Electrolytic Reductive Coupling. XXI.[1] Reduction of Organic Halides in the Presence of Electrophiles

MANUEL M. BAIZER* AND JOHN L. CHRUMA

Central Research Department, Monsanto Company, St. Louis, Missouri 63166

Received November 29, 1971

Controlled potential electrolysis at a mercury cathode was used to effect two-electron reductive cleavages of carbon tetrachloride, ethyl trichloroacetate, ethyl bromoacetate, allyl chloride and bromide, benzyl chloride and bromide, ethyl 4-bromobutyrate, 4-bromobutyronitrile, and chloroacetonitrile in the presence of acrylonitrile, ethyl acrylate, diethyl fumarate, and diethyl maleate. The electrochemically generated anion nucleophilically attacked the acceptor to yield adduct anions. The latter evolved into final products by several routes: (a) by protonation, *e.g.*, 4-trichlorobutyronitrile from CCl_4 and acrylonitrile, (b) by cyclization–displacement of halide, *e.g.*, diethyl 1-chloro-1,2-cyclopropanedicarboxylate from ethyl trichloroacetate and ethyl acrylate, (c) by displacement on halogen of a polyhalo starting material, *e.g.*, diethyl 2,2,4-trichloroglutarate also from ethyl trichloroacetate and ethyl acrylate. The factors that must be considered in the design of these electrochemical syntheses are discussed. Reduction of benzyl chloride in the presence of carbon dioxide led directly to benzyl phenylacetate. Similarly, allyl chloride produced allyl crotonate. Reductive dehalogenative coupling of allyl halides and of ethyl bromoacetate alone are also reported.

Electrolytic reductive cleavage of $E(CH_2)_nL$, in which E is an electron-withdrawing group and L a "leaving" group, in the presence of substituted olefins (*e.g.*, styrene, acrylonitrile) which can trap the radicals or anions resulting from the cleavage has been proposed[2] as a novel synthetic route to polyfunctional molecules. Examples have been presented in which L is phosphonium[3a] or sulfonium.[3b] The present paper concerns related syntheses starting with organic halogen compounds.

There have been numerous studies of the polarography of organic halides in protic and, latterly, in aprotic media[4] and many associated studies concerned with elucidating the mechanism of the cleavage of the carbon–halogen bond.[5] However, not much work has been directed toward involving the dehalogenated fragments in coupling reactions with reagents deliberately added to the electrolysis mixture. As a result of this omission, usually only hydrocarbons, dimers,[6] and symmetrical mercury compounds[7] have been the final products obtained from electrolytic reduction of halides at mercury. Occasionally, electrolyses in the presence of carbon dioxide and identification of the carboxylic acid obtained have been employed, but more as proof that an anionic intermediate had been formed in the reductive cleavage than as a useful synthetic method.[8a] Rifi, however, has obtained acceptable yields of small ring compounds by electrolysis of certain α,ω-dihalides.[9a]

The work reported here was designed to probe the synthetic utility, for preparing coupled products, of reducing certain halides at controlled potential in the presence of an excess of selected acceptors. Carbon tetrachloride (CT), ethyl trichloroacetate (ETA), ethyl bromoacetate (EBA), allyl chloride (AC) and bromide (AB), benzyl chloride (BC) and bromide (BB), ethyl 4-bromobutyrate (EBB), 4-bromobutyronitrile (BBN), and chloroacetonitrile (CAN) were chosen as the halides; acrylonitrile (AN), ethyl acrylate (EA), and diethyl fumarate (DEF)–diethyl maleate (DEM) were the usual acceptors. Occasionally, a halide was reduced in the presence of only starting material or of carbon dioxide. Except where otherwise specified, mercury was the cathode. Yields were not optimized,[9b] and in some cases it was considered sufficient to determine whether or not coupling had occurred.

The organic chemist not conversant with the guidelines of organic electrosynthesis as they apply in this area will be assisted in assessing the rationale of the experiments and the results to be discussed below by considering that[4a] (a) the difficulty of electroreduction—as evidenced by increasing negative voltage required—is iodide < bromide < chloride; (b) monochlorides are reduced in only one discernible two-electron step and are, therefore, cleaved to chloride and a carbanion; (c) controlled potential electrolysis (cpe)[10] allows *gem*-polyhalo compounds to be reduced stepwise with loss of one halide at a time[11]—cpe, likewise, permits one to choose the particular halide–acceptor pair to be used in a coupling experiment so that only the former is reduced at the potential chosen (Table I); (d) the cation of the supporting electrolyte must not be discharged at the voltage needed for the reduction of the halide; (e) slow addition of the halide

---

[1] Paper XX: M. M. Baizer and J. L. Chruma, *J. Electrochem. Soc.*, **118**, 450 (1971).

[2] M. M. Baizer, *J. Org. Chem.*, **31**, 3847 (1966).

[3] (a) J. H. Wagenknecht and M. M. Baizer, *ibid.*, **31**, 3885 (1966); (b) J. H. Wagenknecht and M. M. Baizer, *J. Electrochem. Soc.*, **114**, 1095 (1967).

[4] (a) M. R. Rifi in "Organic Electrochemistry," M. M. Baizer, Ed., Marcel Dekker, New York, N. Y., Chapter 6; (b) C. K. Mann and K. K. Barnes, "Electrochemical Reactions in Nonaqueous Systems," Marcel Dekker, New York, N. Y., 1970, pp 201–244; (c) I. M. Kolthoff and J. J. Lingane, "Polarography," 2nd ed, Vol. II, Interscience, New York, N. Y., 1952, pp 647–651.

[5] *E.g.*, J. W. Sease, F. G. Burton, and S. L. Nickol, *J. Amer. Chem. Soc.*, **90**, 2595 (1968); P. Zuman, "Substituent Effects in Organic Polarography," Plenum Press, New York, N. Y., 1967; J. Simonet, H. Doupeux, P. Martinet, and D. Bretelle, *Bull. Soc. Chim. Fr.*, 3930 (1970).

[6] M. M. Baizer and J. P. Petrovich in "Progress in Physical Organic Chemistry," Vol. 7, A. Streitwieser, Jr., and R. W. Taft, Ed., Interscience, New York, N. Y., 1970, pp 220–223.

[7] *E.g.*, J. Grimshaw and J. S. Ramsey, *J. Chem. Soc. B*, 60 (1968).

[8] (a) *E.g.*, S. Wawzonek, R. C. Duty, and J. H. Wagenknecht, *J. Electrochem. Soc.*, **111**, 74 (1964). (b) F. H. Covitz, *J. Amer. Chem. Soc.*, **89**, 5403 (1967). (c) L. W. Marple, L. E. I. Hummelstedt, and L. B. Rogers, *J. Electrochem. Soc.*, **107**, 437 (1960), had reported finding two one-electron reductions of BB at 1×10^{-5} to 1×10^{-4} *M* in methanol–water–NaOH; these data were later reinterpreted by L. B. Rogers and A. J. Diefenderfer, *ibid.*, **114**, 942 (1967).

[9] (a) M. R. Rifi, *J. Org. Chem.*, **36**, 2017 (1971). (b) Yields are reported here on the basis of quantity of current passed; *i.e.*, they are current efficiencies for the formation of the given products. Except where otherwise indicated, the electrolyses were interrupted after an arbitrary period. Unreduced halo compound, still available in the catholyte, was not determined quantitatively. While chemical yields are therefore not given, they would deviate from current efficiencies only when mechanical losses or unlikely nonelectrochemical reactions between halo compound and medium occurred.

[10] L. Meites, *Pure Appl. Chem.*, **18**, 35 (1969).

[11] (a) S. Wawzonek and R. C. Duty, *J. Electrochem. Soc.*, **108**, 1135 (1961); (b) M. Nagao, N. Sato, T. Akashi, and T. Yoshida, *J. Amer. Chem. Soc.*, **88**, 3447 (1966); (c) P. Iversen, *J. Chem. Educ.*, **48**, 136 (1971).

TABLE I

POLAROGRAPHIC HALF-WAVE POTENTIALS[a]

Halide	Abbreviation	Electrolyte	$-E_{1/2}$ vs. sce	Electrophile	Abbreviation	Electrolyte	$-E_{1/2}$ vs. sce
Allyl bromide	AB	A[b]	1.29[e]	Acrylonitrile	AN	G[g]	2.15
Allyl chloride	AC	A	2.03	Carbon dioxide	CO_2	H[h]	2.3[i]
Benzyl chloride	BC	F[c]	2.25	Diethyl fumarate	DEF	H	1.54
4-Bromobutyronitrile	BBN	A	1.99	Diethyl maleate	DEM	D[j]	1.52
Chloroacetonitrile	CAN	A	1.45	Ethyl acrylate	EA	A	2.12
Chloroform	CF	C[d]	*1.95[f]				
Carbon tetrachloride	CT	C	*0.75[f]				
Ethyl bromoàcetate	EBA	A	0.88				
Ethyl 4-bromobutyrate	EBB	A	2.03				
Ethyl trichloroacetate	ETA	F[c]	0.65[f]				

[a] Taken from the literature (indicated by *) or determined here by standard procedure. Anhydrous DMF, 0.1 *M* supporting electrolyte, 25°. [b] Tetraethylammonium *p*-toluenesulfonate. [c] Tetra-*n*-propylammonium fluoroborate. [d] Tetra-*n*-butylammonium bromide. [e] First wave. Second wave at −1.57 V. [f] First wave. [g] 0.2 *M* tetra-*n*-butylammonium iodide, DMF + 2% water. [h] Tetraethylammonium perchlorate. [i] Acetonitrile as solvent. [j] Lithium chloride.

