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Cathodic Coupling Reactions

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Cathodic coupling reactions, occurring in the electrolysis of mixtures of two activated olefins and of a carbonyl compound with olefins and alkyl halides, as well as reactions occurring in the electrolysis of onium salts in the presence of olefins and chemical reactions catalysed by electrochemically generated anions are examined.
The bibliography includes 55 references.

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I. INTRODUCTION

Numerous studies dealing with the cathodic reduction of an organic compound to a carbanion or a radical in the presence of compounds capable of interacting with them have been published in recent years. It has been established that there is a possibility of the formation of "mixed hydrodimers", which can be the main reaction products under certain conditions. The number of examples of cathodic coupling reactions has become so great that they can be regarded as constituting a kind of electrochemical method of synthesis. It is quite timely to survey the accumulated data.

The study of the mechanism of the cathodic reduction of organic substances has shown that in many instances electron transfer to a molecule gives rise to highly reactive anions or radicals, which react exceptionally readily with certain organic compounds. The use of this phenomenon made it possible to achieve recently an enormous number of syntheses, some of which have no chemical analogs and are therefore of special interest for organic chemists.

The cathodic coupling reaction was achieved for the first time in 1955 by Wawzonek et al.[1], who obtained diphenylsuccinic acid by the electrochemical reduction of styrene dissolved in dimethylformamide in the presence of carbon dioxide. The authors explained the formation of diphenylsuccinic acid by the fact that the addition of two electrons to stilbene results in the formation of a dianion:

$$C_6H_5CH{=}CHC_6H_5 \overset{2e}{\rightleftarrows} C_6H_5\bar{C}H{-}\bar{C}HC_6H_5$$

The latter is stabilised by the addition of two molecules of carbon dioxide and two protons derived from the solvent:

$$C_6H_5\bar{C}H{-}\bar{C}HC_6H_5 \xrightarrow{2CO_2;\ 2H^+} C_6H_5CH(COOH)CHC_6H_5(COOH)$$

However, this study[1] did not arouse much response. At the beginning of the 1960s vigorous investigation of the electrochemical reduction of activated olefins, particularly acrylonitrile, began. This research demonstrated fairly convincingly that the addition of two electrons and one proton results in the formation under these conditions† of a relatively stable anion, which combines in a readily protonating medium with a second proton to form a product without a double bond. In a medium with a limited proton-donating activity, this anion behaves as a powerful nucleophile and can enter into various reactions. In the simplest case the nucleophile adds to the molecule of the initial substance and the addition product is stabilised as a result of protonation with formation of a hydrodimer. A number of reviews have been devoted to the cathodic hydrodimerisation reaction[2,3]; examination of this reaction is outside the scope of the present article, which deals only with the reactions of organic anions with other substances capable of nucleophilic addition.

† Although this view is not in fact generally accepted, it has been confirmed in many investigations.

II. COUPLING OF ACTIVATED OLEFINS

The cathodic hydrodimerisation of activated olefins achieved at the beginning of the 1960s made it possible to undertake the study of the coupling reaction of two different olefins in accordance with the equation

$$X{-}\overset{|}{C}{=}\overset{|}{C}{+}\overset{|}{C}{=}\overset{|}{C}{-}Y \xrightarrow{2e,\ 2H^+} X{-}\overset{|}{\underset{H}{C}}{-}\overset{|}{C}{-}\overset{|}{C}{-}\overset{|}{\underset{H}{C}}{-}Y \quad ;$$

X,Y=CN, COOR, $CONH_2$ etc.

The possibility, in principle, of achieving this reaction was first demonstrated in a study[4] where cathodic coupling reactions of acrylonitrile with benzylideneacetone and mesityl oxide, of diethyl fumarate with methyl vinyl ketone, and of methyl vinyl sulphone with cinnamic acid diethylamide were carried out; a high yield of products was noted. In the above study it was already suggested that only one reactant is reduced at the cathode with formation of organic anions, which interact with the second component.

The real possibility that the cathodic coupling reaction proceeds via this mechanism was demonstrated in relation to the cathodic coupling of acrylonitrile and methyl acrylate[5]. Methyl acrylate is the more readily reducible olefin. When present jointly, the two substances give rise to separate well defined polarographic waves. If methyl acrylate is added to a solution with a constant acrylonitrile concentration, then the acrylonitrile wave begins to decrease with increase of the methyl acrylate concentration. This phenomenon can be explained by the fact that the methyl acrylate anions generated in the first electrochemical stage interact with acrylonitrile, which reduces the concentration of the latter in the layer near the electrode. Thus the cathodic coupling of acrylonitrile with methyl acrylate can be represented by the

following scheme:

$$H_2C{=}CHCOOCH_3 \xrightarrow{2e,\ H^+} \bar{C}H_2CH_2COOCH_3 \ ,$$

$$\bar{C}H_2CH_2COOCH_3 \xrightarrow{H_2C=CHCN} CH_3OOCCH_2CH_2CH_2\bar{C}HCN \ ,$$

$$CH_3OOCCH_2CH_2CH_2\bar{C}HCN \xrightarrow{H^+} CH_3OOCCH_2CH_2CH_2CH_2CN \ .$$

Evidently it follows from this mechanism that the yield of the cathodic coupling reaction product depends to a large extent on the ratio of the reduction potentials of the coupled components and on the potential of the cathode at which the electrolysis is carried out.

A study of the effect of the cathodic potential ϕ on the yield of the cross-coupling product W was undertaken[6]. The following relation was obtained for the diethyl maleate–ethyl acrylate system [here (I) = diethyl maleate dimer and (II) = ethyl acrylate]:

φ, V(sat. cal. e-de)	1.314	1.425	1.500
W, mmole	1.18	5.95	12.10
Yield of (I), mmole	3.64	8.50	6.00
Yield of (II), mmole	-	-	8.66

Evidently at cathodic potentials of 1.314 and 1.425 V only diethyl maleate is reduced and the cross-coupling product is formed exclusively as a result of the interaction of the diethyl maleate anions with ethyl acrylate molecules. A further increase of the cathodic potential favours the formation of the cross-coupling product, but, apart from the ethyl maleate dimer, the electrolysis products indicate the formation of the dimer of the component which is harder to reduce, namely ethyl acrylate. Analogous results were obtained in the electrochemical reduction of the diethyl maleate–acrylonitrile system. On the basis of these results, it was concluded[6] that, if the reduction potentials of two substances A and B differ by ~0.2 V (under effective potentiostatic conditions, the difference can be even smaller) and there is an excess of the harder substance to reduce (suppose that this is substance B), a high yield of the cross-coupling product is observed. The influence of the difference between the reduction potentials ($\Delta E_{1/2}$) of the coupled components on the yield of the cross-coupling product with respect to the current W can be demonstrated in relation to the reaction of acrylonitrile with α,β-unsaturated nitriles B:

B	Methyleneglutaronitrile	1,4-Dicyanobut-1-ene	1-Cyanobuta-1,3-diene
$\Delta E_{1/2}$, V	0.02	0.10	0.17
W, %	35.4	54.3	81.0
References	7	8	9

