Electrolytic Reductive Coupling. IV.[1] Mixed Couplings among Derivatives of α,β-Unsaturated Acids

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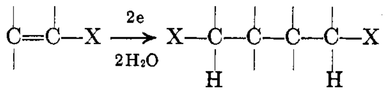
Received December 6, 1963

Electrolytic reductive coupling of derivatives of α,β-unsaturated acids, previously reported as a route to hydrodimers, has been broadened to include mixed reductive couplings among different species. The monomers are linked through their respective β-positions and there is thus provided a new synthesis of cyano esters, ester amides, etc. The factors which lead to the formation of either two or three products in this electrolytic coupling are discussed and illustrated. A novel preparation of lysine involving an electrolytic coupling step is presented. Appropriate derivatives of butadiene (*e.g.*, 1-cyano-1,3-butadiene) couple reductively with derivatives of monoolefinic acids to yield, after hydrogenation, 1,6-disubstituted hexanes. Under forcing conditions diethyl fumarate couples with *two* molecules of acrylonitrile to yield diethyl α,α′-bis(2-cyanoethyl)succinate.

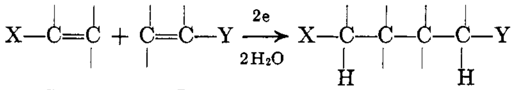
The discovery[2] that a variety of derivatives of α,β-unsaturated acids (I) may be individually hydrodimerized electrochemically in aqueous systems under mildly alkaline conditions provided a novel practical route to many difunctional compounds (II). It is intrinsic in the hydrodimerization process, however, that products II are formed which are symmetrical and which have the functional groups X separated by four carbon atoms.[3] Greater versatility could be achieved if two *different* monomers (I and I′) could be reductively coupled since this would provide a means of obtaining valuable cyano esters, ester amides, etc.



$$\mathrm{C{=}C{-}X} \xrightarrow[2\mathrm{H_2O}]{2e} \mathrm{X{-}\underset{H}{C}{-}C{-}C{-}\underset{H}{C}{-}X}$$

I II

X = -CN, -COOR, -CONR$_2$, etc.

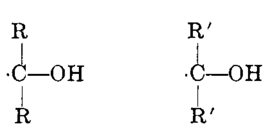


$$\mathrm{X{-}C{=}C} + \mathrm{C{=}C{-}Y} \xrightarrow[2\mathrm{H_2O}]{2e} \mathrm{X{-}\underset{H}{C}{-}C{-}C{-}\underset{H}{C}{-}Y}$$

I I′

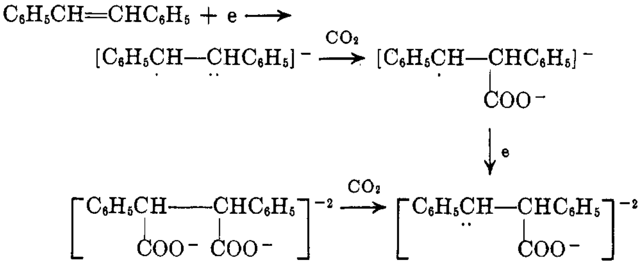
X, Y = -CN, -COOR, -CONR$_2$, etc.

The literature on electrolytic mixed reductive coupling is restricted to the preparation of mixed pinacols in acid medium from a mixture of ketones[4] and the preparation of carboxylic acids by the electrolysis of conjugated olefins in the presence of carbon dioxide.[5] Since it is accepted that pinacol synthesis proceeds *via* a free-radical intermediate (III, IV), it is implicit that



