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Synthesis of Tris[5-(3,5-di-*t*-butyl-4-hydroxyphenyl)-2-thienyl]cyclopropenylium Ion and Its Transformation into the Fully π-Conjugated Dianion

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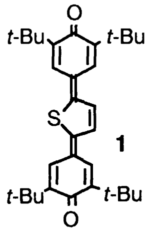
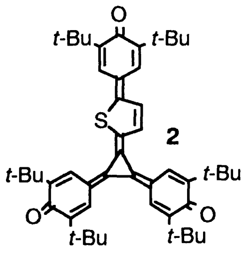
Reaction of trichlorocyclopropenylium ion with 2,5-di-*t*-butyl-4-(2-thienyl)phenol affords the titled cation, which can be transformed into the fully π-conjugated dianion.

Search for the new multistage redox system is attracting current interest from the viewpoint of both the fundamental and applied chemistry. Recently, the composite use of quinone and thiophene as electron-accepting and -donating components was shown to be effective in construction of such redox systems with high amphotericity as exemplified by the compounds **1**1) and **2**.2) On the other hand, we have previously shown that trichlorocyclopropenylium ion ($C_3Cl_3^+$) reacts with thiophene to give tris(2-thienyl)cyclopropenylium ion (**3**$^+$) though in a low yield.3) Here we report the synthesis of the titled cyclopropenylium ion **4**$^+$ by direct reaction of $C_3Cl_3^+$ with a substituted thiophene **6**1) and its transformation into the fully π-conjugated dianion **5**$^{2-}$ in the course of an attempt to generate the tris(thienoquinoid) system **5**.



1



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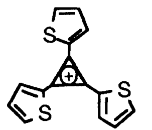
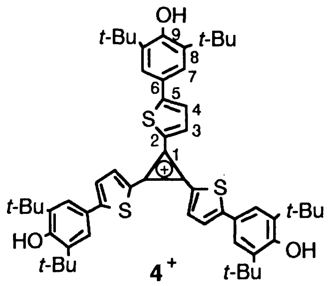
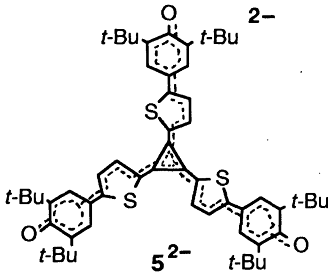


3$^+$

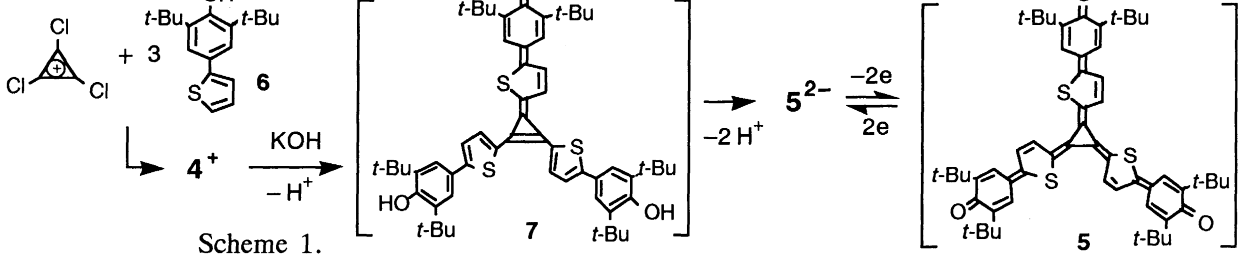


4$^+$



5^{2-}

In a typical procedure (Scheme 1), a stirred and cooled (–30 °C) solution of $C_3Cl_3^+AlCl_4^-$ prepared from tetrachlorocyclopropene and $AlCl_3$ in CH_3CN was allowed to react with a solution of three equivalents of thienylphenol **6** in CH_3CN, and the mixture was stirred at 50 °C for 0.5 h. After quenching with dil. aq. HCl, the product was extracted with CH_2Cl_2. Reprecipitation from CH_2Cl_2/ether and recrystallization from CH_3CN afforded **4**$^+$Cl$^-$ 4) in 37% yield as a red powder, which gradually darkened under air.



Scheme 1.

Deprotonation from the cation **4**$^+$ was shown to occur at pH 5.21 by spectrophotometric titration using citric acid-Na_2HPO_4 buffer in 50% aq. CH_3CN, but **4**$^+$ could not be fully regenerated upon re-acidification indicating the extreme instability of the methylenecyclopropene **7**. Instead, a green-colored dianion **5**$^{2-}$ was generated by direct treatment of **4**$^+$ with an excessive amount of KOH powder in CH_2Cl_2 (or CD_2Cl_2) in a vacuum-sealed tube under sonication, and was satisfactorily characterized by NMR spectroscopy.[5] The equivalency of all the H-7 protons in the ^1H NMR spectrum indicates that the rotation around the C5-C6 bonds in **5**$^{2-}$ is rapid at the NMR time scale presumably due to the low π-bond order. This dianion is unstable even in the degassed solution under vacuum, and was found to undergo gradual decomposition with the half life of about 170 min at room temperature with the concentration of 2×10^{-4} M.

