The final agreement factor was $R = 0.049$ for 2282 observed reflections. A final difference Fourier synthesis did not show any peak higher than ±0.3 e/Å^3. All calculations and drawings were done with the KRIPROG system.[14]

Acknowledgment. The research conducted at the Ohio State University was assisted financially by the U.S. Army Armament Research and Development Command, whom we thank.

Registry No. 4, 96617-85-5; 6, 85850-70-0; 8, 96617-86-6; 9, 96617-87-7.

Supplementary Material Available: A listing of atomic parameters, bond angles, torsion angles, and bond lengths (8 pages). Ordering information is given on any current masthead page. The observed and calculated structure factors for 4 are available from P.E.

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(14) Engel, P. *Acta Crystallogr., Sect. A* 1978, *A34*, 5348.

Chain Reactions Induced by Cathodic Reduction[1]

Tatsuya Shono,* Naoki Kise, Mitsuharu Masuda, and Takeshi Suzumoto

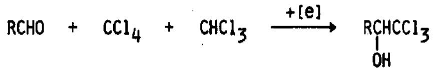
Department of Synthetic Chemistry, Faculty of Engineering, Kyoto University, Yoshida, Sakyo, Kyoto 606, Japan

Received December 20, 1984

Cathodic reduction of a system comprising carbon tetrachloride, chloroform, and an aldehyde led to an effective anionic chain reaction. The best current efficiency observed was about 1 × 10^4%. Such a chain reaction is an effective synthetic method for 1,1,1-trichloro-2-alkanols. The reaction system consisting of methyl trichloroacetate, methyl dichloroacetate, and an aldehyde and several other systems also exhibited a similar pattern of chain reaction.

Chain reaction is one of the useful patterns of reaction in organic synthesis, if the chain reaction is effectively designed and controlled. We have investigated an anionic chain reaction system induced by cathodic reduction. In the first step of the reaction, cathodic reduction of a halide AX forms an anion A^-, which then attacks an electrophile B to yield an intermediate AB^- as shown in Scheme I. This intermediate abstracts a proton from AH, the conjugate acid of A^-, to regenerate the anion A^-. Therefore, when (a) ZX is the only electrochemically reducible reagent in the reaction system, (b) the generated A^- reacts with only B, and (c) AH is more acidic than ABH, the reaction will recur until the electrophiles are completely consumed and will give the product ABH in high current efficiency.

Although such a chain reaction system initiated by cathodic reduction has been reported for a limited case,[2] we have found that this type of chain reaction can be realized more effectively by using carbon tetrachloride, chloroform, and aldehydes as AX, AH, and B, respectively,[4] and it offers a useful method for the synthesis of 1,1,1-trichloro-2-alkanols from aldehydes (eq 1). We have also studied several other chain reaction systems.



$$\mathrm{RCHO} + \mathrm{CCl_4} + \mathrm{CHCl_3} \xrightarrow{+[e]} \mathrm{R\underset{\displaystyle OH}{CH}CCl_3} \quad (1)$$

1

Scheme I

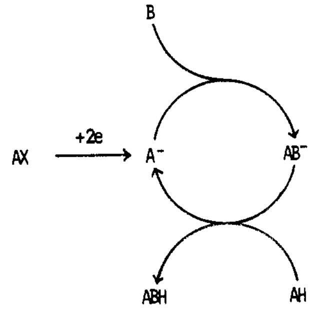


Table I. Electroreduction of the n-C_3H_7CHO-CCl_4-$CHCl_3$ System[a]

solvent	cathode	supporting electrolyte	CE,[b,c] %
DMF	C	Et_4NOTs	732
DMF	Pt	Et_4NOTs	569
DMF	Pb	Et_4NOTs	541
DMF	C	$LiClO_4$	236
$CHCl_3$[d]	C	Et_4NOTs	642
CH_3CN	C	Et_4NOTs	625
THF	C	$LiClO_4$	0
THF	Pb	$LiClO_4$	0
THF	C	(n-octyl)$_3$MeNCl	436
EtOH	C	Et_4NOTs	0

[a] The amounts of n-C_3H_7CHO, CCl_4, and $CHCl_3$ were 100, 10, and 100 mmol, respectively. [b] Current efficiency. [c] Product was $C_3H_7CH(OH)CCl_3$ (**1a**). [d] Excess $CHCl_3$ was used as solvent.

Results and Discussion

Addition of Trichloromethyl Anion to Aldehydes. The reaction conditions of the chain reaction were studied by using butyraldehyde as the typical aldehyde. The ratio of carbon tetrachloride, aldehyde, and chloroform was 1:10:10, and several types of solvent, including chloroform itself, were used as shown in Table I. The cathode material was carbon, platinum, or lead, while the anode was carbon. The current efficiencies summarized in Table I were determined at the time of passing the necessary amount of electricity for the reduction of carbon tetrachloride (2 F/mol of CCl_4). The best current efficiency (732%) given by using the carbon cathode and DMF solvent clearly suggests the recurring nature of this reaction system. The current efficiency, however, changed with increasing amount of electricity passed as depicted in Figure 1. The highest efficiency (2840%) in chloroform solvent was observed when 0.1 F/mol of electricity was passed, whereas passing 0.4 F/mol of electricity gave the

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(1) Electroorganic Chemistry. 88. Preliminary report: Shono, T.; Ohmizu, H.; Kawakami, S.; Nakano, S.; Kise, N. *Tetrahedron Lett.* 1981, *22*, 871.

(2) Baizer and Chruma have reported a chain reaction initiated by the electroreduction of a mixture of carbon tetrachloride (AX), chloroform (AH), and ethyl acrylate or acrylonitrile (B).[3]

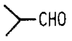
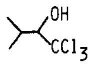
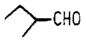
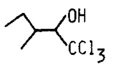
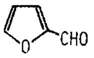
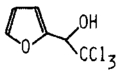
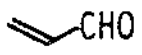
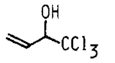
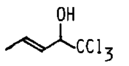
(3) Baizer, M. M.; Chruma, J. L. *J. Org. Chem.* 1972, *37*, 1951.

(4) Karrenbrock and Schäfer have reported the electroreductive coupling of carbon tetrachloride and ethyl trichloroacetate to aldehydes and ketones.[5]

(5) Karrenbrock, F.; Schäfer, H. J. *Tetrahedron Lett.* 1978, 1521.