III IV

in the formation of mixed pinacols one of the two participating ketones must accept an electron at the cathode at about the same cathode voltage as does the other. Three products are formed: two by self coupling and one by cross coupling. In the electrolytic reduction of stilbene in the presence of carbon dioxide, Wawzonek, *et al.*,[5] have proposed that the reaction probably proceeds *via* a stepwise addition of electrons and carbon dioxide, *i.e.*, through an anion free radical, to yield finally *m*-diphenylsuccinic acid. It has been suggested[6] that in hydrodimerization of derivatives of α,β-unsaturated acids (using acrylonitrile as an example), one molecule takes up *two* electrons at the cathode and forms a dicarbanion (V). The unshared electrons at the α-carbon atom are delocalized by resonance interaction with the activating group X or may displace OH$^-$ from water to form a monocarbanion (VI).[7]



$$\mathrm{C_6H_5CH{=}CHC_6H_5} + e \longrightarrow [\mathrm{C_6H_5\dot{C}H{-}\ddot{C}HC_6H_5}]^- \xrightarrow{\mathrm{CO_2}} [\mathrm{C_6H_5\dot{C}H{-}\underset{COO^-}{CHC_6H_5}}]^- \xrightarrow{e}$$

$$\left[\mathrm{\underset{COO^-}{C_6H_5CH}{-}\underset{COO^-}{CHC_6H_5}}\right]^{-2} \xleftarrow{\mathrm{CO_2}} \left[\mathrm{C_6H_5\ddot{C}H{-}\underset{COO^-}{CHC_6H_5}}\right]^{-2}$$

$$\mathrm{CH_2{=}CHX} \xrightarrow{2e} \underset{\mathrm{V}}{[\mathrm{:CH_2:CHX}]^{-2}} + \mathrm{H_2O} \longrightarrow \underset{\mathrm{VI}}{[\mathrm{:CH_2:CH_2{-}X}]^-} + \mathrm{OH^-}$$

The β-position of V or VI then attaches to the β-position of another molecule of polarized (*but not reduced*) starting material to yield the coupled carbanion. On this basis, two types of mixed reductive couplings should be distinguishable: (a) when I and I′ are reduced at about the same cathode voltage,[8] the mixture will be reduced at some intermediate cathode voltage and *three* products should be formed; and (b) when I accepts electrons at a substantially more positive cathode voltage than does I′, controlled electrochemical reduction of the mixture at a cathode voltage close to that for reduction of I alone should produce only *two* products, one by hydrodimerization of I and by mixed

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[1] Paper III: M. M. Baizer and J. D. Anderson, *J. Electrochem. Soc.*, **111**, 226 (1964).

[2] Paper II: M. M. Baizer and J. D. Anderson, *ibid.*, **111**, 223 (1964).

[3] When derivatives of butadiene, *e.g.*, 1-cyano-1,3-butadiene, are used, the functional groups in the hydrodimer may be separated by eight carbon atoms. See ref. 1.

[4] *E.g.*, M. J. Allen, J. A. Siragusa, and W. Pierson, *J. Chem. Soc.*, 1045 (1960).

[5] (a) S. Wawzonek, *et al.*, *J. Electrochem. Soc.*, **102**, 235 (1955); (b) J. W. Loveland, U. S. Patent 3,032,489 (May 1, 1962).

[6] (a) Paper I: M. M. Baizer, *J. Electrochem. Soc.*, **111**, 215 (1964); (b) I. G. Sevast'yanova and A. P. Tomilov, *Zh. Obshch. Khim.*, **33**, 2815 (1963); *Chem. Abstr.*, **60**, 1583*e* (1964).

[7] Evidence for the participation of a dicarbanion in a coupling reaction is presented below.

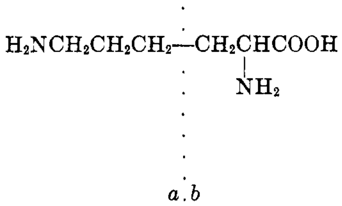
[8] Within *ca.* 0.20–0.25 v.

coupling. No hydrodimer of I′ should be found.[9] Improvement in the yield of mixed product should result from maintaining an excess of I′ in the reaction. These expectations were borne out.