(at a rate sufficient to maintain a reasonable current) to the catholyte containing an excess of acceptor can be used to favor cross-coupling rather than reaction of reduced halide with starting halide; (f) allylic[12] bromides show two one-electron reductions in aprotic media—benzylic bromides have been reported to exhibit one, presumably two-electron, wave polarographically[8] but to yield products arising from both carbanionic[8a] and presumed radical[7] intermediates[13] in macroelectrolyses; (g) nonallylic and nonbenzylic bromides and iodides are considered to be reduced generally in a single two-electron step;[17] (h) since anodic formation of halogen accompanies cathodic reduction of the halide, a divided cell must be used; (i) when it is desired to trap cathodically produced carbanions usefully, it is necessary to minimize the concentration of proton donors present *ab initio* in the catholyte and/or acquired therein by migration of acidic substances from the anolyte—on the other hand, when carbanions couple with anionically polymerizable acceptors, failure to provide conditions for an early termination will lead to oligomers and polymers rather than to simple condensation products. As will be seen below, polymerization can be aborted by making available suitably a proton donor which does not vitiate the initial condensation or an intra- or intermolecular displacement reaction for termination.

Results and Discussion

Carbon Tetrachloride (CT).—The stepwise polarographic reduction of CT in dimethylformamide (DMF) has been discussed.[11a]

$$CCl_4 + 2e^- \longrightarrow Cl^- + \underset{1}{CCl_3^-}$$

$$1 + ZH^{18} \longrightarrow Z + \underset{2}{CHCl_3} \text{ (further reduced, second step)}$$

$$1 \rightleftharpoons \underset{3}{CCl_2} + Cl^-$$

$$3 + 2e^- \longrightarrow \underset{4}{CCl_2^{2-}}$$

$$4 + 2ZH^{18} \longrightarrow 2Z + CH_2Cl_2 \text{ (further reduced, third step)}$$

We have attempted to intercept **1** (before it could significantly dissociate or be protonated) by reducing CCl_4 at the potential of its first wave in the presence of an excess of AN, EA, and DEF or DEM. The results are summarized in Table II.

With AN.—Using a medium of tetraethylammonium *p*-toluenesulfonate dissolved in CH_2Cl_2 containing a small amount of water, the expected[19] product, **6a**, was obtained. The current efficiencey varied from 13 to 40% in the course of the run (expt 1). It is

$$1 + CH_2{=}CHX \longrightarrow \underset{5}{(Cl_3CCH_2CHX)^-}$$

$$5 + ZH \longrightarrow \underset{6}{Cl_3CCH_2CH_2X} + Z$$

$$\mathbf{a},\ X = CN$$
$$\mathbf{b},\ X = COOC_2H_5$$

evident that in this system substantial protonation occurs *after* coupling as well as before. The hydrophobic properties of the cation of the electrolyte used here have been discussed before.[20] It is also clear that in the "chemical" cyanoethylation of chloroform (CF),[19a] which requires large amounts of 40% aqueous benzyltrimethylammonium hydroxide to achieve even an 11% yield of **5a**, water does not fully inhibit the addition of **1** to AN.

---

(12) J. P. Petrovich and M. M. Baizer, *Electrochim. Acta*, **12**, 1249 (1967).

(13) This apparent contradiction arises because of the *assumption* that the formation of certain types of products, *e.g.*, bibenzyl and dibenzylmercury (particularly the latter), from a benzyl halide must proceed *via* a benzyl radical. However, an alternate pathway *via* carbanions can be suggested for the reactions of RX in which R can form a relatively stable carbanion (*e.g.*, allylic, benzylic).

Spontaneous[14] or electrolysis-catalyzed[15] partial formation of RHgX yields a species relatively easily reduced in two successive stages.[15]

$$RHgX \xrightarrow[Hg]{e} R\dot{H}g_n \xrightarrow{e} R^- + nHg$$

Reaction of R^- from the above reaction (or by the 2-e reduction of RX) with RX yields the dibenzyl type of product; displacement of X from RHgX by R^- (or, if RHgX is ionized, reaction of RHg^+ with R^-) yields the dibenzylmercury type without requiring free radicals. Displacements of this type by other stabilized carbanions have been reported.[16]

(14) L. B. Rogers and A. J. Diefenderfer, *J. Electrochem. Soc.*, **114**, 942 (1967).

(15) N. S. Hush and K. B. Oldham, *J. Electroanal. Chem.*, **6**, 34 (1963).

(16) B. L. Dyatkin, S. R. Sterlin, B. I. Martynov, E. I. Mysov, and I. L. Knunyants, *Tetrahedron*, **27**, 2843 (1971); D. Seyberth and J. M. Burlitch, *J. Organometal. Chem.*, **4**, 127 (1965).

(17) However, L. G. Feoktistov and S. I. Zhdanov, *Electrochim. Acta*, **10**, 657 (1965), report two one-electron reductions of 3-iodopropionitrile; J. W. Sease and R. C. Reed, Abstr. 134, Electrochemical Society Meeting, New York (spring 1969), N.Y., obtained hexane, hexene, and dihexylmercury upon reduction of 1-bromohexane.

(18) The solvent and/or tetraalkylammonium cation of the supporting electrolyte functioned as proton donors.

(19) (a) H. A. Bruson, W. Niederhauser, T. Riener, and W. F. Hester, *J. Amer. Chem. Soc.*, **67**, 601 (1945); (b) F. Nerdel, W. Brodowski, J. Buddrus, M. Fligge, P. Weyerstahl, K. Ulm, C. Finger, and D. Klamann, *Chem. Ber.*, **101**, 1407 (1968).

(20) *E.g.*, F. Beck, *Ber. Bunsenges. Phys. Chem.*, **72**, 379 (1968).

TABLE II

REDUCTIVE COUPLINGS WITH CARBON TETRACHLORIDE

		Catholyte Charges			Conditions				
Expt	Solvent, ml[b-d]	Salt (g)	CCl_4,[e,f] mmol	Acceptor (mmol)	−Cath V[g]	Temp, °C	mF[h]	Time, hr	Principal products (%)[a]
1	0.5 H_2O + CH_2Cl_2[b]	A[i] (10.6)	20[f]	AN (300)	1.20	30	3.5	4.5	**6a** (13)
2	0.5 H_2O + CH_2Cl_2[b]	B[j] (5.75)	20[f]	AN (300)	0.95	27	6.4	6.8	**6a** (28)
3	CH_2Cl_2[b]	C[k] (11.2)	10[f]	AN (300)	1.00	27	4.6	5.2	**2**
4	CH_2Cl_2[c]	B (5.0)	10[f]	AN (400)	0.80	30	6.7	6.5	**6a** (207)
5	24.6 $CHCl_3$ + CH_2Cl_2[b]	B (3.75)	10[f]	AN (300)	1.10	28	9.2	7.0	**6a** (143)
6	24.6 $CHCl_3$ + 4.0 H_2O[b]	A (16.0)	20[f]	AN (300)	0.98[m]	26	8.0	3.5	**6a** (347)
7	24.6 $CHCl_3$ + CH_2Cl_2[b]	B (3.75)	30[e]	EA (158)	1.30	16	5.1	3.0	**6b** (114)
8	0.5 H_2O + DMF[c]	A (20.0)	20[e]	EA (200)	1.30	18	6.4	3.5	**6b** (9) + **7** (24.6)
9	DMF[b]	D[l] (0.5)	57[f]	EA (58)	1.41	40	9.3	5.5	Traces of product
10	0.8 H_2O + DMF[d]	A (35.0)	250[e]	EA (254)	1.29	24	138.0	23.0	**2** + **7**
11	DMF[b]	B (2.0)	57[f]	DEF (58)	1.00	40	69.0	25.0	**8** (11.8) + **9** (1.7) + **10** (9.6) + **11** (16.2)
12	4.1 $CHCl_3$ + DMF[b]	B (2.0)	51[f]	DEF (58)	1.20	25	29.0	10.5	**8** (38) + **9** (28) + **10** (49.5)
13	1.0 H_2O + DMF[b]	A (3.6)	51[f]	DEF (58)	1.60	30	11.4	6.0	**2**
14	24.6 $CHCl_3$ + CH_2Cl_2[b]	B (3.75)	20[e]	DEM (122)	1.10	17	12.8	6.0	Traces of **8**, **9**, and **10**

[a] Based on current. [b-d] 60, 80, 140 ml total volume of catholyte, respectively. [e,f] Added gradually, at once, respectively. [g] *Vs.* sce. [h] mF = mA-hr/26.8. [i] Tetraethylammonium *p*-toluenesulfonate. [j] Tetraethylammonium chloride. [k] Tetra-*n*-butylammonium bromide. [l] Lithium chloride. [m] Platinum cathode.

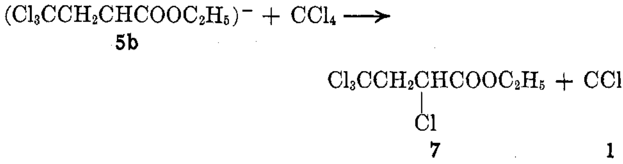
Tetraethylammonium chloride could also be used as electrolyte in the preparation of **6a** (expt 2).

