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Electrolytic Reductive Coupling. XII.[1] Reactions with Styrene of the Intermediates Produced by Electrolytic Reductive Cleavage of Certain Cyanoalkylphosphonium Compounds

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The behavior of compounds $(C_6H_5)_3P^+(CH_2)_nCN\ X^-$ in which $n = 1$–4 was investigated in polarography, microcoulometry, and macroelectrolysis. When $n = 1$, a direct, two-electron reduction to $(C_6H_5)_3P$ and $(CH_2CN)^-$ occurs. A pseudo-one-electron reduction is actually measured, because the $(CH_2CN)^-$ generated exclusively attacks the parent ion to form CH_3CN and $(C_6H_5)_3P{=}CHCN$ thus engaging two molecules of starting material in reaction with two electrons. Large-scale electrolyses in the presence of styrene yield no coupled products or mercurials. When $n = 2$–4, an initial, one-electron reduction is observed indicating the formation first of a discharged onium ion. Depending upon the stability of the latter, it may (a) undergo decomposition at the mercury surface to form "amalgamated" cyanoalkyl radicals which at the first wave rearrange to cyanoalkyl mercurials and at the second wave are reduced to cyanoalkyl anions and (b) migrate away from the cathode before it decomposes, in which case the radicals formed by decomposition enter into reaction with substrates. Bulk electrolyses of the compounds in which $n = 2$–4 in excess styrene yield $C_6H_5(CH_2)_{n+2}CN$ and $[CN(CH_2)_n]_2Hg$.

It has been pointed out previously[2] that mixed reductive coupling between activated olefins I and II, in which E and E′ are the nonreducible electron-withdrawing groups specified in previous papers in


$>C{=}C{<}^{E}$

I


$>C{=}C{<}^{E'}$

II

this series, may lead to either two or three products. If I, *e.g.*, is reduced at a cathode voltage at least about 0.2 v more positive than is II, and if the mixture is electrolyzed at a controlled voltage close to that required for I alone, then only the hydro dimer of I and the mixed coupled product are formed. When, however, the nature of E and E′ (say CN and C_6H_5, respectively) is such that I and II differ greatly in nucleophilicity, then virtually no mixed coupling occurs. Electrolysis of a mixture of acrylonitrile (−1.9)[3] and excess styrene (−2.3)[3] yielded adiponitrile, acrylonitrile hydrooligomers, no polystyrene, and only a trace of 5-phenylvaleronitrile. On the hypothesis[2] that β-to-β electrolytic reductive coupling of activated olefins may represent the first stage of anionic polymerization these results are in agreement with the statement of Fueno, *et al.*,[4] that "the case of polarographic reduction of vinyl monomers is *roughly*[5] parallel to their anionic polymerizability."

While the possibility of reductively coupling acrylonitrile with a more difficultly reducible monomer is therefore poor, another route to such products containing a cyanoethyl moiety is available. A cyanoethyl intermediate (radical, anion) may be generated by electrolytic cleavage[1] of $L^+CH_2CH_2CN$ (where L is a "leaving group"), and this intermediate, now formed in the virtual absence of acrylonitrile,[6] is free to attack other substrate species. Thus electrolysis of β-cyanoethyltriphenylphosphonium *p*-toluenesulfonate in the presence of excess styrene yielded 5-phenylvaleronitrile (and other products). These results and their bearing on the mechanism of the reductive cleavage prompted a broader investigation, the subject of this report, on reductive couplings with $(C_6H_5)_3P^+(CH_2)_n$-CN.[8]

Results and Discussion

Polarography.—The polarographic data for a series of cyanoalkylphosphonium salts are given in Table I.

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[1] Paper XI: M. M. Baizer, *J. Org. Chem.*, **31**, 3847 (1966).

[2] M. M. Baizer, *Tetrahedron Letters*, 973 (1963).

[3] Figures in parentheses refer to the polarographic half-wave (*vs.* the saturated calomel electrode, sce) of the individual compounds.

[4] T. Fueno, K. Asada, K. Morokuma, and J. Furukawa, *J. Polymer Sci.*, **40**, 511 (1959).

[5] Italics ours. Acrylate esters (*ca.* −1.8)[2] and maleate esters (*ca.* −1.4)[2] reduce more easily than acrylonitrile (−1.9)[2] but are not so readily anionically polymerized. Steric factors which are not important when only electrons are added to the β position of activated olefins must play an important role when carbanions are added instead.

[6] The occurrence of any Hofmann-type degradation will lead to some acrylonitrile. The ready cleavage of HX from 3-halopropionitriles makes the latter of dubious value in bulk electrolyses for the generation of cyanoethyl in the absence of acrylonitrile.[7]

[7] L. G. Feoktistov and S. I. Zhdanov, *Izv. Akad. Nauk. SSSR*, 2127 (1962).

[8] The polarography of related sulfonium salts will be reported elsewhere.

TABLE I

POLAROGRAPHIC DATA FOR $(C_6H_5)_3P^+(CH_2)_nCN\ X^-$ IN DIMETHYL SULFOXIDE (DMSO)

Compd	L	n	X	$E_{1/2}$[a]	I_d[b]	Electrolyte
III	$(C_6H_5)_3P$	1	Br	−1.48	0.80	*c*
				−2.26	0.55	
				−2.56	0.44	
IV	$(C_6H_5)_3P$	2	T[d]	−1.74	1.08 (0.77)	*c*
				−2.65	0.81	
IV				−1.76	0.94 (0.79)	*e*
				−2.70	0.75	
V	$(C_6H_5)_3P$	3	Br	−1.80	0.77	*c*
				>−2.5[f]	. . .	
V				−1.81	0.81	*e*
				−2.52	0.42	
				−2.74	0.65	
VI	$(C_6H_5)_3P$	4	Br	−1.83	0.84	*c*
				>−2.5[f]	. . .	
VI				−1.84	0.78	*e*
				−2.60	0.41	
				−2.77	0.37	

[a] *Vs.* sce. Depolarizer concentration, 1 m*M*. [b] $I_d = i_d/\text{cm}^{2/3}t^{1/6}$. [c] Tetrabutylammonium bromide, 0.2 *M*. [d] *p*-Toluenesulfonate. [e] Tetraheptylammonium iodide, 0.2 *M*. [f] Very poorly formed waves.