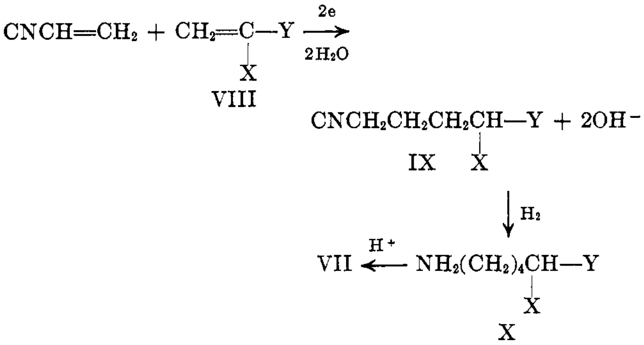
Electrolysis at a mercury cathode of an equimolar mixture of ethyl acrylate (−1.8 v.)[12] and acrylonitrile (−1.9 v.) in aqueous methyltriethylammonium *p*-toluenesulfonate containing sufficient dimethylformamide to ensure homogeneity occurred at −1.83 to −1.85 v. Enough current was passed for only partial conversion[6] of the starting materials. The products isolated were diethyl adipate, ethyl δ-cyanovalerate, and adiponitrile.

A similar electrolysis of diethyl maleate (−1.32 to −1.4 v.) with 2 moles of acrylonitrile (−1.9 v.) at −1.33 v. to −1.40 v. yielded tetraethyl butanetetracarboxylate and diethyl α-(2-cyanoethyl)succinate[13]; no adiponitrile was detectable by vapor phase chromatography.

Since moiety *a* of lysine (VII) can be regarded as being derived from acrylonitrile, and moiety *b* from a suitable derivative of acrylic acid, it appeared likely that VII could be synthesized in a minimum number of steps[14] by a sequence starting with electrolytic reductive coupling of acrylonitrile and an appropriate partner (VII). Since –X and –Y were to become ultimately –NH$_2$ and –COOH, respectively, it was necessary that they survive the electrolysis intact or be reduced only in a manner favoring the synthesis (*e.g.*, $-NO_2 \rightarrow -NH_2$); for the sake of operating simplicity it was desirable that –X and –Y be converted to their respective end functions in one step.


$$H_2NCH_2CH_2CH_2\text{—}CH_2\underset{\substack{|\\ NH_2}}{C}HCOOH$$

VII


$$CNCH{=}CH_2 + CH_2{=}\underset{\substack{|\\ X\\ \text{VIII}}}{C}\text{—}Y \xrightarrow[2H_2O]{2e} \underset{\text{IX}}{CNCH_2CH_2CH_2\underset{\substack{|\\ X}}{CH}\text{—}Y} + 2OH^-$$
$$\downarrow H_2$$
$$\text{VII} \xleftarrow{H^+} \underset{\text{X}}{NH_2(CH_2)_4\underset{\substack{|\\ X}}{CH}\text{—}Y}$$

For illustrative purposes methyl α-acetamidoacrylate[15] (VIII, –X = –NHCOCH$_3$, –Y = –COOCH$_3$) was chosen as the coupling partner for acrylonitrile. A mixture of VIII and a tenfold molar excess of acrylonitrile was electrolyzed in aqueous tetraethylammonium *p*-toluenesulfonate at a mercury cathode. Reduction occurred at *ca.* −1.75 v. (*vs.* the saturated calomel electrode). The cyano ester IX (–X = –NHCOCH$_3$, –Y = –COOCH$_3$) was isolated by fractional distillation. Catalytic hydrogenation of IX in acetic anhydride containing a little sodium acetate using Adams' catalyst or, better, Raney nickel[14] followed by acid hydrolysis of the unisolated amino ester X (X = –NHCOCH$_3$, Y = –COOCH$_3$) yielded lysine dihydrochloride. Partial neutralization with pyridine[16] provided *dl*-lysine monohydrochloride whose infrared spectrum (Nujol mull) was superimposable upon that of a reference sample.[17] While no efforts were made to optimize the yields, it is apparent that the electrolytic coupling is the critical step in the sequence. In this connection, it is interesting that (a) the presence of an α-acetamido group in VIII has not blocked the coupling reaction; (b) the proximity of the cathode voltages for the reduction of methyl α-acetamidoacrylate (−1.75 v.) and acrylonitrile (*ca.* −1.9 v.) leads to the formation of some hydrodimer of the latter (adiponitrile); and (c) selection of a member of class VIII with a more positive reduction potential would therefore minimize by-product formation.

In contrast to the above electrolytic cyanoethylation which leads to a six-carbon chain, ordinary cyanoethylation of α-acylamidomalonates, as in Galat's synthesis of glutamic acid,[18] yields only a five-carbon chain.

