Electrosynthesis of Organic Compounds IV. Synthesis of Some Arylnitromethane Compounds.

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Oxidation of nitromethane has been carried out on platinum anode, at controlled potential of +2.0 V vs SCE, in presence of benzene, toluene, naphthalene, diphenyl ether or 1:4 -dimethoxy benzene to give phenyl nitromethane, p-toluyl -nitromethane, 1-naphthyl nitromethane, p-diphenyl ether nitromethane and 1,4-dimethoxy phenyl-2-nitromethane respectively.The nitromethylation products were isolated.Formation of nitromethyl radical as an intermediate is postulated.

The electrochemical oxidation of nitroalkane anions has been studied polarographically [1,2]. Anodic oxidation of 2-nitrobutane and 2-nitropropane is found to give dimerised products[3]. The electrolysis of trinitromethane in presence of toluene gave 2-phenyl-1,1,1,-trinitroethane[4]. Electrolyzing the nitroethane in the presence of styrene [5,6], did not give any dimerised product. This compound has high oxidation potential value compared with other nitroalkanes.

In continuation of our studies on the synthesis of aryl nitromethane, we started studying the anodic oxidation of nitromethane anions in methanol in presence of appropriate aromatic compound. The results are presented here.

EXPERIMENTAL

MATERIALS:

All starting materials - benzene, toluene, naphthalene, diphenyl ether, 1:4-dimethoxy benzene, nitromethane and methanol - were commercially available. These were purified by standard methods. Their purity was checked by melting point, boiling point or by chromatography.

ELECTROLYSIS CELL:

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

GENERAL PROCEDURE:

A mixture of absolute methanol (30 ml), sodium metal (0.1 gm atom), nitromethane (15 ml) and the aromatic compound (15 ml liquid or 0.02 M solid and 15ml absolute methanol) was placed in the anode compartment. The cathode compartment was filled with 30 ml absolute methanol containing 0.1 gm atom sodium metal. The solution was electrolyzed at 20°C for 48 hrs at potential controlled at + 2.0 V vs SCE. At the end of the electrolysis, the anodic solution was transferred into a distillation flask and the excess methanol was distilled. The residue was then distilled under reduced pressure and the distillates were collected. The residue was extracted with ether and the ether solution was evaporated at atmospheric pressure.

Phenylnitromethane and p-tolueylnitromethane 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-naphthylnitromethane), p-dimethoxybenzene (2-nitromethane)-dimethoxybenzene) and (p-nitromethylphenyl phenyl ether isomers were isolated by column chromatography (silicagel column mixed $CHCl_3$ -hexanes as mobile phases) and identified using authentic samples.

Infrared spectra were obtained using Pye Unicam SP 200 G spectrophotometer with KBr disc.

Also identification of the anodic products was confirmed through their reduction to the corresponding amines.

Formation of small amounts of aromatic aldehydes (α 5%) was also observed and isolated by fractional distillation under reduced pressure or by column chromatography. The aromatic aldehydes were identified using authentic samples, prepared by methods described in literature [8,9,10]

DISCUSSION

The anodic oxidation of nitromethane anions in

TABLE 1

ELECTROSYNTHESIS PRODUCTS NITROMETHANE ANIONS IN THE PRESENCE OF AROMATIC COMPOUNDS.

Aromatic compound	Products: Nitromethane derivatives	%	By product < 5 %
C_6H_6	$C_6H_5CH_2NO_2$	18	C_6H_5CHO
$C_6H_5CH_3$	$p\text{-}CH_3C_6H_4CH_2NO_2$	29	$p\text{-}CH_3C_6H_4CHO$
$C_6H_5OC_6H_5$	$p\text{-}C_6H_5OC_6H_4CH_2NO_2$	39	$p\text{-}C_6H_5OC_6H_4CHO$
$P\text{-}CH_3OC_6H_4OCH_3$	$1,4\text{-}(CH_3O)_2\text{-}C_6H_3CH_2NO_2$	40	$1,4\text{-}(CH_3O)_2\text{-}C_6H_3CHO$
$C_{10}H_8$	$1\text{-}C_{10}H_7CH_2NO_2$	43	$1\text{-}C_{10}H_7CHO$

methanol in presence of benzene, toluene, naphthalene, diphenyl ether and 1,4-dimethoxybenzene was carried out at platinum anode. The isolated products were pheynl nitromethane, p-tolyl-nitromethane, 1-naphthyl nitromethane, p-diphenylether nitromethane and 1,4-dimethoxyphenyl -2-nitromethane as shown in Table 1

The results showed that the yield of nitromethylation of the aromatic compounds increased with increasing the electron density of the aromatic compounds used (diphenyl ether, p-dimethoxybenzene and naphthalene). Following the classical free radical intermediate mechanism of formation of nitroalkane radical [5-6] the formation of nitromethane compounds can be interpreted as follows:

$$CH_2NO_2 \xrightarrow[\text{anode}]{-e^-} \dot{C}H_2NO_2 \xrightarrow{Ar} ArCH_2NO_2$$

where Ar = C_6H_6, $CH_3C_6H_5$, $C_{10}H_8$, $C_6H_5OC_6H_5$ and p- $(CH_3O)_2C_6H_4$.

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