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ELECTROLYTIC REDUCTIVE COUPLING OF ACTIVATED OLEFINS

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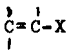
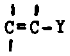
For the past several years we have been engaged in a study of the electrolytic reduction of concentrated water-containing solutions of activated olefins (I, II) in electrolytes A^+Z^- at cathodes of high hydrogen overvoltage. *X* and *Y* are different electron-attracting groups (-CN, -COOR,



$>C{=}C{<}X$

I



$>C{=}C{<}Y$

II

-COOR, $-CONR_2$, 2- and 4-pyridyl, $-PO(OR)_2$, >CO, extended conjugation, $-SO_2-$, etc.) which are selected so that neither they nor the other substituents at the α and β carbon atoms are reduced under the conditions of the electrolysis. *A^+* is a cation that is not discharged at the potential needed for the reduction of the olefins (tetraalkylammonium, tetraalkylphosphonium, trialkylsulfonium and others); *Z^-* is a cation that renders AZ "hydrotropic" (alkarylsulfonate, alkylsulfate and others[1]). This work has yielded an electro-organic reductive condensation method for preparing a

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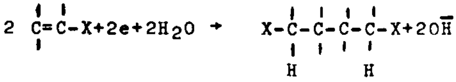
[1] P.S. Putanov and J.D. Babin, *Chim. et ind.* **85**, 263 (1961) and citations therein.

variety of polyfunctional compounds.

When a single olefin (I or II) is employed, the above process is a "hydrodimerization"[2] and yields the hydrodimer III.



$$2\ \mathrm{C{=}C{-}X} + 2e + 2H_2O \rightarrow \mathrm{X{-}\underset{H}{C}{-}C{-}C{-}\underset{H}{C}{-}X} + 2\overline{OH}$$

III

The electrolytic method gives considerably higher yields than Knunyants' alkali metal amalgam procedure[2,3] and often succeeds when the amalgam process fails completely. Among the many olefins we have "hydrodimerized" are: acrylonitrile, α-methylacrylonitrile, ethyl acrylate, ethyl β,β-dimethylacrylate, acrylamide, 2- and 4-vinylpyridines, 9-benzalfluorene and diphenylvinyl phosphine oxide. Activated straight-chain olefins with extended conjugation (1-cyano-1,3-butadiene) as well as cyclic olefins (1-cyano-1-cyclohexene) have been used.

Illustrative is the "hydrodimerization" of ethyl acrylate. The catholyte contained 76.0 g. of stabilized ester, 75.8 g. of a 76.5% aqueous solution of methyltriethylammonium p-toluenesulfonate, and 88.6 g. of dimethylformamide. The anolyte contained 40 ml. of 38% quaternary salt solution. A cathode of 110 ml. mercury (area ca. 55 cm^2) was used in a cell similar to one described[4]. The

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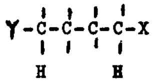
[2] I. L. Knunyants and N. S. Vyazankin, *Izvest. Akad. Nauk S.S.S.R.*, *Otdel. Khim. Nauk* 1957, No. 2,238.

[3] Knunyants' olefins were exclusively derivatives of acrylic acid.

anode was a platinum wire enclosed in an Alundum cup. Electrolysis at 3 amps. was conducted at 35-40° for 2 hr. The cathode voltage was -1.89 to -1.93 (S.C.E.). Dimethylformamide was added to the catholyte from time to time to preserve homogeneity. The pH was controlled at ca. 7-9. At the end of the reaction period, polymerization inhibitor was added, the mercury separated and the catholyte diluted with ca. 500 ml. of water and extracted with six 50-ml. portions of methylene chloride. The extracts were washed, dried and stripped of volatiles on the water bath using an aspirator, The residual liquid (23.6 g., theory 22.6 g.) was vacuum-distilled. After a very small forerun diethyl adipate was collected at 142-148°/30 mm., n_D^{25} 1.4250.

When a mixture of olefins (I *and* II) is electrolyzed two different situations may obtain:

1. When the cathode voltage for the reduction of I is close (within ca. 0.2 v.) to the cathode voltage required for II[5] the mixture will yield three products: hydromer of I, hydrodimer of II and the product of mixed coupling IV:



$$\mathrm{Y{-}\underset{H}{C}{-}C{-}C{-}\underset{H}{C}{-}X}$$

IV

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[4] M. J. Allen, "Organic Electrode Processes", Reinhold Publishing Co., N.Y., 1958, p. 36.

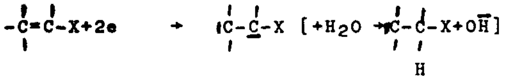
[5] As can be determined polarographically.

For example, the electrolysis of a mixture of ethyl acrylate (ca. -1.8 v. vs. S.C.E.) and acrylonitrile (ca. -1.9 v. vs. S.C.E.) yielded diethyl adipate, adiponitrile and ethyl δ-cyanovalerate.

2. When I reduces at a cathode voltage considerably more positive than is required for II only two products are formed, namely III and IV. Thus electrolysis of a mixture of diethyl maleate (ca. -1.4 v. vs. S.C.E.) and acrylonitrile yielded tetraethyl butanetetracarboxylate, diethyl -(2-cyanoethyl)succinate and no adiponitrile.

Our total results are best accomodated by the following mechanistic proposals.

1. I undergoes an overall two-electron uptake to yield the V dianion[6] (which may under some circumstances undergo neutralization to yield the monocarbanion VI).



$$-\underset{|}{\overset{|}{C}}=\overset{|}{C}-X+2e \rightarrow \underset{|}{\overset{|}{C}}-\underline{\overset{|}{C}}-X\ [+H_2O \rightarrow \underset{|}{\overset{|}{C}}-\underset{\underset{H}{|}}{\overset{|}{C}}-X+O\bar{H}]$$

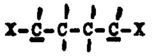
V VI

2. Depending upon the concentration of proton donors and acceptor olefin molecules, the carbanions (V, VI) may now

a. Displace O$\bar{H}$ from water, e.g., and form the dihydro-derivative of I. This occurs in very dilute solutions of olefins.

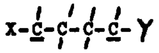
[6] Long after this work was completed, S.I. Zhdanov and L. G. Feoktistov, *Izvest. Akad. Nauk, S.S.S.R., Otdel. Khim. Nauk*, 1963,53 proposed a similar intermediate for the hydrodimerization of acrylonitrile.

b. Engage in nucleophilic attack, via the β-positions of V or VI upon the β-position of other polarized (but not reduced) activated olefin molecules present (I, II) to yield the dianions (VII, VIII) of the coupled product[6]. This step is like the Michael Reaction except that the donor



$X-\underline{C}-C-C-\underline{C}-X$

VII



$X-\underline{C}-C-C-\underline{C}-Y$

VIII

species here is a β-carbanion. It is favored by a high concentration of olefin in the catholyte.

3. If a sufficient concentration of water is available VII and VIII will be neutralized and form coupled product and OH^-.

4. If the concentration of water is very low the condensed carbanion VII may attack additional molecules of I before the process is terminated. From electrolyses of acrylonitrile in dimethylformamide, tetraethylammonium p-toluenesulfonate and a low percentage of water we have obtained "hydrotrimer", "Hydrotetramer" and a new class of low molecular weight polyacrylonitriles.

5. Evidence for the viability of a dicarbanion such as V was obtained in the isolation of diethyl α,α'-bis-(2-cyanoethyl)succinate from the reaction of diethyl maleate and excess acrylonitrile in the presence of a very limited quantity of water.

The initial papers describing the details of this study have been submitted to the Journal of the Electrochemical Society.