An attempt (expt 3) to use tetrabutylammonium ion both as supporting cation and as proton donor was prematurely effective: chloroform but no **6a** was produced.

It appeared that, if chloroform could perform the role of proton donor ZH and, thereby, generate **1**, electroreduction of CCl_4 could serve only a catalytic function, to produce initial quantities of **1** and **5** and, thereafter, to replenish the quantities of **1** which were scavenged by adventitious proton sources. This expectation was realized. **6a** was obtained in greater than 100% current efficiency (expt 4 and 5), even at platinum and in the presence of a saturated aqueous solution of tetraethylammonium *p*-toluenesulfonate (expt 6). Effectively, electroreduction is serving to produce a strong base (**5**); related results have been reported before.[3,21]

Glc analyses of all the above catholytes did not reveal any unknown product corresponding to 2,2-dichlorocyclopropanecarbonitrile which could have been formed by addition of **3** to AN[22] or, alternatively, by intramolecular chlorine displacement–cyclization of **5a**. However, as mentioned below, this type of cyclization was observed in other cases.

With EA.—While electrocatalysis with the system CCl_4–$CHCl_3$ was achieved in one case (expt 7), the results (expt 8–10) were generally less satisfactory than those that had been obtained with AN. Generally, when water was used as the proton donor (expt 8), low yields of **6b** were obtained. The difficulty seemed to reside in the greater criticality of proton-donor control in nucleophilic reactions with EA than with AN:[23] on the one extreme was reduction of CT to chloroform only; on the other, probably oligomerization of EA *via* **5b**. A multiplicity of products was produced. One of these, **7**[24a] (expt 8), is of especial interest because it



$$(Cl_3CCH_2CHCOOC_2H_5)^- + CCl_4 \longrightarrow Cl_3CCH_2\underset{\underset{Cl}{|}}{C}HCOOC_2H_5 + CCl_3^-$$

5b **7** **1**

must have arisen by nucleophilic attack of **5b** upon the chlorine of CT. This type of displacement was also noted when ETA was used in couplings (see below). Nonelectrochemically generated anions have been reported to displace upon the chlorine of CT,[25] but in these cases, because of the very alkaline conditions used, the intermediate chloro products analogous to **7** are further transformed.

Our sample of **7**, collected by preparative glc, had the same retention time (including peak enhancement when fortified by authentic sample) and the identical nmr spectrum as the sample prepared according to the literature.[24a]

Since the reaction of **5b** with CT regenerates **1**, the formation of **7** is an electrocatalytic process; there is no over-all redox reaction.

With DEF.—In the absence of purposely added proton donor (expt 11) the products were **8**, **9**, and two olefinic materials, **10** and **11**. **9** could have arisen by cyclization of the adduct anion **12** or by addition of dichlorocarbene to DEF. Our sample of **10**, collected by preparative glc, had the identical glc retention time

---

[21] P. E. Iversen, *Tetrahedron Lett.*, 55 (1971).

[22] D. Seifert, J. M. Burlitch, R. J. Minasz, J. Y-P. Mui, H. D. Simmons, Jr., A. J. H. Treiber, and S. R. Dowd, *J. Amer. Chem. Soc.*, **87**, 4259 (1965).

[23] M. M. Baizer and J. D. Anderson, *J. Org. Chem.*, **30**, 1357 (1965).

[24] (a) M. Asscher and D. Vofsi, *J. Chem. Soc.*, 1887 (1963), prepared **7** by modulated radical addition of CT to EA. This method has been further studied.[24b] (b) J. Tsuji, XXII IUPAC Congress, Boston, Mass., July 25–30, 1971. (c) Radical additions of methyl dichloroacetate to 1-decene have been reported to give complex mixtures: P. Guerrini, J. Sorba, and D. Lefort, *C. R. Acad. Sci., Ser. C*, **272**, 1690 (1971).

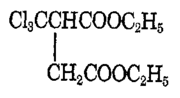
[25] (a) C. Y. Meyers, A. K. Malte, and W. S. Matthews, *J. Amer. Chem. Soc.*, **91**, 7510 (1969); (b) G. Morel, R. Seux, and A. Foucaud, *Tetrahedron Lett.*, 1031 (1971).

TABLE III

REDUCTIVE COUPLINGS WITH ETHYL TRICHLOROACETATE

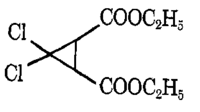
		Catholyte charges			Conditions				
Expt	Solvent, ml[b,c]	Salt (g)	ETA,[f,g] mmol	Acceptor (mmol)	−Cath V[h]	Temp, °C	mF[i]	Time, hr	Principal products (%)[a]
15	DMF[b]	D[e] (0.5)	100[f]	AN (200)[f]	0.84	25	40.0	6.5	**18a** (80) + **17a** (20)
16	7.1 $CHCl_2CO_2Et$ + DMF[b]	B[d] (2.0)	12[f]	EA (180)	0.85	27	24.0	6.0	**18b** (99.9) + **17b** (1.1)
17	9.2 $CHCl_2CO_2Et$ + DMF[b]	D (0.5)	12[g]	EA (180)	0.90	28	25.0	7.5	**18b** (110) + **17b** (43.5)
18	DMF[b]	D (0.5)	145[g]	EA (156)	0.90	45	28.0	7.5	**18b** (86) + **17b** (39)
19	9.0 EtOH + DMF[b] 9.2 $CHCl_2CO_2Et$	D (0.5)	12[g]	EA (180)	0.93	30	21.0	7.0	**18b** (73)
20	DMF[b]	D (0.5)	145[f]	EA (200)	0.97	40	122.0	6.5	**18b** (29) + **17b** (11.4)
21	DMF[c]	D (0.5)	145[f]	DEM (158)	0.75	38	119.0	6.0	**19** (55)

[a] Based on current. [b,c] 60, 80 ml total volume of catholyte, respectively. [d] Tetraethylammonium chloride. [e] Lithium chloride. [f,g] Added gradually, at once, respectively. [h] *Vs.* sce. [i] mF = mA-hr/26.8.

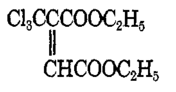


$$\begin{array}{l} Cl_3CCHCOOC_2H_5 \\ \quad | \\ \quad CH_2COOC_2H_5 \end{array}$$

8



9

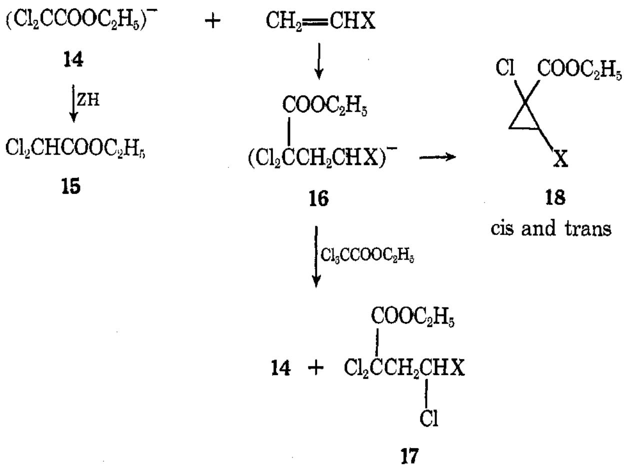


$$\begin{array}{l} Cl_3CCCOOC_2H_5 \\ \quad \| \\ \quad CHCOOC_2H_5 \end{array}$$

10

$C_9H_{12}Cl_2O_4$

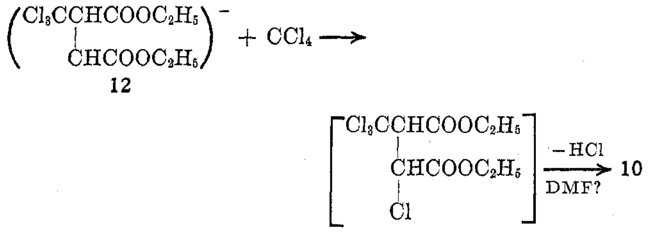
11



a, X = CN
b, X = $COOC_2H_5$

and nmr spectrum with the material prepared according to the literature.[26]

It is reasonable to assume that **13**, formed by a process analogous to that which led to **7**, was dehydrohalogenated by the warm DMF.



13

The bromotrichloromethyl analog of **13** is converted to **10** by cold triethylamine.[26] **11** is an unsaturated diester (ir and nmr) whose detailed structure is uncertain at present.

When CF was used in the catholyte as proton donor (expt 12), **8**, **9**, and **10** were again obtained. The total yield was better than in expt 11.

With DEM.—No coupling products were obtained when water was present (expt 13). With CF as proton donor, very small quantities of **8** (major), **9**, and **10** were detected. It appears that only the DEF present as an impurity in the DEM had reacted.

