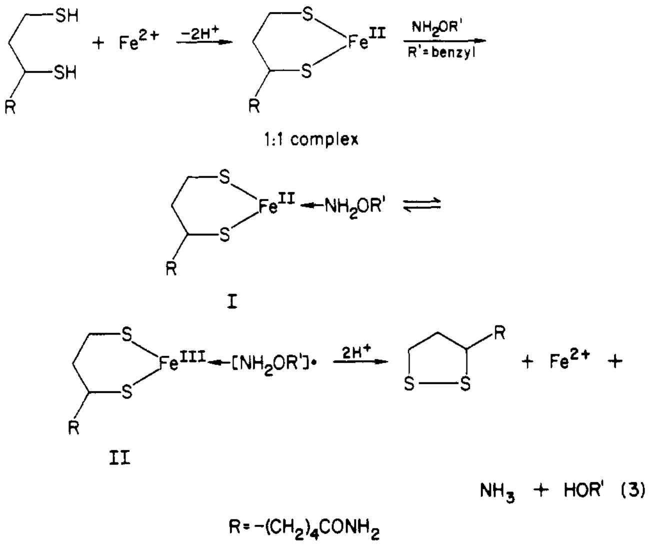
For these reasons, it is suggested that the reduction of *O*-benzylhydroxylamine by DHLAm–Fe(II) proceeds as shown in eq 3. The hydroxylamine coordinates to the thiol–Fe(II) complex to produce intermediates I. The coordinated hydroxylamine then undergoes one-electron reduction to produce intermediate II, which is presumed to be in equilibrium with intermediate I. In the final stage, one-electron transfer from thiol–Fe(III) complex to the hydroxylamino radical occurs by oxidative cyclization of dithiol to disulfide to produce ammonia, the alcohol, ferrous ion, and disulfide.



In conclusion, it is confirmed by spectroscopic and electrochemical methods that a reactive DHLAm–Fe(II) (1:1) complex is formed by mixing DHLAm and ferrous ion. Hydroxylamine derivatives, nitrobenzene, and isoxazole coordinate to the active complex and are reduced, respectively, with oxidative cyclization of DHLAm to LAm.

Experimental Section

Materials and Measurements. The cyclic voltammetric experiments were accomplished by use of a Hokuto Denko Potentiostat PS-1000 and a Function Generator HB-104. A gold-inlay electrode was used as the working electrode in 0.4 M KCl + 0.1 M carbonate buffer (pH 9.8)–ethanol (2:1) solution. The solution in the electrochemical cell was degassed with argon.

Absorption spectra were recorded on a Hitachi 200-10 spectrometer.

Dihydrolipoamide (DHLAm) was prepared by the reduction of lipoamide with sodium borohydride according to the procedure of Reed et al.[9] *o*-Xylene-α,α'-dithiol was prepared as reported already.[10]

Other chemicals used in this study were reagent grade and solvents were purified by the usual methods.

Registry No. DHLAm–Fe(II), 96481-48-0; FeSO$_4$(NH$_4$)$_2$SO$_4$, 10045-89-3; LAm, 940-69-2; DHLAm, 3884-47-7; PhN=NPh, 103-33-3; NH$_2$OCH$_2$Ph, 622-33-3; PhNO$_2$, 98-95-3; PhNHOH, 100-65-2; PhCH$_2$OH, 100-51-6; Au, 7440-57-5; 3,5-dimethylisoxazole, 300-87-8; 6,8-dimercaptooctanoic acid–Fe(II) complex, 96481-53-7; *o*-xylene-α,α'-dithiol–Fe(II) complex, 96481-49-1; 1,4-dimercapto-2,3-butanediol–Fe(II) complex, 96481-50-4; 2,3-dimercaptopropanol–Fe(II) complex, 96481-51-5; benzethiol–Fe(II) salt, 96481-52-6; benzenethiol, 108-98-5; 6,8-dimercaptooctanoic acid, 462-20-4; *o*-xylene-α,α'-dithiol, 41383-84-0; 1,4-dimercapto-2,3-butanediol, 7634-42-6; 2,3-dimercaptopropanol, 59-52-9.