However, the yield of the coupling reaction product is not influenced solely by the cathodic potential and the reduction potentials of the coupled compounds. For example, in the electrolysis of a mixture of acrylonitrile and methyl acrylate the yield of the cross-coupling product depends significantly on the material of the cathode other conditions being equal[5]:

Material of cathode	Graphite	Sn	Pb	Cd	Hg	Al
Yield of ω-cyanovaleric acid ester	50.4	31.0	25.5	22.5	17.3	1.0

The highest yield of cathodic coupling products was obtained at a graphite cathode, which probably indicates a considerable influence of the surface concentration of the reactants. The component ratio also plays a significant role. As a rule, the component which is more difficult to reduce should be present in a greater excess. Thus, when methyl acrylate was coupled with acrylonitrile, the maximum yield of ω-cyanovaleric acid was obtained for a molar reactant ratio of 1 : 12.[5]

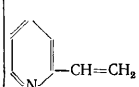
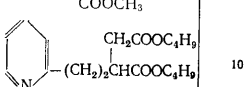
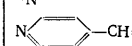
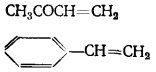
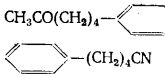
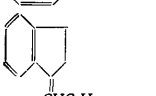
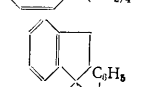
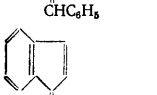
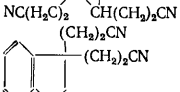
The cross-coupling reactions of the olefins investigated are presented in Table 1, which illustrates effectively the preparative scope of this method. Certain additional information about the olefin coupling reaction can be found in other reviews[2,13].

Subsequent studies showed that alkylidenemalononitriles having the general formula[14]



readily enter into the cathodic coupling reaction with acrylonitrile and methyl acrylate. The nature of the alkyl substituents R′ and R″ has a significant influence on the yield of the coupling products. Certain quantitative characteristics of this reaction are presented in Table 2. It is seen that an increase in the number of carbon atoms in the alkyl group and particularly the branching of the carbon chain lower the yield of the coupling product, evidently in consequence of steric hindrance.

Table 1. The coupling reactions of activated olefins.

Substance A	Substance B	Coupling product	Refs.
$CHCOOC_2H_5$ ‖ $CHCOOC_2H_5$	$H_2C{=}CHCOCH_3$	$CH_2COOC_2H_5$ | $CHCOOC_2H_5$ | $CH_2CH_2COCH_3$	4
$C_6H_5CH{=}CHCOCH_3$	$H_2C{=}CHCN$	$C_6H_5CHCH_2COCH_3$ | CH_2CH_2CN	4
H_3C \ $C{=}CHCOCH_3$ / H_3C	$H_2C{=}CHCN$	$(CH_3)_2CCH_2COCH_3$ | CH_2CH_2CN	4
$CH_3SO_2CH{=}CH_2$	$C_6H_5CH{=}CHCON(C_2H_5)_2$	$C_6H_5CHCH_2CON(C_2H_5)_2$ | $CH_2CH_2SO_2CH_3$	4
$H_2C{=}CHCOOC_2H_5$	$H_2C{=}CHCN$	$CH_2CH_2COOC_2H_5$ | CH_2CH_2CN	9
$CHCOOC_2H_5$ ‖ $CHCOOC_2H_5$	$H_2C{=}CHCN$	$CH_2COOC_2H_5$ | $CHCOOC_2H_5$ | CH_2CH_2CN	9
$H_2C{=}C$ (NHCOCH$_3$, COOCH$_3$)	$H_2C{=}CHCN$	$NC(CH_2)_3CH$ (NHCOCH$_3$, COOCH$_3$)	9
$CHCOOC_4H_9$ ‖ $CHCOOC_4H_9$			10
$CH_3COCH{=}CH_2$		$CH_3CO(CH_2)_4$—	10
	$H_2C{=}CHCN$		11
	$H_2C{=}CHCN$		12
	$H_2C{=}CHCN$		12

One should note that activated olefins are capable of undergoing the cathodic coupling reaction also with alkyl halides[15]. Unfortunately this interesting reaction has been studied only in relation to a few examples.

The electrochemical reduction of a mixture of acrylonitrile and carbon tetrachloride (in methylene chloride plus water as the solvent) in the presence of the Mackie salt (tetraethylammonium toluene-*p*-sulphonate) as the supporting electrolyte led to the formation of trichlorobutyronitrile (with a current yield up to 28%)[15]:

$$H_2C{=}CHCN + CCl_4 \xrightarrow[-Cl^-]{2e,H^+} CCl_3CH_2CH_2CN$$

Carbon tetrachloride is more readily reducible in this system. Evidently, the first stage of the reaction is transfer of the electrons to the carbon tetrachloride molecule and the formation of the ion $\bar{C}Cl_3$, which interacts with acrylonitrile and is then protonated.

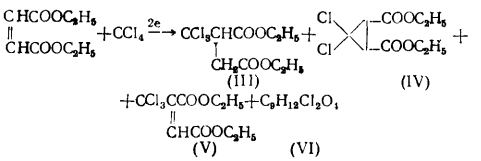
Table 2. The current yields of the products of the cathodic coupling of alkylidenemalononitriles.

R′	R″	Acrylonitrile	Methyl acrylate	R′	R″	Acrylonitrile	Methyl acrylate
CH_3	CH_3	24.0	19.0	CH_3	t-C_4H_9	5.9	7.6
CH_3	C_2H_5	7.6	8.1	C_2H_5	C_2H_5	14.4	14.3
CH_3	iso-C_3H_7	12.5	7.9	$(CH_2)_4$	—	21.0	12.3

The analogous reaction with ethyl acrylate takes place less selectively[15]; a mixture of at least two products is formed:

$$H_2C{=}CHCOOC_2H_5 + CCl_4 \begin{cases} \xrightarrow{2e,H^+} CCl_3CH_2CH_2COOC_2H_5 \ (9\%) \\ \xrightarrow{2e} CCl_3CH_2CHClCOOC_2H_5 \ (24\%) \end{cases}$$

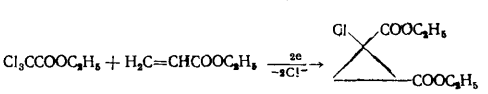
The reaction of carbon tetrachloride with diethyl fumarate is characterised by an even lower selectivity. An interesting feature of this reaction is that, together with products having a linear structure, cyclopropane derivatives are formed:



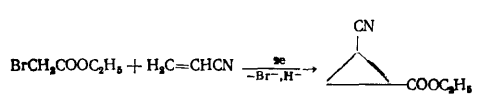
The yields of the individual coupling products (%) depend significantly on the cathodic potential ϕ:

Product	(III)	(IV)	(V)	(VI)
φ = -1.00 V	11.8	1.7	9.6	1.7
φ = -1.20 V	38	28	49.5	—

In the electrolysis of a mixture of ethyl acrylate and ethyl trichloroacetate [in an *N*,*N*′-dimethylformamide (DMF) + dichloroacetic acid mixture as the solvent] in the presence of tetraethylammonium chloride as the supporting electrolyte, the only reaction product is a cyclopropane derivative:



An analogous product is formed on coupling the bromoacetic ester with acrylonitrile (2.8%)[15]:



Allyl bromide reacts with acrylonitrile to form 1-cyanooct-4-ene in 12.6% yield[15]:

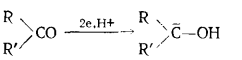
$$H_2C{=}CHCH_2Br + H_2C{=}CHCN \xrightarrow[-Br^-]{2e,H^+} H_2C{=}CH(CH_2)_3CN$$

In conclusion of the discussion of the reactions of activated olefins, mention should be made of their interaction with carbon dioxide. For example, electrolysis of a solution of allyl chloride in DMF with a continuous supply of CO_2 leads to the formation of allyl crotonate in a low yield[15]:

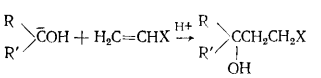
$$H_2C{=}CHCH_2Cl + CO_2 \xrightarrow[-Cl^-]{2e,H^+} CH_3CH{=}CHCOOCH_2CH{=}CH_2 \ .$$

III. REACTIONS OF CARBONYL COMPOUNDS

In the presence of quaternary ammonium salts as supporting electrolytes, aliphatic ketones undergo two-electron reduction. In acid solutions the reduction process is significantly facilitated apparently in consequence of protonation. It has been suggested[2] that in acid media the primary electrode process proceeds in accordance with the equation

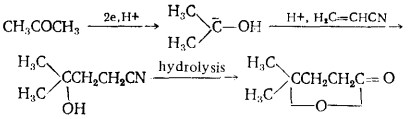


The carbanion formed is capable of adding to Michael acceptors, forming a cross-coupling product:



The reaction has been studied in greatest detail in relation to the cathodic coupling of acetone and acrylonitrile.

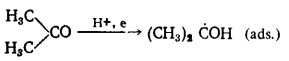
A brief communication[16], showing that the electrochemical reduction of a mixture of acetone and acrylonitrile in 20% sulphuric acid at a controlled potential of the mercury cathode of -1.2 V (sat.cal.e-de) leads to a mixture of γ-hydroxy-γ-methylvaleronitrile and its hydrolysis product γ,γ-dimethylbutyrolactone, was published in 1965; the overall yield of the cross-coupling product was ~70%. Since only acetone undergoes electrochemical reduction under the conditions described (the reduction potential of acrylonitrile in acid solutions is -1.5 V), the authors[16] proposed the following mechanism for the formation of the cross-coupling products:



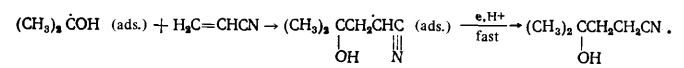
Subsequently this reaction was studied in greater detail[17]. Cyclic voltamperometric data showed that, in an acid solution at a mercury cathode, acetone forms unstable species at a potential of approximately -1.2 V, which undergo reversible oxidation. These species could be detected only at rate of application of potential of 960 V s^{-1}. It has been suggested[17] that these species are of a radical type, since the reduction of acetone is accompanied by the formation of organomercury compounds. The addition of acrylonitrile to the system decreases sharply the surface concentration of these reversibly oxidised species, which indicates their involvement in the interaction with the nitrile. The absence of polyacrylonitrile from the electrolyte solutions shows that the radical species are present on the surface of the electrode and do not diffuse into the bulk of the solution.

The presence of reactive species on the surface of the mercry cathode in the presence of acetone has also been confirmed by the method involving the application of a brief current

pulse against the background of triangular scanning. On the basis of the results, it was suggested[17] that the primary electrode step is the formation of adsorbed radical species:



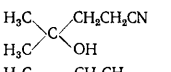
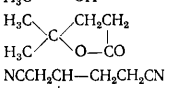
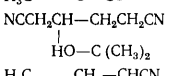
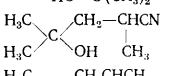
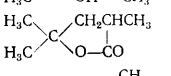
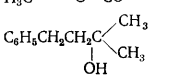
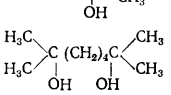
In this case the reaction is first order with respect to acetone; with increase in the acetone concentration to 1 M, the reaction order falls to zero, which shows that molecules of acetone (or of its protonated form) are adsorbed on the electrode before electron transfer. In the second stage of the reaction the adsorbed radicals react with acrylonitrile:



However, although this mechanism agrees with the observed change in the current on pulsation of the potential, it cannot be regarded as rigorously proved, since no direct measurements, indicating the transfer of a single electron to the acetone molecule in the primary electrochemical step, have been made.

Later it was shown[18] that the cathodic coupling of acetone with acrylonitrile can be achieved in a neutral medium at pH 7. The advantage of the neutral medium is that the cross-coupling product is stable under these conditions and the process can be used for the preparative synthesis of γ-hydroxyl-γ-methylvaleronitrile.

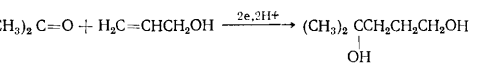
Table 3. The influence of the nature of the olefin on the yield of the product of the cathodic cross-coupling with acetone[18,19] (with respect to the given substance).

Olefin	Coupling product	Yield
Acrylonitrile		73
Methyl acrylate		70
Dicyanobut-1-ene		30
Methacrylonitrile		20
Methyl methacrylate		19
Styrene		8
Butadiene		6

When the reaction is carried out at a graphite cathode in 1 M aqueous solution of dipotassium hydrogen phosphate acidified with phosphoric acid to pH 7 at a temperature of 7–8 °C, a current density of 0.02–0.03 A cm^{-2}, and for a molar acetone : acrylonitrile ratio of 12 : 1, the yield of γ-hydroxy-γ-methylvaleronitrile is 52% with respect to the current and 85% with respect to the reacted acrylonitrile. By measuring the differential capacitance, it was shown that the maximum yield of the cross-coupling product at a mercury cathode is attained under the conditions of the preliminary adsorption of acrylonitrile on the surface of the electrode[18].

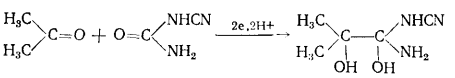
The development of the cathodic coupling of acetone with acrylonitrile on a preparative scale was followed by numerous studies of the applications of this reaction and of its extension to other carbonyl compounds and activated olefins. It was established that acetone enters into the cathodic coupling reaction with numerous activated olefins, forming tertiary alcohols[18,19]. Since the experiments were performed under comparable conditions (graphite cathode, 1 *N* solution of dipotassium hydrogen phosphate, molar ratio acetone : olefin = 10 : 1), it is possible to follow the influence of the nature of the olefin on the yield of the cross-coupling product (Table 3).

