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Novel Method of Oxidation by a Polymeric Reagent Electrochemically Generated and Recycled in Situ. Facile Oxidation of Alcohols

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A polymeric reagent electrochemically generated from crosslinked poly-4-vinylpyridine hydrobromide (1) was found to oxidize secondary alcohols to give the corresponding ketones in the absence of electric current. The exhausted polymeric reagent was regenerated by electrochemical oxidation. Thus a mild method of oxidation was developed which involved an electrochemical process in the presence of 1. Secondary alcohols were oxidized by this method to give the corresponding ketones in high yields, and hydrogen was formed quantitatively as a second product. Since the exhausted polymeric reagent is regenerated by continuous electrochemical oxidation in situ, only a catalytic amount of 1 (based on the alcohol) is required for the reaction, and the method does not consume any chemical oxidant and does not produce any contaminating reduced product. The efficiency of the electric current was very high, and only a slight excess of electricity was required to obtain the ketones in satisfactory yields. This method may remove defects of conventional electroorganic processes such as difficulty in separation and recovery of the electrolytes.

From an environmental point of view considerable attention has recently been focused on insoluble polymeric reagents,[1] since easy recovery of them prevents the leakage of toxic materials. However, regeneration of exhausted polymeric reagents often requires stoichiometric amounts of other chemicals, and the disposal problem of toxic wastes arises from such regeneration processes. In exploring a new methodology which solves this problem, we have now found a novel method of oxidation by a polymeric reagent electrochemically generated from crosslinked poly-4-vinylpyridine hydrobromide (1). Since the exhausted polymeric reagent is regenerated by continuous electrochemical oxidation in situ, the method does not consume any chemical oxidant and does not produce any contaminating reduced product. As an example, electrochemical oxidation of secondary alcohols in acetonitrile in the presence of a catalytic amount of wet 1 gave the corresponding ketones in high yields (eq 1). This is the first

$$\mathrm{RCH(OH)R'} \xrightarrow[\mathrm{1/H_2O/CH_3CN}]{\text{electric current}} \mathrm{RC(O)R'} + \mathrm{H_2} \qquad (1)$$

case of the use of a polymeric reagent which was recycled in situ by the continuous electrochemical regeneration.

Experimental Section

A Trio Model PR-653 regulated DC power supply or a Kikusui Model PAB-32-0.5 regulated DC power supply was used as a source of electric current. ^{1}H NMR spectra were recorded on a Varian T-60A spectrometer in carbon tetrachloride or deuteriochloroform using tetramethylsilane as an internal standard. IR spectra were recorded on a Hitachi Model 215 grating spectrophotometer. GLC analyses were performed on a Shimadzu GC-4B or GC-4C gas chromatograph.

Materials. 4-Vinylpyridine provided by Koei Chemical Co., Ltd., and commercial styrene and divinylbenzene (ca. 55%) were purified by distillation before polymerization. Polyvinyl alcohol (degree of polymerization was 2000) supplied by Wako Pure Chemical Industries, Ltd., was used without further purification. Deionized water was used throughout the experiments. Other chemicals and nitrogen were used as obtained commercially.

Preparation of Crosslinked Poly-4-vinylpyridine. Crosslinked poly-4-vinylpyridine was prepared according to a literature procedure[2] with minor modifications. Polymerization was carried out in a 1-L, three-necked flask equipped with a mechanical stirrer, a reflux condenser, and a gas inlet. Polyvinyl alcohol (2.05 g) was dissolved in 500 mL of boiling water. The solution was stirred under nitrogen at 60 °C, and a mixture of 4-vinylpyridine (30.0 g), styrene (15.1 g), and divinylbenzene (15.1 g) in 30.0 mL of toluene was added. Styrene was used in addition to 4-vinylpyridine and divinylbenzene in order to carry out the suspension polymerization more smoothly. After addition of azobis(isobutyronitrile) (0.45 g) as the initiator, the mixture was heated at 80 °C under slow stirring for 2 h. Polymer beads appeared gradually during this period. The mixture was then heated at 100 °C for 8.5 h. The resin beads were separated by filtration and were washed with water and acetone. After this substance was dried under a reduced pressure, 59.5 g of crosslinked poly-4-vinylpyridine was obtained. The polymer contained 6.34% of nitrogen, indicating that the 4-vinylpyridine content was 48 wt %. The particle diameter was 0.3–1.0 mm in the dry state.

Preparation of Crosslinked Poly-4-vinylpyridine Hydrobromide (1). Crosslinked poly-4-vinylpyridine was preconditioned prior to the preparation of the hydrobromide 1 as follows. A mixture of crosslinked poly-4-vinylpyridine (59.5 g) and aqueous 2 N HBr (430 mL) was stirred overnight at room temperature. The resin beads were separated by filtration, washed with water, and added to aqueous 2 N NaOH (500 mL). After the mixture was stirred overnight at room temperature, the resin beads were separated by filtration and washed with water.