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[9] Reed, L. J.; Koike, M.; Levitch, M. E.; Leach, F. R. *J. Biol. Chem.* **1958**, *232*, 143.

[10] Mayerle, J. J.; Denmark, S. E.; DePamphilis, B. V.; Ibers, J. A.; Holm, R. H. *J. Am. Chem. Soc.* **1975**, *97*, 1032.

Synthesis and X-ray Crystal Structure Analysis of a Vicinally Dinitro-Substituted Bishomopentaprismane

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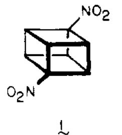
Received November 29, 1984

Oximation of [4]peristylane-2,6-dione (**6**) followed by bromination in buffered aqueous dimethylformamide and trifluoroperacetic acid oxidation delivered chiefly the caged dinitro dibromide **9**. Upon treatment with tri-*n*-butyltin hydride in refluxing benzene, **9** was transformed into the title compound (**4**). No evidence for free radical chain elimination of the nitro groups was seen. Single-crystal X-ray analysis was performed on **4**. Highly strained carbon–carbon single bonds are in evidence as expected. Significantly, the pair of nitro groups bring to **4** a density (1.63 g cm^{-3}) markedly enhanced relative to values exhibited by closely related structures.

The search for energetic compounds having high density has very recently focused on polynitro-substituted cage molecules.[1-3] Properties such as heightened strain energy, molecular compactness, and self-contained oxidizability have been deemed especially important. To this time, 1,4-dinitrocubane (**1**),[1,2] 3,5,5-trinitropentacyclo[5.3.0.0^{2,6}.0^{3,10}.0^{4,8}]decane (**2**),[3a] and 5,5,9,9-tetranitropentacyclo[5.3.0.0^{2,6}.0^{3,10}.0^{4,8}]decane (**3**)[3b] represent the most advanced candidates to have yielded to synthesis.



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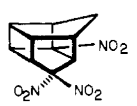

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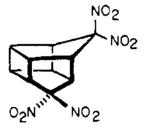

3

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[1] Eaton, P.E.; Ravi Shankar, B. K.; Price, G. D.; Pluth, J. J.; Gilbert, E. E.; Alster, J.; Sanders, O. *J. Org. Chem.* **1984**, *49*, 185.

[2] Griffin, G. W., private communication.

[3] (a) Marchand, A. P.; Suri, S. C. *J. Org. Chem.* **1984**, *49*, 2041. (b) Marchand, A. P.; Reddy, D. S. *Ibid.* **1984**, *49*, 4078.

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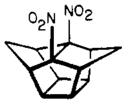
Since the positioning of nitro groups on vicinal carbon atoms had not yet been achieved in molecules of this type and the consequences of this desirable substitution plan were yet unknown, an approach to a prototypical substrate has been developed. Herein is described a synthesis of the bishomopentaprismane 4, whose detailed structure has also been elucidated by X-ray crystallography.

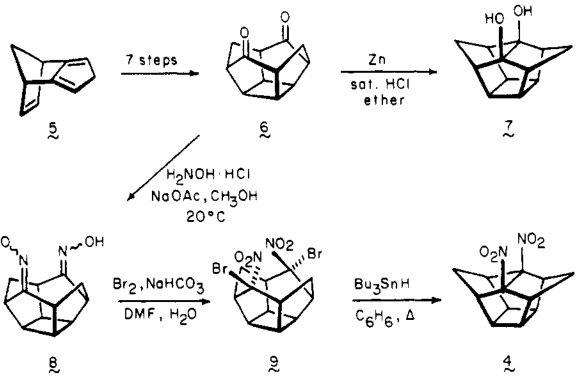


4

Synthesis

The expedient conversion of tricyclo[5.2.1.0^{2,6}]deca-2,5,8-triene (5) to [4]peristylane-2,6-dione (6) has previously been described by us.[4] Twofold oximation of 6 could be accomplished efficiently provided that the reaction was conducted at room temperature.[5] More forcing conditions resulted in decomposition. Bromination of 8 in aqueous dimethylformamide containing sodium carbonate[6] proceeded with predominant exo delivery of the halogen (assumed steric control as observed elsewhere[4]) to give a mixture of bright green dibromodinitroso [4]peristylanes. Direct oxidation of this material with trifluoroperacetic acid according to Nielsen[6] and subsequent recrystallization from ethyl acetate delivered isomerically pure 9 in 8% yield. The highly symmetric nature of 9 follows from its spectra; for example, only four ^{13}C signals are seen.

