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Aromaticity of a Newly Synthesized Azulenone, Cyclohepta[b]thiophen-2-one

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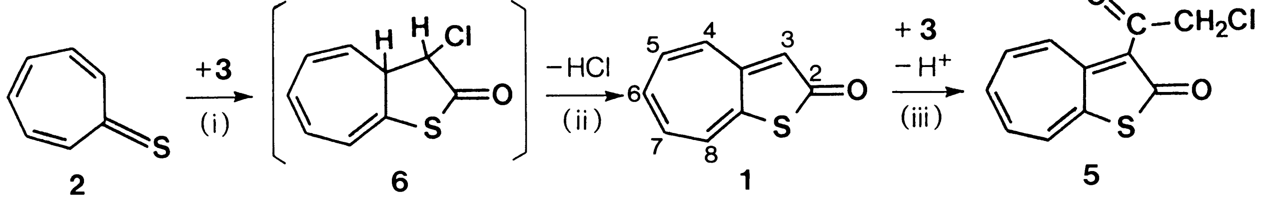
Tropothione reacts with chloroketene to give 1-thia-2-azulenone (**1**) in addition to a 1:2 adduct. An MO calculation suggests that the latter is formed via a novel one-site electrophilic addition of chloroketene to **1**.

Unlike 1-oxa- and 1-aza-2-azulenone,$^{1)}$ 1-thia-2-azulenone (cyclohepta[b]thiophen-2-one) (**1**) is unknown. This compound **1** is expected to have a larger aromatic 10π contribution than its oxygen and nitrogen analogues because of the inclusion of mobile electrons in the sulfur atom. We report herein the first synthesis of **1** (Scheme 1).

The reaction of tropothione$^{2)}$ (**2**) and chloroketene (**3**) [generated in situ from chloroacetyl chloride (**4**) and Et_3N] in benzene at room temperature afforded only a 1:2 adduct **5**,$^{3)}$ deep orange leaflets, mp 226 °C, in 68% yield, but not **1**. The formation of the adduct **5** is interpreted by three steps i, ii, and iii, via the initially expected product **1** followed by electrophilic addition of **3** to the C-3 position of **1**. Finally, the preparation of **1**,$^{4)}$ red needles, mp 88 °C, was accomplished in 72% yield under the controlled HCl elimination (below -60 °C) from the initially formed cycloadduct **6** in the step ii; **4** was slowly added dropwise into a solution of **2** in CH_2Cl_2 containing Et_3N (nucleophile for E2). In both **1** and **5**, the IR spectra indicate the very strong absorptions of the $\nu_{C=O}$ at around 1650 cm^{-1},$^{3,4)}$ demonstrating the pronounced charge separation in these systems.



Scheme 1. Synthesis of **1** and formation route to **5**.

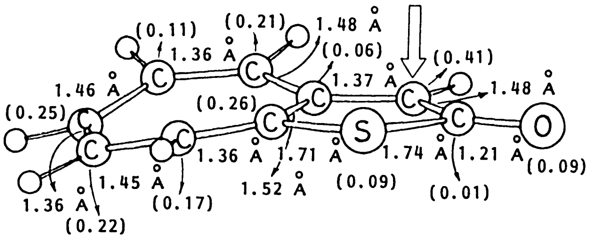


Fig. 1. MNDO optimized geometry of **1**. Numbers in parentheses denote HOMO π electron densities.$^{6)}$

We considered the reaction mechanisms in steps i and iii. In the step i,$^{5)}$ a ketene adds to **2** concertedly in the [$_{\pi}8_s$ + $_{\pi}2_s$] process. Along the Jahn-Teller type distortion of the coupled small-frequency (202 and 518 cm^{-1}, STO-3G) vibrations,$^{6)}$ **3** may provide an appropriate vacant MO for the charge acceptance from HOMO of **2**. The regioselectivity of the unexpected one-site electrophilic addition of the second ketene in the step iii is examined by the frontier electron density of HOMO of **1**. The densities of the HOMO demonstrate clearly that the C-3 is the target for the electrophile (bold arrow in Fig. 1). Ketene reacts usually with olefinic double bonds in the [2 + 2] addition.$^{7,8)}$ The present result of the ready occurrence of the one-site addition to an sp^2 carbon is unprecedented to the best of our knowledge and shows that **1** is enough aromatic to reject the cycloaddition.

References

1) T. Nozoe and K. Kikuchi, "Comprehensive Organic Chemistry," ed by M. Kotake, Asakura, Tokyo (1974), Vol. 13, pp. 535-576.

2) T. Machiguchi, T. Hasegawa, S. Itoh, and H. Mizuno, J. Am. Chem. Soc., 111, 1920 (1989) and references therein.

3) **5**: IR ν_{max} (KBr) 1643 cm^{-1}; UV-vis λ_{max} (Dioxane) 235 (log ε 4.10), 265 (4.14), 298 (4.17), 440 nm (4.06); ^{1}H NMR (400 MHz, CDCl$_3$) δ 4.89 (2H, s, COC$\underline{H}_2$Cl), 7.48-7.57 (2H, complex m, H-6,7), 7.70 (ddd, *J* 11.8, 6.4, and 3.8 Hz, H-5), 7.96 (dd, *J* 6.5 and 3.8 Hz, H-8), 9.44 (d, *J* 11.8 Hz, H-4); MS (75 eV) *m/z* 240/238 (M$^+$, 11/32%), 189 (100).

4) **1**: IR ν_{max} (KBr) 1658 cm^{-1}; UV-vis λ_{max} (EtOH) 248 (log ε 3.67), 294 (3.99), 384sh (4.12), 405 (3.79), 430 nm (3.83); ^{1}H NMR (400 MHz, CDCl$_3$) δ 6.27 (d, *J* 0.9 Hz, H-3), 6.86 (dddd, *J* 9.1, 8.3, 1.0, and 0.9, H-6), 6.92 (ddd, *J* 9.1, 8.9, and 1.7 Hz, H-7), 6.94 (ddd, *J* 10.9, 8.3, and 1.7 Hz, H-5), 7.29 (ddd, *J* 8.9, 1.0, and 0.9 Hz, H-8), 7.36 (dd, *J* 10.9 and 0.9 Hz, H-4); MS (75 eV) *m/z* 162 (M$^+$, 79%), 134 (100).

5) T. Machiguchi and S. Yamabe, Tetrahedron Lett., in press.

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7) S. Patai, "The Chemistry of Ketenes, Allenes and Related Compounds," Wiley, Chichester (1980), Part 1; H. Ulrich, "Ketenes," in "Cycloaddition Reaction of Heterocummulenes," Academic, New York, N. Y. (1967), Chap. 2, pp. 38-109.

8) A recent theoretical study has pointed out that ketene may not play a role at all as an antarafacial component for concerted [2 + 2] cycloadditions. F. Bernardi, A. Bottoni, M. Olivucci, M. A. Robb, H. B. Schlegel, and G. Tonachini, J. Am. Chem. Soc., 110, 5993 (1988).

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