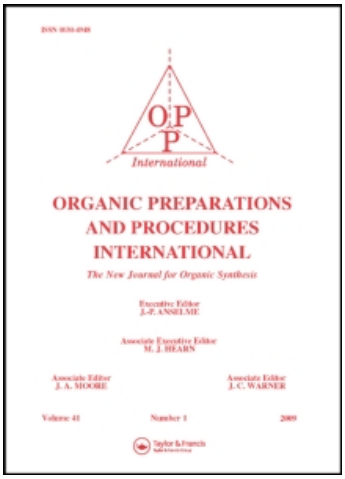


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# FACILE SYNTHESES OF *P*-(DICYANOMETHYLENE)BENZOQUINONES

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and evaporated to dryness. The crude products were dissolved in ethyl acetate and precipitated as their hydrochlorides by addition of conc. hydrochloric acid.

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## FACILE SYNTHESES OF *p*-(DICYANOMETHYLENE)BENZOQUINONES

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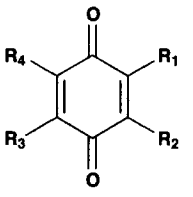
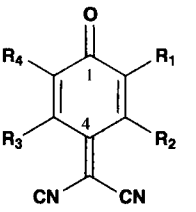
The redox properties of quinones possessing electron-withdrawing substituents have elicited interest in these compounds as electron transport materials in organic photo-conductors.[1] A number of *bis*(dicyanomethylene) compounds (e.g., 7,7,8,8-tetracyano-quinodimethane) have been synthesized from 1,4-cyclohexanediones by the Knoevenagel reaction with malononitrile, followed by oxidation of the resulting product.[2] In contrast, the condensation of 1,4-benzoquinones with malononitrile proceeds *via* a Michael addition at the α-position; subsequent oxidation gives 3-dicyanomethyl-1,4-benzoquinone.[3] When 1,4-benzoquinones sterically hindered at 2,6-position such as **1b**, are condensed with malononitrile and piperidine as catalyst, the product **2b** reacts with the anion of malononitrile at the 7-position; subsequent elimination of HCN affords predominantly 4-tricyanovinylphenol.[4] The

present paper describes the facile syntheses of several mono(dicyanomethylene)benzoquinones substituted at 2,6-position (**2a~2g**) in the presence of $TiCl_4$.[5]

The activation of Lewis acid at an unhindered carbonyl oxygen prevents the Michael addition at the 3-position and leads to the Knoevenagel reaction at the 4-position. However, the use of




**1a-g**




**2a-g**

**1a)** $R_1 = R_4 = CH_3$, $R_2 = R_3 = H$ **1b)** $R_1 = R_4 = t\text{-}C_4H_9$, $R_2 = R_3 = H$
**1c)** $R_1 = s\text{-}C_4H_9$, $R_2 = R_3 = H$, $R_4 = CH_3$ **1d)** $R_1 = R_4 = C_6H_5$, $R_2 = R_3 = H$
**1e)** $R_1 = R_4 = Cl$, $R_2 = R_3 = H$ **1f)** $R_1 = CH_3$, $R_2 = H$, $R_3$, $R_4$ = -(CH=CH)$_2$-
**1g)** $R_1$, $R_2$ = -CH=C(t-$C_4H_9$)-CH=CH-, $R_3$, $R_4$ = -(CH=CH)$_2$-

excess reagents causes the formation of 3-dicyanomethyl-1,4-benzoquinone and 4-tricyanovinylphenol. Thus, equivalent amounts of malononitrile and Lewis acid were used at ice-bath temperature. Since the compounds (**2a-g**) are labile in polar protic solvents and its lability increases with an increase in the half redox potential of the compound, the products were purified by crystallization from aprotic solvents or by column chromatography over neutral aluminum oxide.

**TABLE 1.** Yields and Analytical Data for Compounds **2**

| Compd | Yield % | mp. (°C) | $^1$H NMR δ, ppm | $E_{1/2}$[a] $E^1$ | $E^2$ | Elemental Analysis (Found) C | H | N |
|---|---|---|---|---|---|---|---|---|
| **2a** | 56 | 134-136 | 7.6 | -0.52 | | 71.73 (71.94) | 4.38 (4.36) | 15.21 (15.09) |
| **2b** | 57 | 123-125[b] | 7.4 | -0.62 | | 76.09 (76.33) | 7.51 (7.47) | 10.44 (10.21) |
| **2c** | 52 | 74-76 | 7.5[c] | -0.58 | | 74.31 (74.08) | 6.24 (6.43) | 12.38 (12.17) |
| **2d** | 41[d] | 223-224 | 7.7 | -0.51 | | 81.80 (81.84) | 3.92 (3.94) | 9.09 (9.17) |
| **2e** | 38 | 134(dec.) | 7.8 | -0.32 | | 48.04 (48.29) | 0.90 (1.28) | 12.45 (12.51) |
| **2f** | 61 | 134-135 | | -0.60 | -1.20 | 76.35 (76.21) | 3.66 (3.38) | 12.72 (12.97) |
| **2g** | 33 | 171-175 | | -0.58 | -0.99 | 80.75 (81.02) | 5.16 (5.27) | 8.96 (8.72) |

a) Half redox potential *vs* Ag/AgCl, 0.2M $Et_4NCl$ in $CH_3CN$. b) lit.[3], 124-126°. c) doublet, $J$ = 2.1 Hz. d) Purified by column chromatography (Woelm neutral, Hexane-EtOAc).

