

FORMATION AND TRAPPING OF 1,2-DIMETHYLENEAZULENE

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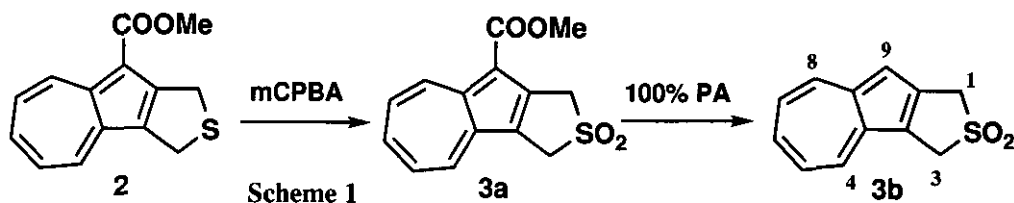
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Abstract - 1,2-Dimethyleneazulenes, an *o*-xylylene type reactive intermediate, have been generated by the heating of 1,3-dihydroazuleno[1,2-*c*]thiophene dioxides. The reactive intermediates were efficiently trapped by dienophiles, such as *N*-phenylmaleimide and diethyl azodicarboxylate, to form [4+2] cycloaddition products in high yields.

The reactive intermediate, *o*-xylylene, has received interest from the theoretical and synthetical points of view, and various reactions for generation of the intermediate have been reported.¹ Although azulene analogs of *o*-xylylene are also interested in the same points of view, none of possible three isomers of such intermediates have been synthesized so far.² We report in this paper on the first formation and trapping of 1,2-dimethyleneazulenes (1) by the thermolysis of 1,3-dihydroazuleno[1,2-*c*]thiophene dioxides (3).

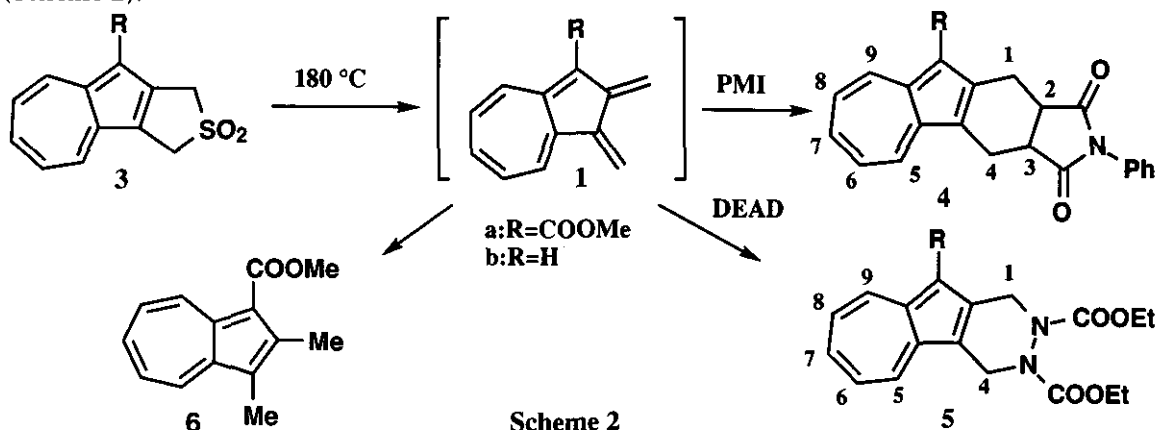
Appropriate precursors (3) were synthesized from methyl 1,3-dihydroazuleno[1,2-*c*]thiophene-9-carboxylate (2).³ Oxidation of 2 with mCPBA in CH₂Cl₂ at 0 °C gave a precursor (3a)⁵ as stable crystals in 92% yield. Demethoxycarbonylation of 3a with 100% phosphoric acid at 90 °C gave another precursor (3b)⁶ in a quantitative yield (Scheme 1). MS spectra of both

3a and 3b showed M^+SO_2 peak as a base peak or a high intense peak instead of molecular ion (M^+) suggesting easy formation of 1,2-dimethyleneazulene (1).