0022-3263/85/1950-2527$01.50/0

Table II. Electroreduction of Systems Containing Other Types of Aldehydes[a]

aldehyde	product	$CHCl_3$ solvent		DMF solvent[d]	
		yield,[b] %	CE,[c] %	yield,[b] %	CE,[c] %
	 **1b**	32	324	68	682 (30)[e]
	 **1c**	28	284	67	670
C_6H_5CHO	$C_6H_5CH(CCl_3)OH$ (**1d**)	42	416	65	653 (70)[e]
p-$CH_3OC_6H_4CHO$	p-$CH_3OC_6H_4CH(CCl_3)OH$ (**1e**)	23	230	46	459
	 **1f**	37	374	55	554
	 **1g**	5.5	55	19	190
	 **1h**	11	112	23	230

[a] The amounts of aldehyde and CCl_4 were 100 and 10 mmol, respectively. [b] Based on aldehyde. [c] Determined by the same manner as Table I. [d] Containing 100 mmol of $CHCl_3$. [e] Reference 4.

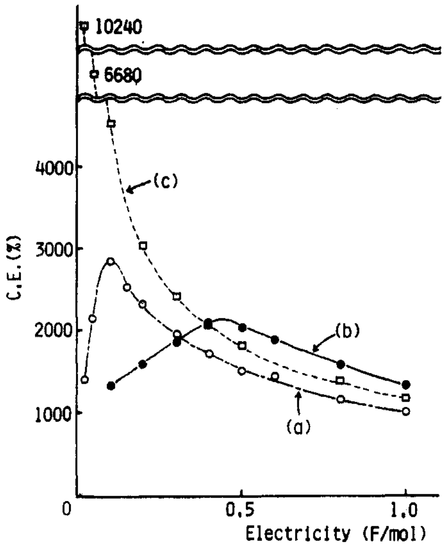


Figure 1. Relation between electricity and current efficiency in the anionic chain reaction, (a) A mixture of n-C_3H_7CHO (100 mmol) and CCl_4 (10 mmol) reduced in $CHCl_3$, (b) A mixture of n-C_3H_7CHO (100 mmol), CCl_4 (10 mmol), and $CHCl_3$ (100 mmol) reduced in DMF, (c) 3 mF of electricity passed to the DMF solution prior to the addition of n-C_3H_7CHO (100 mmol), CCl_4 (10 mmol), and $CHCl_3$ (100 mmol).

highest efficiency (2100%) in DMF solvent. The relatively low current efficiency observed in the early stage of the reaction may suggest that some unknown impurities having proton-donating nature retarded the reaction. Thus, the removal of the impurities contained in the solvent by passing electricity in advance may improve the current efficiency in the early stage. This was actually the case. As shown in Figure 1, passing 0.3 F/mol of electricity to the solvent prior to the addition of reagents clearly improved the efficiency of the early stage, and about 1.2×10^4% was observed in DMF solvent at the stage of passing 0.025 F/mol of electricity.

This cathodic chain reaction was applied to a variety of aldehydes, and the results are shown in Table II. Aromatic and saturated aliphatic aldehydes generally gave reasonable results in DMF solvent, whereas α,β-unsaturated aldehydes showed relatively low current efficiencies. As described above, the electrogenerated trichloromethyl anion adds to the carbonyl group of the aldehyde to yield an intermediate anion which immediately abstracts a proton from chloroform to form the product and regenerate the trichloromethyl anion. Since this process competes with transformation of trichloromethyl anion to dichlorocarbene[6] and since the trichloromethyl anion is not necessarily highly nucleophilic, the current efficiency of this chain reaction is largely affected by the reactivity of the carbonyl compounds.

Table III. Improvement of Chemical Yield of 1 with Changing CCl_4:Aldehyde Ratio[a]

mmol of aldehyde	mmol of CCl_4	yield,[b] %		
		1d	**1e**	**1h**
100	10	65	46	23
50	10	77	58	
30	10			67
10	10	92 (51)[c]	69	
10	30	88 (65)[c]	90	81

[a] A sufficient amount of electricity (2 F/mol) to reduce CCl_4 was passed to DMF solution containing 100 mmol of $CHCl_3$. [b] Isolated yield based on aldehyde. [c] In the absence of $CHCl_3$.

Improvement of Chemical Yields of 1,1,1-Trichloro-2-alkanols. In the previous section, this cathodic chain reaction has been studied mainly from the standpoint of achieving high current efficiencies. The high current efficiencies are, however, not always directly connected with high chemical yields, which are undoubtedly the most important point when this chain reaction is applied to organic synthesis. Thus, the improvement of chemical yields was studied, though it may bring about a decrease in current efficiencies. As shown in Table III, increasing the ratio of carbon tetrachloride to aldehyde led

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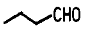
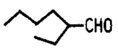
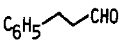
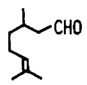
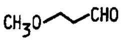
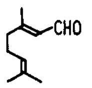
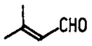
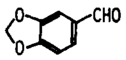
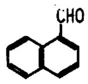
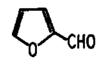
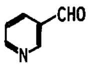
(6) It is well-known that trichloromethyl anion easily decomposes to dichlorocarbene. The formation of dichlorocyclopropane through electroreduction of carbon tetrachloride in the presence of an olefin has also been reported.[7]

(7) (a) Wawzonek, S.; Duty, R. C. *J. Electrochem. Soc.* **1961**, *108*, 1135. (b) Fritz, H. P.; Korntrump, W. *Justus Liebigs Ann. Chem.* **1978**, 1416.