Coulometric values for compounds III–VI indicate initial one-electron reductions in each case. Certain other phosphonium compounds have also been reported to be reduced in a one-electron step.[9–11] It is noteworthy that the cyano group has a definite but decreasing influence upon $E_{1/2}$ when $n = 1$, 2, or 3. This influence[12] does not extend to $n = 4$, for *n*-butyltriphenylphosphonium bromide reduces (−1.84) at about the same voltage as does VI when both are measured using the same electrolyte and solvent.

Compound III shows three reduction waves. The apparent one-electron reduction indicated by the *first wave* is not consistent with our interpretation of the genesis of the products obtained in large-scale reductions (see below); further, the addition of a small amount of acetic acid to the polarographic solution causes the value of I_d to double. This suggests that the one-electron reduction recorded is the resultant of a two-electron reduction and a succeeding chemical reaction which consumes half the starting material as it approaches the mercury drop. When acetic acid is

$$(C_6H_5)_3P^+CH_2CN \xrightarrow{2e} (C_6H_5)_3P + (CH_2CN)^- \qquad (1)$$

$$(C_6H_5)_3P^+CH_2CN + (CH_2CN)^- \longrightarrow (C_6H_5)_3P{=}CHCN + CH_3CN \qquad (2)$$

included, $(CH_2CN)^-$ is discharged as formed, and *all* the phosphonium ion is then available for reduction.[13] The *second wave* for III is the reduction of $(C_6H_5)_3P{=}CHCN$.[16] The *third wave* is due to the reduction of triphenylphosphine.[11]

Two polarograms for IV are shown in Figure 1. With added phenol as a proton donor (curve a) two waves are observed, the second having a large maximum. These waves represent the following reductions (eq 3 and 4). In the absence of phenol (curve b) the

$$\text{first wave, IV} \xrightarrow{1e^-} (C_6H_5)_3\dot{P}CH_2CH_2CN\|Hg_n{}^{18} \longrightarrow (C_6H_5)_3P + Hg_n\|\cdot CH_2CH_2CN^{18} \qquad (3)$$

$$\text{second wave, } Hg\|\cdot CH_2CH_2CN \xrightarrow{1e^-} (-)CH_2CH_2CN \xrightarrow[H^+]{\text{phenol}} CH_3CH_2CN \qquad (4)$$

second wave is absent because IV may serve as proton donor[19] for the neutralization of the anion formed in eq 4; two molecules of IV become involved in a two-electron reduction giving an over-all pseudo-one-electron reduction (eq 5). Although the second wave

$$IV + (-)CH_2CH_2CN \longrightarrow (C_6H_5)_3\overset{+}{P}CH_2\overset{-}{C}HCN + CH_3CH_2CN \qquad (5)$$

does not appear in the absence of phenol, the phenomena causing the maximum still occur to some extent in the absence of phenol and these are the cause of the unusual polarogram. The I_d values for the first wave of IV (Table I) were measured at the top of the "hump," and those in parentheses were measured after the maximum ended. The *second wave* for IV (Table I) is the reduction of triphenylphosphine and is not shown in Figure 1. Controlled-potential coulometry of IV at −2.0 v *vs.* sce verified that a one-electron reduction was involved at the first wave; values for *n* of 1.00 and 0.99 were obtained.

Three polarographic reduction waves were obtained for V and for VI. The *first wave* corresponds to a one-electron reduction of the phosphonium ion. This was verified in the case of V by controlled-potential coulometry at −2.0 v *vs.* sce. The *third wave* is the reduction of triphenylphosphine formed after decomposition of the discharged phosphonium ion. The *second wave* is probably comparable with the second wave obtained for IV in the presence of phenol, that is, reduction of the cyanoalkyl radical to the corresponding anion. The second waves are not due to the reduction of the biscyanoalkylmercury compounds since even biscyanoethylmercury, which should reduce at a more positive potential than biscyanopropylmercury, reduces at $E_{1/2} = -2.74$ v *vs.* sce.[20] It is not possible to eliminate a direct, two-electron reduction of the phosphonium ion at the second wave although one would then expect the I_d value for the second wave to be nearly as high as the I_d value for the first wave. The I_d values for the second wave are only about half as high as those for the first waves indicating that

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(9) E. L. Colichman, *Anal. Chem.*, **26**, 1204 (1954).

(10) L. Horner, F. Röttger, and H. Fuchs, *Chem. Ber.*, **96**, 3141 (1963).

(11) J. H. Wagenknecht, Ph.D. Thesis, State University of Iowa, 1964.

(12) Lüttringhaus[8] has reported the effect of certain substituted alkyl groups, not including cyanoalkyls, upon the $E_{1/2}$ of sulfonium compounds.

(13) Single two-electron reduction waves have been reported for benzyltriphenylphosphonium chloride[10] and tetra-*o*-tolylphosphonium iodide.[9] It seems likely that in these cases the stability of the anions formed by reductive cleavage of the starting compounds favors a two-electron process, but the lower acidity of any of the protons in these phosphonium ions compared with the acidity of the methylene protons of III does not allow a sequence of the type shown in eq 1 and 2 to occur. An analogy to the events depicted in eq 1 and 2 may be found in the lowering of the wave height for acetaldehyde when it is reduced in the presence of formaldehyde;[14] a closer analogy exists in the reduction of acrylonitrile under conditions leading to hydro-oligomerization.[15]

(14) P. Zuman, "Organic Polarographic Analysis," The Macmillan Co., New York, N. Y., 1964, p 8.

(15) M. Murphy, M. G. Carangelo, M. Ginaine, and M. Markham, *J. Polymer Sci.*, **54**, 107 (1961).

(16) The $E_{1/2}$ for $(C_6H_5)_3P{=}CHCN$, independently prepared,[17] was found to be −2.27 v.