Diketone 6 is recognized to undergo pinacol reduction to diol 7 with exceptional ease.[4] This earlier observation prompted us to examine the action of tri-*n*-butyltin hydride in refluxing benzene on 9. The anticipated debrominative transannular cyclization did indeed take place to give 4 in 50% purified yield. We were aware of the readiness with which vicinal dinitro compounds undergo free radical chain elimination (the $E_{RC}1$ process) in the presence of tri-*n*-butylin hydride to produce olefins.[7,8] In the present instance, however, replacement of the two nitro groups by an unsaturated linkage would be accompanied by the buildup of enormous levels of strain and is not readily operative. Relevantly, the presence of AIBN was not necessary to the success of the 9 → 4 transformation. An electron-transfer chain mechanism may therefore not be operative. This feature may explain why the nitro groups in 4 are not subject to denitration by the tin hydride reagent.



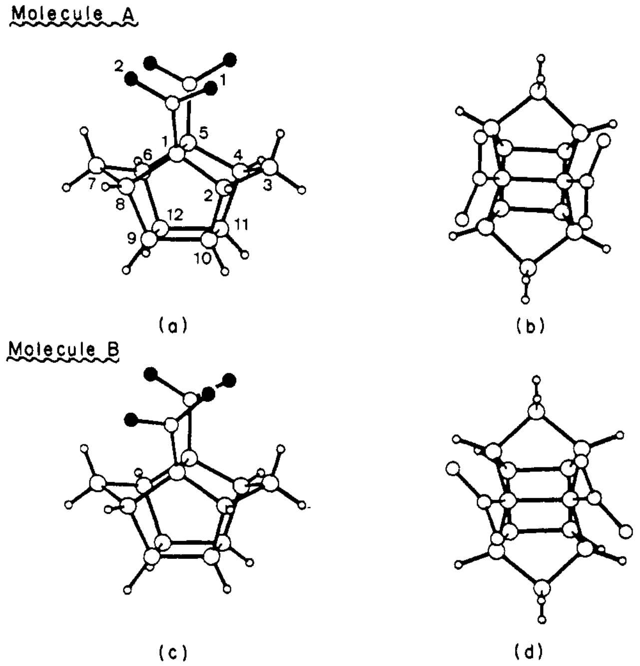


Figure 1. Side and top views of the two independent molecules of 4 in the cell. Structure a illustrates the numbering scheme utilized herein.

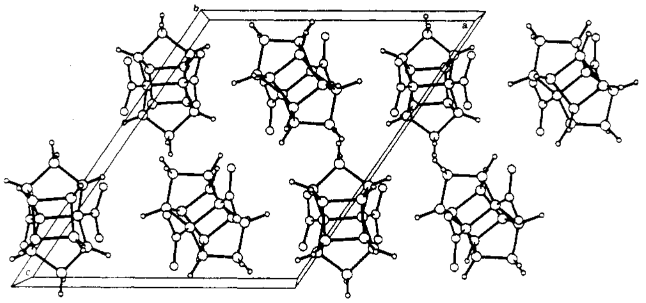


Figure 2. Unit cell of 4 with projection along the *b* axis.

X-ray Crystal Structure Analysis. The asymmetric unit of 4 contains two independent molecules designated as A and B, respectively. As can be seen from Figure 1, the two molecules differ in their orientation of the nitro groups with respect to the bishomopentaprismane framework. The torsion angle O(1)-N(1)-C(1)-C(2) is 16.9° for molecule A and 6.0° for molecule B. The carbocyclic superstructures, however, are virtually identical. The molecules lie on a crystallographic twofold axis characterized as Wyckoff positions 2f and 2e, respectively.

