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Synthesis of 2,3,4,5-Tetra(2-thienyl)cyclopentadienone Exhibiting Considerable Substituent Effects and Synthetic Utility

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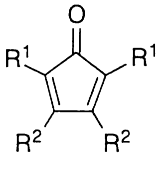
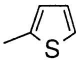
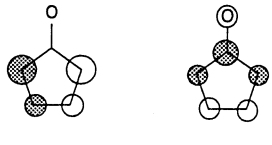
2,3,4,5-Tetra(2-thienyl)cyclopentadienone and the related compounds, here first synthesized, show large bathochromic shift of visible absorptions and appreciably higher amphoteric redox properties than tetraphenylcyclopentadienone; 2-thienyl groups at 2,5-positions exert stronger substituent effects than those at 3,4-positions.

Tetra(2-thienyl)cyclopentadienone (**1a**) would show considerable substituent effects by the thienyl groups compared to tetraphenyl compound (**1d**) and in addition have synthetic utility, for example through cycloaddition reactions, for the synthesis of novel 2-thienyl substituted conjugated molecules. Interest in 2-thienyl group as a substituent mainly lies in (1) its stabilization effects on not only carbocations but also carbanions and radicals[1,2] and (2) ready metalation and functionalization at 5-position allowing further extension of π-systems.[3] The larger MO coefficients (Hückel MO calculation) at 2,5-positions than 3,4-positions of cyclopentadienone graphically shown below suggest stronger electronic effect of 2-thienyl groups at 2,5-positions than those at 3,4-positions. Recently Tamao and coworkers reported the synthesis of thiophene-cyclopentadienone cooligomers;[4] however, (**1a**) has remained unknown. As a part of our studies on novel conjugated molecules incorporating five-membered rings,[2,3] we have synthesized **1a** and related compounds, 2,5-di(2-thienyl)-3,4-diphenyl- and 2,5-diphenyl-3,4-di(2-thienyl)-cyclopentadienone, (**1b**) and (**1c**).

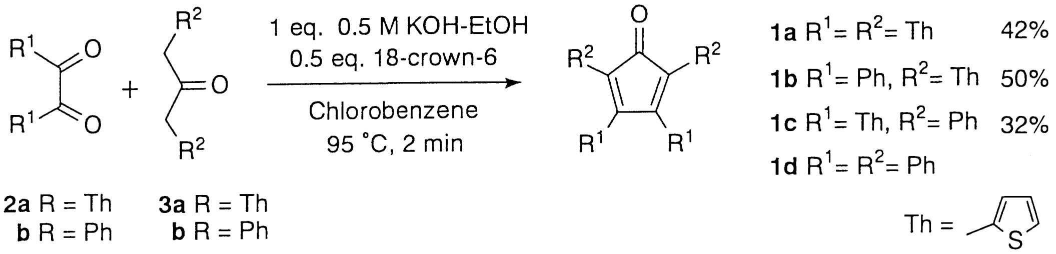


1a $R^1 = R^2 =$ Th
1b $R^1 =$ Th, $R^2 =$ Ph
1c $R^1 =$ Ph, $R^2 =$ Th
1d $R^1 = R^2 =$ Ph

Th =




Tetraphenylcyclopentadienone (**1d**) is readily prepared by alkali-catalyzed condensation of benzil and dibenzyl ketone.[5] The procedure fails, however, to give **1a** from the corresponding diketone **2a**[6] and ketone **3a**.[7] Examinations for the failure revealed lability of **1a** under alkaline conditions probably through deprotonation at 5-positions of the thienyl groups. A modified procedure minimizing contact of **1a** with alkali (see the experimental procedure) was found to give **1a** in moderate yield of about 40% (Scheme 1). Prolonged reaction time rapidly decreased the yield. The procedure also afforded **1b** and **1c** in similar yields.



Scheme 1.

Cyclopentadienones **1a**–**1c**[8] form fairly stable green, blue, and brown crystals, respectively. While 2,5-thienyl compounds **1a** and **1b** show large bathochromic shifts of about 100 nm in the visible absorptions compared to **1d**, 3,4-dithienyl compound **1c** does only slight shift in agreement with the MO consideration (Fig. 1 and Table 1).