(17) S. Trippett and P. M. Walker, *J. Chem. Soc.*, 3874 (1959).

(18) $Hg_n\|$ indicates that the species is adsorbed on the mercury surface and is comparable with the amalgamated radical described by Horner.[10]

(19) The acidity of the proton α to the methylene group has been discussed: M. M. Baizer and J. D. Anderson, *J. Org. Chem.*, **30**, 1357 (1965).

(20) A. P. Tomilov and Yu D. Smirnov, *Zh. Vses. Khim. Obshchestva im. D. I. Mendeleeva*, **10**, 101 (1965); *Chem. Abstr.*, **63**, 3897*g* (1965).

a substantial portion of X, the product of the first reduction (eq 8), is not available for further reduction within the lifetime of the drop. The depletion of X may be due to the decomposition of eq 10 leading to radicals in solution or, less likely within this time period, to dimerization and disproportionation of XII which result in nonelectroreducible species.

Our interpretation of the polarographic data is summarized in eq 6–11.

$$\text{first wave, } (C_6H_5)_3P^+(CH_2)_nCN \xrightarrow[\text{Hg}]{1e} \underset{\text{X}}{(C_6H_5)_3\dot{P}(CH_2)_nCN||Hg_n}\text{[18]} \quad (6)$$

$$X \longrightarrow \underset{\text{XI}}{(C_6H_5)_3\dot{P}(CH_2)_nCN} \text{ (in solution)} + Hg \quad (7)$$

$$X \longrightarrow (C_6H_5)_3P + \underset{\text{XII}}{[\cdot Hg(CH_2)_nCN]} \quad (8)$$

$$\text{second wave, XII} \xrightarrow{1e} Hg + (-)(CH_2)_nCN \quad (9)$$

$$XI \longrightarrow (C_6H_5)_3P + \cdot(CH_2)_nCN \text{ (in solution)}\text{[21]} \quad (10)$$

$$\text{third wave, } (C_6H_5)_3P \xrightarrow{1e} (C_6H_5)_3P\cdot^- \quad (11)$$

No radicals were detected during electrolysis of IV and VI *intra muros* in the esr spectrometer.

Electrolytic Reductive Couplings.—The products obtained from large-scale electrolyses of these onium compounds in the presence of excess styrene are given in Table II. The cathode potential was maintained at the potential of the first polarographic wave during the electrolyses. The electrolyses were usually carried to complete consumption of the onium salts as evidenced by the terminal rise in cathode voltage.

TABLE II

PRODUCTS OBTAINED FROM ELECTROREDUCTIONS OF $(C_6H_5)_3P^+(CH_2)_nCN$ IN THE PRESENCE OF STYRENE

	Yield[a] of product, %			
Product	III	IV	V	VI
$(C_6H_5)_3P$	26.4	58–74	82.5	57
$(C_6H_5)_3PO$	23.6	...	...	...
$CH_3(CH_2)_nCN$	b (0)[c]	b (1)	b (2)	b (3)
C_6H_6	...	14	...	10
$C_6H_5(CH_2)_nCN$	...	13.5 (4)	10 (5)	10 (6)
$[CN(CH_2)_n]_2Hg$	...	b (2)	d (3)	b (4)
$CH_2{=}CHCN$	...	b	...	...
$CN(CH_2)_nCN$	...	b (4)	...	...
$CN(CH_2)_nCHC_6H_5$ $\vert$ $CN(CH_2)_nCHC_6H_5$	...	6 (3)	...	...

[a] Based on one faraday per mole. [b] Products isolated or detected but no yield determined. [c] Values in parenthesis are for *n* in the general formula of the product. [d] Evidence of these compounds is based on nmr spectra.

In the electrolysis of III the absence of 4-phenylbutyronitrile or mercurial among the products supports the mechanism of reduction proposed in eq 1 and 2. Styrene was unable to compete with III for capture of the carbanion formed by reductive cleavage. The $(C_6H_5)_3P{=}CHCN$ formed apparently reacted with water during the work-up to form the $(C_6H_5)_3PO$ actually obtained.[22]

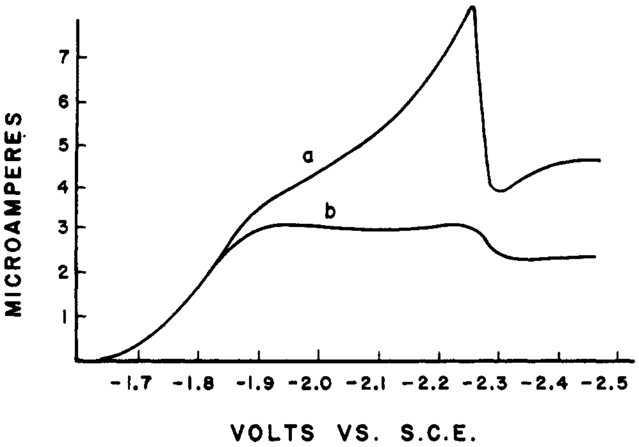


Figure 1.—The polarogram of (a) 1 m*M* triphenylcyanoethylphosphonium *p*-toluenesulfonate in dimethylformamide containing 0.2 *M* tetra-*n*-butylammonium bromide with phenol added and (b) the same without added phenol.

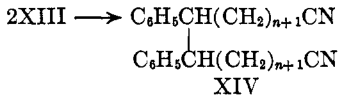
The products obtained from the other phosphonium compounds (n = 2–4) suggest the following general reaction scheme (eq 12–17).

$$XII \longrightarrow 0.5[CN(CH_2)_n]_2Hg + 0.5Hg \quad (12)$$

$$XI \longrightarrow (C_6H_5)_2P(CH_2)_nCN + (C_6H_5)\cdot \xrightarrow{\text{solvent}} C_6H_6 \quad (13)$$

$$XI \longrightarrow (C_6H_5)_3P + \cdot(CH_2)_nCN \xrightarrow{\text{solvent}} CH_3(CH_2)_{n-1}CN \quad (14)$$

$$\cdot(CH_2)_nCN \xrightarrow{\text{styrene}} \underset{\text{XIII}}{C_6H_5\dot{C}H(CH_2)_{n+1}CN} \xrightarrow{\text{solvent}} C_6H_5(CH_2)_{n+2}CN \quad (15)$$



$$2XIII \longrightarrow \underset{\text{XIV}}{\begin{array}{l} C_6H_5CH(CH_2)_{n+1}CN \\ \quad\ \vert \\ C_6H_5CH(CH_2)_{n+1}CN \end{array}} \quad (16)$$

$$XIII \xrightarrow{\text{styrene}} \text{oligomers} \quad (17)$$

The following specific points merit special mention.