Ethyl Trichloroacetate (ETA).—The data are summarized in Table III. Reduction at the first wave yields the carbanion **14**, which has been shown[27] to be a precursor of dichlorocarbene and not of chloroethoxycarbonyl carbene. We, therefore, postulate that in the reductive coupling of ETA with AN and with EA the formation of cyclopropyl derivatives **18**[28] arises by addition of **14** to the acceptor, followed by intramolecular elimination of Cl^-. The intermediary of **16** is unequivocally shown in the formation of **17**[24b] by what must be a displacement reaction of **16** upon the chlorine of ETA. That this type of displacement can occur was shown by treating sodio diethyl malonate with ETA; the products were diethyl chloromalonate and tetraethyl 1,1,2,2-ethanetetracarboxylate.[29]

The above experiments yielded only traces of the linear product (protonated **16**) which is the major product in the addition of ethyl dichloroacetate to AN or EA in the presence of alkali metal alkoxides.[30] In the cited reaction, as in typical Michael-type condensations, the donor—in this case alkyl dichloroacetate—can supply protons to react with **16** and regenerate the attacking anion; in the electrochemical reaction, **16** can abstract a proton from solvent or tetraalkylammonium ion (when used) or from adventitious water or, obviously more advantageously, can achieve stabilization by forming **17** and **18**. Including ethyl dichloroacetate alone (expt 16 and 17) or with ethanol (expt 19) did not in these experiments protonate **16b**. This

---

[26] R. E. Bowman, M. D. Closier, and P. J. Islip, *J. Chem. Soc.*, 3841 (1964).

[27] W. E. Parham and F. C. Loew, *J. Org. Chem.*, **23**, 1705 (1958).

[28] 1-Alkyl-2-chloro-1,2-cyclopropanedicarboxylates have recently been prepared from α-chloroacrylates and ethylzinc chloride: Y. Kawakami and Tsuruta, *Tetrahedron Lett.*, 1173 (1971).

[29] A small yield of dimer was obtained[25b] in the reaction of benzylphenylacetonitrile with carbon tetrachloride and solid potassium hydroxide in *tert*-butyl alcohol.

[30] H. Timmler and R. Wegler, *Angew. Chem.*, **72**, 1001 (1960).

TABLE IV

REDUCTIVE COUPLINGS WITH ETHYL BROMOACETATE

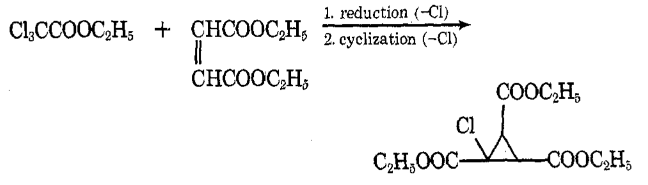
	Catholyte charges				Conditions				
Expt	Solvent, ml[b]	Salt (g)	EBA,[e] mmol	Acceptor (mmol)	−Cath V[g]	Temp, °C	mF[h]	Time, hr	Principal products (%)[a]
22	0.3 H_2O + DMF	A[c] (10.0)	50	Self	1.00	15	48.5	10.8	**20** (19.8) + **21** (51) + **22** (4.3) + **23** (6.6) + **24** (5.7)
23	0.3 H_2O + AN	A (25.0)	50	AN	1.83	20	18.7	5.0	Polymer + **21** + **27a** (34)
24	1.0 H_2O + DMF	A (10.0)	46	AN (300)	1.45	20	50.0	7.0	**21** (95) + **27a** (2.8)
25	0.3 H_2O + DMF	A (10.0)	50	EA (180)	2.00	20	54.0	7.0	**21** (55) + **23** (trace) + **27b** (42.6)
26	0.3 TBP[i] + DMF	A (10.0)	50	EA (180)	1.00	18	25.5	7.5	**21** (73.5)
27	0.3 H_2O + DMF	A (10.0) E[d] (1.0)	37	EA (180)	1.50	20	8.8	7.0	**21** (14.7) + **27b** (76)

[a] Based on current. [b] 60 ml total volume of catholyte. [c] Tetraethylammonium *p*-toluenesulfonate. [d] Tetraethylammonium bromide. [e] Added gradually. [f] Ethyl chloroacetate. [g] *Vs.* sce. [h] mF = mA-hr/26.8. [i] 2,6-Di-*tert*-butylphenol (g).

may reflect a difference in reactivity between the ion pair **16**$^-R_4N^+$ in DMF present in the electrochemical situation and the pair **16**$^-Na^+$ in toluene present in the "chemical" reaction.[30]

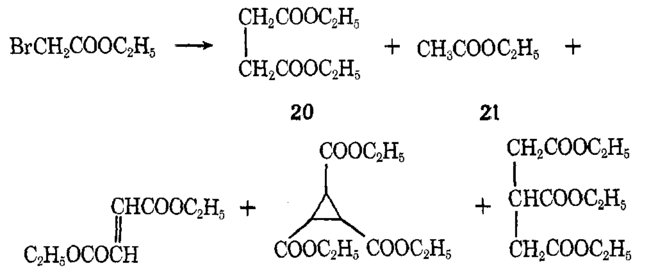
In this case the sequence **14** → **16** → **17** is electrocatalytic, so that the yields reported based on current are not of great significance.

Reductive coupling of ETA with DEM yielded **19** (expt 21).



19

Ethyl Bromoacetate (EBA).—The data are summarized in Table IV. Attempted reductive dehalogenative dimerization (expt 22) in the presence of a small amount of water did, indeed, yield diethyl succinate **20**, but in addition **21**, **22**, **23**, and **24**. By contrast, potassium amalgam reduction of chloroacetic acid esters is reported to yield *ca.* 70% of succinate esters.[31] Our results are best accommodated by the proposal that **25**, the product of the reduction of EBA, functions as a strong base[3,21] and generates **26**. Thereafter, the reaction course is similar to that proposed by Abushanab,[32a] who prepared **26** from ethyl haloacetate and metal–liquid ammonia. We have identified DEF (which he postulated) among the products; in addition, whereas, according to this scheme **23** arises by attack on DEF of **26** followed by ring closure–elimination, attack on DEF by **25** (formed in the electrochemical but not in the nonelectrochemical sequence) leads also to **24**.

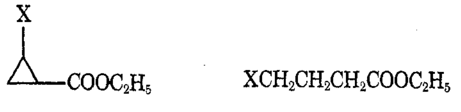


20 **21** **22** **23** **24**

$$BrCH_2COOC_2H_5 \xrightarrow{2e^-} \underset{\textbf{25}}{(CH_2COOC_2H_5)^-}$$

$$\textbf{25} + EBA \longrightarrow \textbf{21} + \underset{\textbf{26}}{(BrCHCOOC_2H_5)^-}$$

With AN.—The major coupled product isolated (expt 23 and 24) was **27a**; no straight-chain condensation product, *i.e.*, **28a**, was found. The formation of both polymer and **27a** in expt 23 may be construed to indicate that **27a** arises *via* addition of **26** to AN followed by ring closure–displacement rather than by prior formation of the carbene from **26**.



27 **28**

a, X = CN
b, X = $COOC_2H_5$

With EA.—The major coupled product was **27b** (expt 25). Again, no **28b** was detected. An attempt (expt 26) to favor the formation of the latter by including 2,6-di-*tert*-butylphenol in the catholyte as a proton donor toward the anion which would be formed if **25** added to EA was unsuccessful; **25** was protonated before condensation and yielded only **21**.

Since "activated" chloride is easily displaced by bromide,[8a] it was possible to use ethyl chloroacetate instead of EBA, include bromide ion in the electrolyte, and still reduce at the potential for EBA (expt 27).

Compounds **23**, **27a**, and **27b** have recently been prepared from ethyl (dimethylsulfuranylidene)acetate, and the appropriate olefin,[33a] the bromo analog of **18b**, but not of **18a**, was similarly synthesized.[33b] An analog of **27b** preponderantly in cis form has been prepared[32b] from ethyl chloroacetate, methyl acrylate, and sodium methoxide at −78°. A new synthesis of analogs of **23**, **27a**, **27b** *via* a copper(I) oxide–isonitrile catalyzed reaction of haloacetates with activated olefins has just appeared.[34] All these methods seem less direct and

---

(31) V. A. Smirnov and A. V. Markova, *Zh. Prikl. Khim.*, **44**, 1364 (1971); *Chem. Abstr.*, **75**, 88065g (1971).

(32) (a) E. Abushanab, *Tetrahedron Lett.*, 2833 (1967), and literature cited therein; (b) A. H. Andrist and P. W. Ford, *Chem. Ind.* (*London*), 930 (1971).

(33) (a) G. B. Payne, *J. Org. Chem.*, **32**, 3351 (1967); (b) G. B. Payne and M. R. Johnson, *ibid.*, **33**, 1285 (1968).

(34) T. Saegusa, Y. Ito, K. Yonezawa, Y. Inubushi, and S. Tomita, *J. Amer. Chem. Soc.*, **93**, 4049 (1971).