Electrochemical redox potentials also clearly reflect the effects of 2-thienyl groups at 2,5-positions. Cyclic voltammetry of **1a**–**1d** show two reversible one-electron reduction and one pseudo-reversible oxidation waves as represented by the voltammogram of **1a**

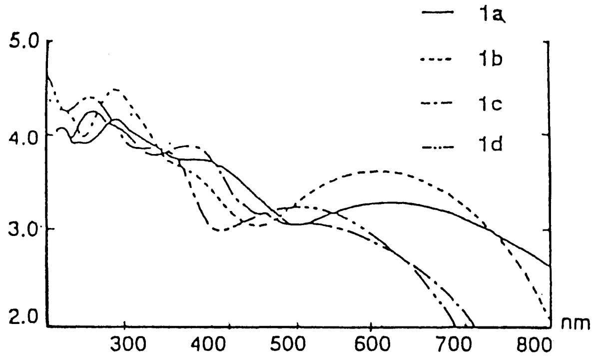


Fig. 1. UV/Vis spectra of **1a-d** in cyclohexane (log ε).

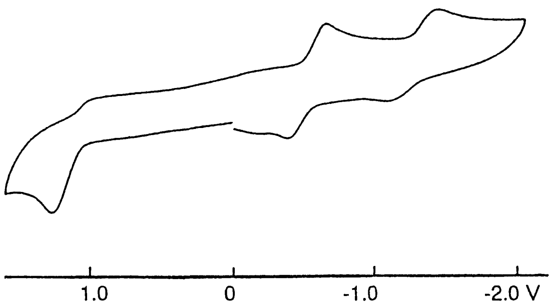


Fig. 2. Cyclic voltammogram of **1a** in DMF at -50 °C.

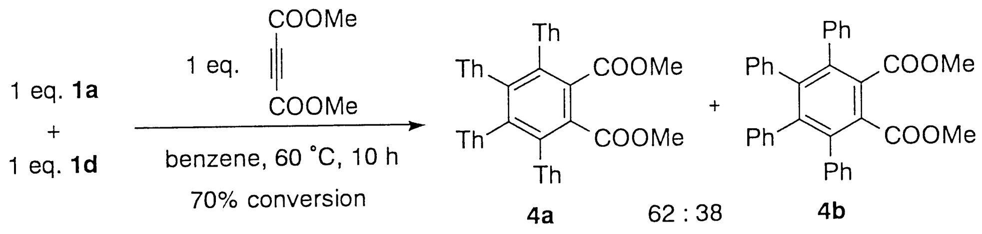
Table 1. Cyclic voltammetric data (E/V) and the longest absorption maxima for **1a - d**

Compounds	Redox potentials[a)]			Longest absorption[d)]
	E^{ox} [b,c)]	E_1^{red}	E_2^{red}	λ max (nm) (log ε)
1a	+1.23	-0.58	-1.33	611 (3.28)
1b	+1.23	-0.68	-1.39	596 (3.61)
1c	+1.54	-0.70	-1.42	508 (3.1)sh
1d	+1.73	-0.83	-1.50	505 (3.17)

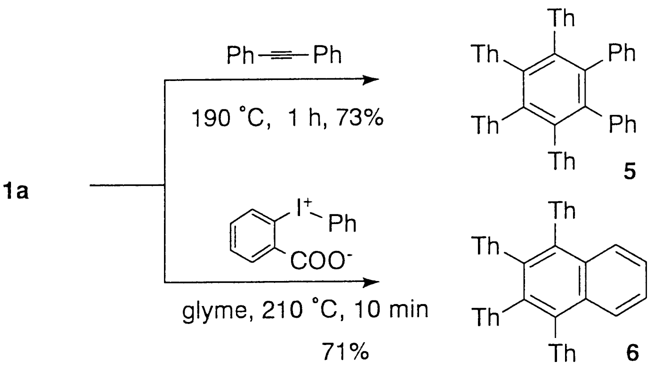
a) Measured *vs.* Ag/AgCl in DMF using Bu_4NClO_4 (0.1 M) as supporting electrolyte at -50 °C; sweep rate = 50 mV•sec^{-1}. b) Pseudo reversible. c) Peak potentials. d) In cyclohexane.

(Fig. 1). Compounds **1a** and **1b** exhibit appreciably low redox potentials with greater change of oxidation potentials from that of **1d**, whereas the change in **1c** is moderate. The numerical sum of E^{ox} and E_1^{red} of **1a** (1.81 V) is the smallest and hence indicates the highest amphoteric redox properties among the reported cyclopentadienone derivatives.9)

Competitive reaction of **1a** and **1b** (1 equiv. each) with dimethyl acetylenedicarboxylate (1 equiv.) at 60 °C in benzene yielded benzene derivatives **4a**10) and **4b**, through Diels-Alder reaction followed by decarbonylation, in 62:38 ratio (Scheme 2; 70% conversion) to indicate a slightly more reactive nature of **1a** over **1d** toward electron deficient dienophiles. This may be due to increase of HOMO energy by the electron-donating 2-thienyl groups. Utility of **1a** for the synthesis of multi-thienylated conjugated molecules are further exemplified by the reactions with diphenylacetylene and benzyne giving **5**10) (73%) and **6**10) (71%), respectively (Scheme 3). Applications of **1a** for the synthesis of novel molecules with physicochemical interest are in progress.