Table IV. Synthesis of 1 from a Variety of Aldehydes[a]

aldehyde	CCl_4:aldehyde	product	yield,[b] %
	1	**1a**	88
	1	**1i**	92
	1	**1j**	86
	1	**1k**	89
	1	**1l**	76
	1	**1m**	62
	3	**1n**	81
	3	**1o**	86
	3	**1p**	76
	3	**1q**	90
$o\text{-}CH_3OC_6H_4CHO$	3	**1r**	91
$m\text{-}CH_3OC_6H_4CHO$	3	**1s**	91
$p\text{-}C_6H_5CH_2OC_6H_4CHO$	3	**1t**	75
	3	**1u**	78
$p\text{-}ClC_6H_4CHO$	3	**1v**	89
	3	**1w**	85
	3	**1f**	77
$p\text{-}CH_3O_2CC_6H_4CHO$	3	**1x**	76
$o\text{-}O_2NC_6H_4CHO$	3	**1y**	86
	3	**1z**	52

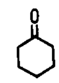
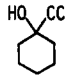
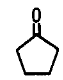
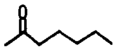
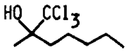
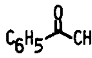
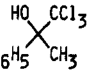
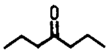
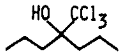
[a] The amount of aldehyde was 10 mmol. The conditions of electrolysis were the same as in Table III. [b] Isolated yield based on aldehyde.

Table V. Base-Catalyzed Reaction of $n\text{-}C_3H_7CHO$ and $CHCl_3$[a]

base[b]	solvent	yield of **1a**,[c] %
KOH	$CHCl_3$[d]	9
KOH	DMF	54
t-BuOK	DMF	50
NaH	DMF	46
electroreduction[e]	DMF	73

[a] 100 mmol of $n\text{-}C_3H_7CHO$ and 100 mmol of $CHCl_3$ were used. [b] 10 mmol. [c] Isolated yield based on $n\text{-}C_3H_7CHO$. [d] Excess $CHCl_3$ was used as solvent. [e] Table I.

Table VI. Electroreduction of CCl_4–$CHCl_3$–Ketone Systems in DMF[a]

		CCl_4:ketone = 0.1[b]		CCl_4:ketone = 3[c]	
ketone	product	yield,[d] %	CE, %	yield,[d] %	CE, %
	 **2a**	9.5	95	61	20
	 **2b**	6.2	62	51	17
	 **2c**	2.2	22	10	3.5
	 **2d**	trace			
	 **2e**	trace			

[a] The conditions of electrolysis were the same as in Table III. [b] The amount of CCl_4 was 10 mmol. [c] The amount of CCl_4 was 30 mmol. [d] Isolated yield based on ketone.

to the improvement of chemical yields. The improved reaction conditions were then applied to a variety of aldehydes and the results are summarized in Table IV.

Although the current efficiencies were less than 100%, aldehydes were consumed completely and converted to 1,1,1-trichloro-2-alkanols **1** in satisfactory yields. Among them, the products **1** transformed from α,β-unsaturated aldehydes showed remarkable increase in the yields. Due to the lower reactivity of aromatic and α,β-unsaturated aldehydes with trichloromethyl anion, however, a significant amount of trichloromethyl anion will decompose without being trapped by aldehydes, and hence it is necessary to generate an excess of trichloromethyl anion to increase the chemical yields.

The lower yield observed in the reaction carried out in the absence of chloroform has clearly shown that chloroform plays important roles in this reaction even though a sufficient amount of carbon tetrachloride is used.

A variety of methods using base catalysts have been studied so far for the preparation of 2-aryl-1,1,1-trichloro-2-ethanols from aromatic aldehydes and chloroform.[8] These base-catalyzed methods, however, gave relatively low yields (34–55%)[8c,e] when aliphatic aldehydes were used, probably due to competitive side reactions such as aldol condensation. Table V shows some examples of yields obtained in the reactions of *n*-butyraldehyde and chloroform using several types of bases[9] and suggests that the cathodic chain reaction always gives better results than the base-catalyzed reactions. The reaction of substituted benzenes with chloral in the presence of Lewis acid catalyst may be an alternative method for the synthesis of 2-aryl-1,1,1-trichloro-2-ethanols.[10] This method is, however, considerably limited since the products are obtained as a mixture of para- and ortho-substituted compounds.

Thus, this electrochemical method is the most convenient method for the synthesis of 1,1,1-trichloro-2-alkanols, since a sole product is obtained in a high chemical yield with a high current efficiency under mild reaction conditions.

Addition of Trichloromethyl Anion to Ketones and Other Nucleophiles. This cathodic chain reaction did not show satisfactory results in the reaction with ketones as exhibited in Table VI. The lower reactivity of ketones with trichloromethyl anion than aldehydes may be responsible for the poor results, since the decomposition of

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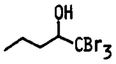
[8] For example: (a) Weizmann, C.; Bergmann, E.; Sulzbacher, M. *J. Am. Chem. Soc.* **1948**, *70*, 1189. (b) Bergmann, E. D.; Ginsburg, D.; Lavie, D. *Ibid.* **1950**, *72*, 5012. (c) Kaspar, E.; Wiechert, R. *Chem. Ber.* **1958**, *91*, 2664. (d) Viehe, H. G.; Valange, P. *Ibid.* **1963**, *96*, 420. (e) Merz, A.; Tomahogh, R. *Ibid.* **1977**, *110*, 96.

[9] Contrary to the electroreductive method, increasing the amount of chloroform in the base-catalyzed reaction led to a drastic decrease in the yield.

[10] For example: (a) Willand, J. R.; Hamilton, C. S. H. *J. Am. Chem. Soc.* **1951**, *73*, 4805. (b) Reeve, W.; Mutchler, J. P.; Liotta, C. L. *Can. J. Chem.* **1966**, *44*, 575.

Table VII. Electroreduction of CBr_4–$CHBr_3$–Aldehyde Systems in DMF

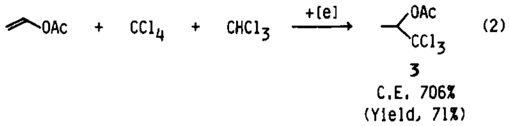
aldehyde	product	CBr_4: aldehyde[a]	*T*, °C	yield,[b] %	CE,[c] %
	 **4a**	0.1[d]	25	13	130
		0.1[d]	0	49	490
		1[e]	0	47	47
		0.1[d]	−50	66	660
		1[e]	−50	58	58
C_6H_5CHO	$C_6H_5CH(CBr_3)OH$ **4b**	0.1[d]	25	25	250
		0.1[d]	0	38	384
		1[e]	0	46	46
		0.1[d]	−50	65	650
		1[e]	−50	82	82

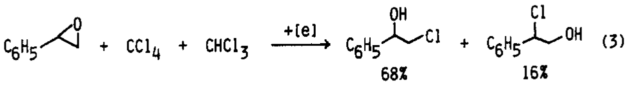
[a] CBr_4, 10 mmol. [b] Isolated yield based on aldehyde. [c] A sufficient amount of electricity to reduce CBr_4 was passed (2 *F*/mol). [d] $CHBr_3$, 100 mmol. [e] $CHBr_3$, 20 mmol.