## EXPERIMENTAL SECTION

Quinones, **1c** and **1d**, were prepared by condensation of sodio nitromalonoaldehyde with 5-methyl-3-heptanone and 1,3-diphenyl-2-propanone, followed by oxidation with lead tetraacetate as descried below.[6] Solvents were dried over a molecular sieve 3A. Other chemicals of reagent grade were used without further purification. $^1$H NMR spectra were recorded on a JNM-PMX60 spectrometer.

**Preparation of 2-*sec*-butyl-6-methyl-1,4-benzoquinone (1c).**- Sodio nitromalonaldehyde (3.9 g, 21 mmol) which had been prepared from mucobromic acid with sodium nitrite was added to a solution of 5-methyl-3-heptanone (3.0 g, 23 mmol) in 60% aq. EtOH containing NaOH (0.5 g). The reaction mixture was stirred at room temperature overnight and heated to reflux for 2 hrs; and then concentrated *in vacuo*. The residue was stirred in 10% HCl , and the resulting brown solid was collected and recrystallized from AcOH-EtOH (1:1) containing one drop of conc. HCl to give 2-*sec*-butyl-6-methyl-4-nitrophenol in 83% yield, mp. 104-106°.

A solution of the above 4-nitrophenol derivative (3.1 g, 15 mmol) and $Pb(OAc)_4$ (3.5 g, 8 mmol) in anhydrous AcOH (50 mL) was stirred at room temperature for 24 hrs, and then extracted with $Et_2O$ (2 x 100 mL). The ethereal extract was washed with $H_2O$, 5% NaOH and $H_2O$, and dried over $Na_2SO_4$ and then concentrated *in vacuo*. The residue was extracted into hexane-EtOAc (4:1) (2 x 50 mL); the solution was filtered through a short silica column (10 cm, Wakogel C-300). Evaporation of the solvents afforded a pale yellow oil (**1c**) in 68% yield. IR (KBr): 1660 (C=O) cm$^{-1}$. $^1$H NMR ($CDCl_3$): δ 0.9 (t, 3H, *J* = 6 Hz, -$CH_2C\underline{H}_3$), 1.1((d, 3H, *J* = 7 Hz, -$CH(CH_3)$-), 1.4 (q, 2H, *J* = 6 Hz, -$CH_2$-), 2.1 (s, 3H, 6-$CH_3$), 2.9 (q, 1H, *J* = 7 Hz, CH), 6.4-6.6 (m, 2H, CH) ppm. Diphenylquinone (**1d**) was prepared similarly in 65% yield, mp. 133-135°, lit.[7] 134-135°.

**Typical Procedure. 4-Dicyanomethylene-2,6-dimethyl-2,5-cyclohexadiene-1-one (2a).**- To a well-stirred solution of 2,6-dimethyl-1,4-benzoquinone (**1a**, 2.0 g, 15 mmol) and malononitrile (1.0 g, 15 mmol) in dichloromethane (150 mL) at ice-bath temperature was added $TiCl_4$ (1.7 mL, 15 mmol) over a period of 10 min under a nitrogen atmosphere and the reaction mixture stirred for 30 min. Then pyridine (7.2 mL, 90 mmol) was added over a period of 15 min. After the addition, the reaction mixture was stirred at room temperature for 5 hrs, and then concentrated *in vacuo*. The residue was extracted into hot hexane (2 x 100 mL), and the hexane solution was washed thoroughly with 10% HCl and water. The solution was dried over $Na_2SO_4$, and concentrated *in vacuo*.. The residue was recrystallized from hexane to yield 1.6g (57%) of **2a** as pale yellow powder. IR (KBr): 3060 (C-H), 2225 (CN), 1640 (C=O) cm$^{-1}$. $^1$H NMR ($CDCl_3$): δ 2.2 (s, 6H, $CH_3$), 7.6 (s, 2H, CH) ppm. MS: 184 ($M^+$, 85%).

**4-Dicyanomethylene-2,6-dichloro-2,5-cyclohexadiene-1-one (2e).**- After the reaction, the reaction mixture was concentrated *in vacuo*, the residue was washed thoroughly in 10% HCl and then water by stirring. The product was extracted into hot EtOAc (2 x 50 mL) and the extract was dried over $Na_2SO_4$, and concentrated *in vacuo*. The orange solid was recrystallized from EtOAc-hexane to give **2e** in 38% yield. IR (KBr): 2250 (CN), 1680 (C=O) cm$^{-1}$. MS: 224 ($M^+$, 2.3%).

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# SYNTHESIS AND CYCLIZATION OF 1-(*N*-NITROAMIDINO)THIOUREAS TO 2,4-DIAMINOTHIAZOLES

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The Hantzsch synthesis of 2-aminothiazoles involves the reaction of a thiourea with a α-haloketone.[1] Despite being a century old, this classic reaction continues to be the mainstay of 2-aminothiazole synthesis and modifications and improvements are still appearing in the literature.[2-4] We have reported[5,6] that the use of 1-amidino-3-(substituted)thioureas in place of simple thioureas in the Hantzsch synthesis leads to 5-acyl-2,4-diaminothiazoles, the amidinothiourea derivative providing the C-N-C-S atoms of the thiazole ring and the remaining C atom arising from the 1α-haloketone. In continuation of this work, we decided to explore the reaction of (*N*-nitroamidino)thioureas (**1**) with α-haloketones. Based on our earlier work,[5,6] the formation of a tentatively assigned thiazoline intermediate (**3**) could be expected, from the initially generated S-alkyl intermediate (**2**), and the former could eliminate either ammonia or nitramine (Scheme). The expulsion of the former would lead to 2-amino-4-(*N*-nitroamino)thiazole derivatives which on reduction, could give hitherto unreported 2-amino-4-hydrazinothiazoles.