FORMATION AND TRAPPING OF 1,2-DIMETHYLENEAZULENE

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Abstract - 1,2-Dimethyleneazulenes, an o-xyylene 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-xyylene, 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-xyylene 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 $M^+\text{-SO}_2$ 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 (127.7 mg) 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) 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


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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