The bishomopentaprismane frame in each instance exhibits nearly C_{2v} symmetry. This symmetry is slightly broken by the nitro groups in molecule A and disturbed considerably in molecule B. The question of whether the different oreientations of the nitro groups in A and B arise solely because of packing requirements in the crystal structure cannot be answered.

Of particular interest are the long C(1)-C(5) single bonds in molecules A (1.593 (3) Å) and B (1.590 (3) Å), which indicate that high levels of strain exist. The long carbon-carbon bonds in the four-membered ring (1.560 (3) and 1.568 (3) Å for A; 1.558 (3) and 1.559 (3) Å for B) have

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(4) (a) Paquette, L. A.; Brown, A. R.; Doecke, C. W.; Williams, R. V. *J. Am. Chem. Soc.* **1983**, *105*, 4113. (b) Paquette, L. A.; Fischer, J. W.; Browne, A. R.; Doecke, C. W. *Ibid.* **1985**, *107*, 686.

(5) Corey, E. J.; Melvin, L. S., Jr.; Haslanger, M. F. *Tetrahedron Lett.* **1975**, 3117.

(6) Nielsen, A. T. *J. Org. Chem.* **1962**, *27*, 1993.

(7) Ono, N.; Miyake, H.; Tamura, R.; Hamamoto, I.; Kaji, A. *Chem. Lett.* **1981**, 1139.

(8) Other reagents are recognized to accomplish the same transformation. (a) Sodium sulfide: Kornblum, N.; Boyd, S. D.; Pinnick, H. W.; Smith, R. G. *J. Am. Chem. Soc.* **1971**, *93*, 4316. (b) Stannous chloride: Fukunaga, K.; Kimura, M. *Bull. Chem. Soc. Jpn.* **1979**, *52*, 1107. (c) Calcium amalgam: Kornblum, N.; Cheng, L. *J. Org. Chem.* **1977**, *42*, 2944.

(9) (a) Ono, N.; Miyake, H.; Tamura, R.; Kaji, A. *Tetrahedron Lett.* **1981**, 1705. (b) Ono, N.; Miyake, H.; Kamimura, A.; Tsukui, N.; Kaji, A. *Ibid.* **1982**, 2957.

been encountered previously in [4]peristylane-2,6-dione (**6**, 1.555 (2) and 1.564 (2) Å)[10] and pentaprismane (mean 1.565 Å).[11] As can be seen from the listing of torsion angles, the five-membered rings adopt half-chair conformations.

The packing arrangement of the molecules in the unit cell is shown in Figure 2. The molecules are held together by van der Waals forces only. The closest intermolecular approach, amounting to 2.73 (3) Å, occurs at O(2B)–H-(2B′). Significantly, the calculated density for **4** (1.63 g cm^{-3}) is markedly enhanced when compared to 1.42 g cm^{-3} for **6**[10] and 1.46 g cm^{-3} for pentaprismanecarboxylic acid.[11]

To a first approximation, therefore, one consequence of positioning a pair of nitro groups on vicinal carbon atoms of a bishomopentaprismane is to produce a substance having appreciably increased density. Additional examples of vicinal dinitro compounds are, of course, necessary to determine the generality of this observation and investigation of this matter is currently under way.

Experimental Section

***exo,exo*-2,6-Dibromo-*endo,endo*-2,6-dinitro[4]peristylane (9).** [4]Peristylanedione (**6**, 300 mg, 1.6 mmol), hydroxylamine (1.11 g, 16 mmol), and sodium acetate (2.62 g, 32 mmol) were stirred together in methanol (30 mL) at room temperature for 4 h. Water (20 mL) was added, and the product was extracted into ethyl acetate (3 × 25 mL). The combined organic phases were washed with saturated sodium bicarbonate solution (25 mL), water (25 mL), and brine (25 mL) prior to drying. Solvent evaporation under reduced pressure afforded oxime **8** (320 mg, 89%) as a colorless solid comprised of two geometric isomers.

