SHORT COMMUNICATION

Electrosynthesis of organic compounds. XI. Synthesis of some arylmalononitrile derivatives

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Received 18 July 1986; revised 21 August 1986

1. Introduction

The electrochemical oxidation of organic compounds containing an active methylene group was first investigated by Mulliken [1] in 1893 and several reviews are now available [2–9]. Various authors [1–9] have suggested a radical coupling mechanism in a manner similar to that of the Kolbe reaction with the difference that no carbon dioxide is evolved. Recently the anodic oxidation of some selected compounds containing an active methylene group, e.g. flourenone derivatives [10], dimethyl malonate [11], nitromethane [12] and malononitrile [13] was carried out in our laboratory.

The chemical synthesis of arylmalononitrile compounds involves several steps and extreme conditions, which motivated us to search for a simple and convenient electrochemical method for synthesis of such compounds. This paper describes the electrochemical oxidation of malononitrile anions in the presence of aromatic compounds.

2. Experimental details

The starting materials were: absolute methanol (Prolabo), malononitrile (Merck), benzene (Prolabo), toluene (Aldrich), naphthalene (Aldrich), anizole (Fluka), chlorobenzene (Fluka) and nitrobenzene (Fluka). These are commercially available and were purified before use.

Authentic samples, namely phenylmalononitrile, *p*-tolylmalononitrile, α-naphthylmalononitrile, *p*-anizylmalononitrile, *p*-chlorophenylmalononitrile, *p*-nitrophenylmalononitrile and 1,1,2,2-tetracyanoethane were prepared according to the literature procedures [14–22].

The electrolysis cell was constructed of two compartments of 125 and 35 ml capacities, separated by a sintered glass No. 2 diaphragm. A platinum anode (2 × 2 cm), a platinum cathode (1 × 1 cm) and a saturated calomel reference electrode were used. An agar salt bridge was used between the surface of the anode and the saturated calomel electrode (SCE). The temperature of the electrolysis was kept constant using an ultrathermostat. The electrolysis was performed under controlled anodic potential conditions using a potentiostat π5848. A gas chromatograph (Perkin–Elmer Sigma 3 B with thermal ionization detector) was used for analysis. IR analysis was carried out using a Beckman spectrophotometer with KBr. Thin layer chromatography (TLC) was carried out on glass plates (5 × 10 cm) covered with silica gel using a mixture of benzene and ether (1 : 1) as solvent. Also, column chromatography separations were performed using silica gel as the stationary phase and petroleum ether (60–80° C), a benzene–ether mixture (1 : 1) and methanol as solvents.

A mixture of 3.3 g (0.02 mol) malononitrile in 50 ml absolute methanol containing 1.15 g atom sodium metal and 50 ml of the liquid aromatic compounds (benzene, toluene, anizole, chlorobenzene, nitrobenzene) and/or 10 g naphthalene was placed in the anode compartment. The cathode compartment was filled with 25 ml absolute methanol containing 0.57 g atom sodium metal. The solution was electrolysed for a period of 24–81 h under a controlled anode potential value of + 1.3 ± 0.03 V vs SCE at 20° C. The colourless solution in the anode compartment became brown, and oily drops were observed on the anode surface during the electrolysis. When the electrolysis was terminated the anodic mixture was transferred into a distillation flask and the excess methanol (or benzene) was distilled under

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Table 1. The anodic oxidation of malononitrile anions in the presence of aromatic compounds at +1.3 ± 0.03 V vs SCE at 20° C

Experiment	*Starting*	*Time (h)*	*Current efficiency (%)*[a]	*Conversion (%)*[b]	*Products (g, %)*
1	$NaCH(CN)_2$	24.0[c]	25.1	68	$[CH(CN)_2]_2$ (1.52, 72.4), $[-C(CN)_2-]_n$ (0.62, 27.6)
2	$NaCH(CN)_2 + C_6H_6$	48.5[c]	10.2	56	$C_6H_5CH(CN)_2$ (0.717, 18), $[CH(CN)_2]_2$ (1.25, 68) $[-C(CN)_2-]_n$ (0.258, 14)
3	$NaCH(CN)_2 + C_6H_5CH_3$	50.0[c]	10.6	62	p-$CH_3C_6H_4CH(CN)_2$ (1.76, 30), $[CH(CN)_2]_2$ (1.08, 53) $[-C(CN)_2-]_n$ (0.34, 17)
4	$NaCH(CN)_2 + C_{10}H_8$	78.0[c]	9.5	83	α-$C_{10}H_7CH(CN)_2$ (3.25, 49.1), $[CH(CN)_2]_2$ (1.05, 38.4), $[-C(CN)_2-]_n$ (0.305, 11.7)
5	$NaCH(CN)_2 + C_6H_5OCH_3$	81.0[d]	17.6	51	p-$CH_3OC_6H_4CH(CN)_2$ (2.1, 47.1), $[CH(CN)_2]_2$ (0.65, 38.0), $[-C(CN)_2-]_n$ (0.24, 14.2)
6	$NaCH(CN)_2 + C_6H_5Cl$	72.0[d]	22.5	54	p-$ClC_6H_4CH(CN)_2$ (2.04, 42.8), $[CH(CN)_2]_2$ (0.71, 39.8), $[-C(CN)_2-]_n$ (0.310, 17.4)
7	$NaCH(CN)_2 + C_6H_5NO_2$	70.0[d]	24.5	59	p-$NO_2C_6H_4CH(CN)_2$ (2.89, 52.1), $[CH(CN)_2]_2$ (0.65, 33.5), $[-C(CN)_2-]_n$ (0.28, 14.4)

[a] Current efficiency = 100 (total yield of products; mol per Faraday passed).