A study of the electrolytic hydrodimerization of 1-cyano-1,3-butadiene had shown[1] that coupling of two molecules occurs mainly through the δ,δ-positions to yield (after catalytic hydrogenation of the intermediate products) sebaconitrile and only to a minor extent through the β,β- (→ 3,4-diethyladiponitrile) and the β,δ-positions (→ 3-ethylsuberonitrile). The preponderance of sebaconitrile indicates clearly that the δ-position of cyanobutadiene is most susceptible to attack by either electrons or carbanions.[19] Therefore, controlled mixed reductive coupling between cyanobutadiene and more difficultly reducible derivative of a monoolefinic acid (which can suffer carbanionic attack only at the β-position) should lead mainly to a straight-chain product.

A mixture of 6.0 moles of acrylonitrile (−1.9 v.) and 1.0 mole of cyanobutadiene (*ca.* −1.5 v.) in 80%

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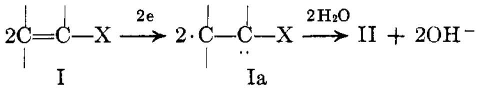
(9) Neglecting the polarographic data[10] which certainly point to a two-electron uptake in the reduction of acrylonitrile, one can visualize hydrodimerization as proceeding *via* coupling of ion-radical intermediates at the free-radical sites,[11] but one cannot apply this concept to the coupling of I


$$2\underset{\substack{|\\ \text{I}}}{\overset{|}{C}}{=}\overset{|}{C}\text{—}X \xrightarrow{2e} 2\cdot\underset{|}{\overset{|}{C}}\text{—}\underset{\substack{\cdot\cdot\\ \text{Ia}}}{\overset{|}{C}}\text{—}X \xrightarrow{2H_2O} \text{II} + 2OH^-$$

and I′ when the cathode voltage is not sufficiently negative for I′ to accept electrons. Attack by the carbanionic end of Ia upon the β-position of I or I′ would lead to α-to-β coupling and not the observed β-to-β coupling. See, however, footnote 18, page 221 of ref. 1.

(10) M. N. Platonova, *J. Anal. Chem. USSR*, **11**, 317 (1956).

(11) M. Szwarc, *Nature*, **178**, 1168 (1956); see also ref. 5a.

(12) Figures in parentheses refer to the cathode potentials *vs.* the saturated calomel electrode for the hydrodimerization of the individual monomer during preparative runs.[2]

(13) P. C. Mitter and A. C. Roy, *J. Indian Chem. Soc.*, **5**, 47 (1928); *Chem. Abstr.*, **22**, 3882[8] (1928).

(14) An elegant short synthesis of lysine from cyclohexanone is described by A. F. Ferris, G. S. Johnson, F. E. Gould, and H. Stange, *J. Org. Chem.*, **25**, 1302 (1960).

(15) E. Rothstein, *J. Chem. Soc.*, 1968 (1949); H. Hellmann, K. Teichmann, and F. Lingens, *Chem. Ber.*, **91**, 2427 (1958).

(16) J. C. Eck and C. S. Marvel, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 374.

(17) Purchased from Nutritional Biochemicals.

(18) A. Galat, *J. Am. Chem. Soc.*, **69**, 965 (1947).

(19) One can conceive of other molecules which would present an intramolecular analog to the mixed coupling of diethyl maleate and acrylonitrile discussed above: molecule (or site) A may more readily accept electrons at the cathode than molecule (or site) B, but B is more subject to carbanionic attack.

aqueous tetraethylammonium *p*-toluenesulfonate was electrolyzed; the cathode voltage was controlled so as not to become more negative than −1.71 v. After removal of the excess starting materials the residue was catalytically hydrogenated. The crude product contained 54.6% suberonitrile. The distilled fraction boiling in the range for suberonitrile and isomers contained 79.6% of the former. This experiment was complicated by (a) the inevitable presence of the hydrodimers of cyanobutadiene[1] and (b) the probable mixed reductive coupling products of cyanobutadiene dimer[1] and acrylonitrile or cyanobutadiene. The highest boiling material collected (222° at 0.47 mm.) had a molecular weight and N content approximating such a "higher" condensation product.

