Electrochemical Synthesis of 2-Phenylethyl Phenyl Acetate at Carbon Anode

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2-Phenylethyl phenylacetate (Benzene acetic acid-2-phenylethyl ester) has been prepared by electrolytic oxidation of 2-phenylethyl alcohol at carbon anode in the presence of iodonium ion, generated by the elctrooxidation of iodide ion. The effect of the molar ratio of 2-phenylethyl alcohol to potassium iodide and the effect of current densities on the yield of 2- pheylethyl phenyl acetate has been studied.

Electrogenerated iodonium ion is a good oxidizing agent (1-3) 2-phenylethyl phenyl acetate, a fungicide (4) and a preservative for sugar preparations(5), is used in pharmaceutical preparations(6). Recently 2-phenylethyl phenyl acetate has been prepared by catalytic dimerization of styrene oxide at 180°C (7). In the present communication we report a simple and efficient electrochemical process for the oxidation of 2-phenylethyl alcohol to the ester, 2-phenylethyl phenyl acetate, using carbon anode. The iodonium ion, generated by the electrolytic oxidation of iodide ion, acts as a catalytic electron carrier.

EXPERIMENTAL

MATERIALS

2-phenylehtyl alcohol (BDH). potassium iodide (BDH) and 2-methyl propan -2-ol (SD's) were used without further purification. Laboratory grade solvents were further distilled and dried prior to use.

CELL ASSEMBLY

Cell assembly was the same as used earlier(1,2). The polarization study was carried out with reference to SCE. It was observed that the current potential behaviour are essentially the same as that of iodide ion in the absence of 2-phenylethyl alcohol, (Fig. 1) confirming that for sucesstul oxidation, current - potential and current-time behaviour of such reactions must remain same(8).

ELECTROLYSIS AND WORK UP

The electrolysis has been carried out varying (i) the molar ratio of 2-phenylethyl alcohol to potassium iodide and (ii) the current density, while keeping all other experimetal conditions as follows: Anolyte is 250 ml.aqueous solution of 2.5 x 10^{-2}M 2-phenylethyl alcohol and potassium iodide; Catholyte is 50 ml. solution of 5% potassium iodide. 2-Methyl propan-2-ol was added as cosolvent in the anolyte to dissolve 2-phenylethyl alcohol. Table 1 shows the experimental details.

After passing the current for calculated time, the anolyte was diluted with equal amount of water, filtered and the filtrate was extracted with chloroform (250 ml x 4). The organic layer was washed with saturated aqueous sodium thiosulphate solution and dried over anhydrous sodium sulphate. The chloroform extract was concentrated under reduced pressure. The product having a faint sweet aromatic odour was identified as 2-phenylethyl-phenyl acetate from TLC and I.R. spectrum (the C=O absorption band is in the region of 1730-1715 cm^{-1} and C-O stretching mode of ester give rise to bands in the 1260-1100 cm region). The experiments were repeated to confirm reproducibility.

RESULTS AND DISCUSSIONS

The electrochemical synthesis of 2-phenylethyl phenyl acetate from 2-phenylethyl alcohol in the presence of iodonium ion proceeds smoothly at carbon anode and the yield varies between 29.8-61.1%. Table 1 shows the effect of molar ratio of 2-phenylethyl alcohol to potassium iodide and the effect of current densities on the yield of 2-phenylethyl phenyl acetate. Lower current density lowers the yield. The yield is also decreased with the increase in molar ratio of 2-phenhylethyl alcohol to potassium iodide. However, the maximum yield obtained was 61.1% when the current density was 1.0997 A dm^{-2} and the molar ratio used was 2:1. The fact is also corroborated from the polarization curve (Fig. 1) in which maximum depolarization is observable at current density 1.0997-Adm^{-2} When the ratio used was 1:1, the yield of product was poor as comparison to that of other ratios.

In this reaction iodonium ion generated by the electrolytic oxidation of iodide ion behaves as

the oxidising agent(9,10) as explained by the reaction mechanism equations(2-4).

The iodide ion formed from iodonium ion (3) is again oxidised at anode to the iodonium ion. The function of the iodonium ion is thus considered as a catalytic oxidising agent and at the same time acting as an electron carrier. During this process of anodic oxidation, the alcohol is directly converted to the ester, The intermediate aldehydes could heardly be isolated since it is used again in the reaction (3,4).

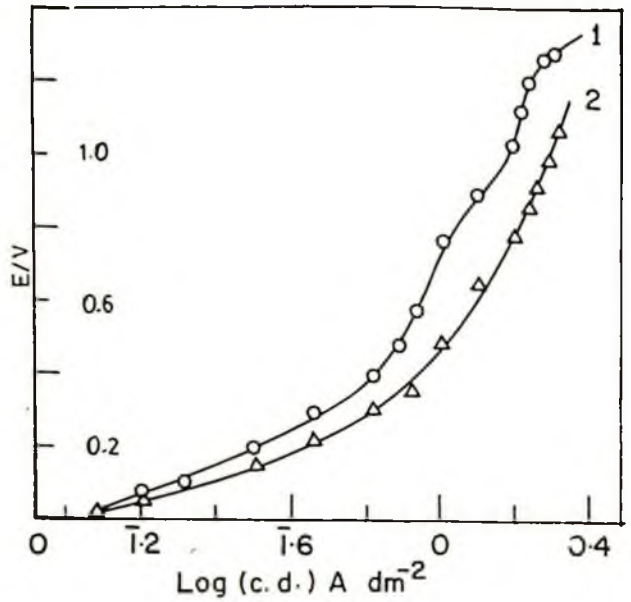


Fig. 1 Polarization curves for the synthesis of 2-Phenylethyl phenylacetate at carbon anode. (1) 250 ml aqueous solution of KI (25 mM) (2) aqueous solution of KI and 2-Phenylethyl alcohol (50 mM) in the molar ratio 1:2

TABLE 1

THE EXPERIMENTAL DETAILS OF ELETROCHEMICAL SYNTHESIS OF 2-PHENYLETHYL PHEYLACETATE AT CARBON ANODE AREA OF THE ELECTRODE = 0.27 Sq. dm. ROOM TEMP. 20-25°C.

S No.	Molar ratio (2-Phenyl-ethyl alcohol/ Potassium iodide)	Current (A)	Electri-city passed$ in F/mole of KI	Yield# (%)	current efficiency (%)
1.	1	0.2	2	29.8	28.6
2.	1	0.3	2	37.3	35.9
3.	2	0.2	4	46.2	44.7
4.	2	0.4	4	61.1	59.3
5.	3	0.2	6	39.6	38.1

$ A little excess of electricity was passed for completion of the reaction.

\# Yield is based on the amount of alcohol taken.

$$I^- \xrightarrow{-2e^-} I^+ \qquad (2)$$

$$R\text{-}CH_2OH + I^+ \xrightarrow{-H^+} [R\text{-}CH_2OI] \longrightarrow [R\text{-}CH{=}O + H^+ + I^-] \qquad (3)$$

$$[R\text{-}CH{=}O + I^+] \longrightarrow [R\text{-}\overset{+}{C}HOI] \xrightarrow[-H^+]{R\text{-}CH_2OH} \left[R\text{-}CH(OCH_2R)\text{-}O\text{-}I\right] \longrightarrow R\text{-}\overset{O}{\overset{\|}{C}}\text{-}O\text{-}CH_2R + H^+ + I^- \qquad (4)$$

Where R = $C_6H_5CH_2$-

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