[b] Conversion = 100 (total yield of products, mol per amount of starting anions, mol).

[c] Current was 0.10–0.02 A (i_d = 12.5–2.5 mA cm^{-2}).

[d] Current was 0.032–0.008 A (i_d = 4–1 mA cm^{-2}).

normal pressure using a rotatory evaporator. The residue was acidified with a dilute solution of HCl and then extracted three times with 100 ml ether (a small amount of the polymerized product did not dissolve and was filtered). The ether extract was washed with water, dried over anhydrous magnesium sulphate, filtered and distilled under normal pressure (to remove the ether) and under reduced pressure (to remove the unreacted aromatic compounds, e.g. toluene, anizole, chlorobenzene, and nitrobenzene). The product mixture was analysed using column chromatography TLC, GLC and IR techniques. The data obtained were compared with those of the authentic samples and found to be identical in all respects.

3. Results and discussion

The kinetic studies showed that the oxidation of malononitrile anions gave only one wave and the half-wave oxidation potential value was +0.87 V vs SCE. The current–potential polarization curves are shown in Fig. 1.

The isolated products were malononitrilation products (phenylmalononitrile, *p*-tolylmalononitrile, α-naphthylmalononitrile, *p*-anizylmalononitrile, *p*-chlorophenylmalononitrile and *p*-nitrophenylmalononitrile) and a dimerization product (1,1,2,2-tetracyanoethane) in addition to a small amount of polymerized compounds. Also, the anodic oxidation of malononitrile anions in absolute methanol under the same conditions gave the dimer 1,1,2,2-tetracyanoethane as major product and polymerized products as minor product (Experiment 1). The results are shown in Table 1.

The following mechanism is postulated. Malononitrile anions are oxidized at the surface of the platinum anode to the corresponding

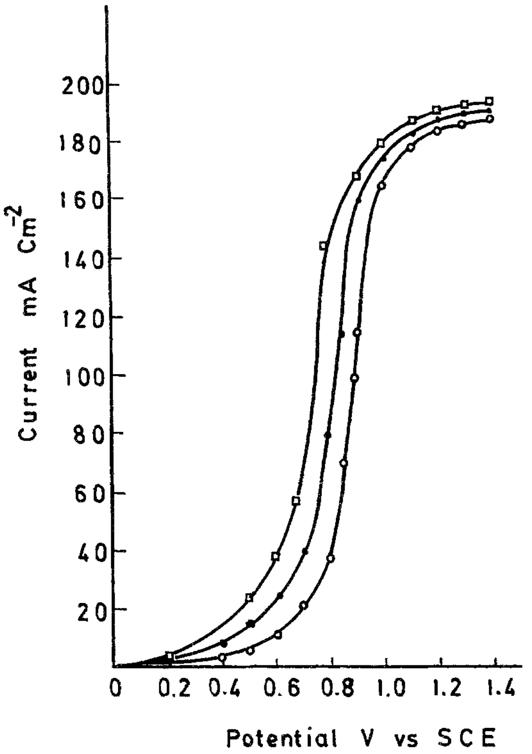

Fig. 1. Anodic oxidation of malononitrile anions in absolute methanol at 20° C. Concentration of malonitrile ($mol\,l^{-1}$): ○, 0.2; ●, 0.3; □, 0.4.

malononitrile radicals, $\dot{C}H(CN)_2$. These radicals are dimerized, polymerized and attack the aromatic compounds present in solution. This mechanism can be represented as follows:

$$\bar{C}H(CN)_2 \xrightarrow[\text{anode}]{-e} \dot{C}H(CN)_2$$
$$\xrightarrow{ArH} ArCH(CN)_2$$
$$\xrightarrow{\text{dimer}} CH(CN)_2CH(CN)_2$$
$$\xrightarrow{\text{polymer}} [-C(CN)_2^{-}-]_n$$

Ar = C_6H_5, p-$CH_3C_6H_4$, $C_{10}H_7$, p-$CH_3OC_6H_4$, p-ClC_6H_4, p-$O_2NC_6H_4$.

It is important to note that the anodic oxidation mechanisms of formation of arylmalononitrile compounds followed the classical free radical intermediate mechanism of formation of malononitrile radicals as in the literature [2–13]. This method can be used successfully for the synthesis of aryl derivatives of malononitrile.

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