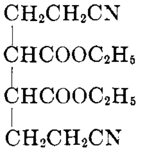
Electrolysis at −1.7 v. of a mixture of 1 mole of cyanobutadiene (*ca.* −1.5 v.) and 8 moles of ethyl acrylate (−1.85 v.) containing acetonitrile as co-solvent yield (after hydrogenation) a cyano ester, which on the basis of analogy we consider to be the straight-chain compound XI.

$$CN(CH_2)_6COOC_2H_5$$

XI

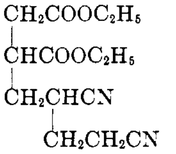
It has been pointed out above that the dicarbanion V formed upon acceptance of 2e at the β-position by an activated olefin may be the reactive species in coupling or that the dicarbanion may first be converted to a monocarbanion VI. A particularly favorable case for determining the viability of V presented itself in the mixed reductive coupling of diethyl fumarate (*ca.* −1.3 v.) and acrylonitrile (−1.9 v.): the ester dicarbanion has symmetry and acrylonitrile is exceptionally susceptible to carbanionic attack. In this electrolysis it was necessary to use a large excess of acrylonitrile and a limited amount of proton donor (in order not to present too great competition for the dicarbanion) but not so little proton donor as to allow anionic polymerization of acrylonitrile to occur.[20]

In the electrolysis diethyl fumarate was added dropwise from a buret to a solution of tetraethylammonium *p*-toluenesulfonate in acrylonitrile containing a small amount of water, and the rate of addition was regulated so as to maintain the cathode voltage at *ca.* −1.4 to −1.5 v. Slightly more current was passed than was necessary for a 2e uptake by the ester. Fractionation yielded, in order of increasing boiling point, diethyl succinate, diethyl succinate, diethyl α-(2-cyanoethyl)succinate, tetraethyl butanetetracarboxylate, and a product containing two cyanoethyl groups.[21] Of the two possible structures of the last product, XII and XIII, XII would *a priori* appear to be favored because in the precursor dianion XIV, the position α to CN might be expected to react with proton donors more readily than the position α to $COOC_2H_5$.[22] Proton magnetic resonance analysis favored XII or XIII.



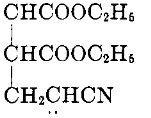
$$\begin{array}{l} CH_2CH_2CN \\ | \\ CHCOOC_2H_5 \\ | \\ CHCOOC_2H_5 \\ | \\ CH_2CH_2CN \end{array}$$

XII



$$\begin{array}{l} CH_2COOC_2H_5 \\ | \\ CHCOOC_2H_5 \\ | \\ CH_2CHCN \\ \quad | \\ \quad CH_2CH_2CN \end{array}$$

XIII



$$\begin{array}{l} \overset{\cdot\cdot}{C}HCOOC_2H_5 \\ | \\ CHCOOC_2H_5 \\ | \\ CH_2\underset{\cdot\cdot}{C}HCN \end{array}$$

XIV

Both the formation of diethyl α-(2-cyanoethyl)succinate and the formation of XII illustrate a point repeatedly demonstrated in mixed reductive coupling, namely that an activated olefin (*e.g.*, diethyl fumarate) may electrochemically form a carbanion capable of participating in Michael adduction even when the corresponding saturated compound (*e.g.*, diethyl succinate) cannot form the carbanion by proton abstraction under Michael conditions.

Experimental[23]

The apparatus and general procedure have been described previously.[6] The catholyte volume in the present experiments was *ca.* 150 ml. and the cathode area 55 cm.² In all cases the acrylonitrile contained a trace of *p*-nitrosodimethylaniline as stabilizer.