Bromine (0.14 mL, 2.8 mmol) was added at room temperature to a mixture of **8** (320 mg, 1.4 mmol) and sodium bicarbonate (590 mg, 7.0 mmol) in dimethylformamide (6 mL) and water (3 mL). Following initial vigorous gas evolution, the reaction mixture took on a dark green hue. After 1 h, the colored contents were poured into water (20 mL), and the product was extracted into dichloromethane (3 × 20 mL). The combined organic layers were washed with water (20 mL) and brine (20 mL), dried, and evaporated. The resulting bright green oil was placed under high vacuum (0.1 torr) for 1 h to remove traces of dimethylformamide. Crystallization occurred during this period, and the green solid was dissolved in dichloromethane (10 mL) and added to cold (0 °C) trifluoroperacetic acid (prepared from 1 mL of 90% hydrogen peroxide and 1 mL of trifluoroacetic anhydride in 10 mL of dichlromethane). The green color was immediately discharged. After 4 h at room temperature, the mixture was poured into water (20 mL), and the aqueous phase was extracted with dichloromethane (2 × 20 mL). The combined organic layers were washed with 10% sodium thiosulfate (20 mL) and saturated bicarbonate solutions (20 mL) and brine (20 mL) before drying. Solvent removal followed by preparative TLC on silica gel (elution with 35% ethyl acetate in petroleum ether) afforded 44 mg (8%) of **9** as colorless crystals: mp 217–219 °C dec (from ethyl acetate); IR (CHI_3, cm^{-1}) 2980, 1555, 1460, 1345, 1300; ^1H NMR (200 mHz, $CDCl_3$) δ 3.9–3.5 (m, 8 H), 2.6–2.2 (m, 2 H), 2.1–1.9 (m, 2 H); ^{13}C NMR ($CDCl_3$) 103.15, 58.02, 44.19, 36.37 ppm.

Anal. Calcd for $C_{12}H_{12}Br_2N_2O_4$: C, 35.32, H, 2.96. Found: C, 34.72; H, 3.12.

Reductive Cyclization of 9. A solution of **9** (50 mg, 0.12 mmol) and tri-*n*-butyltin hydride (76 mg, 0.26 mmol) in benzene (5 mL) under nitrogen was heated at the reflux temperature for 22 h. The cooled reaction mixture was poured into 1 M potassium fluoride solution (10 mL) and extracted with ether (10 mL). The organic phase was washed with water (10 mL) and brine (10 mL), dried, and evaporated to leave a yellow solid. Recrystallization of this material from ethyl acetate afforded **4** as a colorless solid (15 mg, 50%): mp >300 °C dec; IR (KBr, cm^{-1}) 2995, 1545, 1460, 1352, 1345, 810; ^1H NMR (200 MHz, $CDCl_3$) δ 3.23 (m, 4 H), 2.93 (d t, J = 11.5 and 1 Hz, 2 H), 2.85 (m, 4 H), 1.77 (d, J = 11.5 Hz, 2 H); ^{13}C NMR ($CDCl_3$) 109.12, 52.28, 41.40, 40.69 ppm.

Table I. X-ray Crystal Data for 3

formula	$C_{12}H_{12}N_2O_4$	
density, g cm^{-3}	1.63	
space group	$P2/c$	
cell parameters		
a, Å	11.855 (5),[a]	11.660 (3)[b]
b, Å	7.677 (4),[a]	7.669 (2)[b]
c, Å	13.853 (6),[a]	13.723 (10)[b]
β, deg	124.63 (5),[a]	124.63 (5)[b]
molecules per unit per (Z)	4	
radiation	Mo K$\bar{\alpha}$ (λ = 0.71069 Å)	
linear absorption coefficient [μ(Mo K$\bar{\alpha}$)], cm^{-1}	1.34	

[a] At 23 °C. [b] At −140 °C.

X-ray Crystal Structure Determination of 4. Colorless crystals of the dinitrobishomopentaprismane were used. Preliminary Weissenberg photographs with Cu Kα radiation showed that the crystals were strongly twinned. Cutting out a small fragment 0.18 × 0.20 × 0.22 mm in size afforded a suitable single crystal for X-ray analysis. The crystals belong to the monoclinic system. Systematic extinctions are $h0l$, l = $2n + 1$, thus defining the possible space groups $P2_1/c$ and Pc. The reflections $0k0$, $k = 2n + 1$, are very weak and only 050 and 070 could faintly be seen in the diffraction pattern, indicating a true space group $P2_1/c$.