TABLE V

REDUCTIVE COUPLINGS WITH ALLYL HALIDES

	Catholyte charges				Conditions				
Expt	Solvent, ml^b	Salt (g)	Halide^{f,g} (mmol)	Acceptor (mmol)	−Cath V^i	Temp, °C	mF^j	Time, hr	Principal products (%)^a
28	DMF	A^c (10.0)	AC (100)^g	Self	1.845	28	18.5	4.0	**29** (72)
29	DMF	A (10.0)	AC (50)^g	Self	2.25	20	38.5	23.0	**29** (75)
30	DMF	A (10.0)	AB (100)^g	Self	1.00	30	27.0	6.5	**29** (53.5)
31	DMF	A (10.0) E^d (1.0)	AC (32)^g	Self	1.35	27	22.6	22.0	**29** (33.5)
32	DMF	D (0.5)	AB (50)^g	Self	1.80	20	56.0	6.5	**29** (78)
33	CH_2Cl_2	E (7.4)	AB (50)^g	Self	1.62^l	27	1.2	3.0	**29** (trace)
34	DMF	A (10.0)	AB (50)^g	Self	1.56^l	28	5.8	6.5	**29** (35)
35	1.0 TBP^k + DMF	A (10.0)	AB (27)^f	AN (300)	1.60	19	24.2	6.0	**30** (13) + **29** (35) + **32** (12.6)
36	0.2 H_2O + DMF	A (10.0)	AB (45)^f	AN (300)	1.65	28	52.0	7.0	Polymer + **29** (10.5) + **32** (trace)
37	1.0 H_2O + DMF	A (10.0)	AB (50)^f	AN (300)	1.755	25	52.0	5.5	Polymer + **32** (18)
38	2.0 H_2O + DMF	A (10.0)	AB (38)^f	AN (300)	1.86	27	43.4	5.5	**30** + **29** + **32**
39	0.3 TBP + DMF	A (10.0)	AB (21)^f	EA (180)	1.50	21	18.1	6.0	**30** + **29** (55) + **33** (9.3)
40	2.0 H_2O + DMF	A (10.0)	AB (21)^f	EA (180)	1.80	12	33.0	4.5	**33** (4.2)
41	1.0 H_2O + DMF	A (10.0)	AB (8.3)^f	DEM (120)	1.25	16	12.4	4.0	**30** + 18 + **34** (trace)
42	0.2 H_2O + DMF	A (10.0)	AB (4.1)^f	DEM (120)	1.30	17	14.7	7.0	**34** (48.8)
43	DMF	B^e (2.0)	AC (6.3)^f	CO_2^{h}	2.10	25	145.0	10.5	**35**
44	DMF	B (2.0)	AC (4.2)^f	CO_2^{h}	2.05	26	76.0	8.5	**35**

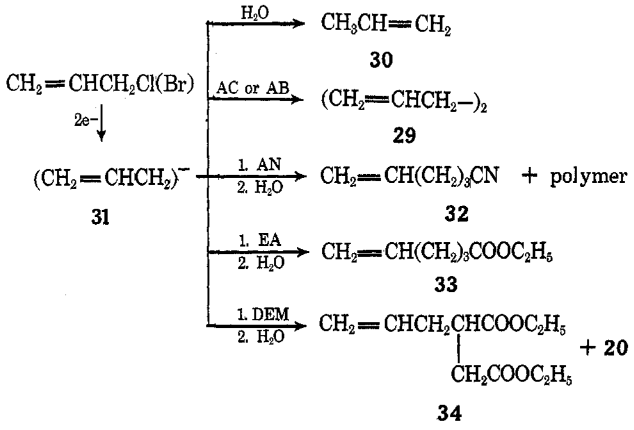
[a] Based on current. [b] 60 ml total volume of catholyte. [c] Tetraethylammonium *p*-toluenesulfonate. [d] Tetraethylammonium bromide. [e] Tetraethylammonium chloride. [f,g] Added gradually, at once. [h] Bubbled continuously through catholyte. [i] *Vs.* sce. [j] mF = mA-hr/26.8. [k] 2,6-Di-*tert*-butylphenol (g). [l] Platinum electrode.

facile than the electrochemical procedure reported here.

Allyl Halides.—The data are summarized in Table V. The dehalogenative coupling of allyl halide to 1,5-hexadiene (**29**) was investigated under a variety of conditions (expt 28–34). Yields were good to excellent; the major by-product was propylene (**30**).

When AC was the halide reduced (expt 28 and 29), a single two-electron step is indicated.[12] The route to **29** is, therefore, *via* the displacement of chloride from AC by the allyl carbanion.[35] The presence of proton donors is injurious to the yield. When, however, allyl bromide (AB)—or AC in the presence of a bromide-containing electrolyte—is used, radical as well as anionic routes to **29** are available. At potentials more anodic than *ca.* −1.5 V (expt 30 and 31) it is likely that **29** was found *via* the electrode product diallylmercury, which easily decomposes on warming.[36,37] The only moderate yields obtained may be due to the difficulty of getting good material and current balances. At potentials more cathodic than *ca.* −1.5 V (expt 32) an anionic course is followed. An attempt to avoid the intervention of mercurials by using a platinum cathode (expt 33 and 34) gave poorer results.

With AN.—The cathode potentials chosen (expt 35–38) were always negative enough to ensure a two-electron[38] reduction of AB. In some cases (expt 37 and 38) they were negative enough to approach AN reduction, since we had previously found[39] that this procedure improves the yield of mixed coupled products. The allyl carbanion **31** formed electrochemically may (a) attack an available proton source to form **30**; (b) attack AB to form **29**; (c) attack AN to form the anion of the coupled product, which anion may be protonated to 5-hexenenitrile (**32**); or (d) react additionally with AN to form polymer. Attempts were made to minimize a (expt 35 and 36) by having a medium of low proton donor availability without encountering d (expt 36 and 37), and to minimize b by adding AB slowly to the catholyte containing an excess of AN. In view of these sometimes contradictory requirements the yields of **32** were low.



With EA.—Reductions at cathode voltages removed from that required for reduction of EA (expt 39) as well as close to it (expt 40) gave poor yields of the coupled product, ethyl 5-hexenoate (**33**).

With DEM.—Because of the relatively positive po-

---

(35) In the formation of **27** from allyl halides and iron powder in DMF, as reported by D. W. Hall and E. Hurley, Jr., *Can. J. Chem.*, **47**, 1238 (1969), the yield is excellent when allyl bromide is used but poor and not greatly improved by addition of a bromide when allyl chloride is used under moderate conditions.

(36) K. V. Vijayaraghavan, *J. Indian Chem. Soc.*, **17**, 589 (1940); A. Kirrmann and M. Kleine-Peter, *Bull Soc. Chim. Fr.*, 894 (1957).

(37) Our identification and analysis of **20** was based on glc and under these conditions diallylmercury and dibenzylmercury decompose to R–R. See footnote 13.

(38) This would be true whether it is the second wave of AB in an anhydrous system that is involved or the merged single two-electron wave of an aqueous system.

(39) M. M. Baizer, J. P. Petrovich, and D. A. Tyssee, *J. Electrochem. Soc.*, **117**, 173 (1970).

TABLE VI

REDUCTIVE COUPLINGS WITH BENZYL HALIDES

	Catholyte charges				Conditions				
Expt	Solvent[b-d]	Salt (g)	Halide[g,h] (mmol)	Acceptor	−Cath V[j]	Temp, °C	mF[k]	Time, hr	Principal products (%)[a]
45	DMF[c]	F[e] (2.26)	BB (100)[h]	Self	1.24	25	104.0	9.0	**37** (49.6) + **38** (34)
46	DMF[d]	F (2.45)	BB (100)[h]	Self	1.24	22	103.0	9.0	**37** (44) + **38** (32) + **36** (9)
47	DMF[d]	F (2.45)	BB (100)[h]	Self	1.10	24	97.0	20.0	**37** (68) + **39** (trace)
48	DMF[b]	B[f] (2.0)	BC (50)[g]	CO_2[i]	2.37	24	95.0	6.0	**38** (2.5) + **40** (42.8)

[a] Based on current. [b-d] 60, 130, 140 ml total volume of catholyte, respectively. [e] Lithium bromide. [f] Tetraethylammonium chloride. [g,h] Added gradually, at once. [i] Bubbled continuously through catholyte. [j] *Vs.* sce. [k] mF = mA-hr/26.8.

tential required for the reduction of DEM, some of it was coreduced during the reduction of AB (expt 41 and 42). This was evidenced by the presence of a significant background current before AB was added and by the presence of diethyl succinate (**20**) among the products. While only a trace of coupled product, diethyl allylsuccinate (**34**), was formed in expt 41, reducing the amount of water in the catholyte to 0.2 ml (expt 42) resulted in a moderately good yield.

With CO_2.—Electrolysis in the presence of CO_2 has been used as a means of trapping anion radicals[40] and anions from hydrocarbons and halides,[8a] respectively. Good[40a] to very poor[8a] yields of acids have been obtained.

In expt 43 and 44 neither 3-butenoic nor crotonic acid was obtained in more than trace amounts.[41] The major coupling product was allyl crotonate (**35**). While the multiplicity of products did not permit a meaningful determination of the current efficiency, this one-step synthesis of the ester is arresting. It was examined in greater detail in the reduction of benzyl chloride described later.

Reaction of the allyl carbanion with CO_2 yields a carboxylate anion, **36**, which under conditions prevailing in the catholyte[42] must become crotonate rather than 3-butenoate. The counterion is tetraethylammonium. In the presence of excess active halide (AC) the salt is rapidly converted to ester. It was established independently that tetraethylammonium carboxylates are rapidly converted to esters with active and even only moderately active halides in DMF.[43]

$$\mathbf{31} + CO_2 \longrightarrow$$

$$[CH_2{=}CHCH_2COO^- \rightleftarrows \underset{\mathbf{36}}{CH_3CH{=}CHCOO^-}]R_4N^+$$

$$\mathbf{36} + AC \longrightarrow \underset{\mathbf{35}}{CH_3CH{=}CHCOOCH_2CH{=}CH_2}$$

Since **35** was present in only dilute solution and since the electrolysis was carried out at too positive a potential for reduction of **35** ($-E_{1/2} = -2.31$ V), no hydrodimerization[42] which would have led to diallyl 3,4-dimethyl adipate occurred.