(1) The small amount of acrylonitrile formed during the electrolysis of IV may be due to a Hofmann degradation of IV[23] or, more likely, an intramolecular nucleophilic displacement[17] of $(C_6H_5)_3P$ from the zwitterion formed in eq 5.

(2) The adiponitrile may be formed by electrochemical hydrodimerization of some of the acrylonitrile liberated or by attack upon acrylonitrile of the β-cyanoethyl carbanion arising according to eq 4; we consider it much less likely in view of the excess of styrene present that it arises from coupling of cyanoethyl radicals, present in low concentration, which have been formed by decomposition of XI in the bulk of the solution (eq 14).

(3) The only example of bimolecular mixed coupled product (XIV) actually isolated and identified was the one in which n = 2. The dinitrile obtained was con-

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[21] Those radicals formed in solution are likely to undergo other reactions before they could reach the mercury surface. We would offer the more general hypothesis that when organometallics are formed at an electrode they arise *via* electronic reorganization of the electrode–organic moiety complex—followed where appropriate by dimerization and disproportionation—rather than *via* attack of a returning "free" radical upon the electrode.

[22] It was established separately that $(C_6H_5)_3P{=}CHCN$ dissolved in DMF–water was completely decomposed to $(C_6H_5)_3PO$ in less than 2 hr at 25°.

[23] Hofmann degradation would be expected to lead predominantly to $(C_6H_5)_3PO$ and CH_3CH_2CN; for analogous cases, see H. Hoffmann, *Ann.*, **634**, 1 (1959).

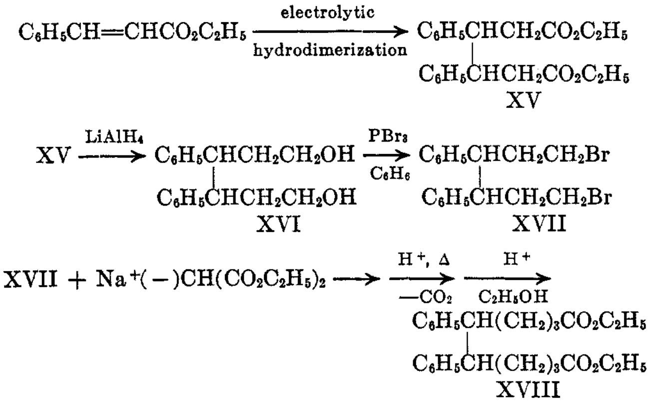
TABLE III

CONDITIONS FOR THE ELECTROREDUCTION OF III–IX IN THE PRESENCE OF STYRENE[a]

			Catholyte								
Expt	Cell	Compd	Wt, g	Moles	Ml of DMF[b]	Electrolyte,[c] g	Anolyte	Temp, °C	Amp	Cathode voltage *vs.* sce	Faradays
1	A	III	25	0.065	200	None	*d*	40–60	0.5	−1.1 to −1.5	0.065
2	A	IV	97.4	0.2	130	None	*e*	15	1.5	−1.58 to −1.60	0.2
3	B	IV	73	0.15	150[f]	25	*g*	20	0.25–0.20	−1.56 to −1.75	0.156
4	A	V	25	0.061	200	None	*d*	35–40	0.5	−1.60 to −1.75	0.065
5	A	VI	25	0.059	200	None	*d*	55–60	0.5	−1.50 to −1.60	0.065
6	A	VI	25	0.059	200	None	*d*	35	0.5	−1.55 to −1.71	0.073
7	B	VI	25	0.059	200	25	*h*	30	0.3–0.05	−1.65 to −1.85	0.059
8[i]	B	VI	25	0.059	200	None	*h*	30	0.30	−0.8 to −2.30	0.048

[a] Styrene (30 ml) was used in each run. [b] Dimethylformamide. [c] Tetraethylammonium *p*-toluenesulfonate. [d] Tetra-*n*-butylammonium bromide in dimethylformamide. [e] Tetraethylammonium *p*-toluenesulfonate in dimethylformamide. [f] Dimethyl sulfoxide was the solvent in this experiment. [g] A mixture of dimethyl sulfoxide, hexene, and tetra-*n*-butylammonium bromide. [h] A mixture of dimethylformamide, hexene, and tetra-*n*-butylammonium bromide. [i] A platinum foil cathode was used.

verted to the corresponding diester identical with XVIII independently prepared by the following sequence.[24]



$$C_6H_5CH{=}CHCO_2C_2H_5 \xrightarrow[\text{hydrodimerization}]{\text{electrolytic}} \begin{array}{c} C_6H_5CHCH_2CO_2C_2H_5 \\ | \\ C_6H_5CHCH_2CO_2C_2H_5 \\ \text{XV} \end{array}$$

$$\text{XV} \xrightarrow{LiAlH_4} \begin{array}{c} C_6H_5CHCH_2CH_2OH \\ | \\ C_6H_5CHCH_2CH_2OH \\ \text{XVI} \end{array} \xrightarrow[C_6H_6]{PBr_3} \begin{array}{c} C_6H_5CHCH_2CH_2Br \\ | \\ C_6H_5CHCH_2CH_2Br \\ \text{XVII} \end{array}$$

$$\text{XVII} + Na^{+}(-)CH(CO_2C_2H_5)_2 \longrightarrow \xrightarrow[-CO_2]{H^{+},\ \Delta} \xrightarrow[C_2H_5OH]{H^{+}} \begin{array}{c} C_6H_5CH(CH_2)_3CO_2C_2H_5 \\ | \\ C_6H_5CH(CH_2)_3CO_2C_2H_5 \\ \text{XVIII} \end{array}$$

(4) The structures of the mercurials obtained are based on nmr data and structure proof of one representative, biscyanobutylmercury. The latter reacted with HCl to form valeronitrile and cyanobutylmercuric chloride. The nmr spectrum consisted of a triplet at τ 8.92 for the methylenes α to mercury, a multiplet centered at 8.25 for the β and γ methylenes, a triplet at 7.68 for the methylenes α to the nitrile, and a small triplet at 9.79 due to splitting of the methylene α to the mercury by Hg^{199}. The other half of this splitting would be under the β and γ methylene peaks.