Scheme 2.



Scheme 3.

Experimental procedure for **1a**: To a preheated solution of **2a** (1.0 g, 4.5 mmol), **3a** (0.5 g, 2.25 mmol) and 18-crown-6 (0.26 g, 0.5 mmol) in dichlorobenzene (10 ml) at 95 °C was added a 0.5 M KOH-EtOH solution (5 ml) all at once. The mixture was stirred at 95 °C for 2 min, and poured into an ice-water. Extraction with benzene-hexane (1:1), usual work-up, and chromatogaphy on silica-gel eluted with 20% benzene-hexane gave 348 mg (42%) of **1a** from green fractions.

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7) **2a** was prepared from tosylmethylisocyanide (TosMIC) and 2-chloromethylthiophene through the van Leusen's method (O.Possel and A.M.van Leusen, Tetrahedron Lett., **1977**, 4229).

8) All the new compounds gave satisfactory elemental analyses and spectral data. **1a**: green plates; mp 203 °C; ^{1}H NMR (270 MHz, $CDCl_3$) δ = 7.05 (6H, m), 7.30 (2H, dd, J = 5.2, 1.0 Hz), 7.47 (2H, dd, J = 5.2, 1.0 Hz), 7.48 (2H, dd, J = 4.0, 1.0 Hz); ^{13}C NMR (68.5 MHz, $CDCl_3$) δ = 120.92, 126.99, 127.32, 128.16, 128.93, 129.15, 129.71, 132.26, 133.53, 145.09, 197.31; IR (KBr, C=O) ν = 1714 cm^{-1}. **1b**: blue plates; mp 209 °C; ^{1}H NMR δ = 6.91 (2H, dd, J = 5.3, 4.0 Hz), 7.08 (4H, m), 7.19 (2H, dd, J = 5.3, 1.0 Hz), 7.28 (6H, m), 7.35 (2H, dd, J = 4.0, 1.0 Hz); ^{13}C NMR δ = 119.32, 126.97, 127.06, 128.14, 128.34, 128.52, 128.72, 132.85, 133.39, 152.69, 199.21; IR ν = 1715 cm^{-1}. **1c**: red brown plates; mp 171 °C; ^{1}H NMR δ = 6.74 (2H, dd, J = 4.0, 1.0 Hz), 6.95 (2H, dd, J = 5.0, 4.0 Hz), 7.30 (10H, m), 7.36 (2H, dd, J = 5.0, 1.0 Hz); ^{13}C NMR δ = 126.71, 127.10, 128.18, 128.34, 128.83, 130.25, 130.64, 130.69, 133.91, 146.94, 198.63; IR ν = 1695 cm^{-1}.

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10) **4a**: oil; ^{1}H NMR (270 MHz, $CDCl_3$) δ = 3.59 (6H, s), 6.54 (2H, dd, J = 3.6, 1.0 Hz), 6.69 (2H, dd, J = 5.0, 3.6 Hz), 6.88 (4H, m), 7.10 (2H, dd, J = 5.0, 1.0 Hz), 7.24 (2H, dd, J = 4.0, 1.0 Hz). **5**: colorless crystals; mp 200 °C; ^{1}H NMR δ = 6.62 (2H, dd, J = 3.6, 1.3 Hz), 6.68 (2H, dd, J = 5.0, 3.6 Hz), 7.00 (4H, m), 7.06 (2H, dd, J = 5.0, 1.3 Hz), 7.32 (2H, dd, J = 5.0, 1.5 Hz), 7.46 (2H, m), 7.84 (2H, m). **6**: colorless crystals; mp 300 °C; ^{1}H NMR δ = 6.45 (2H, dd, J = 3.7, 1.0 Hz), 6.58 (2H, dd, J = 5.2, 3.6 Hz), 6.60 (2H, dd, J = 3.7, 1.4 Hz), 6.67 (2H, dd, J = 4.9, 3.6 Hz), 6.91 (10H, m), 6.98 (2H, dd, J = 4.9, 1.0 Hz), 7.06 (2H, dd, J = 5.2, 1.4 Hz).

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