Electrochemical Carbon-skeleton Rearrangements catalysed by Hydrophobic Vitamin B_{12} immobilised in a Polymer-coated Electrode

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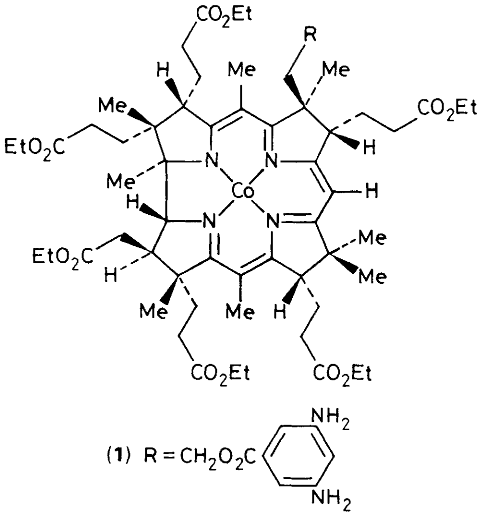
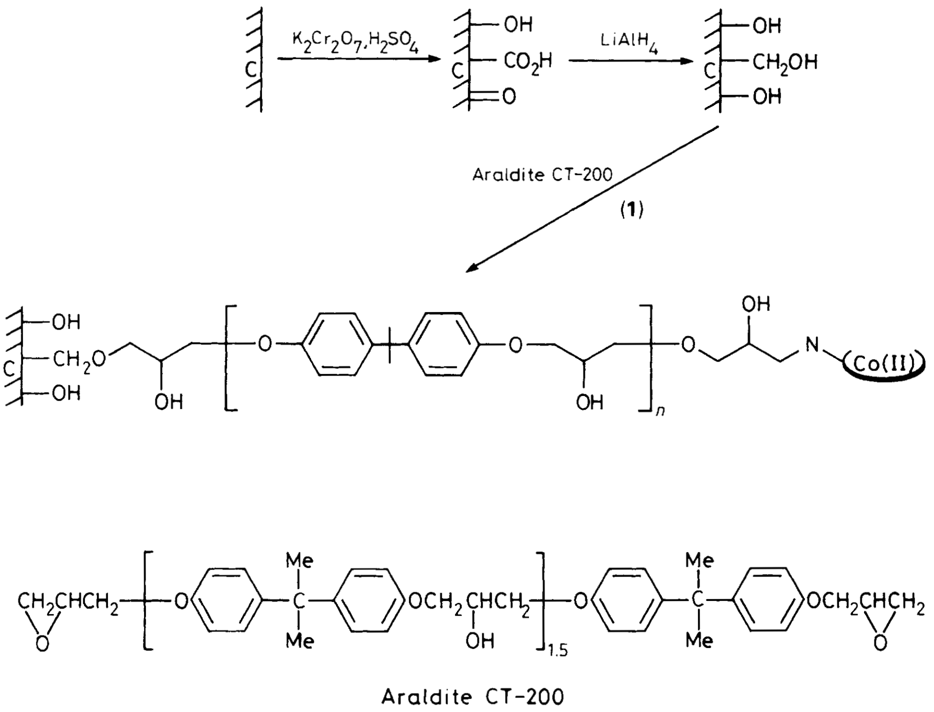
A glassy carbon electrode was coated with a polymer species derived from a hydrophobic vitamin B_{12} and Araldite CT-200, and the immobilised cobalt complex catalysed the electrochemical carbon-skeleton rearrangements of alkyl halides having electron-withdrawing groups.

Much of the current interest in polymer-coatings on electrode surfaces originated in the hope that catalytically active species incorporated into the polymers may exert efficient catalytic activity.[1] Such modified electrodes are generally considered to hold many advantages, such as utilization of small amounts of catalyst species, ready separation of products, and performance of specific electro-syntheses. We have previously demonstrated that carbon-skeleton rearrangements, which are specific reactions mediated by vitamin B_{12}-dependent enzymes,[2] were catalysed by hydrophobic vitamin B_{12} derivatives under electrochemical conditions.[3] Improvement of the catalytic efficiency was expected to result from immobilisation of a hydrophobic vitamin B_{12} on an electrode. In this regard, Scheffold *et al.* prepared a polymer-coated electrode, in which a vitamin B_{12} derivative was anchored, and used it for the exclusive formation of valeronitrile,[4] but did not try to examine the reactions characteristic of vitamin B_{12} enzymes. We now report the preparation of a polymer-coated electrode, in which a hydrophobic vitamin B_{12} is immobilised, by a modification of Scheffold's method, and its catalytic efficiency in carbon-skeleton rearrangement reactions.