Ethyl δ-Cyanovalerate.—The catholyte contained 80 g. (0.80 mole) of ethyl acrylate, 42.4 g. (0.80 mole) of acrylonitrile, 80 g. of 76.5% methyltriethylammonium *p*-toluenesulfonate, and 42 g. of dimethylformamide. Electrolysis at 3 amp. was carried out at 40° for 3 hr. A total of 4 ml. of acetic acid was added dropwise to the catholyte in this period to maintain the pH at *ca.* 8. The catholyte then was diluted with twice its volume of water, the mercury separated, and the solution was extracted with five 50-ml. portions of methylene chloride. The extracts were washed with water and dried over Drierite. Volatile materials were removed on a water bath with an aspirator. The residues from two similar runs (total 53.2 g.) were fractionated through a Todd column. Each fraction was analyzed by vapor phase chromatography for diethyl adipate (total 3.5 g.), ethyl δ-cyanovalerate (total 15.1 g.), and adiponitrile (total 17.0 g.). The infrared spectrum of the cyanovalerate was superimposable upon that of an authentic sample.

Diethyl α-(2-Cyanoethyl)succinate.—The catholyte consisted of 86.0 g. (0.50 mole) of diethyl maleate, 53.0 g. (1.0 mole) of acrylonitrile, 98.5 g. of 86.5% tetraethylammonium benzenesulfonate, and 10 g. of dimethylformamide. Electrolysis at 3 amp. proceeded for 3 hr. at 30°. A total of 2.5 ml. of acetic acid was used for pH control. The combined methylene chloride extracts from two identical runs were fractionated through a Todd column and yielded, after combination and redistillation of similar fractions, 70.9 g. of tetraethylbutanetetracarboxylate, b.p. 159–160° (0.85 mm.), $n^{25}D$ 1.4427, and 7.1 g. of slightly impure[24] diethyl α-(2-cyanoethyl)succinate, b.p. 126–130° (0.65 mm.), $n^{25}D$ 1.4408.

Anal. Calcd. for $C_{11}H_{17}NO_4$: C, 58.13; H, 7.54; N, 6.17; mol. wt., 227. Found: C, 58.13; H, 7.53; N, 7.80; mol. wt., 212.

No adiponitrile was found by vapor phase chromatographic examination of the forerun boiling up to 143° (1 mm.).

Electrolytic Reductive Coupling of Acrylonitrile and Methyl α-Acetamidoacrylate.—A solution of 14.3 g. (0.1 mole) of the ester and 53.0 g. (1.0 mole) of acrylonitrile (containing a trace of *p*-nitrosodimethylaniline as stabilizer) in 70 g. of 69% aqueous tetraethylammonium *p*-toluenesulfonate was electrolyzed at 20°. An average of 2.0 amp. was passed through the cell. After 6.8 amp.-hr. the catholyte was diluted with twice its volume of water and treated in the usual manner in the presence of hydroquinone. After removal of solvent and excess acrylonitrile, the residual liquid (17.2 g., $n^{25}D$ 1.4564) was slowly distilled through a microapparatus equipped with a fraction cutter.

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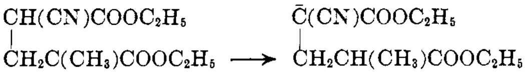
(20) This type of reaction will be discussed in a subsequent paper.

(21) The fractions were monitored by infrared analysis. The appearance, disappearance, and final reappearance of −CN absorption as the boiling points increased was a convenient means of locating the respective products.

(22) An example in which a carbanion with the charge α to an ester group rearranges to the isomer with the charge α to the cyano group is cited by E. D. Bergmann, D. Ginsburg, and R. Pappo, *Organic Reactions*, **10**, 186 (1959).



$$\begin{array}{l} CH(CN)COOC_2H_5 \\ | \\ CH_2C(CH_3)COOC_2H_5 \end{array} \longrightarrow \begin{array}{l} \bar{C}(CN)COOC_2H_5 \\ | \\ CH_2CH(CH_3)COOC_2H_5 \end{array}$$

(23) Melting points and boiling points are uncorrected. The cathode used was mercury in all cases.

(24) A purer sample was obtained in the diethyl fumarate experiment described below.

After recovery of 2–3 g. of starting ester, there was obtained 4.4 g. of adiponitrile and 5.9 g. of crude product, b.p. 180–190° (0.24 mm.). Redistillation yielded **methyl α-acetamido-δ-cyanovalerate** (IX), b.p. 166–174° (0.20 mm.), n^{25}_{D} 1.4680.

