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An Efficient Synthesis of Quinone Derivatives of Thieno[3,2-b]thiophene and Thieno[3,2-b]thieno[2',3'-d]thiophene and Their Spectral Properties

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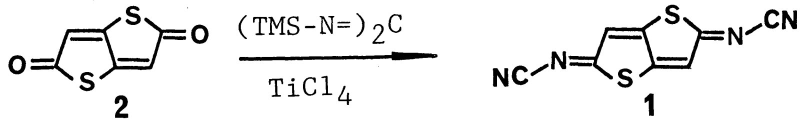
The quinones of the condensed thiophenes were prepared in good yields by use of an elimination reaction of di-tert-butoxy derivatives. The redox and UV-spectral properties of these compounds are demonstrated.

Considerable interest has been focused on the synthesis of new electron acceptors for the development of organic metals.1) Acceptors, other than simple derivatives of TCNQ, that are of current interest include fused-ring TCNQ derivatives and TCNQ analogues of hetero-aromatics.2) These developments owe greatly to the $TiCl_4$-mediated Knoevenagel reaction that has been explored by Hünig.3) Recently, Hünig et al. have reported also a preparation of dicyanodiimine acceptor **1** and its derivatives by applying such an improved Knoevenagel reaction for thieno[3,2-b]thiophenes **2** and found that those form highly conducting charge-transfer complexes.4) The quinone precursor 2, however, is not easily obtained: the literature procedure provides **2** only in an extremely poor yield as a by-product.5) On this basis we are prompted to report an alternative and more general synthesis of quinone **2** that has recently been explored in this laboratory.

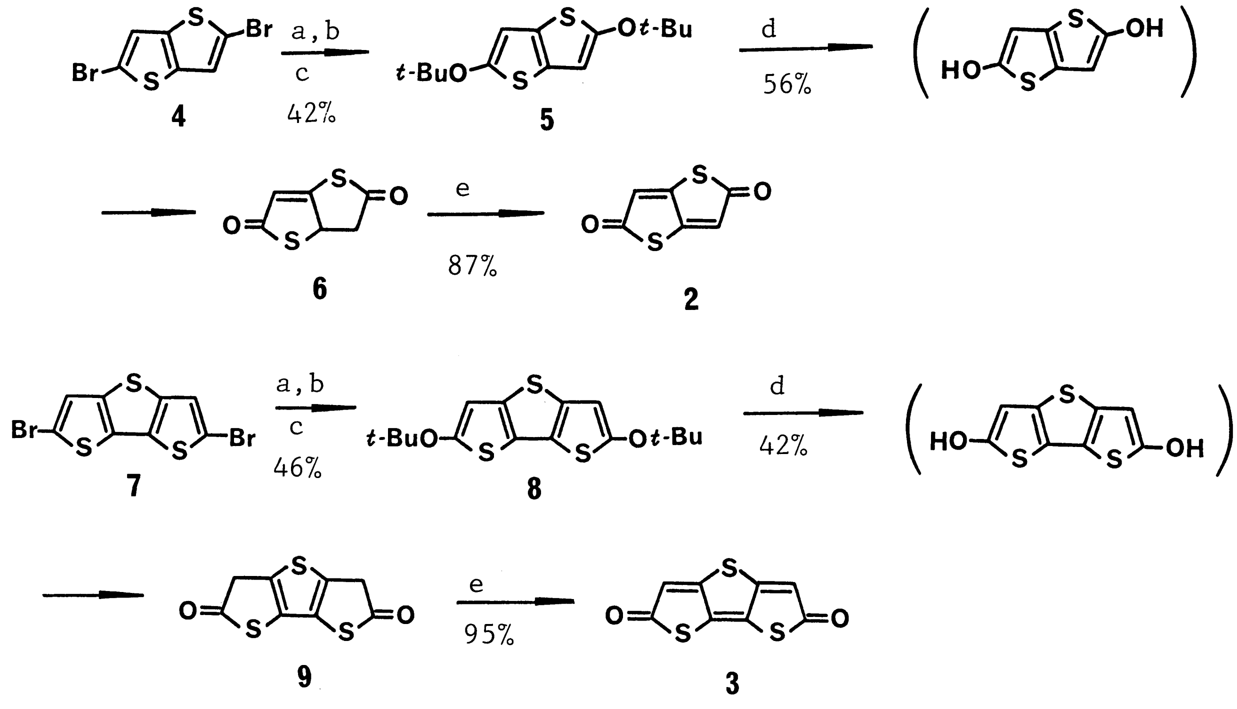


The synthetic sequence of **2** is outlined in Scheme 1. For the preparation of **5** it is essential to utilize the Grignard reagent in place of the lithium reagent. Thus, dibromo compound **4** was dilithiated by 2 equiv. of n-BuLi and then converted to the Grignard reagent by treating in ether with $MgBr_2$ which was prepared from 1,2-dibromoethane and Mg. The resulting solution was allowed to react with t-butyl perbenzoate in ether at 0 °C to give **5** in 42% yield.