It follows from Table 3 that the highest yields of the cross-coupling products have been obtained from acrylonitrile and methyl acrylate, i.e. compounds with a strongly polarised bond. Unexpectedly, acetone undergoes the coupling reaction (albeit with a low yield) with olefins of low polarity such as styrene and butadiene. The yields of the coupling products can apparently be increased, since it has been reported that acetone has been coupled with styrene to give a yield of 42%, with butadiene to give a yield of 32%, and with stilbene to give a yield of 45%. The experimental conditions were not described in detail[20]. It has also been reported[21] that the coupling of acetone with allyl alcohol was achieved to give a high yield of product; electrolysis of a mixture of these substances in an aqueous solution of potassium phosphate at a graphite cathode yielded 2-methylpentane-2,5-diol:

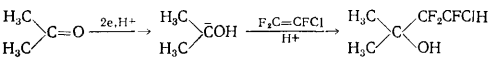


The yield of product was ~70% with respect to the current and 95–98% with respect to the reacted allyl alcohol.

The cross-coupling of acetone with cyanourea was described comparatively recently[22]:



At a mercury cathode in 40% sulphuric acid solution acetone couples with chlorotrifluoroethylene to give a current yield of ~43%.[23] The following reaction mechanism has been proposed:

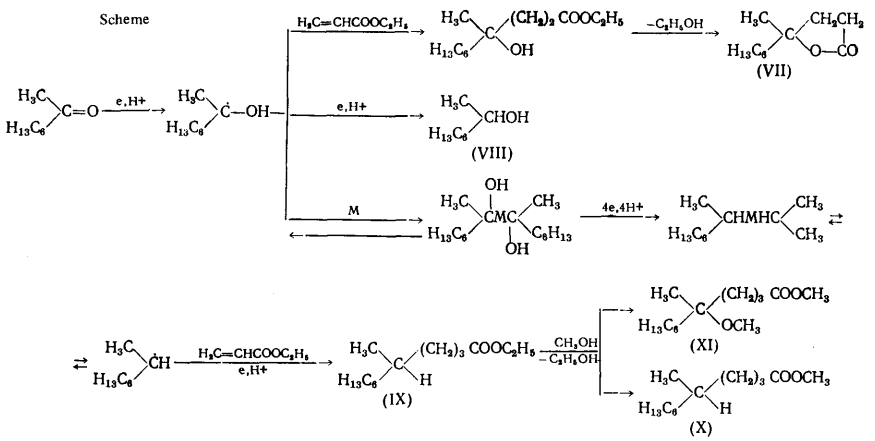


This reaction resembles the radical addition of 2-propanol to chlorotrifluoroethylene.

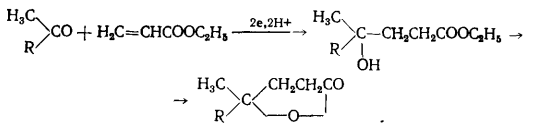
Apart from acetone, many other aliphatic ketones undergo the coupling reaction. It was already mentioned in an early study[16] that ethyl methyl ketone and diethyl ketone undergo the coupling reaction with acrylonitrile, giving current yields of 60 and 30% respectively. Under the same conditions, i.e. in an acid medium, the coupling of acetone with methyl pentyl and hexyl methyl ketones was achieved[24], giving overall yields of coupling products of 70 and 72% respectively. Thus the coupling reaction in an acid medium is also entirely suitable for preparative purposes with high aliphatic ketones.

However, we may note that in an acid medium a considerable proportion of the hydroxynitrile formed (~30%) hydrolyses[24]. It is therefore more convenient to couple the ketone with an

Scheme



acrylate ester, for example ethyl acrylate:



In this case the reaction is no longer complicated by the hydrolysis and fairly high yields of lactones were obtained under the same conditions:

Ketone	$CH_3COC_2H_5$	$CH_3COC_3H_7$	$CH_3COC_5H_{11}$	$CH_3COC_6H_{13}$
Yield, %	80	70	74	42

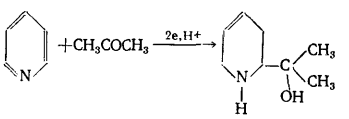
When ketones are coupled with acid ester, side products are always formed[24]. The processes occurring in the electrolyis of a mixture of a ketone and an ester are presented in the Scheme below (M is the material of the cathode).

During the coupling of ethyl acrylate with hexyl methyl ketone in aqueous methanol, the formation of the main product, which is the γ-lactone (VII), is accompanied by that of 2-octanol (VIII), the amount of which increases as the potential is displaced to the cathodic region, ethyl 4-methyldecanoate (IX), considerable amounts of which have been noted only at a more cathodic potential, as well as small amounts of its methyl ester (X) together with traces of methyl 4-methoxy-4-methyldecanoate (XI).[24] Apart from the products indicated, also detected were insignificant amounts of hydrocarbons with molecular weights of 224 and 226, which were identified as 7,8-dimethyltetradecane and 7,8-dimethyltetradodecane respectively, and diisopropylmercury; pinacone was not detected as a side product.

In electrolysis in a neutral medium a smaller amount of side products is found[19]. Table 4 presents data for the cathodic coupling of various aliphatic ketones with acrylonitrile and methyl acrylate. A distinct decrease in the reactivity of the ketone with increasing complexity of its carbon skeleton is obseerved in both acid and neutral media.

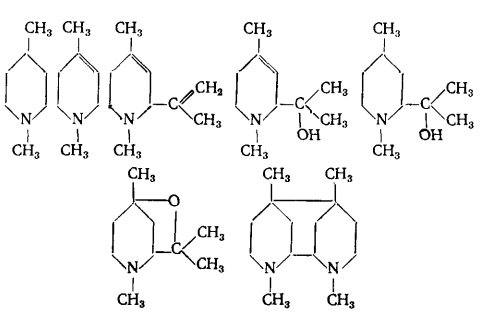
The coupling reaction of higher aliphatic ketones with unsaturated hydrocarbons has been studied in detail[25]. The electrolyte used in the experiments was tetraethylammonium toluene-*p*-sulphonate. The correct choice of solvent is very important in this instance. Preliminary experiments showed that cathodic coupling does not occur in *t*-butyl alcohol, *N*,*N*-dimethylformamide, the monomethyl ether of diethylene glycol, and s-butyl alcohol; in methanol reaction proceeds with an insignificant yield. Mixed solvents proved to be most effective: isopropyl alcohol (20%)–dioxan (80%) and isopropyl alcohol (25%)–dimethyl ether of triethylene glycol (75%). At a graphite electrode coupling proceeds with a higher yield than at a mercury electrode (Table 5).

Interesting information concerning the cathodic coupling of acetone with pyridine has been published in a communication[26], whose authors showed that in an acid medium the reaction is directed preferentially to the α-position and proceeds with partial hydrogenation of the pyridine ring:

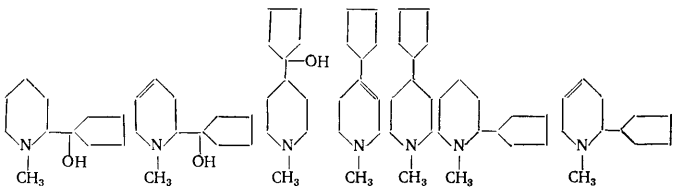


A more detailed investigation of this process showed[27] that the best electrode material in this instance is mercury. Under comparable conditions, the yields of the cross-coupling product at mercury, lead, and cadmium cathodes are 85, 59, and 39% respectively. Cathodic coupling requires the use of acid solutions, since cross-coupling products have not been detected in an alkaline solution. Both an increase in the length of the carbon chain of the aliphatic ketone and the introduction of substituents into the pyridine ring reduce the yield of the coupling product.

