Use of Ion Exchange Resins to Trap Electrogenerated Intermediates: Acetamidation of Hydrocarbons†

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Summary Trapping by a sulphonic acid ion exchange resin of nitrilium ions produced *via* anodic oxidation of hydrocarbons permits an easy recovery of modified resin by filtration; treatment of the resin with aqueous sodium hydroxide solution liberates amide products and re-regenerates the original resin.

In a process termed a 'wolf and lamb' reaction it has been shown[1] that two reagents possessing high reactivity toward each other are rendered inactive by attachment to separate polymer substrates. When suspended in a common solvent no direct reaction occurs. However elegant transformations can be achieved by reaction of a solute with one polymer bound reagent to give an intermediate, which can be transported through the solution to give products by reaction of this intermediate with the second polymer bound reagent. Replacement of one polymer bound reagent by an electrode might permit this concept to be extended to electrochemical processes.

Two schemes (reactions 1 and 2) can be envisaged.

$$\text{Reactant} \xrightarrow{\text{electrode}} \text{electrogenerated soluble intermediate} \xrightarrow[\text{reagent}]{\text{polymer bound}} \text{polymer-bound intermediate} \xrightarrow{\text{hydrolysis}} \text{product} + \text{regenerated polymer} \qquad (1)$$

$$\text{Reactant} \xrightarrow[\text{reagent}]{\text{polymer bound}} \text{soluble intermediate} \xrightarrow{\text{electrode}} \text{soluble product} \qquad (2)$$

The second of these schemes may be used to study the electrochemistry of otherwise inaccessible intermediates but is not discussed further here. The first scheme permits the trapping of unstable electrogenerated intermediates and is illustrated here by the trapping of nitrilium ions produced *via* anodic oxidation of hydrocarbons.

Adamantane was oxidized conventionally[2] in a divided cell in acetonitrile at a platinum electrode using $Bu^n_4NBF_4$ as electrolyte. In the anolyte compartment a cation exchange resin carrying sulphonic acid groups (Dowex 50W-X8; 100—200 mesh) was present as a suspension. Adamantane is oxidized to give the 1-adamantyl carbonium ion, trapped by solvent to give the nitrilium ion. The nitrilium ion is captured by the resin. When electrolysis is complete filtration affords the resin, from which *N*-(1-adamantyl)acetamide is isolated readily by addition of aqueous sodium hydroxide solution followed by ether extraction. The results of this and related oxidations are given in the Table.

Table

Starting material	Anode potential/V	Product	% Yield[a]	Literature yield in absence of added resin
Adamantane	2·45	*N*-(1-Adamantyl)acetamide	85	74[b]
Cyclohexene	2·00	*N*-(Cyclohex-3-enyl)acetamide	63	17[c]
Toluene	2·20	*N*-Benzylacetamide	17	—[d]
p-Xylene	1·80	*N*-(4-Methylbenzyl)acetamide	27	—[d]
Durene	1·40	*N*-(2,4,5-Trimethylbenzyl)acetamide	52	38[e]
Hexamethylbenzene	1·25	*N*-(2,3,4,5,6-Pentamethylbenzyl)acetamide	88	88[f]

[a] Isolated yield of crystalline amide based on initial weight of hydrocarbon added. [b] See ref. 2. [c] See T. Shono and A. Ikeda, *J. Amer. Chem. Soc.*, 1972, **94**, 7892. [d] No data available for isolated yields. See L. Eberson and B. Olofsson, *Acta Chem. Scand.*, 1969, **23**, 2355. [e] Very low yields (*ca.* 1%) are obtained in very dry acetonitrile comparable to that used for the experiments with resin. Higher yields are obtained under less rigorously dry conditions. See L. Eberson and K. Nyberg, *Tetrahedron Letters*, 1966, 2389. See footnote f. [f] See A. Bewick, G. J. Edwards, J. M. Mellor, and B. S. Pons, *J.C.S. Perkin II*, 1977, 1952.

Isolation of amides *via* this trapping technique is an improvement over existing methods because (i) product isolation is greatly simplified and the often difficult separation of organic products from electrolyte salts is obviated. A chromatographic purification is unnecessary. (ii) Intermediates and products are protected from secondary electrode processes and hence yields of isolated products are improved; note cyclohexane and durene. (iii) Fouling of the anode by polymeric materials, often a problem in anodic oxidations, is greatly reduced.

It is important to note that this simple resin could be used successfully at such high anodic potentials without any appreciable degradation.

(*Received*, 8*th May* 1978; *Com.* 485.)

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† Information protected by U.K. Patent application No. 5550 (1978).

[1] B. J. Cohen, M. A. Craus, and A. Patchornik, *J. Amer. Chem. Soc.*, 1977, **99**, 4165.
[2] G. J. Edwards, S. R. Jones, and J. M. Mellor, *J.C.S. Perkin II*, 1977, 505.