(5) When platinum rather than mercury is used as a cathode, no analogs of X and XII are formed, and more products arising from the reaction of free radicals in solution are obtained. Electrolysis of VI at platinum in the presence of excess styrene gave a nitrile-containing polystyrene.

Experimental Section[25]

The polarographic data were obtained using a Sargent Model XXI polarograph. Electrode constants were m = 2.216 mg/sec, t = 3.43 sec, and $m^{2/3}t^{1/6}$ = 2.08 $mg^{2/3}sec^{-1/2}$ at a mercury column height of 90 cm. The cells were immersed in a thermostated water bath at 25 ± 0.1°. Coulometric data were obtained using a Beckman Electroscan 30. Nuclear magnetic resonance analyses were carried out with a Varian A-60 nuclear magnetic resonance spectrometer. Preparative gas chromatography utilized a F & M Model 770 preparative gas chromatograph with a 12 ft × 3/4 in. column packed with 18% Carbowax 20 M–1% $AgNO_3$ on Chromasorb W. Analytical gas chromatography was carried out with 3 m × 1/4 in. columns packed with 18% Carbowax 20–1% $AgNO_3$ on Chromasorb W, 3% XE-60 on Teflon, 3% Flexol 8N8 on Teflon, or silicone grease on Chromasorb W. In general vpc analyses were done on two or more columns to ensure the identity of the peak. The vpc rapid-scan mass analyses were carried out with a F & M Model 810 dual hydrogen flame chromatograph attached to a C.E.C 21-130 mass spectrometer modified for rapid scan. Electron spin resonance analyses were carried out with an X-band Varian epr spectrometer with 100-kc modulation.

The dimethyl sulfoxide (Matheson Coleman and Bell) used for polarography was distilled at reduced pressure from a small amount of sodium hydride, bp 58–60° (5 mm). The dimethylformamide was distilled before use. Styrene (Eastman) was distilled *in vacuo* just before use and stabilized with hydroquinone. Both tetrabutylammonium bromide (Eastman) and tetraheptylammonium iodide (Eastman) were recrystallized from ethyl acetate before use. Tetraethylammonium *p*-toluenesulfonate (Alfred Bader Chemical Co.) was recrystallized from acetone.

The electrolytic cell used in most of the bulk electrolyses and the general operating procedure has been described[26] (cell A). In some cases a glass H-type cell (cell B) was used. The cathode compartment had a capacity of 200 ml and was fitted with a mercury pool contact, stirrer, thermometer, and reference electrode. The anode compartment (separated from the cathode compartment by a medium-porosity glass frit) had a capacity of 75 ml and was fitted with a platinum foil anode. The anolyte used in cell B was a mixture of solvent, tetrabutylammonium bromide, and cyclohexene. The bromine formed at the anode reacts with the cyclohexene. The procedure was adopted to prevent formation of acidic products which diffuse to the catholyte when tetraethylammonium *p*-toluenesulfonate is used in the anolyte. In most cases an Analytical Instruments, Inc., current integrator was used during the electrolyses.

The conditions for the **electroreduction of III–VI in the presence of styrene** are summarized in Table III. The isolation and identification of products from individual runs follow.

Experiment 1.—The solvent was removed from the catholyte by distillation at reduced pressure. The Dry Ice–acetone cooled trap from this distillation contained acetonitrile (vpc). The residue after distillation was treated with 500 ml of water and extracted with ether. Evaporation of the ether extract yielded a residue which contained no nitrile (infrared). Several washings of the residue with boiling hexane yielded 4.25 g (23.6%) of triphenylphosphine oxide, mp 154–155°, which crystallized from the cooled hexane extracts. Evaporation of the hexane mother liquor yielded a residue of 4.5 g (26.4%) of triphenylphosphine, mp 74–76° after recrystallization from ethanol.

Experiment 2.—The mercury was separated, and the catholyte was diluted with ice water and extracted with six portions of ether and then one portion of methylene chloride. From the dried ether extract first the ether was distilled at atmospheric pressure and than a fraction was collected in a Dry Ice–acetone trap at 60–70° (15 mm) (bath temperature). The latter contained excess styrene, some DMF, AN, and propionitrile. It was fractionated in the presence of hydroquinone through a

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[24] An attempt to prepare XVIII in one step by electrohydrodimerization of ethyl styrylacrylate failed: coupling occurred β rather than δ to the ester group. See the Experimental Section.

[25] Boiling points are not corrected.

[26] M M. Baizer, *J. Electrochem. Soc.*, **111**, 215 (1964).

Todd–Vigreux column collecting the portion boiling at 63–95°. This fraction contained (vpc identification and analysis) 0.45 g of AN and 0.35 g of propionitrile. The undistilled material in the ether fraction (44.5 g) solidified. Crystallization from alcohol yielded 28.2 g (0.11 mole) of triphenylphosphine. The alcoholic mother liquor was distilled yielding (1) 4.3 g (0.027 mole) of 5-phenylvaleronitrile, bp 80–92° (0.3 mm), $n^{24}\text{D}$ 1.5140, hydrolyzed to 5-phenylvaleric acid identical with an authentic sample (Aldrich); (2) 5.4 g (0.021 mole) of triphenylphosphine, bp 142–152° (0.35 mm), mp 76.5–78°; (3) an intermediate, syrupy fraction, 1.1 g $n^{24}\text{D}$ 1.5780, bp, 155–170° (0.35 mm); (4) 2.1 g, bp 170–197° (0.35 mm); (5) a normal distillation residue of 1.0 g. The material of fraction 4 after crystallization and recrystallization from alcohol yielded dimer XIV ($n = 2$) melting at 93–95°.