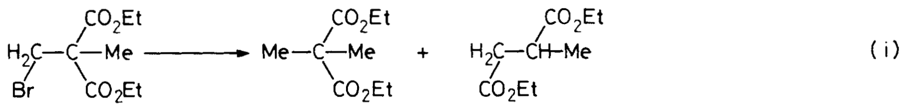
The hydrophobic vitamin B_{12} derivative (**1**), having a 3,5-diaminobenzoyl moiety at its peripheral site, was prepared from cyanocobalamin according to a modification of reported procedures.[4,5] Several procedures for chemical pretreatments of electrodes have been proposed for anchoring catalytically



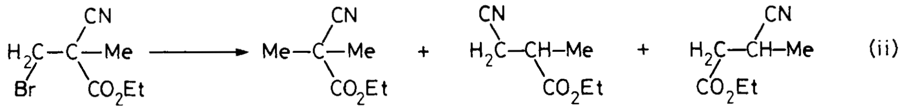
(**1**) R = CH_2O_2C–



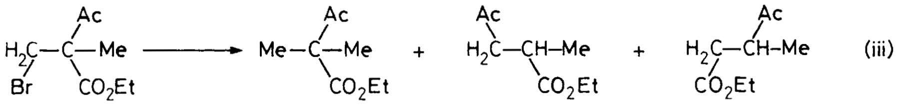
Scheme 1



(2)	(2a)	(2b)
-2.0 V *vs.* S.C.E.	2%	18-25%
-1.5 V *vs.* S.C.E.	2%	2%



(3)	(3a)	(3b)	(3c)
-2.0 V *vs.* S.C.E.	3-5%	trace	10-20%
-1.5 V *vs.* S.C.E.	3%	1%	2%



(4)	(4a)	(4b)	(4c)
-2.0 V *vs.* S.C.E.	1-2%	30-39%	trace
-1.5 V *vs.* S.C.E.	1%	6-10%	trace

active functional groups on the carbon electrode. We first thoroughly oxidised the surface of a glassy carbon electrode with a sulphuric acid solution of potassium dichromate,[6] and then reduced it with lithium aluminium hydride in order to introduce hydroxy groups on the electrode surface, which had been polished with 1 μm diamond paste in advance. The electrode surface was coated with a polymer species formed with the hydrophobic vitamin B_{12} derivative (**1**) and a polymeric monomer, Araldite CT-200 (supplied by Ciba-Geigy, Japan), as described in the literature[4] (Scheme 1). The apparent coverage of the surface with the immobilised hydrophobic vitamin B_{12} was evaluated from the charge under the reductive $Co^{II/I}$ wave by cyclic voltammetry;[7] 4×10^{-9} mol cm^{-2}. This value is in good agreement with the total quantity of the cobalt species present evaluated by *X*-ray fluorescence spectroscopy. Electrochemical measurements made it clear that electron transfer between the carbon electrode and the hydrophobic vitamin B_{12} took place readily in the polymer-coated electrode.

The catalytic function of the modified polymer-coated electrode was investigated for the carbon-skeleton rearrangement reactions of alkyl halides (**2**), (**3**), and (**4**), having electron-withdrawing groups such as carboxylate, acetyl, and cyano, under electrochemical conditions in *N,N*-dimethylformamide (DMF). The substrates and the corresponding products are shown in equations (i)—(iii). The electrolysis was carried out in a cylindrical three-electrode cell in the manner previously described.[3] A DMF solution of the substrate (100 mg, 10^4—10^5 fold with respect to the molar quantity of the hydrophobic vitamin B_{12} immobilised on the electrode) and tetrabutylammonium tetrafluoroborate (TBAF) was electrolysed at an appropriate potential, and the products were analysed and identified by g.l.c. and n.m.r. methods, as given in equations (i)—(iii); unreacted substrates were also present. The following features became apparent. (a) The carbon-skeleton rearrangement products (**2b**), (**3c**), and (**4b**) were the major products at -2.0 V *vs.* standard calomel electrode (S.C.E.). This is the first successful example of a carbon-skeleton rearrangement being caused by a modified electrode. (b) The yields based on the hydrophobic vitamin B_{12} were quite large at -2.0 V *vs.* S.C.E.; turnover number, 10^3—10^4 in 8—10 h. The conversion rates of the substrates were in the range 20—40% for this reaction period. (c) Even at a lower reduction potential, -1.5 V *vs.* S.C.E., the isomerization products (**2b**), (**3b**), (**3c**), (**4b**), and (**4c**) were obtained in significant yields relative to the corresponding reduction products (**2a**), (**3a**), and (**4a**), though the isomerized products were scarcely obtained at this potential in homogeneous solution systems without immobilisation of the catalyst species.[3]

The polymer matrix seems to provide an efficient micro-environmental effect in the rearrangement reaction catalysed by the hydrophobic vitamin B_{12} in a manner similar to that observed for the similar reaction carried out in an 'octopus azaparacyclophane', even though the reaction mechanisms are different.[8]

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