

Studies on Electrolytic Substitution Reactions

V. Observation of a Rearrangement during the Cathodic Reduction of Neophyl Chloride¹

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Recent studies²⁻⁵ on the cathodic reduction of halides have centered on the problem of defining the orientation of the C—X dipole with regard to the electrode in the rate-determining step, *i.e.* to find out whether the S_N2-like mechanism proposed by Elving and Pullman⁶ is correct, and to elucidate the nature of the subsequent steps leading to products. We now wish to report a case of a rearrangement during the course of a cathodic reduction of a halide, a phenomenon not encountered previously.

Neophyl chloride^a (10 mmoles) in *N,N*-dimethylformamide (analytical grade,

^a The product was distilled twice through a column of ten theoretical plates and the purity of it was carefully checked by VPC before use. Considerable care must be exercised during this procedure, since dehalogenation with formation of 3-phenyl-2-methylpropene and 1-phenyl-2-methylpropene occurs very easily. At temperatures below 110° (both in injection chamber and column) the sample used in the electrolysis experiments was gas chromatographically homogeneous on several columns (a 2 m × 0.3 cm 10% Apiezon L on Chromosorb P column was the best one). At higher temperatures, olefin formation interfered with the analytical procedure.

The NMR-spectrum of the sample revealed no impurities even at high attenuation.

^b The anode was a piece of Pt foil, placed in a separate anode compartment. The electrode potential was controlled by means of the Model 557 Potentiostat from Amel, Milan, Italy.

45 ml) and water (7.0 ml) with tetrabutylammonium tosylate (4.0 g) as supporting electrolyte was electrolyzed at a mercury cathode at -2.4 V *vs.* the saturated calomel electrode.^b In order to have a further check on the homogeneity of the neophyl chloride, samples were withdrawn at intervals and analyzed by VPC.^c The hydrocarbon fraction contained *t*-butylbenzene as the major product and a rearrangement product, isobutylbenzene,^d as a minor component. The composition of the product mixture at different stages of the run is given in Table 1. Small amounts ($\approx 0.3\%$) of a coupling product, bineophyl, could also be detected. As shown in the table, the current yield of hydrocarbons is not very high, presumably due to competition from water reduction. In runs without any added water present, the current yield of the same hydrocarbon mixture rose to about 60%. The mercury surface remained shiny during the runs, indicating that no formation of tetrabutylammonium amalgam took place.⁸

Experiments carried out with acetonitrile saturated with tetrabutylammonium tosylate as the electrolyte gave the same hydrocarbon mixture in a current yield of about 50%. On the contrary, no reduction products were observed when dioxane/water (45:7) was used as the solvent system.

The formation of a rearrangement product during the cathodic reduction of neophyl chloride might in principle be taken as evidence for an S_N1-like reaction mechanism, in which R—X dissociates into an ion pair under the influence of the strong electric field near the electrode, followed by electron transfer from the cathode to the cation. However, in view of the fact that the neophyl cation rearranges completely

^c This procedure would have revealed if any halide capable of giving isobutylbenzene by cathodic reduction and with a different half-wave potential from that of neophyl chloride was present in the sample. In such a case, a definite trend in the product composition with conversion would have been observed.

^d Identified by gas chromatographic and mass spectral comparison with an authentic sample.

Table 1. Cathodic reduction of neophyl chloride, $C_6H_5C(CH_3)_2CH_2Cl$.

% of theoretical amount of charge passed, calc. for a 2-electron process	Yield of hydro- carbons, %	Current yield %	Composition of product, %	
			<i>t</i> -BuPh	<i>i</i> -BuPh
70	13	19	93.7	6.3
132	39	30	93.7	6.3
200	56	28	93.6	6.4
270	75	28	93.2	6.8

when generated by solvolysis,⁹ the rearrangement observed here is preferably viewed as a radical one. The neophyl radical is known to rearrange with ease,^{10,11} although not as completely as the corresponding cation, and the migration aptitude of the phenyl group is influenced by substituents in a characteristic manner,¹¹ almost independently of the mode of generation of the radicals. Moreover, it has been shown that the small proportion of rearrangement products (1–6 %) formed in the reaction between neophyl chloride and magnesium is most likely formed *via* neophyl radicals.¹² The close similarity between cathodic reduction at the mercury electrode and dissolving metal reductions noticed previously^{3,4} is again apparent.

The observation of this cathodic rearrangement provides another probe into the complex mechanism of electrolytic halide reductions. A study of substituent effects along the lines outlined by Röchardt¹¹ might give valuable information about the intermediacy of radicals in halide reductions at electrodes.

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