The coupling of 4-methylpyridine with acetone and of *N*-methylpyridinium with cyclopentanone has been studied in detail[28]. It was found that in both cases the coupling involves the 2-position of the pyridine ring. However, according to the authors[28], these reactions are of no preparative interest in view of their low selectivity. Thus the formation of the following products was observed in the electrolysis of a mixture of acetone and *N*,4-dimethylpyridinium:

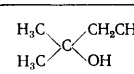
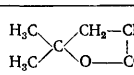
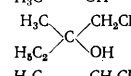
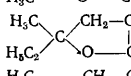
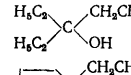
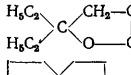
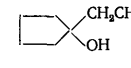
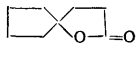


while the products



were isolated in the reduction of *N*-methylpyridinium with cyclopentanone. Further investigation of this reaction showed that the hydrocarbons are formed as a result of the reduction of the tertiary alcohols formed in the first stage of the cross-coupling reaction[29].

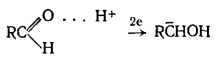
Table 4. The influence of the structure of the ketone on the yields of the products of the cathodic coupling of aliphatic ketones with acrylonitrile and methyl acrylate[19].

Ketone	Product of coupling with acrylonitrile*	Yield, %	Product of coupling with methyl acrylate**	Yield, %
Acetone		50		70
Ethyl methyl ketone		35		30
Diethyl ketone		28		21
Cyclopentanone		13		19

*Graphite cathode, 1 *N* solution of dipotassium hydrogen phosphate.

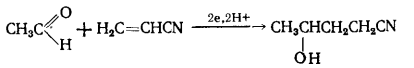
**Mercury cathode, 20% sulphuric acid.

The cross-coupling processes involving aliphatic aldehydes have been studied in less detail. As in the reduction of aliphatic ketones, the reduction of aliphatic aldehydes gives rise to a single two-electron wave[30] and it has been established that the protonated form of the aldehyde is electrochemically active[31]. The first stage of the electrochemical reduction of aliphatic aldehydes involves the formation of an anion:



This anion readily reacts with Michael acceptors.

The first report of the possibility, in principle, of the cathodic coupling reaction with activated olefins appeared in a Japanese patent[32]. Later this reaction was investigated in greater detail. For example, it has been shown[33] that the electrochemical reduction of a mixture of acetaldehyde and acrylonitrile leads to the formation of a hydroxynitrile (1-cyano-3-hydroxybutane) in a high yield:



If acrylic acid or its esters are used instead of acrylonitrile, then in both instances the reduction leads to the formation of γ-lactones, since the γ-hydroxyacids and their esters, formed initially, are unstable under the electrolysis conditions and hydrolyse with formation of the corresponding lactones[34], for example:

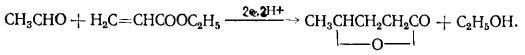
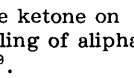
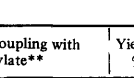
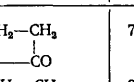
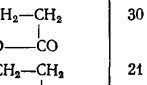
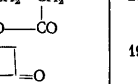
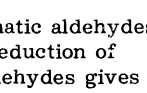
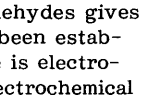
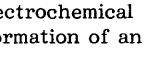


Table 5. Products of the coupling of aliphatic ketones RCOR′ with olefins (cathodic current density 0.014 A cm^{-2}).

R	*R′*	Coupling product	Yield, % w.r.t. ketone	Yield, % w.r.t current
CH_3	CH_3		18	15
CH_3	C_2H_5		22	18
CH_3	C_3H_7		18	15
CH_3	C_6H_{13}		20	17
CH_3	C_7H_{15}		18	15
CH_3	C_8H_{19}		17	14
CH_3			12	10
CH_3			5	4
C_3H_7	C_3H_7		8	6.5
CH_3*	C_2H_5		10	8
CH_3**	C_2H_5		14	12
CH_3***	CH_3		10	10

*Hex-1-ene. ** Dec-1-ene. ***Penta-1,3-diene. In the remaining cases the olefin was oct-1-ene.

The available information about the cathodic coupling of aldehydes with activated olefins is presented in Table 6. [These data refer to the electrolysis of weakly acid solutions (pH4–6) using a graphite cathode[35]]. It has been shown that, under the conditions described by Tomilov and coworkers[34,35], there is a possibility of the cross-coupling of aldehydes also with alkyl halides. Thus the electrochemical reduction of acetaldehyde in the presence of carbon tetrachloride involves the following process:



An analogous reaction has been observed when other halogeno-compounds were used, such as methylene chloride, allyl chloride, chloroform, etc. The cross-coupling of aldehydes is carried out at the graphite cathode in potassium phosphate solutions in a weakly acid medium (pH 2.0–2.5). The required pH is maintained by the gradual addition of phosphoric acid to the cathodic compartment during electrolysis. Table 7 shows the products obtained in the interaction of aliphatic aldehydes with alkyl halides.

Table 6. Products of the cathodic coupling of aliphatic aldehydes with activated olefins[34,35].

Aldehyde	Olefin	Coupling product	Yield, %	
			w.r.t. current	w.r.t substance
CH_3CHO	$H_2C=CHCOOCH_3$	$CH_3CHCH_2CH_2C(=O)-O$	99	92
CH_3CHO	$H_2C=CHCOOH$	ditto	14	52
CH_3CHO	$H_2C=CHCH_2Cl$	$CH_3CHCH_2CH=CH_2$ (OH)	34	82
CH_3CHO	$H_2C=CHCH_2OH$	$CH_3CHCH_2CH_2CH_2OH$ (OH)	—	19
CH_3CH_2CHO	$H_2C=CHCOOCH_3$	$CH_3CH_2CHCH_2CH_2CO$ (O)	86.0	91
CH_3CH_2CHO	$H_2C=CHCOOH$	ditto	20	59
CH_3CH_2CHO	$H_2C=CHCN$	$CH_3CH_2CHCH_2CH_2CN$ (OH)	68	91
CH_3CH_2CHO	$H_2C=CHCH_2OH$	$CH_3CH_2CHCH_2CH_2CH_2OH$ (OH)	6	25
$CH_3CH_2CH_2CHO$	$H_2C=CHCH_2Cl$	$CH_3CH_2CH_2CHCH_2CH_2CH_2Cl$ (OH)	42	86
CH_3CHO	$H_2C=CHCN$	$CH_3CHCH_2CH_2CN$ (OH)	80	93

Table 7. Products of the cross-coupling of aldehydes with alkyl halides[34,35].