Anal. Calcd for $(C_{11}H_{12}N)_2$: C, 83.49; H, 7.64; N, 8.85. Found: C, 83.07; H, 7.41; N, 8.87.

The residue from the methylene chloride extract (2.7 g) contained mainly 5-phenylvaleronitrile (vpc).

Hydrolysis of XIV ($n = 2$) with aqueous hydrochloric acid yielded the corresponding diacid, mp 177–178°, of undetermined stereochemistry.

Anal. Calcd for $C_{22}H_{26}O_4$: C, 74.55; H, 7.39. Found: C, 74.55; H, 7.62.

Esterification with ethanol and *p*-toluenesulfonic acid yielded the diester, bp 180° (0.05 mm), $n^{23}\text{D}$ 1.5190, whose nmr spectrum was identical (except for shoulders and broadening of peaks due to a mixture of *dl* and *meso* isomers) with that of diethyl 5,6-diphenyldecanedioate prepared by the independent synthesis described later below.

Experiment 3.—Vpc analysis of the solvent removed from the catholyte by distillation at reduced pressure (5 mm) indicated the presence of 1.7 g (14.5%) of benzene. The residue, after solvent removal, was treated with cold ethanol to precipitate 25.5 g of triphenylphosphine. Evaporation of the ethanol mother liquor yielded an oil which was found to contain biscyanoethylmercury by its characteristic nmr pattern.

Experiment 4.—The work-up, which was as described for experiment 3, yielded a small amount of butyronitrile (vpc), 13.5 g of triphenylphosphine (87.5%), and 1.1 g (10%) of 6-phenylcapronitrile, bp 100–110° (0.7 mm). Hydrolysis of the 6-phenylcapronitrile with basic peroxide yielded 6-phenylcaproamide, mp 93.5–94° (lit.[27] mp 94–96°). A considerable amount of mercury was formed during distillation of the products.

Anal. Calcd for $C_{12}H_{17}NO$: C, 75.35; H, 8.96. Found: C, 75.80; H, 9.11.

Experiment 5.—The work-up, which was as described for experiment 3, yielded a small amount of valeronitrile (vpc), 9.5 g (57%) of triphenylphosphine, 1.5 g (10%) of 7-phenylheptanonitrile, bp 110–130° (0.3 mm) [lit.[28] bp 173–178° (15 mm)], and 1.1 g of mercury (obtained in product distillation). The 7-phenylheptanonitrile was purified by preparative vpc. The nmr spectrum of purified material contained a multiplet at τ 8.58 (7.8 H) for the four isolated methylenes, a triplet at 7.83 (2.1 H) for the methylene α to the nitrile, a triplet at 7.42 (2.1 H) for the methylene α to the phenyl, and a single peak 2.87 (5 H) for the hydrogens on the benzene ring. Vpc mass spectral anaysis showed the parent ion of 7-phenylheptanonitrile at *m/e* 187.

Experiment 6.—A second electrolysis was carried out essentially as the first. After solvent removal approximately 1 g of biscyanobutylmercury was obtained by chromatographing on alumina and eluting with benzene. The mercurial was distilled in a short-path distillation apparatus at reduced pressure (0.2 mm), $n^{23}\text{D}$ 1.5238. The nmr spectrum is described in the Discussion. Treatment of the biscyanobutyl mercury in ether with anhydrous HCl yielded valeronitrile (vpc) and a solid precipitate, cyanobutylmercuric chloride, mp 76–77° dec.

Anal. Calcd for C_5H_8ClHgN: C, 18.87; H, 2.53; Cl, 11.15; Hg, 63.04; N, 4.40. Found: C, 18.80; H, 2.70; Cl, 10.98; Hg, 63.01; N, 4.39.

Experiment 7.—A third electrolysis was carried out, this time in cell B. Distillation of the catholyte at 10 mm to remove solvents yielded 0.5 g (10%) of benzene (vpc).

Experiment 8.—A fourth electrolysis was carried out like the third, except that a platinum foil cathode was used. Removal of the solvent by distillation at reduced pressure left a residue which upon addng to a large excess of methanol yielded a white, gummy mass. Repeated reprecipitation of this material by dissolving it in benzene and adding this solution dropwise to methanol yielded 4 g of polystyrene, softens at 78–90°. The infrared spectrum (film) was identical with that of an authentic sample except for a small adsorption at 4.5 μ, indicating nitrile.

Anal. Calcd for $(C_8H_8)_n$: C, 92.26; H, 7.74. Found: C, 91.06; H, 7.85; N, 0.70.

Preparation of Diethyl 5,6-Diphenyldecanedioate (XVIII).—The electrohydrodimerization of ethyl cinnamate was carried out by a general procedure previously described.[29] Treatment of the product with ethanol caused one of the isomers of the *dl-meso* mixture to precipitate nearly quantitatively. The liquid isomer of XV, diethyl 3,4-diphenyladipate, obtained by evaporation of ethanol from the mother liquor, was used in the next step.

A mixture of 100 g of the liquid isomer, 1 l. of dry tetrahydrofuran (THF), and 11 g of lithium aluminum hydride ($LiAlH_4$) was refluxed for 2 days under N_2. The excess $LiAlH_4$ was decomposed with water and after filtering the THF was stripped from the solution. Chromatography of the crude product on alumina, eluting first with benzene and then with methanol, yielded, in the methanol eluate, 20 g (26%) of XVI, 3,4-diphenylhexane-1,6-diol,[30] bp 172° (0.1 mm), mp 95–97°.

Anal. Calcd for $C_{18}H_{22}O_2$: C, 79.96; H, 8.20. Found: C, 80.15; H, 8.43.

