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CYCLOPROPANES. XX. ELECTROCHEMICAL REDUCTION OF (+)-S-1-BROMO-1-METHYL-2,2-DIPHENYLCYCLOPROPANE[1]

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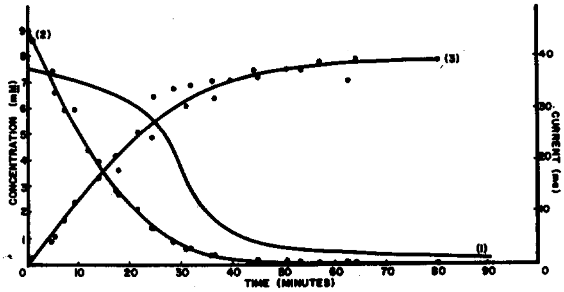
In order to gain some insight into the mechanism of metallation and of homogeneous and heterogeneous dissolving metal reductions, we have undertaken a study involving the reduction of optically active (+)-(S)-1-bromo-1-methyl-2,2-diphenylcyclopropane. This system is ideally suited for such an investigation since the optical purities and the absolute configurations of both the starting material and the product, 1-methyl-2,2-diphenylcyclopropane, are known[2]. Moreover, in contrast to most other tertiary halides, this system is unique in that it is relatively stable toward SN_1 solvolysis, thus permitting us to remove from consideration the incursion of a cationic intermediate[3]. Finally, the optical fate of the 1-methyl-2,2-diphenylcyclopropyl radical[4] as well as the anion[5] has been established, the former leading to complete racemization and the latter to almost complete retention of optical activity. The above observations will be used as our probe into the mechanisms of these reductions as they have been previously used for the metallation reaction[6,7].

As a first approximation we view metallation, dissolving metal reductions and electrolytic reductions as a single class of reactions differing only in the ease with which electrons are transferred to the substrate. In a sense they are all examples of electrolytic type reactions.

We have previously reported on the metallation[6,7] reaction and we wish now to describe our results on electrolytic reduction.*

Repeated controlled potential electrolyses of (±)-1-bromo-1-methyl-2,2-diphenylcyclopropane (3-10 mM in 0.10 M tetraethylammonium bromide in acetonitrile, using compartmented cells and three-electrode configurations) at -2.7 volts vs. S.C.E. produced the hydrocarbon, 1-methyl-2,2-diphenylcyclopropane, in 93% yield. Current integration indicated that 1.98 ± .03 electrons per molecule reacted. Variation of current with time during the controlled potential electrolysis was not exponential but decayed as shown in Fig. I. This type of curve can be interpreted as being indicative of

FIG. I



Controlled Potential Electrolysis of 1-Bromo-1-methyl-2,2-diphenylcyclopropane.
Curve 1. Electrolysis current vs. time.
Curve 2. Substrate concentration vs. time.
Curve 3. Hydrocarbon concentration vs. time.

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* There is a good deal of current interest in the general area of electrolytic reduction of alkylhalides, i.e., N.S. Hush, K.B. Oldham, J. Electroanal. Chem., 6, 34 (1963); A. Streitweiser, Jr., C. Perrin, J. Am. Chem. Soc., 86, 4938 (1964); I.W. Sease, P. Chang, J.L. Groth, ibid., p. 3154; F.L. Lambert, A.H. Albert, J.P. Hardy, ibid., p. 3155; L.G. Feoktistov, S.I.Zhdanov, Electrochim. Acta, 10, 657 (1965).

an intermediate being formed prior to hydrocarbon formation.* This hypothesis was reinforced by kinetic analysis of product formation versus substrate disappearance. Comparison of curves 1 and 2 in Fig. I show that at the start of the reaction, current is not at all proportional to concentration of substrate, but that the rate of substrate disappearance is much greater than the change in current. In addition, the initial consumption of substrate is faster than the formation of product.

Two likely intermediates were considered, 1-methyl-2,2-diphenylcyclopropylmercuric bromide and di-1-methyl-2,2-diphenylcyclopropylmercury.. The former was shown not to be involved by comparing its cyclic voltammetry curve with that of 1-bromo-1-methyl-2,2-diphenylcyclopropane, Fig. II, a

FIG. II

A

B

Cyclic Voltammetry Curves. Reduction current upward, negative potentials to the right. See text for peak potentials.

a. 1-Bromo-1-methyl-2,2-diphenylcyclopropane at 8.9 volts/sec. sweep rate.

b. 1-Methyl-2,2-diphenylcyclopropylmercuric bromide at 12.8 volts/sec. sweep rate.

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* Since the current-time curve of this shape could be caused by limiting by the potentiostat or by uncompensated ohmic drop between the reference and working electrodes, these factors were carefully considered. In all experiments, electrolysis current and total cell voltage drop were well within the capabilities of the potentiostat. The reference probe tip was kept from 2 to 15 mm from the cathode pool. Maximum electrolysis current was usually less than 30 ma and one run was made with a maximum current of 5 ma to assure that uncompensated resistance drop would be small. In all cases the current-time curve had the shape illustrated in Fig. I. In other work we have observed unusual current-time curves which were caused by resistance-drop artifacts. In these cases, substrate concentration-time curves have had the same shape as the current-time curves.

and b. The curve for the bromide shows two reduction peaks at -2.70 and -1.28 volts vs. S.C.E. and one oxidation peak at -0.96 volts.