A solution of **5** in benzene was refluxed in the presence of p-toluenesulfonic acid for 2 h. The product isolated in 56% was not 2,5-dihydroxythieno[3,2-b]thiophene but its ketone form **6**, being confirmed by its ^{1}H-NMR spectra ($CDCl_3$): δ 6.41 (1H, d, J=2.7 Hz), 4.94 (1H, ddd, J=2.7 Hz, 7.5 Hz, 12.0 Hz), 3.53 (1H, dd, J=7.5 Hz, 15.2 Hz), 2.84 (1H, dd, J=12.0 Hz, 15.2 Hz). It has been observed that all the 2-hydroxylthiophenes exist as thiolen-2-ones.6) Also for thieno[3.2-b]thiophenes, no evidences for the presence of the hydroxyl form were obtained in the oxidation products of the corresponding boronic acids.7)

The dehydrogenation of **6** was accomplished by refluxing with DDQ in dioxane for 5 h to afford **2** in 87% yield as a yellow crystal (Table 1).

Quinone derivative **3** of thieno[3,2-b]thieno[2',3'-d]thiophene was also prepared according to a similar procedure as that employed for **2**. The elimination of isobutylene from the di-t-butoxythienothienothiophene **8** produced ketone **9** as revealed by the ^{1}H-NMR spectra ($CDCl_3$); δ 3.92 (s). This compound was dehydrogenated by DDQ to give quinone **3** in 95% yield as a red crystal (Table 1).



Scheme 1. (a) n-BuLi, Et_2O, -30 °C, 30 min; (b) $MgBr_2$ (from $BrCH_2CH_2Br$ and Mg, Et_2O, reflux, 1 h), reflux, 1 h; (c) t-BuOOCOPh, 0 °C→r.t., 18-24 h; (d) TosOH, benzene, reflux, 2 h; (e) DDQ, dioxane, reflux, 5 h.

Table 1. The properties of quinones **2** and **3**

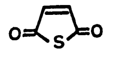
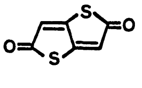
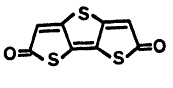
Compd	Color	Mp $\theta_m/^{\circ}C$	IR[a)] ν/cm^{-1}	^1H-NMR[b)] δ/ppm	CV[c)]/V vs. S.C.E. E^1	 E^2	 ΔE
2	yellow	168-169	1700, 1730	6.4(s)	-0.63	-1.43	0.80
3	red	203(dec.)	1700	6.3(s)	-0.46	-1.01	0.55

a)Nujol. b)$CDCl_3$. c)DMF, $(n\text{-}Bu)_4NClO_4$, 500 mV/s.

The cyclic voltammograms of **2** and **3** exhibited two reversible one-electron reduction potentials (Table 1). The electron affinity of **2** is comparable to that of benzoquinone (E^1=-0.62 V, E^2=-1.28 V vs. S.C.E.) and was not sufficient to form charge-transfer complexes with tetrathiafulvalene (TTF). For extended acceptor system **3**, the second reduction (i.e., radical anion to dianion) occurs at a significantly lower potential than that for **2**. This indicates that stretching of the molecules stabilizes the dianion state due to reduction of on-site Coulombic repulsion.

The electronic spectra of **2** and **3** consist of an intense π-π^* absorption band and a weak band extending to UV region, which is assignable to n-π^* transition. Table 2 summarizes the absorption data for **2** and **3** together with those of a lower homologue, i. e., thiomaleic anhydride.[8)]

Table 2. Electronic spectra[a)] of a series of the quinones

Compd		λ_{max} /nm (ϵ)
	b)	318 (620), 230 (9300)
	**2**	396 (70), 304 (13800)
	**3**	456 (40), 376 (26800) 360 (23900)

a) In CH_2Cl_2. b) Ref. 8.

The π-π^* absorption maxima are shifted 70 nm to longer wavelength as the number of the thiophene ring increases. This increase in λ_{max}, per one ring added, is considerably large. Thus, the quinones of linearly condensed thiophenes[9)] provide a new π-system that would be useful not only as a precursor of organic metals but also as a building block for chromotropic materials.

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