Electrochemical Synthesis of Compounds of General Formula $(R^1CH_2{\cdot}CR^2{\cdot}Y)_2$

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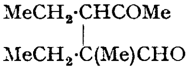
Summary The anodic oxidation of organic acids, R^1CO_2H, in the presence of substrates of the type $CH_2 = CR^2{\cdot}Y$ (Y = CHO, COMe, CO_2Et, and CN) leads with good yields to duplication products of general formula $(R^1{\cdot}CH_2{\cdot}CR^2{\cdot}Y)_2$.

OXIDATIVE addition of anions to organic substrates has been widely studied.[1] It is known that the anodic oxidation of certain anions of organic acids R^1CO_2H leads by a Kolbe reaction to $R^1{\cdot}R^1$ duplication compounds, but the fixation of the R^1 intermediate radical has so far been observed only in ethylenes, or dienes[2] or aromatic compounds.[3]

We used as substrates the compounds, $CH_2{=}CR^2{\cdot}Y$ (Y=CHO, COMe, CO_2Et, or CN) in which the ethylenic double bonds are activated by the electron withdrawing groups Y.† The electrolysis was carried out in a diaphragm cell, the substrate being introduced only in the anodic compartment. A platinum sheet was used as anode at a potential of >2 V.[4] The medium used was 8 N water–acetonitrile.

TABLE

Substrate	Anion	Products		Yield (%)
$CH_2{=}C(Me)CHO$	$MeCO_2^-$	$[MeCH_2{\cdot}C(Me)CHO]_2$		80
	$EtCO_2^-$	$[Pr^nC(Me)CHO]_2$		80
	$Pr^nCO_2^-$	$[Bu^nC(Me)CHO]_2$		70
	$(Me)_2CH{\cdot}CH_2CO_2^-$	$[(Me)_2CH{\cdot}(CH_2)_2{\cdot}C(Me)CHO]_2$		50
$CH_2{=}CH{\cdot}COMe$	$MeCO_2^-$	$[MeCH_2CHCOMe]_2$	*meso*	25
			dl	24
	$CD_3CO_2^-$	$[CD_3CH_2CHCOMe]_2$	*meso*	25
			dl	24
	$Et{\cdot}CO_2^-$	$[Pr^nCHCOMe]_2$	*meso*	24
			dl	24
$CH_2{=}C(Me)COMe$	$MeCO_2^-$	$[MeCH_2{\cdot}C(Me)COMe]_2$	*meso*	56
			dl	20
	$CD_3{\cdot}CO_2^-$	$[CD_3CH_2C(Me)COMe]_2$	*meso*	56
			dl	20
$CH_2{=}CHCO_2Et$	$MeCO_2^-$	$[MeCH_2{\cdot}CHCO_2Et]_2$		70
$CH_2{=}CH{\cdot}CN$	$MeCO_2^-$	$[MeCH_2{\cdot}CHCN]_2$	*meso*	48
			dl	52
Mixture of $CH_2{=}CH{\cdot}COMe$ and $CH_2{=}C(Me)CHO$	$MeCO_2^-$	 $\begin{array}{l}MeCH_2{\cdot}CHCOMe\\ \quad\quad\quad\ \ \vert\\ MeCH_2{\cdot}C(Me)CHO\end{array}$		23

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† Ref. 26 indicates that a product from two methyl groups and two molecules of acrylonitrile had been obtained in attempts to initiate the electrochemical polymerisation of acrylonitrile in acetic acid. Present work allows us to assign a structure to this product.

The products (see Table) were studied by n.m.r. and mass spectrometry. Where two diastereoisomers were separated, structures were assigned by chemical means and by comparison with compounds of known configuration.

The generalisation of this reaction to other substrates is being studied. Reaction mechanisms will be discussed elsewhere.

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