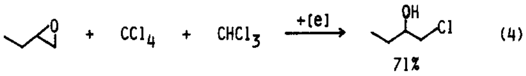
trichloromethyl anion may be faster than the reaction of the anion with ketones.

Vinyl acetate used as a nucleophile gave the coupling product **3** with high current efficiency (eq 2), while isopropenyl acetate was completely unreactive. Other nucleophiles such as epoxides gave chlorohydrins (eq 3 and 4). Esters, acid anhydrides, and aliphatic halides did not give any product.

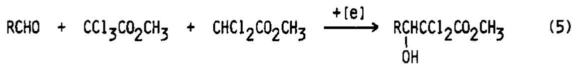
Addition of Tribromomethyl Anion to Aldehydes. The reaction system consisting of carbon tetrabromide, bromoform, and aldehydes gave similar products, 1,1,1-tribromo-2-alkanols **4**, but with low current efficiencies (Table VII). The low efficiencies were explained by the instability of tribromomethyl anion, since the reactions carried out at −50 °C gave much better current efficiencies and satisfactory chemical yields.







Addition of Dichloro(methoxycarbonyl)methyl Anion to Aldehydes. The anion chain reaction also took place when a mixture of methyl trichloroacetate, methyl dichloroacetate, and aldehydes was electrochemically reduced and gave methyl 2,2-dichloro-3-hydroxyalkanoates **5** with reasonable current efficiencies (eq 5) (Table VIII).



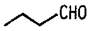
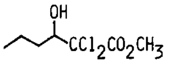
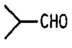
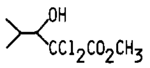
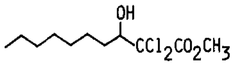
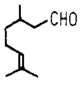
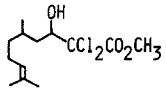
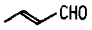
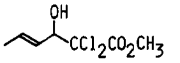
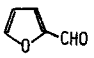
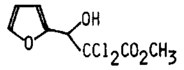
$$RCHO + CCl_3CO_2CH_3 + CHCl_2CO_2CH_3 \xrightarrow{+[e]} \underset{OH}{RCH}CCl_2CO_2CH_3 \quad (5)$$

5

As was expected, a current efficiency of about $1 \times 10^4\%$ was observed at the initial stage of the reaction. The chemical yields could be improved by increasing the ratio of methyl trichloroacetate and methyl dichloroacetate to aldehydes, though the current efficiencies decreased considerably.

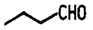
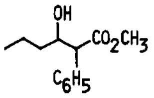
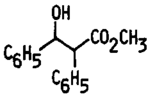
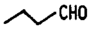
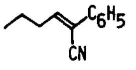
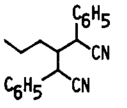
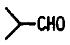
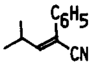
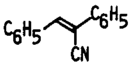
Other Anionic Chain Reaction Systems. This electroreductive chain reaction is not limited to systems of carbon tetrachloride plus chloroform and methyl trichloroacetate plus methyl dichloroacetate, but any system that satisfies the conditions described above will lead to the chain reaction.

Table VIII. Electroreduction of $CCl_3CO_2CH_3$–$CHCl_2CO_2CH_3$–Aldehyde Systems in DMF[a]

		$CCl_3CO_2CH_3$:$CHCl_2CO_2CH_3$:aldehyde		
		1:10:10[b]		1:2:1[b]
aldehyde	product	yield,[c] %	CE, %	yield[c] = CE, %
	 **5a**	47	469	65
	 **5b**	16	158	44
	 **5c**	32	315	73
	 **5d**			64
	 **5e**	9.1	91	54
C_6H_5CHO	$C_6H_5CH(CCl_2CO_2CH_3)OH$ (**5f**)	20	199	48
p-$CH_3OC_6H_4CHO$	*p*-$CH_3OC_6H_4CH(CCl_2CO_2CH_3)OH$ (**5g**)	14	135	32
	 **5h**	30	301	58

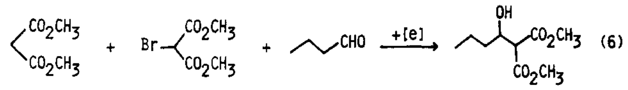
[a] A sufficient amount of electricity (2 F/mol) to reduce $CCl_3CO_2CH_3$ was passed. [b] $CCl_3CO_2CH_3$, 10 mmol. [c] Isolated yield based on aldehyde.

Table IX. Electroreduction of the Systems of Active Methylene Compounds, Their Halides, and Aldehydes

aldehyde (100 mmol)	AH (100 mmol)	AX (5 mmol)	product	yield,[a] %	CE,[b] %
	$C_6H_5CH_2CO_2CH_3$	$C_6H_5CHBrCO_2CH_3$	 7a	56 (63:37)[c]	1114
C_6H_5CHO	$C_6H_5CH_2CO_2CH_3$	$C_6H_5CHBrCO_2CH_3$	 7b	35 (65:35)[c]	696
	$C_6H_5CH_2CN$	$C_6H_5CHBrCN$	 8	14	280
			 9	42	840
	$C_6H_5CH_2CN$	$C_6H_5CHBrCN$	 10	81	1610
C_6H_5CHO	$C_6H_5CH_2CN$	$C_6H_5CHBrCN$	 11	71	1420

[a] Isolated yield based on aldehyde. [b] A sufficient amount of electricity (2 F/mol) to reduce AX was passed. [c] Diastereomeric ratio.

Thus, it may be expected that a combination of an active methylene compound and its halogenated compound forms the system of AH and AX of the chain reaction. The cathodic reduction of a system of dimethyl malonate, dimethyl bromomalonate, and *n*-butyraldehyde indeed gave the product 6 with high current efficiency (eq 6), though the same product is easily obtained by the reaction of methyl malonate and *n*-butyraldehyde using weak-base catalyst in a good yield.