Benzyl Halides (Table VI).—Dehalogenative coupling of BB at −1.24 V (expt 45 and 46) yielded mainly dibenzylmercury (**37**), toluene (**38**), and in expt 46 a small amount of bibenzyl (**39**). A later run (expt 47), made purely for the purpose of preparing **37**, provided the latter in good yield with only a trace of **39**.[44] Similar results have been reported before using a methanolic LiCl system.[7]

$$C_6H_5CH_2Br \xrightarrow[Hg]{\text{reduction}} \underset{\mathbf{37}}{(C_6H_5CH_2)_2Hg} + \underset{\mathbf{38}}{C_6H_5CH_3} + \underset{\mathbf{39}}{(C_6H_5CH_2)_2}$$

Reduction of BC in the presence of CO_2 (expt 48) at −2.37 V led directly[45] to benzyl phenylacetate (**40**) in good yield. A reported[8a] reduction of 10 ml of BC in DMF containing a bromide electrolyte at "semicontrolled potential" had yielded 0.1 g of phenylacetic acid after 1.68 A-hr of electrolysis. The ester **40** was, undoubtedly, formed by the same circumstances that obtained in the formation of **35** (*vide supra*).

$$2C_6H_5CH_2Cl \xrightarrow[CO_2]{2e^-} \underset{\mathbf{40}}{C_6H_5CH_2COOCH_2C_6H_5} + 2Cl^-$$

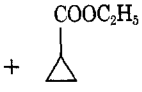
Miscellaneous Halides (Table VII).—Since the reduction of this group of halides required rather negative cathode voltages, the electrolyses were carried out at cathode voltages sufficient to reduce the acceptors. It has been shown[1] that this procedure can lead to reductive coupling; self-coupling of the acceptor must now, however, generally be expected.

CAN and/or bromoacetonitrile[8a] with EA (expt 49) gave a mixture of *cis*- and *trans*-**27a** which had previously been obtained (above) from EBA and AN. The two pairs of reagents are, therefore, commutative for the preparation of **27a**. The analytical method did not allow any acetonitrile formed to be differentiated from EA; no diethyl adipate (**41**) or linear condensation product, *i.e.*, **28a**, was found. The sequence leading to **27a** may well be similar to the one discussed above in the EBA experiments.

EBB reduced alone (expt 50) gave ethyl butyrate (**42**), a small yield of ethyl cyclopropanecarboxylate (**43**), and a trace of ethyl 4-acetoxybutyrate (**44**). Since a few drops of acetic acid had been added occasionally to the catholyte to keep it from getting excessively alkaline, **44** is, undoubtedly, an artifact, a solvolysis product of EBB. The formation of *any* **43** under these mild conditions is remarkable. It sug-

$$\underset{\text{EBB}}{Br(CH_2)_3COOC_2H_5} \xrightarrow[\text{trace HOAc}]{}$$

$$\underset{\mathbf{42}}{CH_3(CH_2)_2COOC_2H_5} + $$



43

$$+ \underset{\mathbf{44}}{CH_3COO(CH_2)_3COOC_2H_5}$$

---

[40] (a) S. Wawzonek, E. W. Blaha, R. Berkey, and M. E. Runner, *ibid.*, **102**, 235 (1955); (b) R. Dietz and M. E. Peover, *Discuss. Faraday Soc.*, **45**, 154 (1968); (c) J. W. Loveland, U. S. Patent 3,032,489 (1962); *Chem. Abstr.*, **57**, 4470 (1962); S. Wawzonek and D. Wearing, *J. Amer. Chem. Soc.*, **81**, 2067 (1959).

[41] Glc examination of silylated electrolysis products compared with silylated authentic acids.

[42] M. R. Ort and M. M. Baizer, *J. Org. Chem.*, **31**, 1646 (1966).

[43] J. H. Wagenknecht, unpublished work in this laboratory.

[44] Analysis by nmr. In glc **26** decomposes quantitatively to **27**.

[45] Glc analysis of the catholyte. No phenylacetic acid or benzyl alcohol were present.

TABLE VII

REDUCTIVE COUPLINGS WITH MISCELLANEOUS HALIDES

	Catholyte charges				Conditions				
Expt	Solvent, ml[b]	Salt (g)	Halide[e,f] (mmol)	Acceptor (mmol)	−Cath V[g]	Temp, °C	mF[h]	Time, hr	Principal products (%)[a]
49	0.3 H_2O + DMF	A[c] (10.0) E[d] (2.0)	CAN (50)[e]	EA (180)	2.25	15	38.0	6.5	**27a** (43.5)
50	DMF	A (10.0)	EBB (80)[f]	Self	2.28	22	82.0	22.0	**42** (82) + **43** (17) + **44** (1.3 g)
51	0.5 H_2O + DMF	A (10.0)	EBB (40)[e]	EA (180)	2.22	22	55.6	7.0	**41** + **43** + **44**
52	1.0 H_2O + DMF	A (10.0)	EBB (33)[e]	AN (300)	2.31	25	40.0	6.0	Polymer + **45** + **43** + **44**
53	0.5 H_2O + DMF	A (10.0)	BBN (50)[e]	EA (180)	2.22	25	42.5	6.0	**41**
54	1.0 H_2O + DMF	A (10.0)	BBN (50)[e]	AN (300)	2.22	25	40.0	5.5	Polymer + **45**

[a] Based on current. [b] 60 ml total volume of catholyte. [c] Tetraethylammonium *p*-toluenesulfonate. [d] Tetraethylammonium bromide. [e,f] Added gradually, at once. [g] *Vs.* sce. [h] mF = mA-hr/26.8.

$$\text{EBB} \xrightarrow{2e} {}^{-}\text{CH}_2\text{CH}_2\text{CH}_2\text{COOC}_2\text{H}_5$$

45

gests that reduction of EBB yielded the anion **45**, which abstracted a proton from the α position of EBB to yield **42** and **46**; the usual intramolecular elimination–

$$\mathbf{45} + \text{EBB} \longrightarrow \mathbf{42} + \underset{\mathbf{46}}{\text{BrCH}_2\text{CH}_2\bar{\text{C}}\text{HCOOEt}}$$

ring closure of **46** formed **43**. "Standard" cyclization of BBN requires either strong alkali, which leads to cyclopropanecarboxylic acid,[46a] or the use of sodium in liquid ammonia if the nitrile is desired;[46b] neither method is probably suitable for preparing **43** directly from EBB.

Reduction of EBB in the presence of EA (expt 51) yielded **43**, **44**, and **41** but no coupled product; in the presence of AN instead of EA (expt 52) only adiponitrile (**45**) was found.

BBN (expt 53 and 54) yielded no coupling products.

TABLE VIII

WORK-UP AND ANALYSES OF CATHOLYTES

Expt	Work-up procedure-glc column/conditions
1–6, 16, 17, 19, 38, 41, 43	A-I
7,[a] 8,[b] 21,[a,b] 40, 42	D-I
9, 13	A-II
10, 48[d,e]	A-II, then D-II
11,[a,b], 12,[a,b] 14, 15[a,b]	D-II
18,[a,b] 20,[a] 39	A-I, then D-I
22–24, 51–54	D-III
25,[a] 26, 35, 36, 45, 49[a,b]	A-III, then D-III
27, 28, 30–34, 44[d]	A-III
29[a]	B-III
46, 50	A-III, then C, then D-III
47[c]	C

[a] Products also isolated by fractional distillation and structures confirmed. [b] Products also isolated by preparative-scale glc; a 3 ft × $^3/_4$ in. stainless steel column packed with 16% SE-52 on Chromosorb W (60–80 mesh) was used. The carrier flow rate and column temperature were selected to give the highest resolution of components to be collected. Collections were made in cooled glass capillary tubes. [c] Analysis by nmr. [d] Catholyte silylated prior to analysis: to 10μl in a screw-cap vial was added 20 μl of Regisil (Regis Chemical Co.), and the mixture was warmed 10 min before analysis. [e] Catholyte acidified prior to work-up.

Experimental Section[47]

Equipment.—The potentiostat used was a 1.6-A model, Chemical Electronics Co., Newcastle, England. Total current passed was measured using a Lectrocount, Royson Engineering Co., Hatboro, Pa. Polarograms were obtained with a Sargent Model XXI polarograph. Ir spectra were obtained with a Beckman Microspec instrument. Nmr spectra were determined at 60 Mc with a Varian A-56/60 or T-60 spectrometer; the chemical shifts are expressed in δ (parts per million) relative to tetramethylsilane as an internal standard. Analytical glc determinations were made using a Hewlett-Packard 5750 model; preparative glc experiments employed the Model 770 F & M instrument. Electrolysis Cell No. 1 was an H-cell similar to that described by Lingane.[48] The erlenmeyer (cathode) compartment had a minimum capacity of *ca.* 130 ml and was separated from the cylindrical anode compartment by a 30-mm diameter medium-porosity glass frit. The cathode mercury, 50 ml, had an area of 50 cm^2. The anode was a platinum foil cylinder, 20 × 30 cm. Mechanical stirring was used in the cathode chamber, magnetic stirring in the anode chamber. The top of the cathode compartment was fitted with a ground-glass multiport head to which thermometer, buret, condenser, etc., could be attached. The reference sce was held rigidly in place; the salt bridge, drawn to a capillary, was positioned about 1 mm above the mercury. H-Cell no. 2 was constructed of two cylindrical members; the horizontal section contained a 30-mm-diameter medium-porosity glass frit. The cathode (15 ml when mercury) had an area of 15.5 cm^2. The anode was a platinum foil, area 5.8 cm^2. The volume was *ca.* 60 ml on each side. Stirring and auxiliary inlets were similar to those of cell no. 1.