Determination of the lattice parameters and the intensity measurements was made with the Nonius CAD4 diffractometer using graphite-monochromatized Mo Kα radiation. The cell parameters were calculated by a least-squares procedure from 15 reflections in the range 12° < θ 41° measured at 23° and at −140 °C. The crystal date are summarized in Table I.

All independent reflections in the range $2° < 2\theta < 60°$ were measured at T = −140 °C. The orientation of the crystal was controlled every 100 reflections, and the intensities of the $\bar{2}\bar{1}\bar{1}$ and 421 refelctions were checked every 2.8 h. During the measurement, no significant deviation could be observed. A total of 3103 reflections was measured. After multiple measurements were averaged, 2934 independent reflections remained, of which 652 were unobserved with $I < 2.58\sigma(I)$. The intensities were corrected for Lorenz and polarization effects. An absorption correction was not considered necessary because of the low absorption coefficient. The intensities were transformed into normalized E values, which show a statistical distribution corresponding to a centrosymmetric crystal. An attempt to solve the crystal structure in the pseudo space group $P2/c$ with direct methods gave a rough model that, however, could not be refined beyond R = 0.43. This model could be improved in the subgroup $P2/c$ with a tangent refinement,[12] after the pseudosymmetry was broken by rotating one of the two independent molecules around the b axis by an arbitrary angle of 20°. The complete structure was then found in a subsequent Fourier synthesis. The refinement with block-diagonal least-squares calculations did not converge smoothly. At several times some of the atoms had to be moved in order to realize further progress. This behavior is often met in pseudosymmetric structures because of the systematic overlap in the Patterson synthesis and the final result may not be very accurate. The hydrogen atoms could all be seen in a difference Fourier synthesis. In the last cycles of refinement the hydrogen atoms were included with isotropic temperature factors. For the oxygen, nitrogen, and carbon atoms, anisotropic temperature factors were used. The minimized function was

$$\sum_{H}\left[|F_o(H)| - \frac{1}{k}\left|F_c(H)\right|\right]^2$$

Atomic scattering factors were taken from Ibers and Hamilton.[13]

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[10] Engel, P.; Fischer, J. W.; Paquette, L. A. *Z. Kristallogr.* **1984**, *166*, 225.

[11] Engel, P.; Eaton, P. E.; Ravi Shankar, B. K. *Z. Kristallogr.* **1982**, *159*, 239.

[12] Karle, J.; Hauptman, K. *Acta Crystallogr.* **1956**, *9*, 635.

[13] Ibers, J. A.; Hamilton, W. C. "International Tables for X-Ray Crystallography"; Kynock Press: Birmingham, England 1974; Vol. IV, p 71.

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]

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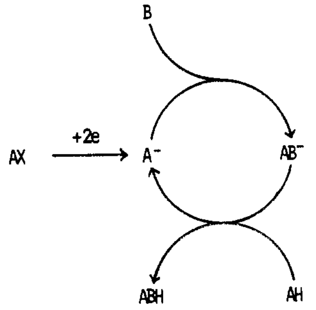
Received December 20, 1984

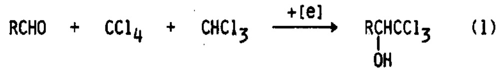
Cathodic reduction of a system comprising carbon tetrachloride, chloroform, and an aldehyde led to an effective anionic chain reaction. The best current efficiency observed was about 1×10^4%. Such a chain reaction is an effective synthetic method for 1,1,1-trichloro-2-alkanols. The reaction system consisting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

Scheme I



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.



$$\mathrm{RCHO} + \mathrm{CCl_4} + \mathrm{CHCl_3} \xrightarrow{+[e]} \underset{\displaystyle \mathrm{OH}}{\mathrm{RCHCCl_3}} \quad (1)$$

1

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

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	$(n\text{-octyl})_3MeNCl$	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.

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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