Anal. Calcd. for $C_9H_{14}N_2O_3$: C, 54.53; H, 7.12; N, 14.14; mol. wt., 198. Found: C, 54.87; H, 6.87; N, 14.25; mol. wt., 197.

IX Conversion to *dl*-Lysine Monohydrochloride.—A suspension of 3.8 g. of IX, 0.75 g. of Raney nickel,[14] and 1.0 g. of anhydrous sodium acetate in 15 ml. of acetic anhydride was shaken at room temperature with hydrogen at 50-lb. initial pressure for 4 hr. in a Parr apparatus. The mixture was filtered. Volatile materials were removed *in vacuo*. The sirupy residue was heated under reflux with 20 ml. of concentrated HCl for 7 hr. Volatile products were again removed *in vacuo*. The residual sirup was dissolved in 20 ml. of hot absolute ethanol, treated with charcoal, and filtered. Addition of an excess of dry ether precipitated 5.5 g. of a gum which was dissolved in 30 ml. of hot absolute ethanol and treated with 1.0 ml. of pyridine. After refrigeration, a small quantity of pyridine hydrochloride was removed. Addition of 10 drops of pyridine precipitated crude *dl*-lysine monohydrochloride. Further crops were obtained from the filtrate by careful addition of pyridine. The crude product was dissolved in 3 ml. of water, treated with charcoal, and filtered. Addition of 25 ml. of absolute ethanol followed by refrigeration yielded pure white crystals, 0.37 g., m.p. 264°.

In another preparation in which Adams' catalyst was used instead of Raney nickel the purified product melted at 267°.

Suberonitrile.—The catholyte contained 98 g. (1.8 moles) of acrylonitrile and 18.3 g. (0.23 mole) of freshly distilled 1-cyano-1,3-butadiene dissolved in 115 g. of 80% tetraethylammonium *p*-toluenesulfonate. The cathode voltage was regulated manually at −1.69 to 1.71 v. (*vs.* the saturated calomel electrode). The initial amperage was 3.0 and this was gradually reduced to 0.25 toward the end of the run. A total of 10.6 amp.-hr. (coulometer) was used. The temperature was maintained at 25° and the pH at *ca.* 8. The residual liquid, after removal of materials volatile at 30 mm. on the water bath, weighed 25.9 g. It was dissolved in 90 ml. of absolute ethanol containing 1.00 g. of 5% palladium on carbon and hydrogenated at room temperature at an initial pressure of 36 lb. The uptake was 14.25 lb., 0.166 mole (calcd. for hydrogenation of 1,6-dicyano-2-hexene, 15.4 lb., 0.179 mole). The saturated product (25.3 g.) was distilled. The first cut, 16.5 g., b.p. 150 (2.9 mm.) to 162° (3.2 mm.), n^{25}_{D} 1.4428, was virtually pure suberonitrile.

Anal. Calcd. for $C_8H_{12}N_2$: C, 70.54; H, 8.88; N, 20.57; mol. wt., 136. Found: C, 70.41; H, 9.09; N, 20.75; mol. wt., 138.

The final cut, b.p. 222 (0.47 mm.) to 226° (0.55 mm.), n^{25}_{D} 1.4732, had a molecular weight of 204–210 and 21.3% N, indicating a product with three nitrogen atoms.

Ethyl 7-Cyanoheptanoate.—The catholyte contained 88 g. (0.88 mole) of ethyl acrylate (stabilized by hydroquinone), 8.7 g. (0.11 mole) of cyanobutadiene, 43 g. of acetonitrile, and 99 g. of 80% tetraethylammonium *p*-toluenesulfonate. The cathode voltage was regulated at −1.67 to −1.70 v. which required gradually lowering the amperage from 2.7 to 0.25. A total of 5.0 amp.-hr. was passed. The operating temperature was 30–35°. The recovered crude product (12.4 g.) was hydrogenated as above and the saturated products were fractionated through a 2-ft. jacketed Vigreux column. The fractions (4.1 g.) containing the product of mixed coupling, b.p. 155–175° (18 mm.), were combined and refractionated to yield pure product boiling at 162–164° (18 mm.), n^{25}_{D} 1.4342.

