspension of 50.8 g (0.153 mol) of vacuum-dried **1** in 300 cm^3 of dry *t*-butyl alcohol for 2 h[2)] to give 24.26 g (68.6%) of 2,6-dimethyl-3,5-nonamethylenepyridine, bp 140—142 °C/3 Torr; UV_{max} (cyclohexane) 197 (log ε 4.3), 217 (3.9), 273 (3.5) and 280^{sh} nm (3.5); IR (liquid film) 2930, 2855, and 1445 cm^{-1}; PMR ($CDCl_3$) δ=1.04 (10H, m, *c*), 1.64 (4H, m, *b*), 2.64 (4H, t, J=6.5 Hz, *a*), 2.41 (6H, s, CH_3) and 7.20 (1H, s, 4-H).

The pyridine [5.13 g (0.222 mol)] was mixed with 5 cm^3 (0.08 mol) of methyl iodide. After 12 h, an additional 5 cm^3 of methyl iodide was added. After 12 h, removal of excess methyl iodide (reduced pressure) left **2** as a yellowish hygroscopic crystalline mass.

*4,8-Dimethyl-5,7-nonamethyleneazulene (**3**).* *A. From **1**.* To sodium cyclopentadienide prepared from 4.6 g (0.07 mol) of cyclopentadiene and 2.9 g (0.06 mol) of sodium hydride in 30 cm^3 of THF under dry nitrogen, was added 6.7 g (0.02 mol) of **1** in 15 cm^3 of THF (30 min) and the mixture stirred for 2 h. Two-thirds of the solvent was removed, 300 cm^3 of water was added, and the whole was extracted several times with petroleum ether. The solvent was evaporated and the residue chromatographed on 20 g of silica gel (petroleum ether eluant). Extraction of the blue-green fraction with 85% phosphoric acid, dilution of the extracts with ice water, extraction of the aqueous solution with petroleum ether, evaporation of the solvent, and chromatography with petroleum ether of the residue on 25 g of silica gel gave 16.7 mg (0.3%), mp *ca.* 89 °C.

The crude product (66.8 mg, 0.239 mmol) in petroleum ether was retreated with 85% phosphoric acid as described above. Chromatography on 25 g of silica gel (petroleum ether) and rechromatography on 7 g of silica gel (hexane-benzene, 9:1) gave 23.4 mg of **3** as blue-violet crystals. Passage over Amberlite IRC-50 (CG-50 type) (80% ethanol) gave 9.82 mg (0.04%) of violet plates from 80% ethanol, mp 109—110 °C; pure by GLC, UV$_{max}$ (cyclohexane) 253 (log ε 4.71), 292 (4.87), 298 (4.85), 340 (3.97), 350 (4.06), and 365 nm (3.87); 565^{sh} (ε 829), 581 (875), 600 (816), 627^{sh} (666), 660^{sh} (361), and 690 nm (196). IR (CCl$_4$) 2920, 2850, and 1460 cm^{-1}. PMR (CCl$_4$, 90 MHz), δ= 1.25 (10H, broad s, *c*), 1.78 (4H, m, *b*), 2.88 (6H, s, CH$_3$), 3.05 (4H, m, J=6.0 Hz, *a*), 7.19 (1H, dd, J=4.0 and 1.5 Hz, 1- or 3-H), 7.28 (1H, m, overlapping 7.19 signal, 1- or 3-H), 7.48 (1H, q, J=4.0 Hz, 2-H) and 7.61 (1H, s, 6-H). MS m/e 280 (M$^+$ for C$_{21}$H$_{28}$, base peak) [M$^+$=280.218 (C$_{21}$H$_{28}$= 280.219)].

B. From **2**.[11] Sodium cyclopentadienide (from 3.8 g (0.078 mol) of sodium hydride and 7.4 cm^3 (0.09 mol) of cyclopentadiene) in 10 cm^3 of THF was added to the vacuum dried (CaCl$_2$) pyridinium iodide (**2**) from 0.222 mol of pyridine. The mixture was stirred for 2.5 h and the solvent was removed. A petroleum ether solution of the violet solid was washed (H$_2$O), dried (Na$_2$SO$_4$), separated from the solvent, and chromatographed on 80 g of silica gel (petroleum ether-benzene, 9:1). The green zone (86.23 mg) was purified as described for the crude product in *A* to give 2.12 mg (0.034%) of **3**.

A solution of **3** in trifluoroacetic acid showed PMR signals corresponding to **4**, δ=1.33 (10H, *c*), 2.10 (4H, *b*), 3.05 (6H, 4-CH$_3$ and 8-CH$_3$), 3.46 (4H, *a*), 4.20 (2H, 1-CH$_2$), 7.68 (2H, 2-H and 3-H), and 8.78 (1H, 6-H).

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