A solution of 3a (99.5 mg, 0.36 mmol) in dibutyl phthalate (5 mL) was heated at 180°C under an Ar atmosphere in the presence of *N*-phenylmaleimide (PMI) (249 mg, 4 mol eq.) for 5 h. After removing of the solvent under reduced pressure, chromatography of the products with a silica gel column eluted with benzene gave 4a (127.7mg)⁷ in 92% yield. The spectral data of 4a were well consistent with the assigned structure of [4+2] cycloadduct of the expected intermediate (1a) with PMI. The thermal reaction of 3a in the presence of diethyl azodicarboxylate (DEAD) gave also a cycloadduct (5a)⁸ in a quantitative yield.

The thermal reaction of 3b in the presence of PMI under the same conditions gave an adduct (4b) (violet prisms, mp 183-184 °C). These results clearly indicate the generation of the reactive intermediate (1), 1,2-dimethyleneazulenes, from 3 under the reaction conditions (Scheme 2).



Heating of a solution of 3a in dibutyl phthalate in the absence of a trapping reagent gave methyl 2,3-dimethylazulene-1-carboxylate (6) in only 20% yield without recovery of 3a. Synthetic studies by the application of 1 are now in progress.

REFERENCES AND NOTES

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2. 2,6-Dimethyleneazulene has been synthesized: N. Kato, Y. Fukazawa, and S. Ito, *Tetrahedron Lett.*, 1976, 2045; R. Lohoway and P. M. Keehn, *J. Am. Chem. Soc.*, 1977, **99**, 3797.
3. K. Fujimori, T. Fujita, K. Yamane, M. Yasunami, and K. Takase, *Chem. Lett.*, 1983, 1721.
4. All new compounds gave satisfactory results of elemental analyses. Spectral data of adducts were shown for **4a** and **5a**. The spectral data of **4b** were well consistent with the assigned structure.
5. **3a**: Violet micro needles, mp 213-213.5 °C; MS (70 eV, 210 °C) m/z 276 (M⁺, 5.1%), 212 (M⁺-SO₂, 72.9%), 154 (212-COOMe, 100%); IR (KBr) 1689, 1312, 1121, 534 cm⁻¹; ¹H NMR (90 MHz, CDCl₃) δ=3.89 (3H, s, COOMe), 4.76 (2H, br s, CH₂-3), 4.54 (2H, br s, CH₂-1), 7.75 (3H, mc, H-5,6,7), 8.08 (1H, d, J=9.6 Hz, H-4), 8.56 (1H, d, J=9.6 Hz, H-8).
6. **3b**: Blue prisms, mp 160 °C (decomp); MS (25 eV, 80 °C) m/z 218 (M⁺, 7.8%), 154 (M⁺-SO₂, 100%); IR(KBr) 1309, 1126 cm⁻¹; ¹H NMR (90 MHz, CDCl₃) δ=4.66 (4H, br s, CH₂-1,3), 7.25 (1H, s, H-9), 7.45 (3H, mc, H-5, 6, 7), 8.09 (1H, d, J=9.6 Hz, H-8), 8.34 (1H, d, J=9.6 Hz, H-4).
7. **4a**: Blue plates, mp 199 °C; IR (KBr) 1709, 1695, 1439, 1391, 1205, 1127 cm⁻¹; ¹H NMR (90 MHz, CDCl₃) δ=3.60(4H, mc, H-1, 2, 3, 4), 3.96 (3H, s, COOMe), 7.35 (8H, mc, H-6, 7, 8, Ph), 8.31 (1H, d, J=9.6 Hz, H-5), 9.94 (1H, d, J=9.6 Hz, H-9).
8. **5a**: Violet micro prisms, mp 117-118 °C; MS (25 eV, 100 °C) m/z 386 (M⁺, 42.1%), 297 (100%); ¹H NMR (90 MHz, CDCl₃) δ=1.30 (6H, t, J=7.2 Hz, COOCH₂CH₃), 3.97 (3H, s, COOMe), 4.24 (4H, q, J=7.2 Hz, COOCH₂CH₃), 4.75 (2H, mc, H-1), 5.65 (2H, mc, H-4), 7.65 (3H, mc, H-6, 7, 8), 8.20 (1H, d, J=9.6 Hz, H-5), 9.63 (1H, dm, J=9.6 Hz, H-9).

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