# FORMATION AND TRAPPING OF 1,2-DIMETHYLENEAZULENE

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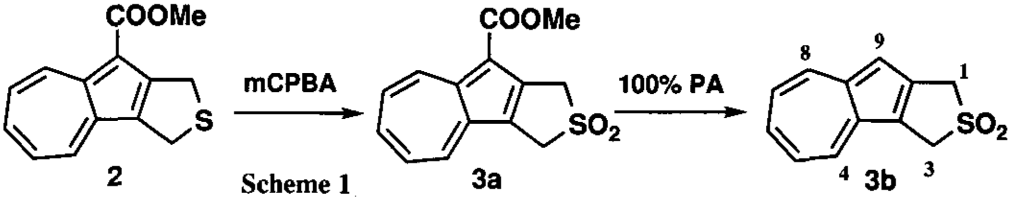
*Abstract* - 1,2-Dimethyleneazulenes, an *o*-xylylene type reactive intermediate, have been generated by the heating of 1,3-dihydroazuleno[1,2-*c*]thiophene dioxides. The reactive intermediates were efficiently trapped by dienophiles, such as *N*-phenylmaleimide and diethyl azodicarboxylate, to form [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 $CH_2Cl_2$ 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

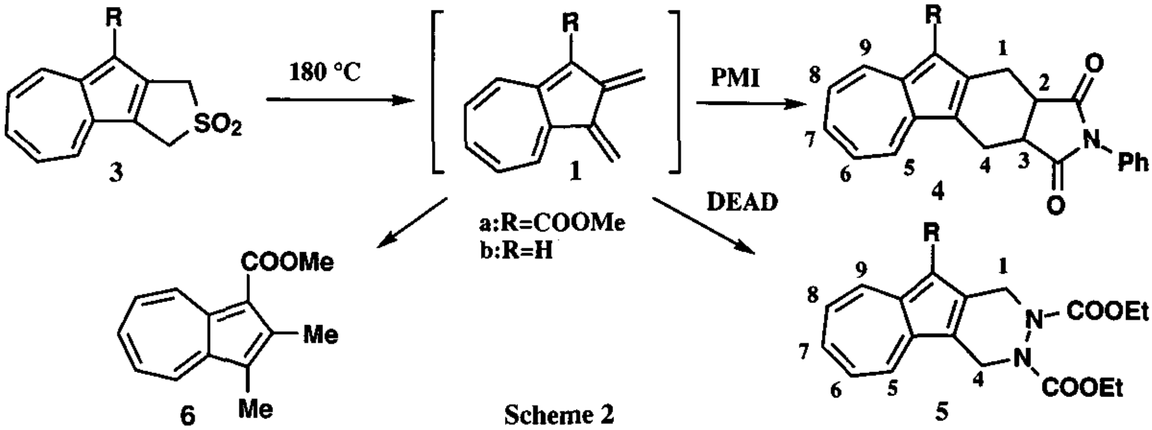
**3a** and **3b** showed $M^+$-$SO_2$ peak as a base peak or a high intense peak instead of molecular ion ($M^+$) suggesting easy formation of 1,2-dimethyleneazulene (**1**).



Scheme 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).



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. Luhowy 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 ($M^+$-$SO_2$, 72.9%), 154 (212-COOMe, 100%); IR (KBr) 1689, 1312, 1121, 534 $cm^{-1}$; $^1H$ NMR (90 MHz, $CDCl_3$) δ=3.89 (3H, s, $COO\underline{Me}$), 4.76 (2H, br s, $CH_2$-3), 4.54 (2H, br s, $CH_2$-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 ($M^+$-$SO_2$, 100%); IR(KBr) 1309, 1126 $cm^{-1}$; $^1H$ NMR (90 MHz, $CDCl_3$) δ=4.66 (4H, br s, $CH_2$-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, $CDCl_3$) δ=3.60(4H, mc. H-1, 2, 3, 4), 3.96 (3H, s, $COO\underline{Me}$), 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, $CDCl_3$) δ =1.30 (6H, t, J=7.2 Hz, $COOCH_2C\underline{H}_3$), 3.97 (3H, s, COOMe), 4.24 (4H, q, J=7.2 Hz, $COOC\underline{H}_2CH_3$), 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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