6
C.E. 1600%
(Yield, 80%)

On the other hand, the reaction of methyl phenylacetate or phenylacetonitrile with aldehydes usually requires relatively strong-base catalysts. Thus, the chain reaction systems comprising these compounds are useful in organic synthesis as shown in Table IX, since the mild and neutral reaction conditions of the chain reaction do not bring about unexpected side reactions.

Application of the Products Obtained by Cathodic Chain Reaction to Organic Synthesis. As shown in our previous preliminary studies and in other references, the products obtained through this anionic chain reaction are highly useful as starting materials in organic synthesis. Although details will be described in our future reports, some examples are briefly shown below.

The hydrolysis of 1,1,1-trichloro-2-alkanols 1 and 1,1,1-tribromo-2-alkanols 4 yields α-methoxy or α-hydroxy carboxylic acids.[11] Compounds 1 can also be transformed through further electroreduction to chloromethyl ketones,[12] α-methoxy aldehydes, and α-hydroxy aldehyde dimethyl acetals.[13] The last transformation allows one-carbon elongation of carbohydrates.[13] Furthermore, methyl 2,2-dichloro-3-hydroxyalkanoates 5 can stereoselectively be converted to methyl 2,3-dihydroxyalkanoates, and this method enables us to elongate stereoselectively the carbon chain of carbohydrates as shown in our previous report.[14]

Experimental Section

General Procedure for Anionic Chain Reaction. A solution of 10 g (330 mmol) of tetraethylammonium *p*-toluenesulfonate in 60 mL of solvent was put into the cathodic (45 mL) and anodic (15 mL) chambers of the electrolysis cell (100-mL beaker) equipped with carbon-rod electrodes and a ceramic diaphragm. To the catholyte were added given amounts of AX, AH, and B. In the case of using chloroform as AH, it was also employed as solvent. Stirred with a magnetic bar and cooled with a water bath, the catholyte was electrochemically reduced with a constant current of 0.1 A. After 2 *F* of electricity per mole of AX was passed, the catholyte was poured into 300 mL of a saturated solution of sodium chloride and extracted with three 100-mL portions of ether. The combined ethereal solution was dried over anhydrous magnesium sulfate and evaporated. The product was isolated from the residue by fractional distillation or column chromatography on silica gel.

Synthesis of 1,1,1-Trichloro-2-alkanols. Electroreduction was carried out under the conditions shown in Tables I, II, and VI using carbon tetrachloride (10 mmol), chloroform (100 mmol or as solvent), and an aldehyde or ketone (100 mmol) as AX, AH, and B, respectively.

The reaction was followed by sampling the catholyte at regular intervals and the current efficiency was determined by GLC analysis. Figure 1 was obtained by this method using *n*-butyraldehyde as B.

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[11] For example: (a) Reeve, W.; Woods, C. W. *J. Am. Chem. Soc.* **1960**, *82*, 4062. (b) Compere, E. L., Jr. *J. Org. Chem.* **1968**, *33*, 2565. (c) Compere, E. L., Jr.; Shochravi, A. *Ibid.* **1978**, *43*, 2702.

[12] Shono, T.; Kise, N.; Yamazaki, A.; Ohmizu, H. *Tetrahedron Lett.* **1982**, *23*, 1609.

[13] Shono, T.; Ohmizu, H.; Kise, N. *Tetrahedron Lett.* **1982**, *23*, 4801.

[14] Shono, T.; Kise, N.; Suzumoto, T. *J. Am. Chem. Soc.* **1984**, *106*, 259.

Improvement of chemical yields was achieved by increasing the ratio of carbon tetrachloride to carbonyl compounds as shown in Tables III, IV, and VI.

Synthesis of 2-Acetoxy-1,1,1-trichloropropane. Carbon tetrachloride (10 mmol), chloroform (100 mmol), and vinyl acetate (100 mmol) were used as AX, AH, and B, and the solvent was DMF.

Reaction of Epoxides. A mixture of carbon tetrachloride (50 mmol), chloroform (100 mmol), and an epoxide (10 mmol) was reduced in DMF solvent.

Synthesis of 1,1,1-Tribromo-2-alkanols. Electroreduction of carbon tetrabromide (AX), bromoform (AH), and an aldehyde (B) was performed under the reaction conditions exhibited in Table VII.

Synthesis of Methyl 2,2-Dichloro-3-hydroxyalkanoates. Methyl trichloroacetate, methyl dichloroacetate, and an aldehyde were used as AX, AH, and B, and the molar ratios of the reactants are given in Table VIII.

Electroreduction of the Systems of Active Methylene Compounds, Their Halides, and Aldehydes. Electroreduction was carried out in DMF solvent by using an active methylene compound (100 mmol), its halide (5 mmol), and an aldehyde (100 mmol) as AX, AH, and B.

Identification of Products. **1,1,1-Trichloropentan-2-ol (1a)**,[15] **3-methyl-1,1,1-trichlorobutan-2-ol (1b)**,[8e] **1-phenyl-2,2,2-trichloroethanol (1d)**,[8e] **1-(4-methoxyphenyl)-2,2,2-trichloroethanol (1e)**,[8e] **1-(1-furyl)-2,2,2-trichloroethanol (1f)**,[10a] **1,1,1-trichloro-3-buten-2-ol (1g)**,[16] **1,1,1-trichloro-3(*E*)-penten-2-ol (1h)**,[17] **1,1,1-trichlorononan-2-ol (1i)**,[18] **3-ethyl-1,1,1-trichloroheptan-2-ol (1j)**,[19] **4-phenyl-1,1,1-trichloro-3(*E*)-buten-2-ol (1o)**,[20] **4-methyl-1,1,1-trichloro-3-penten-2-ol (1q)**,[15] **1-(2-methoxyphenyl)-2,2,2-trichloroethanol (1r)**,[8b] **1-(3-methoxyphenyl)-2,2,2-trichloroethanol (1s)**,[8b] **1-(4-chlorophenyl)-2,2,2-trichloroethanol (1v)**,[16] **1-(trichloromethyl)cyclohexanol (2a)**,[8e] **1-(trichloromethyl)cyclopentanol (2b)**,[8e] **2-methyl-1,1,1-trichloroheptan-2-ol (2c)**,[21] **1-chloro-2-phenylethanol**,[22] **1-chloro-2-butanol**,[23] **1-phenyl-2,2,2-tribromoethanol (4b)**,[20] **methyl 2,2-dichloro-3-hydroxy-4-methylpentanoate (5b)**,[24] **methyl 2,2-dichloro-3-hydroxy-3-phenylpropanoate (5f)**,[25] **methyl 2,3-diphenyl-3-hydroxypropanoate (7b)**,[26] and **2,3-diphenylpropenenitrile (11)**[27] were identified by comparison of their spectroscopic behaviors with those described in the references or with authentic samples. The other products were confirmed by spectroscopic and elemental analyses as shown below.