Aldehyde	Alkyl halide	Coupling product	Yield, %	
			w.r.t current	w.r.t substance
CH_3CHO	CCl_4	CH_3CHCCl_3 (OH)	72	83
CH_3CHO	$CHCl_3$	$CH_3CHCHCl_2$ (OH)	54	79
CH_3CHO	CH_2Cl_2	CH_3CHCH_2Cl (OH)	4.8	89
CH_3CHO	$H_2C=CHCH_2Cl$	$CH_3CHCH_2CH=CH_2$ (OH)	34.0	82
CH_3CH_2CHO	CCl_4	$CH_3CH_2CHCCl_3$ (OH)	77.0	86
CH_3CH_2CHO	$CHCl_3$	$CH_3CH_2CHCHCl_2$ (OH)	54.6	87
$CH_3CH_2CH_2CHO$	$H_2C=CHCH_2Cl$	$CH_3CH_2CH_2CHCH_2CH=CH_2$ (OH)	42.0	86

All the examples examined above refer to reactions of aliphatic carbonyl compounds. This type of reaction is not characteristic of aromatic carbonyl compounds. However, in a concentrated aqueous solution of the Mackie salt, it was possible to achieve the cathodic coupling of benzophenone with ethyl acrylate[20]. The yield of the cross-coupling product, γγ-diphenyl-γ-butyrolactone, is ~25%:

$$(H_5C_6)_2CO + H_2C{=}CHCOOCH_3 \xrightarrow{2e,2H^+} (H_5C_6)_2C(CH_2{-}CH_2)O{-}C{=}O$$

Acrylonitrile has been coupled with benzophenone and benzaldehyde under similar conditions[11]. In the latter case the reaction proceeds in accordance with the equation

$$C_6H_5C(=O)H + 2H_2C{=}CHCN \xrightarrow{3e,3H^+} C_6H_5CH(OCH_2CH_2CN)CH_2CH_2CN$$

An unusual type of cathodic coupling reaction has been observed[36] in the electrochemical reduction of an anhydrous mixture of benzaldehyde and ethyl iodide, which was saturated with tetraethylammonium iodide to make it electrically conducting. The following reaction takes place at a copper cathode with a low yield:

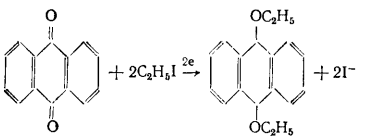
$$C_6H_5CH(=O) + 2C_2H_5I \xrightarrow{2e} C_6H_5CH(OC_2H_5)C_2H_5 + 2I^-$$

It leads to the formation of the ethyl ether of ethylphenylmethanol[36]; its mechanism has not been studied.

When a mixture of benzophenone and ethyl iodide was electrolysed in *N*,*N*-dimethylformamide, ethyldiphenylmethanol was obtained[37]:

$$C_6H_5CC_6H_5(=O) + C_2H_5I \xrightarrow{2e,H^+} C_6H_5C(C_2H_5)(OH)C_6H_5 + I^-$$

The ethyl ether of 9,10-hydroanthroquinone is obtained from anthraquinone and ethyl iodide[38]:



IV. CATHODIC REDUCTION OF 'ONIUM SALTS

Conditions favourable for the reduction of 'onium cations are created in the electrolysis of solutions of 'onium salts in a medium with low conductivity or in aprotic solvents. The reduction of the cation is followed by its decomposition, leading to the generation of unstable reactive species. When the solution contains substances reacting with these species, a kind of cathodic coupling reaction takes place.

This type of reaction was achieved for the first time in relation to the generation of cyanomethylene anions[39]:

$$[(H_3C)_2SCH_2CN]^+ \xrightarrow{2e} (CH_3)_2S + \bar{C}H_2CN$$

The electrolysis of a solution of this salt in the presence of acrylonitrile yielded glutarodinitrile with a current yield of 83%. The reaction apparently proceeds as follows:

$$\bar{C}H_2CN + H_2C{=}CHCN \xrightarrow{H^+} CNCH_2CH_2CH_2CN$$

The electrolysis of a dimethylbenzylsulphonium salt in the presence of acrylonitrile under the same conditions gave a 68%

yield of 3-phenylbutyronitrile[39]:

$$(CH_3)_2\overset{+}{S}CH_2C_6H_5 + H_2C{=}CHCN \xrightarrow{2e,H^+} C_6H_5CH_2CH_2CH_2CN + S(CH_3)_2$$

An analogous reaction takes place with phosphonium salts[40], but the yields of coupling products are appreciably lower (on average, they do not exceed 10–13%). It has been suggested[40] that the reaction proceeds via an intermediate stage involving the formation of an organomercury compound:

$$(C_6H_5)_3\overset{+}{P}(CH_2)_nCN \xrightarrow[Hg]{e} (C_6H_5)_3\dot{P}(CH_2)_nCN \| Hg \rightarrow$$
$$\rightarrow \begin{cases} \rightarrow (C_6H_5)_3P + [Hg(CH_2)_nCN]^{\cdot} \\ \rightarrow (C_6H_5)_3\dot{P}(CH_2)_nCN + Hg \rightarrow (C_6H_5)_3P + {}^{\cdot}(CH_2)_nCN \rightarrow \end{cases}$$
$$\xrightarrow{C_6H_5HC=CH_2} C_6H_5\dot{C}H(CH_2)_{n+1}CN \xrightarrow{e,H^+} C_6H_5(CH_2)_{n+2}CN$$

The nitriles of phenylvaleric ($n = 2$), phenylcaproic ($n = 3$), and phenyloenanthic ($n = 4$) acids have been synthesised in this way. Unfortunately, owing to the low yields, this reaction is hardly likely to find preparative applications. In the electrolysis of phosphonium salts with $n = 1$ neither dimerisation products nor organomercury compounds were detected.

V. OTHER REACTIONS INVOLVING ELECTROCHEMICALLY GENERATED ANIONS

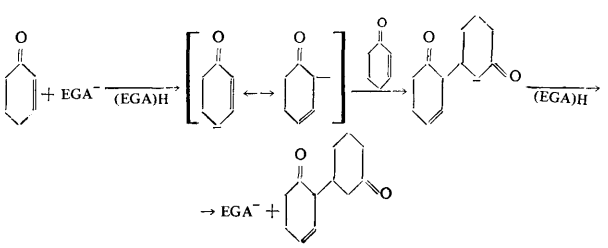
Attempts have been made recently to carry out electrochemically certain classical reactions of organic synthesis, which proceed via a stage involving an organic anion, using the electric current to generate the latter. One of the most promising features of this field of research involves the Michael reaction.

The initiation of the Michael reaction by electrochemically generated anions (EGA^-), which behave as a strong base (for example, in the condensation of malonic ester with acrylonitrile), can be represented by the following equations:

$$EGA^- + CH_2(COOC_2H_5)_2 \rightleftarrows (EGA)H + \bar{C}H(COOC_2H_5)_2 \quad ,$$
$$\bar{C}H(COOC_2H_5)_2 + H_2C{=}CHCN \rightarrow (C_2H_5OOC)_2CHCH_2\bar{C}HCN \quad ,$$
$$(C_2H_5OOC)_2CHCH_2\bar{C}HCN + CH_2(COOC_2H_5)_2 \rightarrow$$
$$\rightarrow (C_2H_5OOC)_2CHCH_2CH_2CN + \bar{C}H(COOC_2H_5)_2 \quad .$$

For the reaction to go virtually to completion, catalytic amounts of EGA^- are sufficient. The process described has been carreid out[41] using azobenzene, which on reduction in an aprotic medium gives rise to the fairly active dianions $C_6H_5\bar{N}-\bar{N}C_6H_5$, as the source of EGA^-.[42] The experiments carried out in the above study[41] showed that it is sufficient to add to the solution 0.0025 mole of azobenzene per mole of malonic ester for the above reaction to take place with a yield of 75%.