Crosslinked poly-4-vinylpyridine hydrobromide (1) was freshly prepared immediately before use. A mixture of the preconditioned crosslinked poly-4-vinylpyridine (2.0 g) and aqueous 2 N HBr (52 mL) was stirred overnight at room temperature, and the resin beads were separated by filtration followed by washing with 1 L of water. The amount of HBr bound to the resin was determined by back-titration with standard 0.1 N HCl using phenolphthalein as indicator after reaction with excess 0.1 N NaOH overnight at room temperature. The crosslinked poly-4-vinylpyridine hydrobromide contained 45 wt % of water. Elemental analysis of the dry resin showed the contents of 4.85% of N and 21.95% of Br, indicating that 79% of the pyridyl group in the resin was converted to the hydrobromide form. The particle diameter was 0.3–1.1 mm in the wet state.

Crosslinked poly-4-vinylpyridine hydrochloride was prepared in a similar way.

Resins. For comparison, two commercial resins were used in this work. Amberlite IRA-400 supplied by Rohm and Haas Co. was used as a strong base anion-exchange resin, which had a styrene–divinylbenzene matrix with a quaternary ammonium group. The resin was preconditioned and transferred to the bromide form by employing the column method as follows: (1) washing with methanol, (2) washing with water, (3) washing with aqueous 2 N NaOH, (4) washing with water, (5) washing with aqueous 2 N HBr, (6) washing with water, (7) repeating steps 3–6

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(1) For example: (a) Overberger, C. G.; Sanness, K. N. *Angew. Chem.* **1974**, *86*, 139–145; (b) Neckers, D. C. *J. Chem. Educ.* **1975**, *52*, 695–702.

(2) Fréchet, J. M. J.; Farrall, M. J.; Nuyens, L. J. *J. Macromol. Sci., Chem.* **1977**, *A11*, 507–514.

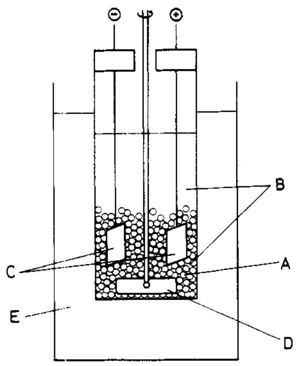


Figure 1. Cell for electrochemical reaction: A, resin beads; B, solvent or solution; C, platinum electrodes; D, stirrer; E, water bath.

several times, (8) slow contact with 2 N NaOH, (9) washing with water, (10) slow contact with 2 N HBr, (11) washing with water. The resin in the bromide form contained 35 wt % of water and was directly used for the electrochemical reaction. The amount of Br bound to the resin was determined by titration with standard 0.1 N $AgNO_3$ using eosine as indicator after treatment with a large excess of aqueous 1 N KNO_3.

Amberlite IRA-94 supplied by Rohm and Haas Co. was used as a weak base anion-exchange resin, which had a styrene–divinylbenzene matrix with a tertiary amino group. The resin was preconditioned by employing the column method as follows: (1) washing with methanol, (2) washing with water, (3) washing with aqueous 2 N HBr, (4) washing with water, (5) washing with aqueous 2 N NaOH, (6) washing with water, (7) repeating steps 3–6 several times.

The preconditioned resin (3.0 g) was transferred to the hydrobromide form by treatment with 100 mL of aqueous 2 N HBr overnight at room temperature under stirring, followed by washing with 1 L of water. The resin contained 56 wt % of water and was directly used for the electrochemical reaction. The amount of HBr bound to the resin was determined by back-titration with standard 0.1 N HCl using phenolphthalein as indicator after treatment with a large excess of 0.1 N NaOH overnight at room temperature.

Electrochemical Generation of Oxidizing Reagent from Crosslinked Poly-4-vinylpyridine Hydrobromide (1). A mixture of 1 (3.50 g, wet) containing 6.97 mmol of HBr and 3.0 mL of acetonitrile was placed in an undivided 15-mL glass cell equipped with platinum electrodes (10 × 10 × 0.5 mm) parallel to each other with about 10 mm of space between them. A diagram of the cell is shown in Figure 1.

A constant current (60 mA) was passed through the mixture with slow stirring at 50 °C. The initial potential between the electrodes was about 15 V, and this gradually increased to 35 V until 10.1 mF of electricity was passed. The resin beads were then separated by filtration and were washed with acetonitrile and water. The polymeric reagent thus obtained was allowed to react with 2-octanol (619 mg, 4.75 mmol) in 3.0 mL of acetonitrile at 50 °C for 20 h in the absence of electric current under stirring. GLC analysis of the reaction mixture showed the formation of 1.07 mmol of 2-octanone. The product was isolated and identified by comparison of its ^1H NMR and IR spectra with those of an authentic material.