3-Methyl-1,1,1-trichloropentan-2-ol (1c): bp 90 °C (16 mm); IR (neat) 3450 (OH), 810 (CCl) cm^{-1}; NMR (CCl_4) δ 0.60–2.53 (m, 9 H), 3.46 (s, 1 H), 3.80–4.03 (m, 1 H). Anal. Calcd for $C_6H_{11}OCl_3$: C, 35.06; H, 5.40; Cl, 51.76. Found: C, 34.94; H, 4.61;f Cl, 51.47.

4-Phenyl-1,1,1-trichlorobutan-2-ol (1k): bp 103 °C (1 mm); IR (neat) 3400 (OH), 810 (CCl), 785 cm^{-1}; NMR (CCl_4) δ 1.52–3.11 (m, 4 H), 3.27 (br s, 1 H), 3.87 (dd, 1 H, J = 2, 10 Hz), 7.16 (s, 5 H). Anal. Calcd for $C_{10}H_{11}OCl_3$: C, 47.37; H, 4.37; Cl, 41.95. Found: C, 47.66; H, 4.41; Cl, 41.76.

4,8-Dimethyl-1,1,1-trichloro-7-nonen-2-ol (1l): bp 99–101 °C (1 mm); IR (neat) 3400 (OH), 810 (CCl), 770 cm^{-1}; NMR (CCl_4) δ 0.70–2.27 (m, 16 H), 2.76 (br s, 1 H), 3.93–4.21 (m, 1 H), 5.11 (t, 1 H, J = 6 Hz). Anal. Calcd for $C_{11}H_9OCl_3$: C, 48.28; H, 7.00; Cl, 38.87. Found: C, 48.39; H, 7.08; Cl, 38.62.

4-Methoxy-1,1,1-trichlorobutan-2-ol (1m): bp 120–123 °C (30 mm); IR (neat) 3400 (OH), 820, 795 (CCl) cm^{-1}; NMR (CCl_4) δ 1.46–2.61 (m, 2 H), 3.35 (s, 3 H), 3.46–3.79 (m, 2 H), 3.51 (br s, 1 H), 4.17 (dd, 1 H, J = 2.5, 10 Hz). Anal. Calcd for $C_5H_9O_2Cl_3$: C, 28.94; H, 4.37; Cl, 51.27. Found: C, 28.34; H, 4.52; Cl, 51.24.

2-Acetoxy-1,1,1-trichloropropane (3): bp 75 °C (22 mm); IR (neat) 1750 (C=O), 822, 780 (CCl) cm^{-1}; NMR (CCl_4) δ 1.55 (d, 3 H, J = 6 Hz), 2.10 (s, 3 H), 5.40 (q, 1 H, J = 6 Hz). Anal. Calcd for $C_5H_7O_2Cl_3$: C, 29.22; H, 3.43; Cl, 51.77. Found: C, 29.47; H, 3.48; Cl, 51.30.

1,1,1-Tribromopentan-2-ol (4a): mp 55–56 °C; IR (KBr) 3420 (OH), 735, 705 (CBr) cm^{-1}; NMR (CCl_4) δ 1.02 (t, 3 H, J = 7 Hz), 1.33–2.33 (m, 4 H), 2.69–2.84 (m, 1 H), 3.72–3.94 (m, 1 H). Anal. Calcd for $C_5H_9OBr_3$: C, 18.47; H, 2.79; Br, 73.82. Found: C, 18.62; H, 2.88; Br, 73.55.

Methyl 2,2-dichloro-3-hydroxyhexanoate (5a): bp 112–114 °C (15 mm); IR (neat) 3470 (OH), 1735 (C=O), 850 (CCl) cm^{-1}; NMR (CCl_4) δ 0.93 (t, 3 H, J = 7 Hz), 1.17–2.00 (m, 4 H), 2.47 (br s, 1 H), 3.90 (s, 3 H), 4.00–4.23 (m, 1 H). Anal. Calcd for $C_7H_{12}O_3Cl_2$: C, 39.09; H, 5.62; Cl, 32.97. Found: C, 39.44; H, 5.88; Cl, 32.59.

Methyl 2,2-dichloro-3-hydroxydecanoate (5c): bp 109 °C (1 mm); IR (neat) 3470 (OH), 1740 (C=O), 850 (CCl) cm^{-1}; NMR (CCl_4) δ 0.93 (t, 3 H, J = 7 Hz), 1.10–2.00 (m, 12 H), 2.50 (br s, 12 H), 3.88 (s, 3 H), 3.95–4.20 (m, 1 H). Anal. Calcd for $C_{11}H_{20}O_3Cl_2$: C, 48.71; H, 7.43; Cl, 26.15. Found: C, 49.00; H, 7.55; Cl, 25.89.

Methyl 2,2-dichloro-5,9-dimethyl-3-hydroxy-8-decenoate (5d): bp 118 °C (1 mm); IR (neat) 3500 (OH), 1765, 1750 (C=O), 860 (CCl), 765, 705 cm^{-1}; NMR ($CDCl_3$) δ 0.90–1.07 (m, 3 H), 1.13–2.20 (m, 7 H), 1.62 (s, 3 H), 1.69 (s, 3 H), 2.67 (br s, 1 H), 3.92 (s, 3 H), 4.31 (dd, 1 H, J = 2.5, 9 Hz), 5.11 (t, 1 H, J = 7 Hz). Anal. Calcd for $C_{13}H_{22}O_3Cl_2$: C, 52.53; H, 7.46; Cl, 23.86. Found: C, 52.93; H, 7.50; Cl, 23.47.

