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A NOVEL CHAIN REACTION INDUCED BY CATHODIC REDUCTION. ADDITION OF TRICHLOROMETHYL ANION TO ALDEHYDES OR VINYL ACETATE[1]

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A novel chain reaction induced by cathodic reduction was found in the reaction system consisting of carbon tetrachloride, chloroform, and electrophiles such as aldehydes or vinyl acetate. The current efficiency of addition of trichloromethyl anion to electrophiles was extremely high. Synthesis of an analogue of ethyl chrysanthemate using this new reaction was also described.

Generally speaking, chain reaction is one of the ideal patterns of reaction in organic synthesis, if the chain reaction is effectively designed and controlled. As shown in the general equations, 1—3, we have found a novel chain reaction system induced by cathodic reduction. In the first step of the reaction, cathodic reduction of AX forms anions A^-, which then attack electrophiles B to yield intermediates $[AB]^-$. The intermediates abstract a proton from solvents AH regenerating the first anions A^-. Therefore, if the anions A^- react with only B, the reaction will recur until the electrophiles are completely consumed, and will give high current efficiency.

$$AX \xrightarrow{+\ 2e} A^- + X^- \qquad (1)$$

$$B + A^- \longrightarrow [AB]^- \qquad (2)$$

$$[AB]^- + AH \longrightarrow ABH + A^- \qquad (3)$$

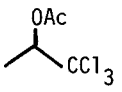
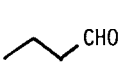
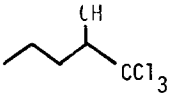
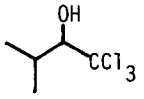
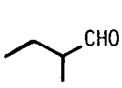
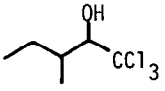
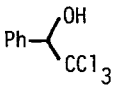
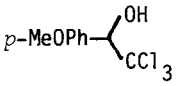
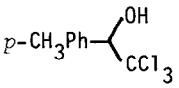
A chain reaction system using carbon tetrachloride as AX, aldehydes or vinyl acetate as B, and chloroform as AH was found in the present study.

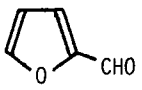
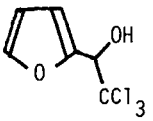
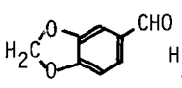
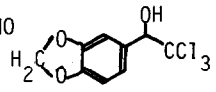
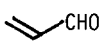
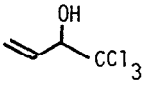
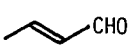
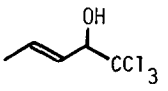
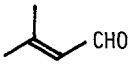
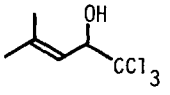
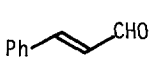
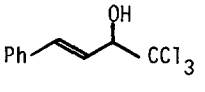
$$\begin{matrix} RCHO \\ (CH_2{=}CHOAc) \end{matrix} + CCl_4 \xrightarrow[CHCl_3]{+\ 2e} \begin{matrix} R\text{-}CH(OH)CCl_3 \\ (CH_3CH(OAc)CCl_3) \end{matrix} \quad \mathbf{1}$$

A typical procedure is as follows. A solution of 10 g (0.033 mol) of tetraethylammonium *p*-toluenesulfonate in 70 ml of chloroform or *N*,*N*-dimethylformamide containing 0.1 mol of chloroform was used as catholyte and anolyte, which were placed in a cell equipped with carbon rod electrodes and a ceramic diaphragm. To the catholyte was added 0.01 mol of carbon tetrachloride and 0.1 or 0.05 mol of aldehydes or vinyl acetate. The catholyte was

stirred with a magnetic bar and electrochemically reduced with a constant current of 0.1 A. The current efficiency and chemical yield were followed by glc method. After 2 *F*/mol of electricity based on carbon tetrachloride was passed, the product was isolated by distillation or column chromatograph. Results obtained by using a variety of electrophiles are shown in Table 1, in which the molar ratio of carbon tetrachloride to electrophiles is 1 : 10 or 1 : 5 unless otherwise stated.