Anal. Calcd. for $C_{10}H_{17}NO_2$: C, 65.54; H, 9.35; N, 7.64. Found: C, 65.44; H, 9.74; N, 7.43.

Higher boiling fractions contained mixtures of the cyano ester and sebaconitrile.

Diethyl α,α'-Bis(2-cyanoethyl)succinate.—The catholyte contained 100 ml. of acrylonitrile, 1.5 ml. of diethyl fumarate, 1.0 ml. of water, and 50 g. of tetraethylammonium *p*-toluenesulfonate. The anolyte contained 20 g. of 60% quaternary salt. During the electrolysis the cathode voltage was maintained at −1.48 to −1.50 v. by dropwise addition of 14.9 ml. of diethyl fumarate over a period of 7 hr. The temperature was 25° for the first 90 min. and 40° thereafter. The amperage was in the range of 1.50–0.50, total 6.0 amp.-hr. The crude product (21.0 g.) was fractionated through a 2-ft. Vigreux column. The fraction boiling at 129° (0.45 mm.), n^{25}_{D} 1.4430, was pure diethyl α-(2-cyanoethyl)succinate.

Anal. Found: C, 58.11; H, 7.53; N, 6.28.

Intermediate fractions were shown by vapor phase chromatographic analysis to consist of mixtures of tetraethyl butanetetracarboxylate and diethyl α-(2-cyanoethyl)succinate. The highest boiling fraction was redistilled and the product collected at 176–178° (0.25 mm.), n^{25}_{D} 1.4565.

Anal. Calcd. for $C_{14}H_{20}N_2O_4$: C, 59.98; H, 7.19; N, 9.99. Found: C, 59.75; H, 7.18; N, 10.19.

The proton magnetic resonance spectrum was determined at room temperature on the Varian A-60 spectrometer operating at 60 Mc./sec. Spectro Grade chloroform and carbon tetrachloride were used as solvents and tetramethylsilane as internal standard. The spectrum of the sample was obtained in *ca.* 25% solution by volume. The proton magnetic resonance spectra of known model compounds [adiponitrile and diethyl α-(2-cyanoethyl)succinate] were obtained by the same technique. The τ-values and the intensities of the signals of the unknown were used to assign the nonequivalent nuclei in a direct comparison with the model compounds: 8.7 (for 6.2 H of $CH_2\,C\mathit{H}_3$), 8.0 (for 4.1 H of $-C\mathit{H}_2$-CN), 7.4 (for 4.0 H of $-C\mathit{H}_2—C<$), 6.4 (for 1.9 H of $>C\mathit{H}$-C), and 5.8 (for 3.8 H of $—O—C\mathit{H}_2—$). These data indicated that structure XII was more probable than structure XIII.

Acknowledgment.—All instrumental analyses were performed by Donald Beasecker's group The proton magnetic resonance spectra were obtained and interpreted by Louis Boros.

Photolysis of Nortricyclanone Tosylhydrazone Sodium Salt

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Received October 30, 1963

Photochemical decomposition of nortricyclanone tosylhydrazone sodium salt (1) pursues a course rather different from that of the pyrolysis. 3-Nortricyclyl *p*-tolyl sulfone (5) is formed in yields as high as 50% under *aprotic* conditions. Irradiation of 1 in the presence of free nortricyclanone tosylhydrazone gives nortricyclanone N-tosyl-3-nortricyclylhydrazone (6), identical with a sample prepared by an independent synthesis. Mechanistic implications of these observations are discussed briefly.

Thermal decomposition of *p*-toluenesulfonylhydrazone (tosylhydrazone) salts has become an important method for the generation of carbenes.[1] Dauben's observation that irradiation of camphor tosylhydrazone sodium salt gave high yields of tricyclene, presumably *via* the carbene, suggested that photochemical decomposition of tosylhydrazone salts parallels closely the thermal process.[2] In a study of the behavior of nortricyclanone tosylhydrazone sodium salt (1) we have

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(1) See, for example, E. Chinoporos, *Chem. Rev.*, **63**, 235 (1963).

(2) W. G. Dauben and F. G. Willey, *J. Am. Chem. Soc.*, **84**, 1497 (1962).