SHORT COMMUNICATION

Electrosynthesis of organic compounds. IV. Synthesis of some arylnitromethane compounds

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1. Introduction

The electrochemical oxidation of nitroalkane anions polarographically has been carried out previously [1, 2]. Dimerized products of the anodic oxidation of 2-nitrobutane and 2-nitropropane were obtained [3, 4]. The electrolysis of trinitromethane in the presence of toluene gave 2-phenyl-1,1,1-trinitroethane [4, 5]. No dimerized product was obtained by electrolysing the nitroethane in the presence of styrene [6–8] as the nitroethane has a high oxidation potential value compared with the above electrolysed nitroalkanes.

As a result of interest in [9, 10] and the search for a convenient method to synthesize aryl nitromethane, we began to study the anodic oxidation of nitromethane anions in methanol in the presence of benzene, toluene, naphthalene, diphenyl ether and 1,4-dimethoxybenezene at a controlled anodic potential (+ 2.0 V vs SCE).

2. Experimental details

2.1. *Electrolysis cell*

This was constructed of two compartments separated by sintered glass No. 2 as the diaphragm. The electrodes used were a platinum anode (1.5 x 1.5 cm), a platinum cathode (1.0 x 1.0 cm) and a saturated calomel electrode as a reference electrode. The desired temperature was obtained using an Ultrathermostat (20° C). The electrosynethesis was performed under controlled anodic potential (+ 2.0 V vs SCE) using a potentiometer.

2.2. *General procedure*

A mixture of absolute methanol (30 ml) or 45 ml (in the case where a solid investigated material was used), sodium metal (0.1 g atom), nitromethane (15 ml) and the investigated compound (15 ml liquid or 0.02 M solid) was placed in the anode compartment. The cathode compartment was filled with 30 ml of absolute methanol containing 0.1 g atom sodium metal. The solution was electrolysed for 48 h at a controlled potential (+ 2.0 V vs SCE) at 20° C. During electrolysis, the current was 0.12 A. Accordingly, the current density was 26.6 mA cm^{-2} and the charge passed was 0.028 F mol^{-1}. At the end of the electrolysis, the anodic solution was transferred into a distillation flask and the excess methanol was distilled under atmospheric pressure. The residue was distilled under reduced pressure and the distillates were collected. The residue was extracted with ether and the ether solution was evaporated at atmospheric pressure.

Nitromethylbenzene and *p*-(nitromethyl)-toluene were isolated by fractional distillation under reduced pressure. These products were identified by comparison of their IR spectra, R_f values and elemental analysis with those of the authentic samples.

Anodic nitromethylation products from naphthalene [1-(nitromethyl)naphthalene], *p*-dimethoxybenzene[1,4-dimethoxy-2-(nitromethyl)benzene] and diphenyl ether [(1-nitromethyl)-4-phenoxy benzene] were isolated by column chromatography (silica gel, mixed $CHCl_3$–hexanes as mobiles phases) and identified using authentic samples.

Infrared spectra were obtained using a Pye Unicam SP 200G spectrophotometer with KBr disc and identification of the anodic products was confirmed through their reduction to the corresponding amines.

The formation of small amounts of aromatic aldehydes (< 5%) was also observed and these were isolated by fractional distillation under

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Table 1. Electrosynthesis products from the oxidation of nitromethane anions in the presence of aromatic compounds

Aromatic compound	*Products*			
	Nitromethane derivatives	*Yield m mol (g)*	*Current efficiency (%)**	*Byproduct (< 5%)*
C_6H_6	$C_6H_5CH_2NO_2$	5.03(0.69)	18	C_6H_5CHO
$C_6H_5CH_3$	p-$CH_3C_6H_4CH_2NO_2$	8.11(1.22)	29	p-$CH_3C_6H_4CHO$
$C_6H_5OC_6H_5$	p-$C_6H_5OC_6H_4CH_2NO_2$	10.87(2.49)	39	p-$C_6H_5OC_6H_4CHO$
p-$CH_3OC_6H_4OCH_3$	1,4-$(CH_3O)_2C_6H_3CH_2NO_2$	11.11(2.20)	40	1,4-$(CH_3O)_2C_6H_3CHO$
$C_{10}H_8$	1-$C_{10}H_7CH_2NO_2$	11.44(2.24)	43	1-$C_{10}H_7CHO$

* Current efficiency was calculated based on the actual amount of nitromethane anions involved in electrolysis.

reduced pressure or by column chromatography. The aromatic aldehydes were identified using authentic samples.

All the starting materials used were commercially available. The chemicals were subjected to further purification by known methods and their purity checked by boiling point or melting point determination and/or by chromatography.

2.3. *Preparation of authentic samples*

Nitromethylbenzene and 1-(nitromethyl)-naphthalene were prepared as described earlier [11, 12], p-(nitromethyl)toluene, 1-(nitromethyl)-4-phenoxy benzene and 1,4-dimethoxy-2-(nitromethyl)benzene were also prepared by a method described in the literature [13].

3. Results and discussion

The anodic oxidation of nitromethane anions in methanol in the presence of benzene, toluene, naphthalene, diphenyl ether and 1,4-dimethoxybenzene was carried out at a platinum anode. The isolated products were nitromethylbenzene, p-(nitromethyl)toluene, 1-(nitromethyl)-naphthalene, 1-(nitromethyl)-4-phenoxy benzene and 1,4-dimethoxy-2-(nitromethyl)benzene as shown in Table 1.

The results obtained showed that the yield of nitromethylation of the investigated aromatic compounds increased with increasing electron density of the aromatic compounds used (i.e. diphenyl ether, p-dimethoxybenzene and naphthalene).

The formation of nitromethane compounds can be interpreted in terms of the formation of a free radical intermediate $^{\cdot}CH_2NO_2$, which attacks the aromatic nucleus forming the corresponding aryl nitromethane products. The mechanism can be visualized as follows:

$$^{-}CH_2NO_2 \xrightarrow[\text{anode}]{-e} {}^{\cdot}CH_2NO_2 \xrightarrow{\text{Ar}} ArCH_2NO_2$$

where Ar is C_6H_6, $CH_3C_6H_5$, $C_{10}H_8$, $C_6H_5OC_6H_5$ and p-$(CH_3O)_2\,C_6H_4$.

It is important to mention that the mechanism of formation of aryl nitromethane products followed the classical free radical intermediate mechanism of formation of nitroalkane radicals as in the literature [3–8].

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