Table 1

Electrophile	Product[a]	B.P., °C/mmHg	$\frac{\text{Electrophile}}{CCl_4}$	Solvent	Yield, %[b]	Current Efficiency, %
CH_2=CHOAc		70—71/20	10	$CHCl_3$	71	706
		84—85/18	10	$CHCl_3$	64	642
			10	DMF	73	732
		80—82/17	10	$CHCl_3$	32	324
			10	DMF	68	682
		90/16	10	$CHCl_3$	28	284
			10	DMF	67	670
PhCHO		138—139/15	10	$CHCl_3$	42	416
			10	DMF	65	653
			5	DMF	77	385
p-MeOPhCHO		122—124/1	10	$CHCl_3$	23	230
			10	DMF	46	459
			5	DMF	58	290
p-CH_3PhCHO		96—98/1	5	DMF	76	378

		87—90/13	10	$CHCl_3$	37	374
			10	DMF	55	553
			5	DMF	81	403
p-ClPhCHO	*p*-ClPh-CH(OH)-CCl_3	110—111/1	5	DMF	69	345
o-NO_2PhCHO	*o*-NO_2Ph-CH(OH)-CCl_3	125/1	5	DMF	75	375
		125—126/1	5	DMF	53	265
			10	$CHCl_3$	5.5	55
		70/18	10	DMF	19	190
			3	DMF	51	153
			10	$CHCl_3$	11	112
		74—76/12	10	DMF	23	230
			3	DMF	67	201
		101—102/16 m.p. 76—77°	3	DMF	70	210
		120/1	3	DMF	56	168

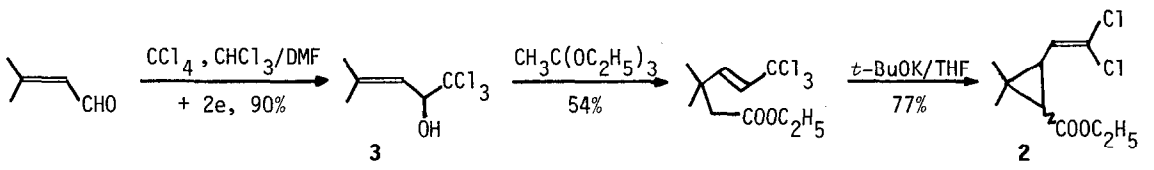
a. All the products gave satisfactory data in spectroscopic and elemental analyses.

b. Isolated yield based on electrophile.

As Table 1 clearly shows, the current efficiency determined when 2 *F*/mol of electricity based on carbon tetrachloride[2] was passed is sufficiently high to support the recurring nature of the reaction system. The highest current efficiency, some 1×10^3%, was observed when about 1 *F*/mol of electricity was passed. Chemical yields can be improved by raising the molar ratio of carbon tetrachloride to electrophiles, but the current efficiency will be lowered. For example, in case of *p*-methoxybenzaldehyde, the yield was 90% when the molar ratio of carbon

tetrachloride to the aldehyde was 3 : 1. The compounds like **1** may be synthesized from carbonyl compounds and chloroform or carbon tetrachloride by chemical methods[3] or an electrochemical method,[4] though the versatility, yields, and reaction conditions are not satisfactory from the view point of organic synthesis.

The significance of this new cathodic anion chain reaction may be shown by a new synthetic route of an analogue of ethyl chrysanthemate **2**[5] using this chain reaction as a key process, in which one of the key intermediates **3** was obtained from prenyl aldehyde in a yield of 90%.[6] The compound **2** is one of the components of useful insecticides.



cis : *trans*=2 : 7

References and Notes

1) Electroorganic Chemistry. 47.

2) In this reaction system, cathodically most reducible compound is carbon tetrachloride, so that the current efficiency was determined at the stage where theoretical amount of electricity to reduce carbon tetrachloride was passed.

3) a) J. Mathieu and J. Weill-Raynal, "Formation of C-C Bonds", Vol. 1, pp. 260-263, Georg Thieme Publishers, Stuttgart, 1973.
   b) M. Fedorymski, I. Gorzkowska, and M. Makosza, *Synthesis*, **1977**, 120.
   c) A. Merz and R. Tomahogh, *Chem. Ber.*, **110**, 96 (1977).

4) F. Karrenbrock and H. J. Schäfer, *Tetrahedron Lett.*, **1978**, 1521.

5) Y. Nakada, R. Endo, S. Muramatsu, J. Ide, and Y. Yura, *Bull. Chem. Soc. Jpn.*, **52**, 1511 (1979), and references cited therein.

6) The molar ratio of carbon tetrachloride to prenyl aldehyde is 3 : 1.

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