Furthermore, EGA^- can also be used to obtain dimerisation products when the same substance can behave as the donor and acceptor in the Michael reaction[41]. The reaction involving cyclohex-2-en-1-one can be formulated thus:



The dimer was obtained in 65 mole % yield with reduction of only 0.13 mole % of the monomer[41]. The reactions given in Table 8 were carried out similarly. However, in most cases there is no need to introduce a special substance generating anions. The acceptor itself can function as a substance of this kind. Thus in the above reaction of malonic ester with acrylonitrile, acrylonitrile can function as the source of EGA^- [41]:

$$H_2C{=}CHCN \xrightarrow{2e,H^+} \bar{C}H_2CH_2CN$$

Table 8. Examples of dimerisation reactions initiated by EGA^-.[41]

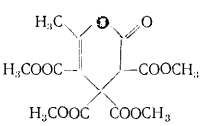
Monomer	Dimer	Amount of reduced monomer, %	Yield of dimer, %
$H_2C{=}CHCH_2CN$	$CNCH_2CH_2CH_2CHCH{=}CH_2$ (CN)	1.0	35
$CH_3OOCCH_2C{=}CHCOOCH_3$ (COOCH₃)	$CH_3OOCCH_2CHCH_2COOCH_3$ (COOCH₃)	1.5	88
	$CH_3OOCCH{=}CCHCOOCH_3$ (COOCH₃)		
$C_2H_5OOCCH_2CH{=}CHCOOC_2H_5$	$C_2H_5OOCCH_2CHCH_2COOC_2H_5$ ($C_2H_5OOCCH{=}CHCHCOOC_2H_5$)	2.0	50

At a mercury cathode in solution in *N*,*N*-dimethylformamide in the presence of tetrabutylammonium fluoroborate as the supporting electrolyte the coupling reaction proceeds with a yield of 18.5% when 0.024 of a faraday of electricity per mole of acrylonitrile is passed through the system. Under these conditions, the coupling of ethyl acrylate with malonic ester was carried out to give a yield of 77% after passing 0.055 of a faraday of current[41].

$$CH_2(COOC_2H_5)_2 + H_2C{=}CHCOOC_2H_5 \xrightarrow{2e,H^+} (C_2H_5OOC)_2CH{-}CH_2CH_2COOC_2H_5$$

The coupling of methyl ethylenetetracarboxylate with methyl pyruvate proceeds to give a yield of 60% [41]:

$$(CH_3OOC)_2C{=}C(COOCH_3)_2 + CH_3COCH_2COOCH_3 \xrightarrow{2e}$$



The yield of the product of the coupling reaction between ethyl ethylenetetracarboxylate and malonic ester is 93%. All the reactions examined are undoubtedly of preparative value. Their characteristic feature is that the electric current is used solely to regenerate the catalyst of the chemical reaction.

The familiar Wittig reaction involves the conversion of carbonyl compounds under the influence of ylids, which are usually obtained by treating a quaternary phosphonium salt with phenyl-lithium:

$$((C_6H_5)_3\overset{+}{P}CH_3)Br + C_6H_5Li \rightarrow (C_6H_5)_3\overset{+}{P}\cdot\bar{C}H_2 + LiBr + C_6H_6$$

Ylids are also formed electrochemically in the electrolysis of phosphonium and sulphonium salts[43,44]. The electrochemical generation of ylids includes oxidation-reduction and acid–base reactions. This process can be achieved by electrolysing a mixture of a phosphonium salt and a substance which readily gives rise to organic anions, for example, azobenzene[45]. The electrolysis of such a mixture at the azobenzene reduction potential (−0.90 V) leads to the formation of the

anions of the latter, which split off protons from the phosphonium salt with formation of an ylid; next the yild interacts with a carbonyl compound, for example, benzaldehyde. The overall mechanism of the reactions can be expressed by the following equations:

$$C_6H_5N{=}NC_6H_5 \xrightarrow{2e} C_6H_5\bar{N}{-}\bar{N}C_6H_5 \text{ (reduction)},$$

$$(C_6H_5)_3\overset{+}{P}CH_2C_6H_5 \xrightarrow{1/2C_6H_5\bar{N}-\bar{N}C_6H_5} (C_6H_5)_3\overset{+}{P}{-}\bar{C}HC_6H_5 + $$

$$+ 1/2C_6H_5NHNHC_6H_5 \text{ (abstraction of a proton)},$$

$$(C_6H_5)_3\overset{+}{P}{-}\bar{C}HC_6H_5 \xrightarrow{C_6H_5CHO} (C_6H_5)_3PO + C_6H_5CH{=}CHC_6H_5 \text{ (Wittig reaction)}.$$

It has been shown[45] that the Wittig reaction takes place with a high yield in the electrolysis of a mixture of azobenzene, benzyltriphenylphosphonium bromide, and benzaldehyde in anhydrous *N*,*N*-dimethylformamide containing lithium bromide. According to the authors[45], the electrochemical version of the Wittig reaction has definite advantages, since it becomes possible to establish readily the required concentration of the base by regulating the current and hence side reactions can be virtually eliminated.

Another example of this reaction is provided by the electrochemical version of the Stevens rearrangement, which involves the conversion of an ammonium salt into a tertiary amine under the influence of, for example, sodium amalgam {Na[Hg]}:

$$C_6H_5COCH_2\overset{+}{N}(CH_3)_2CH_2C_6H_5\ Br^- \xrightarrow{Na[Hg]} \left[C_6H_5CO\bar{C}H\overset{+}{N}(CH_3)_2CH_2C_6H_5\right] \rightarrow C_6H_5COCHN(CH_3)_2CH_2C_6H_5 .$$

In this case azobenzene cannot be used as a depolariser, because it is reduced at a more negative potential than benzyldimethylphenacylammonium bromide. However, the initial substance itself can be employed as the depolariser[46]. The overall chain of processes occurring can be represented by the equation

$$2C_6H_5COCH_2\overset{+}{N}(CH_3)_2CH_2C_6H_5 \xrightarrow[DMF/LiCl]{2e} C_6H_5COCH_3 + C_6H_5CH_2N(CH_3)_2 +$$

$$+ C_6H_5CO\bar{C}H\overset{+}{N}(CH_3)_2CH_2C_6H_5 \rightarrow C_6H_5COCHN(CH_3)_2CH_2C_6H_5$$

The reductive acetylation reaction is an example of the use of electrochemically generated bases for organic synthesis. This process was initially investigated in relation to the acetylation of *N*-heterocyclic compounds[47]. The cathodic acetylation reaction consists of the electrolysis of a mixture of nitro- or nitroso-compounds with acetic anhydride in solution in anhydrous acetonitrile. A 0.8 M solution of sodium perchlorate is used as the supporting electrolyte:

$$RNO_2 \xrightarrow{e} [RNO_2]^{\cdot-} \xrightarrow[-AcO^-]{Ac_2O} \left[RN(O)OAc\right]^{\cdot} \xrightarrow[-AcO^-]{e,Ac_2O} RN(OAc)_2$$

For a nitroso-compound, the process can be formulated as follows:

$$RNO \xrightarrow{e} [RNO]^{\cdot-} \xrightarrow[-AcO^-]{Ac_2O} [RNOAc]^{\cdot} \xrightarrow[-AcO^-]{e,Ac_2O} RN(OAc)Ac$$

N-Substituted *N*,*O*-diacetylhydroxylamines have been obtained from various nitroso-compounds with the following yields[48]: CH_3NO_2—54%; $t\text{-}C_4H_9NO_2$—47%; $t\text{-}C_4H_9NO$—57%; $C_6H_5NO_2$—55%; C_6H_5NO—71%; $p\text{-}CH_3C_6H_4NO_2$—77%; $C_6H_4(NO_2)_2$—87%. This reaction is undoubtedly of preparative value.