In order to examine the redox properties of the dianion **5**$^{2-}$, cyclic voltammetry[6] was conducted for the CH_2Cl_2 solution of **5**$^{2-}$ freshly generated in a vacuum-sealed cell cooled at −20 °C. Upon scanning the range of −0.8 to +1.2 V vs. SCE, a quasi-reversible wave with E_{pa} +0.00 V and E_{pc} -0.21 V vs. SCE was observed. From the comparison with the data for the compound **2** and those for the triquinocyclopropane,[7] we presume that this wave with $E_{1/2}$ -0.10 V corresponds to a nearly one-step, two-electron transfer from the dianion **5**$^{2-}$ to yield **5**. The Coulombic repulsion in **5**$^{2-}$ is apparently minimized due to the extensive delocalization of π-electrons. On the other hand, a stronger and irreversible oxidation peak was observed at +1.10 V.

Attempts to chemically convert dianion **5**$^{2-}$ into the quinoid system **5** by the use of $K_3Fe(CN)_6$ or PbO_2 resulted in color change of the solution from dark green to dark blue, but the direct spectral observation of **5** could not be made even by the reaction in a degassed solution, suggesting the extreme instability of **5**.

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References

1) K. Takahashi, T. Suzuki, K. Akiyama, Y. Ikegami, and Y. Fukazawa, *J. Am. Chem. Soc.*, **113**, 4576 (1991).
2) K. Takahashi and M. Ogiyama, *Tetrahedron Lett.*, **32**, 3507 (1991).
3) K. Komatsu, I. Tomioka, and K. Okamoto, *Tetrahedron Lett.*, **1978**, 803.
4) **4**$^+$Cl$^-$: mp 190.0-191.5 °C (dec); ^1H NMR (270 MHz, CD_2Cl_2) δ 8.72 (d, J=3.9 Hz, 3H, H-3), 7.78 (d, J=3.9 Hz, 3H, H-4), 7.67 (s, 6H, H-7), 4.50 (br s, 3H, OH), 1.53 (s, 54H, CH_3); ^{13}C NMR (67.8 MHz, CD_2Cl_2) δ 164.7 (s, C-1), 157.6 (s, C-9), 144.8 (d, C-3), 138.1 (s, C-2 or 5), 131.3 (s, C-5 or 2), 126.6 (d, C-4), 124.6 (d, C-7), 124.0 (s, C-6), 118.3 (s, C-8), 34.9 (s, $C(CH_3)_3$), 30.6 (q, CH_3); IR (KBr) ν 1388 (br s, C_3^+) cm^{-1}; UV-vis (CH_2Cl_2) λ_{max} 271 nm (log ε 4.52), 294 (4.36 sh), 400 (4.50 sh), 479 (4.92 sh), 505 (4.95). Anal. Found: C, 71.87; H, 7.60; Cl, 3.81; O, 5.77; S, 10.17. Calcd for $C_{57}H_{71}ClO_4S_3$ (monohydrate, **4**$^+$Cl$^-\cdot H_2O$): C, 71.92; H, 7.52; Cl, 3.72; O, 6.72; S, 10.11%.
5) **5**$^{2-}$: ^1H NMR (270 MHz, CD_2Cl_2) δ 7.22 (s, 6H, H-7), 6.90 (d, J=3.6 Hz, 3H, H-3), 6.70 (d, J=3.6 Hz, 3H, H-4), 1.37 (s, 54H, CH_3); ^{13}C NMR (67.8 MHz, CD_2Cl_2, −50 °C) δ 153.3, 146.4, 139.1, 136.4, 135.4, 130.0, 124.9, 122.4, 33.9, 29.5 (one of the sp^2-carbon signals is missing due to the low signal-to-noise ratio); UV-vis (CH_2Cl_2) λ_{max} 300 nm (log ε 4.41), 335 (4.41), 370 (4.33 sh), 430 (4.27), 455 (4.24), 572 (4.20 sh), 640 (4.55), 693 (4.68).
6) Conducted in a vacuum-sealed three-electrode cell, composed of Pt-wire working and counter electrodes and a Ag-wire reference electrode, with Bu_4NClO_4 as supporting electrolyte. The potential value was corrected with reference to ferrocene (+0.374 V vs. SCE) added from a side arm immediately after the measurement.
7) K. Komatsu and R. West, *J. Chem. Soc., Chem. Commun.*, **1976**, 570.

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