To a mixture of 20 g of 3,4-diphenylhexane-1,6-diol, 125 ml of benzene, and 4 ml of pyridine at 10° was added 44 g of freshly distilled phosphorus tribromide. The mixture was stirred at 60° for 2 hr and then poured onto ice. This mixture was extracted with benzene. Distillation of the benzene extract yielded 20 g (68%) of XVII, 1,6-dibromo-3,4-diphenylhexane,[31] bp 178° (0.1 mm). The material was recrystallized from ethanol giving white crystals, mp 62–64°.

Anal. Calcd for $C_{18}H_{20}Br_2$: C, 54.56; H, 5.09; Br, 40.34. Found: C, 54.88; H, 5.20; Br, 39.73.

To a mixture of 20 ml of DMF and 1.5 g of 55% sodium hydride dispersion was added 4.86 g of diethyl malonate. To this mixture was added 6 g of the above 1,6-dibromo-3,4-diphenylhexane. This mixture was stirred at 100° for 2 hr and then poured into water. The aqueous mixture was extracted with dichloromethane. The residue after solvent removal from the organic extract was refluxed with 50 ml of concentrated hydrochloric acid for 24 hr. The acid solution was extracted with dichloromethane, and the residue obtained upon evaporation of the dichloromethane was heated at about 150° for 24 hr. The cooled material was treated with 5% sodium hydroxide and this extracted with dichloromethane. The aqueous layer was acidified with hydrochloric acid yielding 2 g (37%) of crude 5,6-diphenyldecanedioic acid,[30] mp 205–208°. Recrystallization from ethanol yielded 1 g, mp 207–208°.

Anal. Calcd for $C_{22}H_{26}O_4$: C, 74.54; H, 7.39. Found: C, 74.34; H, 7.14.

About 1 g of the diacid was esterified with ethanol and *p*-toluenesulfonic acid yielding a few drops of XVIII, diethyl-5,6-diphenyldecanedioate,[30] bp 194–195° (0.1 mm), $n^{24}\text{D}$ 1.5200.

Anal. Calcd for $C_{26}H_{34}O_4$: C, 76.06; H, 8.36. Found: C, 76.04; H, 8.03.

The nmr spectrum of XVIII consisted of a multiplet at τ 2.99 (10 H) for the aromatic hydrogens, a quartet at 5.98 (4 H), and a triplet at 8.86 (6 H) for the ethoxy groups, a multiplet at 7.20 (4 H) for the hydrogens α to the phenyls, a triplet at 7.87 (4 H) for the methylenes α to the carbonyl groups, and a multiplet at 8.45 (8 H) for the methylenes β and γ to the carbonyl groups.

Preparation of Triphenylcyanomethylphosphonium Bromide (III).—Triphenylphosphine (94.4 g, 0.36 mole) was quaternized with 27.2 g (0.36 mole) of chloroacetonitrile in 40 ml of ethyl acetate by refluxing for 90 min. The crude chloride (82.5% yield) was dissolved in water and filtered to remove a trace of insoluble material. To the clear filtrate was added an excess of potassium bromide solution. The precipitated quaternary bromide was recovered and recrystallized from alcohol, mp 251–253° (lit.[31] mp 256–258°).

Preparation of Triphenylcyanoethylphosphonium *p*-Toluenesulfonate (IV).—The method employed was an adaptation of one

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[27] E. Wenkert and B. F. Barnett, *J. Am. Chem. Soc.*, **82**, 4671 (1960).

[28] J. V. Braun, *Ber.*, **44**, 2877 (1911).

[29] M. M. Baizer and J. D. Anderson, *J. Electrochem. Soc.*, **111**, 223 (1964).

[30] The stereochemistry was not determined.

[31] G. P. Schiemenzet and H. Engelhard, *Chem. Ber.*, **94**, 578 (1961).

developed[32] for the preparation of the corresponding bromide. A mixture of 131 g (0.5 mole) of triphenylphosphine, 95 g (0.5 mole) of *p*-toluenesulfonic acid monohydrate, and 100 ml (excess) of stabilized acrylonitrile was heated for 40 min under reflux. Volatile materials were then removed on the water bath *in vacuo*. The residue was taken up in 300 ml of water and filtered. The filtrate was concentrated to dryness *in vacuo*. The residue was recrystallized from acetone yielding 220 g (90.6%) of product, mp 104–105.5°.

Anal. Calcd for $C_{28}H_{26}NO_3PS$: C, 68.97; H, 5.38; P, 6.15; S, 6.58. Found: C, 68.86; H, 5.40; P, 6.32; S, 6.62.

Preparation of Triphenylcyanopropylphosphonium Bromide (V).—This salt was prepared from triphenylphosphine and 4-bromobutyronitrile in refluxing benzene or ethyl acetate. The product (79.5%) after recrystallization from ethanol melted at 218–219°.

Anal. Calcd for $C_{22}H_{21}BrNP$: C, 64.39; H, 5.13; Br, 19.48. Found: C, 64.32; H, 5.25; Br, 19.60.

Compound VI was prepared similarly from 5-bromovaleronitrile. After several days of reflux, 78.5% of crude product was obtained which, after recrystallization from ethanol, melted at 223–224°.

Anal. Calcd for $C_{23}H_{23}BrNP$: C, 65.09; H, 5.44; Br, 18.83. Found: C, 65.11; H, 5.46; Br, 19.01.

Attempted Structure Proof of XIV *via* Ethyl Styrylacrylate.—Styrylacrylic acid was prepared on the scale reported.[33] The crude product (90.0 g) was esterified with ethanol and *p*-toluenesulfonic acid. The esters were fractionated through a 2-ft Vigreu column yielding (1) 43.1 g, bp 135° (1.2 mm) to 138° (1.3 mm), $n^{23}\mathrm{D}$ 1.6148, and (2) 8.9 g, bp 139–145° (1.2 mm), $n^{23}\mathrm{D}$ 1.6130, along with higher boiling residue. Vpc examination showed that each fraction contained two isomers (geometric). Fraction 1 was analyzed.

