LONG-CHAIN SUBSTITUTED TETRACYANOQUINODIMETHANES: A CONVENIENT SYNTHETIC APPROACH

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ABSTRACT

2-Alkylcyclohexane-1,4-diones, key precursors of TCNQ derivatives, have been synthesized by modified Birch reduction of 2,5-dimethoxybenzoic acid by Li and Et_2NH in an ultrasonic bath and subsequent alkylation.

Derivatives of tetracyanoquinodimethane (TCNQ) exhibit strong electron-accepting properties and are widely employed as components for charge transfer complexes and ion radical salts with metal-like conductivity. Surface-active derivatives of TCNQ have been used for fabrication of Langmuir-Blodget (LB) films with unusual photophysical behavior.¹ The presence of a long alkyl chain in such compounds should increase the solubility of their complexes with electron donors in nonpolar solvents, and allows studies of electron transfer phenomena in solutions. However, to the best of our knowledge, a systematic study of such complexes and LB films has never been attempted, owing to the tedious and poorly reproducible synthetic procedures published to date.

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Indeed, the best yields of derivatives **5** have been obtained using 2-alkyl-cyclohexane-1,4-diones (**4**) as precursors. There are three synthetic routes toward 2-alkylcyclohexane-1,4-diones (**4**) known: 1) Hydrogenation of 2-alkylhydroquinones by hydrogen in the presence of Raney nickel as a catalyst at high temperatures and at high pressures, giving rise to 2-alkyl-1,-4-cyclohexanedioles, which can be further oxidized to corresponding diones **4**.² The known multistep low-yield synthetic route to 2-alkylhydroquinones presents a severe limitation for the practical use of this method; 2) Birch reduction of poorly available 2-alkyl-1,4-dimethoxybenzenes with sodium or lithium at low temperatures in liquid ammonia/THF or Et₂O mixture;²⁻⁵ and 3) Reduction of commercially available 2,5-dimethoxybenzoic acid (**1**) by lithium in liquid ammonia with subsequent alkylation.^{6,7}



The last method is the most attractive; however, according to our experience, it gives low yields in cases when long-chain alkylhalides (practically insoluble in the reaction mixture) are used for alkylation of salt 2.

We describe here a novel way for reduction of acid 1 in solvent system HMPA-Et₂NH-THF close to room temperature and alkylation, especially with long-chain alkyl halides. The alkylation with hexadecylhalides already has been described in our previous paper.⁸ The ¹H NMR and IR spectra, as well as melting points, in comparison with those described in the literature, and satisfactory elemental analysis for unknown compounds (4 and 5, $R = C_{13}H_{27}$, $C_{17}H_{35}$), conform as to their structure and are of sufficient purity (Tables 1, 2).

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Alkyl halide RX	Yield	M.p. °C	¹ H NMR, CDCl ₃ δ, ppm	
C ₁₂ H ₂₅ I	45	70 ^{2,6}	0.86, t, 3H; 1.25, m, 22H; 2.45, m, 1H; 2.69, m, 6H.	
$C_{13}H_{27}I$	46	66–67	0.86, t, 3H; 1.23, m, 24H; 2.43, m, 1H; 2.67, m, 6H.	
C ₁₅ H ₃₁ Br	43	78^{2}	0.87, t, 3H; 1.27, m, 28H; 2.41, m, 1H; 2.7, m, 6H.	
C ₁₆ H ₃₃ I	41	$80 - 81^{18}$	0.87, t, 3H; 1.26, m, 30H; 2.45, m, 1H; 2.68, m, 6H.	
C ₁₇ H ₃₅ Br	43	81-82	0.85, t, 3H; 1.23, m, 32H; 2.41, m, 1H; 2.69, m, 6H.	
C ₁₈ H ₃₇ I	36	87 ^{2–4}	0.84, t, 3H; 1.24, m, 34H; 2.44, m, 1H; 2.67, m, 6H.	

Table 1. Characterization of Synthesized 2-Alkylcyclohexane-1,4-diones 4

Table 2. Characterization of Alkyltetracyanoquinodimethanes 5

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R	Yield	M.p. °C	¹ H NMR, CDCl ₃ δ, ppm		
C ₁₂ H ₂₅	64	119-120 ^{2,6}	0.89, t, 3H; 1.29, s, 18H; 1.52, m, 2H; 3.0, t, 2H; 7.32, s, 1H; 7.54, d, 1H; 7.61, d, 1H.		
$C_{13}H_{27}$	58	119–120	0.87, t, 3H; 1.27, s, 20H; 1.52, m, 2H; 2.99, t, 2H; 7.32, s, 1H; 7.49, d, 1H; 7.59, d, 1H.		
C15H31	47	120 ²	0.88, t, 3H; 1.28, s, 24H; 1.53, m, 2H; 2.97, t, 2H; 7.31 s, 1H; 7.54 d, 1H; 7.59 d, 1H.		
C ₁₆ H ₃₃	38	120–121 ⁸	0.89, t, 3H; 1.26, s, 26H; 1.51, m, 2H; 2.97, t, 2H; 7.32, s, 1H; 7.53, d, 1H; 7.62, d, 1H.		
C ₁₇ H ₃₅	41	122–123	0.87, t, 3H; 1.28, s, 28H; 1.55, m, 2H; 3.01, t, 2H; 7.30, s, 1H; 7.48, d, 1H; 7.56, d, 1H.		
C ₁₈ H ₃₇	44	124 ^{2–4}	0.87, t, 3H; 1.25, s, 30H; 1.53, m, 2H; 2.98, t, 2H; 7.34, s, 1H; 7.51, d, 1H; 7.57, d, 1H.		

EXPERIMENTAL

A General Procedure for Preparation of 2-Alkylcyclohexane-1,4-diones (4)

To a solution of 1.82 g (0.01 mol) 2,5-dimethoxybenzoic acid in 20 mL THF and 12 mL HMPA (fresh-distilled solvents) under argon, 4 mL diethylamine was added. After the formation of diethylammonium salt was complete, 0.15 g (0.021 mol) lithium was added. The reduction was carried out in an ultrasonic bath at 10° -15°C and took about 20–30 min. A solution

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of alkyl halide (0.01 mol) in 15 mL THF was added dropwise until the red color disappeared. After 1 h, pale yellow reaction mixture was diluted with 150 mL of water, acidified with hydrochloric acid to $pH\sim1$, THF was distilled off, and the mixture was refluxed for 2.5 h, maintaining $pH\sim1$ (if necessary, adjusted by hydrochloric acid). After cooling, the precipitated solid was collected and recrystallized from ethanol. Resulting alkylcyclohexanediones **4** can be used for synthesis of TCNQ without additional purification.

A General Procedure for Preparation of 2-Alkyl Substituted TCNQ (5)

Cyclohexanedione 4 (0.002 mol), malonodinitrile (0.004 mol) and 0.05 g β -alanine in a mixture of 5 mL of THF and 1 mL H₂O were refluxed for 7 h. After cooling to room temperature, 40 mL of water was added and the product was extracted with 50 mL CHCl₃. Extract was dried over MgSO₄ and evaporated in vacuo. The residue was dissolved in 15 mL of MeCN and 0.6 g bromosuccinimide in 5 mL of MeCN was added. Pyridine (0.24 mL) was added to the reaction mixture after 30 min. After an additional 10 min, H₂O (50 mL) was added. The product was collected by filtration and dried at room temperature. Purification of TCNQ derivatives can be carried out by column chromatography using any appropriate solvent systems.

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Accepted May 31, 2000