Reagents and Starting Materials.—The DMF was purified as previously described.[49] Allyl bromide (AB), bp 70°, and allyl chloride (AC), bp 45°, were redistilled from high-quality supplies. Acrylonitrile (AN), bp 78°, and ethyl acrylate (EA), bp 99°, were likewise redistilled and stored over a trace of *p*-nitrosodimethylaniline. The stabilizer was not removed before electrolyses. Benzyl bromide (BB), chloroacetonitrile (CAN), diethyl fumarate (DEF), and ethyl bromoacetate (EBA) were all Eastman White Label and used as received. Carbon tetrachloride (CT) and chloroform (2) were Mallinckrodt AR. 4-Bromobutyronitrile (BBN) and 2,6-di-*tert*-butylphenol (DBP) were Aldrich products used as received. Benzyl chloride (BC) was Fisher Reagent Grade and methylene chloride was Fisher Certified. Ethyl trichloroacetate (ETA) was prepared from the acid (Aldrich) by the Fischer–Speyer method. Diethyl maleate (DEM) was MC and B material redistilled, bp 80° (2 mm); glc analysis showed *ca.* 11% DEF content. Ethyl 4-bromobutyrate (EBB) was prepared according to the literature.[50] Tetraethylammonium chloride (Eastman) was dried in a vacuum oven at 100°. Tetraethylammonium bromide (Eastman) was recrystallized from ethanol, and tetraethylammonium *p*-toluenesulfonate (Aldrich) was recrystallized twice from acetone before similar drying. Lithium chloride and bromide (Fisher Certified) were

---

[46] (a) C. M. McCloskey and G. H. Coleman, *Org. Syn.*, **24**, 36 (1944); (b) M. J. Schlatter, *ibid.*, **23**, 20 (1943).

[47] Melting points are corrected; boiling points are uncorrected.

[48] J. J. Lingane, C. G. Swain, and M. Fields, *J. Amer. Chem. Soc.*, **65**, 1348 (1943).

[49] J. P. Petrovich, M. M. Baizer, and M. R. Ort, *J. Electrochem. Soc.*, **116**, 749 (1969).

[50] H. Lapin, V. Arsenyevic, and A. Horeau, *Bull. Soc. Chim. Fr.*, 1700 (1960).

TABLE IX

ANALYTICAL AND NMR SPECTRAL DATA

	Calcd, %			Found, %				
Compd	C	H	Cl[a]	C	H	Cl	Solvent	Spectral data,[b] δ, ppm
6b							CCl_4	4.15 (2 H, q, CH_2), 2.91 (4 H, m, 2 CH_2), 1.3 (3 H, t, CH_3)
7							CS_2	2.8–4.6 (5 H, m, 2 CH_2 and CH), 1.3 (3 H, t, CH_3)
8	37.20	4.48	36.70	37.16	4.58	36.06	$CDCl_3$	3.8–4.5 (5 H, m, 2 CH_2 and CH), 3.1 (2 H, m, CH_2), 1.32 (3 H, t, CH_3), 1.25 (3 H, t, CH_3)
9	42.50	4.72	27.80	42.48	4.79	24.13	$CDCl_3$	4.0–4.5 (4 H, m, 2 CH_2), 3.6 (2 H, s, 2 CH), 1.35 (3 H, t, CH_3), 1.25 (3 H, t, CH_3)
10							$CDCl_3$	5.5 (1 H, s, CH), 4.5 (4 H, q, 2 CH_2), 1.33 (6 H, t, 2 CH_3)
11	42.40	4.71	27.90	43.17	5.00	26.97	$CDCl_3$	7.52 (1 H, s, CH), 5.6 (1 H, s, CH), 4.34 (4 H, q, 2 CH_2), 1.36 (3 H, t, CH_3), 1.34 (3 H, t, CH_3)
17a[c]	34.37	3.27	43.53	34.83	3.50	42.93	$CDCl_3$	4.82 (1 H, t, CH), 4.36 (2 H, q, CH_2), 3.28 (2 H, q, CH_2), 1.38 (3 H, t, CH_3)
17b	37.13	4.49	36.48	36.95	4.34	36.27	$CDCl_3$	4.0–4.7 (5 H, m, 2 CH_2 and CH), 2.9–3.6 (2 H, m, CH_2), 1.34 (6 H, 2 t, 2 CH_3)
18a[d]	48.41	4.61	20.46	48.55	4.56	21.08	$CDCl_3$	4.38 (2 H, q, CH_2), 1.6–2.4 (3 H, m, CH_2 and CH), 1.4 (3 H, t, CH_3)
18b	48.98	5.90	16.01	48.96	5.86	16.75	$CDCl_3$	4.15 (4 H, 3 q, 2 CH_2), 1.50–2.80 (3 H, m, CH and CH_2), 1.28 (6 H, 3 t, 2 CH_3)
19	49.23	5.81	12.14	49.17	5.79	12.68	$CDCl_3$	4.2 (6 H, 2 q, 3 CH_2), 3.05 (2 H, q, 2 CH), 1.3 (9 H, 2 t, 3 CH_3)

[a] Compounds with Cl α to ester or nitrile are relatively unstable and tend to give low Cl analyses. *Cf.* data of ref 24. [b] Included, if not previously reported, even for known compounds. [c] Calcd: N, 5.73. Found: N, 5.62. [d] Calcd: N, 8.07. Found: N, 8.19.

dried *in vacuo* at >150°. Tetra-*n*-butylammonium bromide (Eastman) was recrystallized from ethyl acetate and air dried.

Reference Compounds.—The 4-trichlorobutyronitrile (**6a**)[19a] was converted to ethyl 4-trichlorobutyrate (**6b**) *via* the imino ether.[51] Ethyl 2,4,4,4-tetrachlorobutyrate (**7**),[24a] diethyl 2-trichloromethylfumarate (**10**),[26] triethyl cyclopropanetricarboxylate (**23**),[32] ethyl 4-cyanobutyrate (**28a**),[50] 5-hexenenitrile (**32**),[52] ethyl 5-hexenoate (**33**),[52] diethyl allylsuccinate (**34**),[53] benzyl phenylacetate (**40**),[54] and ethyl 4-acetoxybutyrate (**44**)[55] were prepared by the methods cited. Ethyl dichloroacetate (**15**) and triethyl 1,2,3-propanetricarboxylate (**24**) were prepared from the acids (Aldrich) by the Fischer–Speyer method. Allyl crotonate (**35**) was similarly prepared from the acid (Eastman). Diethyl succinate (**20**) (Eastman), ethyl acetate (**21**) (Mallinckrodt), diethyl cyclopropane-1,2-dicarboxylate (**27b**) (Aldrich), diethyl glutarate (**28b**) (Aldrich), 1,5-hexadiene (**29**) (Eastman), propylene (**30**) (Matheson), dibenzylmercury (**37**) (K and K), toluene (**38**) (Mallinckrodt), bibenzyl (**39**) (Eastman), diethyl adipate (**41**) (Aldrich), ethyl butyrate (**42**) (Eastman), ethyl cyclopropanecarboxylate (**43**) (Aldrich), and adiponitrile (**45**) (Textiles Division, Monsanto) were commercially available. Ethyl 2-cyanocyclopropanecarboxylate (**27a**) prepared here had the same boiling point, nmr spectrum, and mass spectrum as reported for this compound in the literature.[33a]

General Electrolysis Procedure.—The cell, which had been oven-dried overnight, was quickly assembled under nitrogen with needed auxiliary equipment (stirrer, thermometer, etc.) and placed in a bath which could be used for warming or cooling. The catholyte charges and the conditions of the electrolyses are indicated in Tables II–VII. The anolyte had the same supporting electrolyte—plus halide, if necessary, to assure that halogen would be preferentially discharged—and solvent as were used for the catholyte; in addition, 1–2 ml of an olefin (*e.g.*, 1-hexene or 1-decene) was included to trap the halogen to be liberated. The catholyte was purged with pure nitrogen for 15–30 min before the beginning of an electrolysis. When it was desired that only the organic halide be reduced, the catholyte was checked in the absence of the organic halide at the cathode voltage to be used, to make sure that only negligible quantities, if any, of other reducible species were present. If, during the electrolysis, there was indication of migration of electrolyte solution (usually anolyte to cathode chamber at high currents), additional supporting electrolyte was added to the chamber that had lost volume. At the end of the electrolysis the catholyte was worked up and analyzed by one or more of several procedures detailed below; the anolyte was examined by glc for olefin dihalides when it appeared that some of the latter may have migrated to the catholyte.

Work-Up and Analyses of Catholytes.—The catholyte was treated in one of the following ways: procedure A, it was analyzed directly by glc; procedure B, it was carefully heated and the distilled materials (at 1 atm) were collected for analysis; procedure C, it was poured onto ice, and the precipitated product was removed by filtration, washed, and dried; procedure D, it was poured onto ice and extracted three times with methylene chloride. The combined extracts were washed, dried over $MgSO_4$, and heated to expel solvent. The residue was analyzed by glc.