Data on the electrochemical acetylation and alkylation in the cathodic cleavage of disulphides are of interest[49,50]. The reaction is carried out in dimethyl sulphate or in *N*,*N*-dimethylformamide. A mixture of a disulphide with an alkyl halide or acetic anhydride is electrolysed. Alkylation and acetylation are observed in the former and latter case respectively:

$$RSSR \xrightarrow{2e} 2RS^- \xrightarrow[2R'X]{} 2RSR' + 2X^-$$

$$\xrightarrow[2Ac_2O]{} 2RSAc + 2AcO^-$$

The experiments showed that methylene chloride can be most conveniently used as the methylating agent[49]. The yields of methylation products obtained under these conditions in solution in *N*,*N*-dimethylformamide in the presence of lithium chloride as the supporting electrolyte are listed in Table 9.

Table 9. The yields of the products of the electrochemical methylation of disulphides[49].

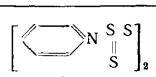
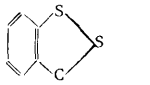
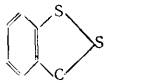
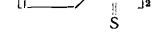
Starting material	Yield, %	Starting material	Yield, %
$[C_6H_5CH_2S]_2$	82		78
$[C_6H_5S]_2$	83		
$[p\text{-}CH_3C_6H_4S]_2$	85		85
$[C_6H_5COS]_2$	70		
$[o\text{-}NO_2C_6H_4S]_2$	91		78
$[o\text{-}C_2H_5OC_6H_4S]_2$	89		
		$[(CH_3)_2NCS]_2$	81
			88

Table 10. Electrochemical alkylation and acylation of disulphides[49].

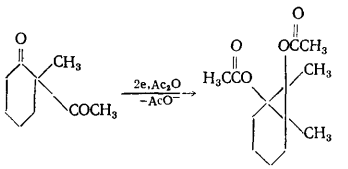
Initial disulphide	Electrode reagent	Yield of cathodic coupling product, %
CH_3SSCH_3	$C_6H_5CH_2Cl$	63
$CH_3COSSCOCH_3$	$C_6H_5CH_2Cl$	76
$C_6H_5SSC_6H_5$	$C_6H_5CH_2Cl$	92
$C_6H_5CH_2SSCH_2C_6H_5$	$CH_3CHClCH_3$	75
$C_6H_5CH_2SSCH_2C_6H_5$	$(CH_3CO)_2O$	83
$o\text{-}O_2NC_6H_4SSC_6H_4NO_2\text{-}o$	$(CH_3CO)_2O$	68
ditto	CH_3COCl	39
»	CH_3I	84
»	$(CH_3O)_2SO_2$	91
»	$(CH_3CH_2O)_2SO_2$	76
$(CH_3)_2NC(S)SSC(S)N(CH_3)_2$	$(CH_3)_2NCOCl$	37
$C_6H_5COSSCOC_6H_5$	CH_2Br_2	66

Somewhat lower yields have been obtained using other alkylating agents, but they nevertheless remain within limits adequate for a preparative process (Table 10).[49] The advantage of the electrochemical alkylation of disulphides over known chemical methods is that the electrochemical procedure makes it possible to obtain thioethers even when the corresponding thiols are unstable or do not exist at all[49].

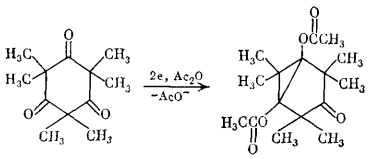
The study of the polarographic behaviour of benzophenone in solution in acetonitrile showed that the addition of acetic anhydride to the solution suppresses the second benzophenone reduction wave. Preparative electrolytic processes carried out at the potential of the first wave showed that benzophenone is acetylated under the conditions indicated[51]:

$$(C_6H_5)_2C{=}O \xrightarrow{+e} [(C_6H_5)_2C{-}O]^{\cdot-} \xrightarrow[-AcO^-]{Ac_2O} [(C_6H_5)_2COAc]^{\cdot} \xrightarrow{+e}$$
$$\rightarrow [(C_6H_5)_2COAc]^- \xrightarrow[-AcO^-]{Ac_2O} (C_6H_5)_2C(COCH_3)OAc \quad .$$

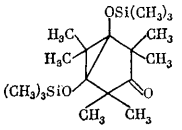
The electrochemical acetylation of diketones was achieved analogously[52]. An acetylated internal cyclisation product has been obtained by the reduction of 2-acetyl-2-methylcyclohexanone in solution in acetonitrile in the presence of tetraethylammonium bromide as the supporting electrolyte at a potential of -2.8 V (sat.cal.e-de) and with continuous supply of acetic anhydride:



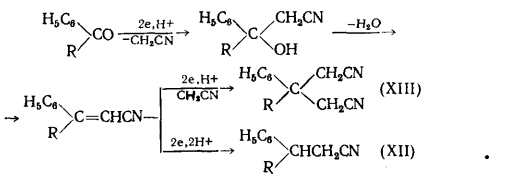
The reduction of 2,2,4,4,6,6-hexamethylcyclohexane-1,3,5-trione takes place similarly, the yield of the acetylation product reaching 71%:



If chlorotrimethylsilane is added to the solution instead of acetic anhydride, an unstable trimethylsilyl derivative is formed[53]:



An unusual reaction has been observed in the reduction of aromatic ketones in anhydrous acetonitrile; 3-substituted propionitriles and glutaronitriles are formed under these conditions[54]. In order to explain this reaction, it has been assumed that the anion formed as a result of electron transfer to a molecule of the carbonyl compound exhibits such a high proton affinity that a proton is abstracted from a solvent molecule, generating the anion $\bar{C}H_2CN$:



For acetophenone, the yields of products (XII) and (XIII) are 35–50% and 35–45% respectively. Related carbonyl compounds—benzaldehyde and benzophenone—give rise to similar products. A more detailed study of the reaction mechanism[55] confirmed the involvement of the $\bar{C}H_2CN$ anions.

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Thus cathodic coupling reactions are not only of theoretical but also of practical interest, since they extend significantly the applications of electrochemical methods in the synthesis of organic compounds. It is therefore of interest to carry out further studies in this field.

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