The -2.70-volt peak represents the initial reaction; the -0.96-volt peak indicates oxidation of the initial reaction product. The -1.28-volt peak is reduction of a product of the -0.96-volt oxidation. These assignments are indicated for several reasons. A one-cycle potential sweep, -0.7 to -2.7 volts vs. S.C.E., applied after the solution has been stirred and then allowed to come to rest shows no -1.29-volt peak but does show the other two. A two-cycle sweep within the same limits shows only the -2.70-volt and -0.96-volt peaks on the first cycle, but all three on the second. If when a signal like Fig. IIa is being observed, the sweep length is reduced from the right while the positive limit is kept as shown, the -0.96-volt and the -1.28-volt peaks disappear when the right hand sweep limit reaches a point corresponding to the foot of the -2,70-volt peak. All peaks again are observed if the sweep is lengthened to include the -2.70-volt peak. If the solution is stirred while a signal like Fig. IIa is being observed, the -2.70-volt peak increases and the other two decrease. This indicates that the reactant for the -2.70-volt peak is furnished from the bulk of the solution but that reactants for the other two are not.

The cyclic voltammetry curve for 1-methyl-2,2-diphenylcyclopropylmercuric bromide is shown in Fig. IIb. Three peaks are observed at -0.69, -0.86 and -2.04 volts vs. S.C.E. In this case, the two more positive peaks appear to be a reversible couple. Unlike the two positive peaks in Fig. IIa, they do not represent reaction of products from the more negative reaction, but can be observed independent of it. A current-potential curve for a mixture of the cyclopropyl bromide and cyclopropylmercuric bromide under the conditions for Fig. IIa shows all of the peaks for the mercury compound but only the main peak for the bromide. If a curve like Fig. IIa is being observed and the mercury compound is added, the -0.96-volt and the -1.28-volt peaks disappear and the three peaks for the mercury compound appear simultaneously.

Significant concentrations of cyclopropylmercuric bromide cannot be formed as an intermediate in the reduction of alkyl bromide because the former is more easily reduced than the latter. On the other hand, dicyclopropyl mercury is more difficult to reduce than the bromide. At the potential used for cyclopropylbromide reduction, the dialkylmercury reacts only slowly to form the hydrocarbon. Accordingly, it is a possible intermediate in the alkyl bromide reduction.*

To ascertain that cyclopropyl bromide reduction does involve formation and subsequent reaction of a stable organomercury intermediate, samples of the reaction mixture were analyzed for mercury by wet oxidation and subsequent dithizone color formation. A solution containing 126.4 μmoles of cyclopropyl bromide was electrolyzed. Samples were taken when one third the expected number of coulombs had passed and when the reaction was complete. On analysis of these samples together with a blank similarly electrolyzed, no detectable mercury (< 0.1 μg/ml) was found in either the blank or the final sample. The intermediate sample contained 1.6 μmoles of mercury (45 μg/ml).

Finally, controlled potential electrolysis of (+)-S-1-bromo-1-methyl-2,2-diphenylcyclopropane under the conditions used for the racemic bromide yielded the hydrocarbon, $[\alpha]_{5461}$ -38.1° (optical purity[2] 25%).

We view the reduction as occurring in the following manner:

(1) $R\text{-}Br + e^- \rightarrow [R\dot{-}Br]^-$

(2) $[R\dot{-}Br]^- \rightarrow R\cdot + Br^-$

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* In the case of 1-iodo-1-methyl-2,2-diphenylcyclopropane, in which the potential for reduction is lower, -1.7 volts vs. S.C.E., di-1-methyl-2,2-diphenylcyclopropylmercury can be isolated from the reaction.

(3) $R\cdot + e^- \rightarrow R^-$

(4) $R\cdot + Hg^o \rightarrow RHg_n^{\cdot}$

(5) $RHg_n^{\cdot} + e^- \rightarrow R^- + Hg^o_n$

(6) $RHg_n\cdot + RHg_n\cdot \rightarrow RHg_nR \rightarrow RHgR + Hg^o_{n-1}$

(7) $R_2Hg + e^- \rightarrow R^- + RHg\cdot \xrightarrow{Hg^o} RHg_n\cdot$

(8) $R^- + (Et)_3NBr \rightarrow RH + CH_2{=}CH_2 + (Et)_3N + Br^-$

As in the cases of direct metallation[6,7], we view the reaction as occurring at the metal surface. An electron is transferred from the surface to the σ* antibonding orbital of the carbon-bromine bond to produce the anion-radical (1). The anion-radical can then dissociate at the surface to the 1-methyl-2,2-diphenylcyclopropyl radical (2) which can undergo a number of indistinguishable reactions. The radical may pick up another electron to yield the anion (3), or since mercury is a good radical trap, the radical may become adsorbed on the mercury surface (4) from which it can either take on another electron to yield the anion (5) or meet up with another adsorbed radical to produce a dicyclopropylmercury (6). The formation of the dicyclopropylmercury alone or in combination with the adsorbed radical type intermediates accounts for the observation that the substrate disappears at a faster rate than product appears. The dicyclopropylmercury can then accept an electron to produce the anion and a cyclopropylmercury radical which in combination with the mercury surface becomes an adsorbed radical (7) which can be recycled through path (5) or (6). The anions formed in (3), (5) and (7) react at the surface with the electrolyte, tetraethylammonium bromide, in an elimination reaction to produce the hydrocarbon, ethylene and triethylamine, all of which have been identified in the reaction mixture.

The reaction of lithium metal with the optically active bromide produces a product which has retained its optical activity to the extent of

46%[7]. Reaction with magnesium results in 13-18% retention of optical activity with overall retention of configuration. The observation that the hydrocarbon produced in the electrolytic reduction has retained 25% of its optical activity (63% retention of configuration) is consistent with the surface nature of this reaction as has been discussed previously[6,7].

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