Methyl 2,2-dichloro-3-hydroxy-4-hexenoate (5e): bp 84 °C (1 mm); IR (neat) 3450 (OH), 1730 (C=O), 850 (CCl), 760, 695 cm^{-1}; NMR (CCl_4) δ 1.86 (d, 3 H, J = 5 Hz), 3.30 (br s, 1 H), 3.87 (s, 3 H), 4.59 (d, 1 H, J = 5.5 Hz), 5.59–6.23 (m, 2 H). Anal. Calcd for $C_7H_{10}O_3Cl_2$: C, 39.46; H, 4.73; Cl, 33.28. Found: C, 39.42; H, 4.82; Cl, 32.75.

Methyl 2,2-dichloro-3-hydroxy-3-(4-methoxyphenyl)propanoate (5g): bp 130–131 °C (1 mm); IR (neat) 3450 (OH), 1765, 1745 (C=O), 860, 835 (CCl), 730, 695 cm^{-1}; NMR (CCl_4) δ 3.90 (s, 6 H), 4.15 (br s, 1 H), 5.23 (s, 1 H), 7.07 (d, 2 H, J = 9 Hz), 7.35 (d, 2 H, J = 9 Hz). Anal. Calcd for $C_{11}H_{12}O_4Cl_2$: C, 47.33; H, 4.33; Cl, 25.41. Found: C, 47.74; H, 4.30; Cl, 24.94.

Methyl 2,2-dichloro-3-furyl-3-hydroxypropanoate (5h): bp 118 °C (1 mm); IR (neat) 3500 (OH), 1770, 1750 (C=O), 865, (CCl), 745, 695 cm^{-1}; NMR (CCl_4) δ 3.86 (s, 3 H), 4.00 (br s, 1 H), 5.30 (s, 1 H), 6.25–6.40 (m, 1 H), 6.45 (d, 1 H, J = 3 Hz), 7.30–7.43 (m, 1 H). Anal. Calcd for $C_8H_8O_4Cl_2$: C, 40.19; H, 3.37; Cl, 29.66. Found: C, 40.84; H, 3.45; Cl, 28.98.

Methyl 3-hydroxy-2-phenylhexanoate (*threo*-7a): mp 42–43 °C; IR (KBr) 3420 (OH), 1740 (C=O), 735, 700 cm^{-1}; NMR (CCl_4) δ 0.81 (t, 3 H, J = 7 Hz), 1.00–1.67 (m, 4 H), 2.68 (br s, 1 H), 3.42 (d, 1 H, J = 9 Hz), 3.63 (s, 3 H), 3.83–4.22 (m, 1 H), 7.24 (s, 5 H). Anal. Calcd for $C_{13}H_{18}O_3$: C, 70.24; H, 8.16. Found: C, 70.24; H, 8.34.

***erythro*-7a**: IR (neat) 3500 (OH), 1735 (C=O), 700 cm^{-1}; NMR (CCl_4) δ 0.90 (t, 3 H, J = 7 Hz), 1.11–1.71 (m, 4 H), 2.09 (br s, 1 H), 3.40 (d, 1 H, J = 7 Hz), 3.61 (s, 3 H), 3.91–4.19 (m, 1 H), 7.28 (s, 5 H). Anal. Calcd for $C_{13}H_{18}O_3$: C, 70.24; H, 8.16. Found: C, 69.99; H, 8.39.

2-Phenyl-2-hexenenitrile (8): IR (neat) 2225 (CN), 1170, 1010, 765, 695 cm^{-1}; NMR (CCl_4) δ 1.03 (t, 3 H, J = 7 Hz), 1.23–1.93 (m, 2 H), 2.56 (q, 2 H, J = 8 Hz), 6.70 (t, 1 H, J = 8 Hz), 7.13–7.63 (m, 5 H). Anal. Calcd for $C_{12}H_{13}N$: C, 84.17; H, 7.65. Found: C, 84.20; H, 7.79.

2,4-Diphenyl-3-(1-propyl)pentanedinitrile (9): IR (neat) 2250 (CN), 765, 735, 700 cm^{-1}; NMR (CCl_4) δ 0.67–2.33 (m, 8 H), 2.50–3.33 (m, 2 H), 7.25 (br s, 10 H). Anal. Calcd for $C_{21}H_{22}N_2$: C, 83.29;f H, 6.99. Found: C, 83.38; H, 7.21.

4-Methyl-2-phenyl-2-pentenenitrile (10): IR (neat) 2220 (CN), 755, 695 cm^{-1}; NMR (CCl_4) δ 1.12 (s, 3 H), 1.23 (s, 3 H),

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2.72–3.42 (m, 1 H), 6.51 (d, 1 H, $J = 10$ Hz), 7.24–7.66 (m, 5 H). Anal. Calcd for $C_{12}H_{13}N$: C, 84.17; H, 7.65. Found: C, 88.26; H, 7.80.

Base-Catalyzed Reaction of *n*-Butyraldehyde and Chloroform. To a solution of *n*-butyraldehyde (100 mmol) and chloroform (100 mmol) in DMF (50 mL) was added a suspension of base (10 mmol) in DMF (10 mL) at 0 °C for 1 h. After the mixture was stirred at 0 °C for 4 h, it was poured into 300 mL of a saturated solution of sodium chloride and extracted with ether. After evaporation of ether, **1a** was isolated by distillation.

Acknowledgment. T.S. wishes to thank the Ministry of Education, Science, and Culture, Japan, for the Grant-in-Aid for Scientific Research (B) (Grant 59470079).

