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INTRAMOLECULAR ELECTROLYTIC REDUCTIVE COUPLING OF ACTIVATED OLEFINS: A NOVEL ROUTE TO CYCLIC COMPOUNDS

James D. Anderson and Manuel M. Baizer

Central Research Department, Monsanto Company,
St. Louis, Missouri 63166

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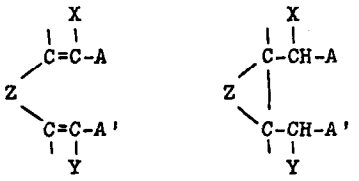
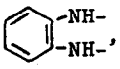
The general scope of intermolecular electrolytic reductive coupling of activated olefins has been outlined (1) and detailed examples of the application of this method to several classes of these olefins have been published (2). Intramolecular electrolytic reductive coupling of diolefins I, under active investigation in This Laboratory, has now been found to be a novel route to carbocyclic and heterocyclic compounds (II) functionally substituted on the side-chain. These products are not readily accessible by alternate syntheses.



A and A' are electron-withdrawing groups.
X and Y are electron-withdrawing groups or H.

I II

a, Z = $(CH_2)_4$, A=A'=$COOC_2H_5$, X=Y=H

b, Z =  , A=A'=X=Y=$COOC_2H_5$

The following may serve as an example of the formation of a cyclohexane derivative by this procedure. The electrolytic cell used was identical to the one previously described (3). The catholyte contained 40.0 g. (0.157 mole) of diethyl 2,8-decadiene-1,10-dioate (4) (Ia), 70.7 g. of acetonitrile, 26.9 g. of tetraethylammonium p-toluenesulfonate, and 10 ml. of water. The electrolysis was carried out at 2 amps. and 25° until a total of 4.2 amp.-hr. were passed. The cathode voltage was -1.91 to -1.96 (vs. S.C.E.) during the run. The catholyte was diluted with water and extracted with ether to remove the products and recovered starting material. Distillation of the residue followed by v.p.c. analyses of the distillation cuts showed the presence of 13.4 g. (0.052 mole) of trans- and 5.3 g. (0.021 mole) of cis-

diethyl 1,2-cyclohexanediacetate. The fraction boiling at 91° (0.16 mm.), n_D^{25} 1.4560, contained 83% of the trans isomer and 17% of the cis isomer [lit. (5): cis-diethyl ester n_D^{20} 1.4581, trans-diethyl ester n_D^{20} 1.4566]. Mass spectrograph, n.m.r., and elemental analyses of the above-mentioned fraction were consistent with the cyclohexane-diacetate structure. Assignment of the isomers was based on a collection of the trans- peak via preparative scale v.p.c. and conversion of the diester to the corresponding dicarboxylic acid, m.p. 164.5-165.5°, [lit. (6): m.p. 167°]. The yield of the diethyl 1,2-cyclohexanediacetates was 90.5% based on current input (two-electron uptake per mole).

An example of the formation of a heterocyclic ring system by this method is presented. The electrolytic cell was the same as used in the first example. The catholyte contained 40.0 g. (0.089 mole) of o-bis-(β-dicarbethoxy-vinylamino) benzene (7) (Ib), 104.0 g. of acetonitrile, 28.0 g. of tetraethylammonium p-toluenesulfonate, and 12.0 g. of water. The electrolysis was carried out at 2 amps. and 25° until a total of 4.77 amp.-hr. were passed. The cathode voltage was -1.73 to -1.85 (vs. S.C.E.) during the run. The catholyte was worked up as previously described. Evaporation of the extracting solvent (methylene chloride)

yielded a residue which was recrystallized from methanol, m.p. 94.5°. The product, 2,3-bis-(dicarbethoxymethyl)-1,2,3,4-tetrahydroquinoxaline, weighed 34.4 g. (0.077 mole) which corresponds to an 86% yield of pure product based on current input (two-electron uptake per mole). [Calcd. for $C_{22}H_{30}N_2O_8$: C, 58.65; H, 6.71; N, 6.22; mol. wt., 450. Found: C, 58.60; H, 6.73; N, 6.18; mol. wt. (in benzene), 451.] N.m.r. analysis was consistent with the structure. It was also found that the product is thermally decomposed quantitatively at about 160° into diethyl malonate and quinoxaline.

One significant difference between inter- and intra-molecular electrolytic reductive coupling is the fact that, where ring closure has been favored, the intra-molecular reaction has been found to be independent of initial concentration of the starting diolefin (3). As a corollary, the yield of cyclic product is essentially the same when the reaction is taken to partial or to complete conversion.

There is indication that radical intermediates are not involved in these couplings and that considerable stereo-selectivity may be evidenced.

The full scope of this reaction, including the size of the carbocyclic rings that may be constructed, the hetero-atoms that may be included, and the mechanism of the coupling will be reported elsewhere.

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