Depending on the nature of the products, three different columns and conditions were employed in the glc analyses: (I) 6 ft × $^1/_8$ in. S.S. 3% OV-101 on Chromosorb W (80–100 mesh), 100° → 250° at 20°/min; (II) 6 ft × $^1/_8$ in. S.S. 10% SE-52 on Chromosorb W (80 mesh), 100° → 225° at 10°/min; (III) 10 ft × $^1/_8$ in. S.S. 5% FFAP + 1% Carbowax 20M on Chromosorb G (80–100 mesh), 60° (3 min post-injection interval) → 220° at 30°/min. The work-up and glc analytical procedures used in all experiments are gathered in Table VIII.

Identification of Products.—Comparison of glc retention times under identical conditions including the peak enhancement method was always employed. In addition, in many cases (Table VIII, footnote *b*) preparative glc was used to collect samples of electrolysis products whose physical properties and nmr spectra were compared with those of authentic samples. New analytical and spectral data are given in Table IX.

Detailed Procedure for a Representative Run (**Experiment 35, Table V**).—To the catholyte compartment of cell no. 2, equipped in this case additionally with a buret, was added the mercury, 15.8 g (0.3 mol) of AN, 1.0 g of 2,6-di-*tert*-butylphenol, 10.0 g of tetraethylammonium *p*-toluenesulfonate, and sufficient DMF to make 60 ml. The buret contained 3.3 g (0.027 mol) of AB. The stirred catholyte was purged with pure nitrogen for 15 min. The anolyte contained the tosylate salt and 1.0 g of tetraethylammonium chloride dissolved in DMF to the same liquid level as in the catholyte. Passage of current at −1.60 V *vs.* sce showed that the "background" current was 6 mA. Addition of AB was then begun at a rate sufficient to maintain a current of 120–140 mA. After the AB had been added, electrolysis was

---

(51) H. Henecka in Houben-Weyl, "Methoden der Organischen Chemie," 4th ed, Vol. VIII, Georg Thieme Verlag, Stuttgart, 1952, p 536.

(52) F. B. LaFarge, N. Green, and W. A. Gersdorff, *J. Amer. Chem. Soc.*, **70**, 3709 (1948).

(53) K. Alder, F. Pascher, and A. Schmitz, *Ber.*, **76**, 27 (1943).

(54) M. Gomberg and C. C. Buchler, *J. Amer. Chem. Soc.*, **42**, 2059 (1920).

(55) E. V. Spencer and G. F. Wright, *ibid.*, **63**, 1281 (1941).

continued to reduce the residual AB in the catholyte until the current dropped to 12 mA. The total electrolysis time was 6.0 hr; 0.0243 F had been passed.

A sample of the catholyte was directly analyzed by glc for **30** and **29** using *m*-xylene as an internal standard. The catholyte was then poured onto ice and extracted three times with CH_2Cl_2. The combined extracts were washed and dried over $MgSO_4$. The filtered solution was stripped of low-boiling components on a rotary evaporator using an aspirator and warm-water bath. The residue (10.0 g) was examined by glc for **32** using an authentic reference sample and then analyzed quantitatively using ethyl benzoate as an internal standard.

Reaction of Diethyl Malonate with Ethyl Trichloroacetate.—To 50 ml of pure DMF contained in a four-necked 500-ml flask equipped with thermometer, mechanical Trubore stirrer, and drying tube was added 2.2 g (0.05 mol, dry basis) of 54.7% sodium hydride (Metal Hydrides). Then 16.0 g (0.10 mol) of diethyl malonate was added slowly while the temperature was kept below 40° by cooling in an ice–water bath. When hydrogen evolution had ceased, a clear, very pale yellow solution resulted. This was further cooled and then 9.6 g (0.05 mol) of ethyl trichloroacetate was added in 10 min with vigorous stirring at a temperature of 27°. Turbidity appeared a few minutes after addition was complete. Stirring was continued (arbitrarily) for 5 hr at room temperature. The mixture was poured onto 200 g of ice (alkaline solution) and extracted twice with 50-ml portions of CH_2Cl_2. The combined extracts were washed twice with water, dried over $MgSO_4$, filtered, and warmed on a hot water bath to expel CH_2Cl_2. The residual liquid (24.0 g) was analyzed by glc and found to contain (in order of elution) (a) ethyl dichloroacetate (3.2 g), (b) ethyl trichloroacetate (0.42 g), (c) diethyl malonate (6.3 g), (d) diethyl chloromalonate (5.1 g), and (e) tetraethyl ethane-1,1,2,2-tetracarboxylate (3.2 g). A sample of d was collected by preparative glc. Its nmr spectrum ($CDCl_3$) showed δ 4.83 (1 H, s, CH), 4.29 (4 H, q, 2 CH_2), and 1.34 (6 H, t, 2 CH_3) and was virtually identical with Sadtler Spectrum No. 1880 for the bromo analog.

In another similar experiment e was collected by distillation at 125–139° (0.25 mm). The product solidified in the receiver. After crystallization from ethanol, it melted at 75–76°, undepressed when admixed with authentic material.

Registry No.—**6b**, 20101-80-8; **7**, 25335-12-0; **8**, 34405-06-6; **9**, 34405-07-7; **10**, 34405-08-8; **17a**, 34405-09-9; **17b**, 34405-10-2; *cis*-**18a**, 34405-11-3; *trans*-**18a**, 34405-12-4; *cis*-**18b**, 34405-13-5; *trans*-**18b**, 34405-14-6; **19**, 34405-15-7; BC, 100-44-7; BBN, 5332-06-9; CAN, 107-14-2; CF, 67-66-3; CT, 56-23-5; EBA, 105-36-2; EBB, 2969-81-5; ETA, 515-84-4; AN, 107-13-1; CO_2, 124-38-9; DEF, 623-91-6; DEM, 141-05-9; EA, 140-88-5; AB, 106-95-6; AC, 107-05-1.

Acknowledgment.—We wish to thank Dr. John H. Wagenknecht for discussions on polarographic results, Dr. Pierre A. Berger for detailed nmr analysis of **17b**, and Clarence Robb for preparing an authentic sample of **10**.

Oxidative Carbon–Carbon Coupling. II. The Effect of Ring Substituents on the Oxidative Carbon–Carbon Coupling of Arylmalonic Esters, Arylmalonodinitriles, and Arylcyanoacetic Esters

H. A. P. DE JONGH,* C. R. H. I. DE JONGE, H. J. M. SINNIGE, W. J. DE KLEIN,
W. G. B. HUYSMANS, AND W. J. MIJS

Corporate Research Department, Akzo Research Laboratories, Arnhem, Holland

W. J. VAN DEN HOEK AND J. SMIDT

Laboratorium voor Technische Natuurkunde, Technische Hogeschool, Delft, Holland

Received October 14, 1971

Arylmalonic esters and arylmalonodinitriles can be coupled oxidatively to the corresponding bibenzyls. Good yields of dimers are obtained when a para substituent (CH_3, Cl) is introduced, which inhibits the formation of higher oligomers through benzylic C–para C coupling. Substitution at *both* ortho positions and the para position (CH_3) in phenylcyanoacetic esters completely inhibits C–C coupling by steric crowding. Ketene imines are formed instead by C–N coupling. Substitution at *one* ortho position (CH_3) partially gives the usual C–C coupling together with benzylic C–para C coupling (oligomer formation) in case of a free para position and C–N coupling (ketene imine formation) in case of a CH_3-substituted para position. The thermal dissociation of the dimers into radicals is confirmed by esr analysis. From nmr line width measurements kinetic parameters for the dissociation reaction are obtained.

The oxidation of benzyl cyanides, α substituted with ester, acyl, or amide groups to give high yields of C–C dimers, has been described in the previous paper.[1] On thermal treatment the C–C dimers showed a reversible radical dissociation–recombination attended with oligomerization *via* benzylic C–para C coupling in the case of free para positions. Attempts to extend this oxidative dimerization reaction to unsubstituted phenylmalonic esters failed; only low yields of dimers were obtained, presumably owing to formation of higher oligomers. The present paper describes the oxidation of para-substituted arylmalonic esters and arylmalonodinitriles. The effect of both *o*- and *p*-CH_3 substituents on the oxidative coupling of arylcyanoacetic esters is also reported.

Arylmalonic Ester 1a–c.—The oxidation of **1a–c** has been carried out at room temperature with $KMnO_4$, $K_3Fe(CN)_6$, and $[Cu(OH)(TMEDA)]_2Cl_2$–oxygen (TMEDA = *N,N,N′,N′*-tetramethylethylenediamine) (*cf.* Table I).

With the first two oxidants, the C–C coupled dimers **2b** and **2c** were formed in high yield, whereas dimer **2a** was only produced as a minor product. In agreement with these results the oxidation of diester **1a** with dibenzoyl peroxide at 100° (neat) has been reported to give only 10% of dimer **2a**.[2] From gel permeation

---

(1) H. A. P. de Jongh, C. R. H. I. de Jonge, and W. J. Mijs, *J. Org. Chem.*, **36**, 3160 (1971).

(2) T. Suehiro, *Nippon Kagaku Zasshi*, **79**, 457 (1958); *Chem. Abstr.*, **54**, 4486*g* (1960).