Registry No. **1a**, 6111-12-2; **1b**, 32766-45-3; **1c**, 78409-34-4; **1d**, 2000-43-3; **1e**, 14337-31-6; **1f**, 70033-16-8; **1g**, 815-00-9; **1h**, 96349-56-3; **1i**, 4776-43-6; **1j**, 82772-36-9; **1k**, 82772-38-1; **1l**, 82772-37-0; **1m**, 85363-86-6; **1n**, 96349-57-4; **1o**, 96349-58-5; **1p**, 96349-59-6; **1q**, 6111-14-4; **1r**, 58369-59-8; **1s**, 59424-91-8; **1t**, 75820-73-4; **1u**, 7228-30-0; **1v**, 5333-82-4; **1w**, 19126-05-7; **1x**, 96349-60-9; **1y**, 62798-94-1; **1z**, 67916-20-5; **2a**, 3508-84-7; **2b**, 10292-51-0; **2c**, 96349-61-0; **2d**, 90347-44-7; **2e**, 6111-25-7; **3**, 19376-15-9; **4a**, 96349-62-1; **4b**, 38158-81-5; **5a**, 96349-63-2; **5b**, 29804-78-2; **5c**, 96349-64-3; **5d**, 96349-65-4; **5e**, 96349-66-5; **5f**, 16715-03-0; **5g**, 96349-67-6; **5h**, 96349-68-7; *threo*-**7a**, 96349-70-1; *erythro*-**7a**, 82584-40-5; *threo*-**7b**, 17226-94-7; *erythro*-**7b**, 17226-93-6; **8**, 6519-09-1; **9**, 96349-69-8; **10**, 6519-10-4; **11**, 2510-95-4; CCl_4, 56-23-5; $CHCl_3$, 67-66-3; *n*-C_3H_7CHO, 123-72-8; *i*-C_3H_7CHO, 78-84-2; $CH_3CH_2CH(CH_3)CHO$, 96-17-3; C_6H_5CHO, 100-52-7; *p*-$CH_3OC_6H_4CHO$, 123-11-5; $CH_2{=}CHCHO$, 107-02-8; (*E*)-$CH_3CH{=}CHCHO$, 123-73-9; $CH_3(CH_2)_6CHO$, 124-13-0; $CH_3(CH_2)_3CH(CH_2CH_3)CHO$, 123-05-7; $C_6H_5(CH_2)_2CHO$, 104-53-0; $(CH_3)_2C{=}CH(CH_2)_2CH(CH_3)CH_2CHO$, 106-23-0; $CH_3O(CH_2)_2CHO$, 2606-84-0; $CH_3(CH_2)_2CH{=}CHCHO$, 505-57-7; (*E*)-$C_6H_5CH{=}CHCHO$, 14371-10-9; (*E*)-$(CH_3)_2C{=}CH(CH_2)_2C(CH_3){=}CHCHO$, 141-27-5; $(CH_3)_2C{=}CHCHO$, 107-86-8; *o*-$CH_3OC_6H_4CHO$, 135-02-4; *m*-$CH_3OC_6H_4CHO$, 591-31-1; *p*-$C_6H_5CH_2OC_6H_4CHO$, 4397-53-9; *p*-ClC_6H_4CHO, 104-88-1; *p*-$CH_3O_2CC_6H_4CHO$, 1571-08-0; *o*-$O_2NC_6H_4CHO$, 552-89-6; $CH_3CO(CH_2)_4CH_3$, 110-43-0; $C_6H_5COCH_3$, 98-86-2; $CH_3(CH_2)_2CO(CH_2)_2CH_3$, 123-19-3; CBr_4, 558-13-4; $CHBr_3$, 75-25-2; $CCl_3CO_2CH_3$, 598-99-2; $CHCl_2CO_2CH_3$, 116-54-1; $C_6H_5CH_2CO_2CH_3$, 101-41-7; $C_6H_5CHBrCO_2CH_3$, 3042-81-7; $C_6H_5CH_2CN$, 140-29-4; $C_6H_5CHBrCN$, 5798-79-8; $CH_2{=}CHOAc$, 108-05-4; $C_6H_5CH(OH)CH_2Cl$, 1674-30-2; $C_6H_5CHClCH_2OH$, 1004-99-5; $CH_3CH_2CH(OH)CH_2Cl$, 1873-25-2; furfural, 98-01-1; piperonal, 120-57-0; 1-naphthalenecarboxaldehyde, 66-77-3; nicotinaldehyde, 500-22-1; cyclohexanone, 108-94-1; cyclopentanone, 120-92-3; phenyloxirane, 96-09-3; ethyloxirane, 106-88-7.

Steady-State and Laser Flash Photolysis Studies of Bridgehead-Substituted Dibenzobarrelenes[1]

Bulusu A. R. C. Murty,[2a] Sreedharan Pratapan,[2a] Challa V. Kumar,[2] Paritosh K. Das,*[2b] and Manapurathu V. George*[2]

Department of Chemistry, Indian Institute of Technology, Kanpur 208016, India, and Radiation Laboratory and Department of Chemistry, University of Notre Dame, Notre Dame, Indiana 46556

Received September 11, 1984

The photochemistry of bridgehead-substituted dibenzobarrelenes **1a–h** (Scheme I) has been investigated by steady-state photolysis, product analysis, and time-resolved laser flash photolysis. 4b-Substituted dibenzosemibullvalenes **8b,c,f,g** are formed as major photoproducts from dibenzobarrelenes **1b,c,f,g**, bearing acetoxy, formyl, ethyl, and methoxy 9-bridgehead substituents, whereas 8b-substituted dibenzosemibullvalenes (or products derived from them) (**7** and **6e**) are formed from 9-hydroxy- and 9-cyano-substituted dibenzobarrelenes **1a,e**. Laser flash photolysis gives rise to transient phenomena attributable to the triplets of dibenzobarrelenes ($\phi_T = 0.2$–0.7 in benzene). These are characterized by broad and diffuse absorption spectra, short lifetimes (0.07–11 μs), and varying degrees of quenchability by azulene, ferrocene, β-carotene, and *p*-methoxyphenol. The rate constants for triplet quenching by the latter quenchers as well as oxygen and di-*tert*-butylnitroxy radicals are presented.

Several reports have appeared on the phototransformations of barrelenes and different barrelene derivatives.[3] Barrelenes undergo facile photoisomerization to give the corresponding semibullvalenes, under triplet-sensitized irradiation, whereas on direct irradiation, cyclooctatetraene derivatives are formed. Vinylic and bridgehead substituents affect the stabilities of the diradical intermediates and thereby influence the regioselectivities of these rearrangements.[4-8] Electronegativities of the bridgehead substituents[8] and the presence of methoxycarbonyl and similar groups on the vinyl moiety, which can stabilize adjacent radical sites through π-delocalization,[4] are factors that affect the stabilities of such diradical intermediates. In addition, the presence of proximal hydroxy and acetoxy groups also stabilizes radical sites by through-space interactions, in some cases.[5,6]

Earlier,[9] we have shown that dibenzobarrelenes containing 1,2-dibenzoylalkene moieties prefer to undergo the di-π-methane rearrangement (Zimmerman rearrangement)[3b] than the 1,2-dibenzoylalkene rearrangement.[10] In

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(1) Document No. NDRL-2616 from the Notre Dame Radiation Laboratory.

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0022-3263/85/1950-2533$01.50/0