Anal. Calcd for $C_{13}H_{14}O_2$: C, 77.20; H, 6.97. Found: C, 77.09; H, 6.90.

Forty grams (0.198 mole) was hydrodimerized to partial conversion (2.70 amp-hr) according to the general procedure described.[29] The crude product, after removal of 17.9 g of starting material by fractional distillation, was 20.1 g of a syrupy, yellow liquid. Addition of ethanol caused precipitation of 5.7 g of one of the isomers (XIX), mp 130–130.5°, of **diethyl 3,4-bisstyryladipate.**[34] The alcoholic mother liquor (XX) contained other isomers.

Anal. Calcd for $C_{26}H_{30}O_4$: C, 76.89; H, 7.44. Found: C, 76.87; H, 7.45.

XIX (4.9 g) was suspended in 60 ml of ethanol, 0.5 g of 5% palladium on charcoal was added, and the mixture was hydrogenated on a Parr shaker at an initial pressure of 31 psi. The theoretical amount of hydrogen (2.0 psi) was taken up in 30 min. Fractionation of the filtered solution yielded 4.2 g, bp 203° (0.25 mm) to 208° (0.25 mm) (main portion) to 210° (0.30 mm), $n^{24}\mathrm{D}$ 1.5190, of **diethyl 3,4-bis-2-phenethyladipate** (XXI). Vpc examination (silicone grease at 250°) showed only one component.[31]

Anal. Calcd for $C_{26}H_{34}O_4$: C, 76.06; H, 8.35. Found: C, 75.73; H, 7.46.

Hydrolysis of XXI with 1:1 hydrochloric acid–water followed by reprecipitation of the crude diacid product from alkaline solution and recrystallization from dilute ethanol yielded XXII, **3,4-bis-2-phenethyladipic acid,**[30] mp 136–138°.

Anal. Calcd for $C_{22}H_{26}O_4$: C, 74.55; H, 7.39. Found: C, 74.58; H, 7.62.

Catalytic hydrogenation of XX according to the procedure described above yielded (1) 3.3 g of XXI isomer, bp 201–212° (0.2 mm), $n^{23}\mathrm{D}$ 1.5230, and (2) 8.8 g of XXI isomer, bp 212° (0.25 mm) to 214° (0.30 mm), $n^{23}\mathrm{D}$ 1.5224. Hydrolysis of product 1 with concentrated hydrochloric acid yielded a diacid, mp 158–159° (from ethanol), which on reesterification produced as ester, XXIII, bp 170° (0.07 mm), $n^{24}\mathrm{D}$ 1.5190. The nmr spectrum of this compound consisted of a singlet at τ 2.90 (10 H) for the aromatic hydrogens, a quartet at 5.96 (4 H), and a triplet at 8.81 (6 H) for the ethoxy groups, a triplet at 7.50 (4 H) for the methylenes α to the phenyl groups, a broad singlet at 7.85 (4 H) for the methylenes α to the carbonyl groups, and a multiplet at 8.47 (6 H) for the hydrogens β and γ to the phenyl groups. This spectrum differs from that of XVIII given above.

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(32) H. Hoffmann, *Chem. Ber.*, **94**, 1331 (1961).

(33) A. G. Anderson and S. Y. Wang, *J. Org. Chem.*, **19**, 277 (1954).

(34) This structure is inferred from the nmr data given below for the saturated ester.

Electrolytic Reductive Coupling. XIII.[1] Intramolecular Reductive Coupling. Electrohydrocyclization[2]

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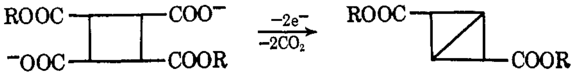
Electrolytic reductive coupling has been extended to intramolecular reactions which have been found capable of yielding a wide variety of cyclic compounds. A series of bisactivated olefins, $ROOCCH{=}CH(CR_2)_nCH{=}CHCOOR$, gave high yields of ring compounds by β-to-β coupling when *n* was 1, 2, 3, and 4; the proposed mechanism of the reaction explained the fact that only acyclic products were formed when *n* was greater than 4. The reaction was also useful in the syntheses of bicyclic and heterocyclic compounds. Thus, the electrolysis of *cis*-diethyl 1,3-cyclopentanediacrylate gave *trans*-diethyl 2,3-norbornanediacetate and the electrolysis of 1,2-bis(2-ethoxycarbonylvinyloxy)ethane gave 2,3-bis(ethoxycarbonylmethyl)-1,4-dioxane. A variation of the reaction gave a cyclic product by an electrolytic displacement reaction: dimethyl *o*-[(bis-β-ethoxycarbonyl)vinyl]phenethylsulfonium *p*-toluenesulfonate gave 3-indanylmalonate.

The development of synthetic methods for the preparation of cyclic compounds has engaged the interest of many investigators. The numerous *chemical* methods that have become available have been reviewed.[3] Little has been reported on direct *electrochemical* routes to cyclic compounds. Attempts to prepare cycloalkanes *via* Kolbe reactions with dicarboxylic acids had been unsuccessful[4] until Vellturo and Griffin[5] described the preparation of a bicyclobutane derivative by this procedure.



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[2] Preliminary communication: J. D. Anderson and M. M. Baizer, *Tetrahedron Letters*, 511 (1966).

[3] See, for example, (a) E. Vogel, *Angew. Chem.*, **72**, 4 (1960); (b) M. Julia, *Rec. Chem. Progr.*, **25**, 3 (1964); (c) L. I. Belinkii, *Russ. Chem. Rev.*, 551 (1964); (d) E. H. Rodd, "Chemistry of Carbon Compounds," Vol. 2A, Elsevier Publishing Co., New York, N. Y., 1953; (e) K. T. Finley, *J. Chem. Educ.*, **42**, 536 (1965).

[4] G. E. Svadkovskya and S. A. Voitkevich, *Russ. Chem. Rev.*, 161 (1960), and references contained therein.

[5] A. F. Vellturo and G. W. Griffin, *J. Am. Chem. Soc.*, **87**, 3021 (1965).