Regeneration of the Exhausted Polymeric Reagent. The exhausted polymeric reagent was isolated from the above reaction mixture and was washed with acetonitrile and ether. After soaking in water for 0.5 h, the resin beads were separated by filtration. A mixture of the resin beads and 3.0 mL of acetonitrile was placed again in the electrolysis cell, and a constant current (60 mA) was passed. After 10.1 mF of electricity was passed, the resin beads were separated by filtration and were washed with acetonitrile and water. Thus regenerated polymeric reagent was allowed to react with 2-octanol (603 mg, 4.63 mmol) in 3.0 mL of acetonitrile at 50 °C for 20 h in the absence of electric current under stirring. GLC analysis of the reaction mixture showed the formation of 0.83 mmol of 2-octanone.

Electrochemical Oxidation of Alcohols in the Presence of Crosslinked Poly-4-vinylpyridine Hydrobromide (1). The reactions were carried out in an undivided cell equipped with platinum electrodes as shown in Figure 1. An alcohol (20.0 mmol) and 1 (3.50 g (wet), which contained 5.1–7.5 mmol of HBr) were allowed to react in 3.0 mL of acetonitrile at 50 °C with a constant electric current (60 mA) under slow stirring. The applied electric potential was 10–30 V. After 2.4 mF/mol of electricity (based on the alcohol) was passed (ca. 21.5 h), the mixture was analyzed by GLC. The products were isolated by collection using GLC or by distillation from the reaction mixture and were identified by comparison of their ^1H NMR and IR spectra with those of authentic materials. The polymer beads can be reused several times with little loss of activity. In this case, the resin beads were recovered by filtration and were washed with acetonitrile and ether. After the beads were soaked in water for 2 h at room temperature, excess water was removed by filtration, and the resin beads were used for the electrochemical reaction.

For comparison, several other resins, aqueous HBr solution, and pyridine hydrobromide salt were used as the precursors of the oxidizing reagents. These experiments were carried out in a similar manner.

Polymeric Reagent Prepared by Treatment of Crosslinked Polyvinylpyridine with Aqueous Bromine. Crosslinked poly-4-vinylpyridine beads (1.60 g, dry) were suspended in 16 mL of water. Bromine (0.11 mL, 2.15 mmol) was added dropwise at room temperature with stirring. After the addition was completed, the mixture was stirred for 5 h. The polymer beads were separated by filtration and were washed extensively with water. The polymeric reagent thus obtained (3.06 g, wet) was allowed to react with 2-octanol (673 mg, 5.17 mmol) in 3.0 mL of acetonitrile at 50 °C for 15 h. GLC analysis of the reaction mixture showed the formation of 1.30 mmol of 2-octanone.

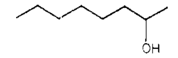
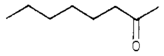
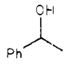
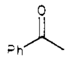
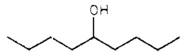
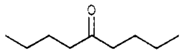
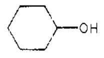
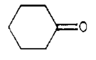
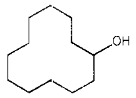
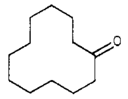
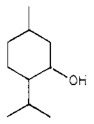
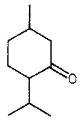
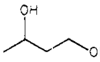
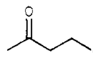
Results and Discussion

We found that a polymeric oxidizing reagent was generated from crosslinked poly-4-vinylpyridine hydrobromide (1) by an electrochemical process. The electrochemical reaction was carried out in a cell equipped with platinum electrodes by using acetonitrile as solvent without use of specific electrolyte. A diagram of the cell is shown in Figure 1. As an example, 3.50 g (wet) of 1 containing 6.97 mmol of HBr and 3.0 mL of acetonitrile was placed in the cell, and a constant electric current (60 mA) was passed through the mixture with slow stirring at 50 °C. At first, the electric potential between the electrodes was 15 V but gradually increased to 35 V until 10.1 mF of electricity was passed. Then the polymer beads were separated by filtration. Thus-obtained polymeric reagent was found to react with 4.75 mmol of 2-octanol in 3.0 mL of acetonitrile in the absence of electric current to give 1.07 mmol of 2-octanone during 20 h at 50 °C. (See the Experimental Section for details.) The precursor 1 itself did not show the ability to oxidize 2-octanol under the conditions.

The exhausted polymeric reagent was found to be regenerated by the electrochemical process. For example, the polymer beads were isolated from the above reaction mixture by filtration. Thus recovered polymer beads and 3.0 mL of acetonitrile were placed in the cell, and a constant electric current (60 mA) was passed again in a similar manner. After 10.1 mF of electricity was passed, the polymer beads were separated by filtration. Thus-regenerated polymeric reagent was found to react with 4.63 mmol of 2-octanol in 3.0 mL of acetonitrile in the absence of electric current to give 0.83 mmol of 2-octanone during 20 h at 50 °C. (See the Experimental Section for details.)

These observations prompted us to develop a mild method of oxidation which involved an electrochemical process in the presence of 1 without use of a specific electrolyte. The reactions were carried out in the cell shown in Figure 1 with 20.0 mmol of alcohol and 3.50 g (wet) of 1 containing 5.1–7.5 mmol of HBr in 3.0 mL of acetonitrile as the solvent at 50 °C. A constant electric

Table I. Oxidation of Alcohols by Polymeric Reagent Electrochemically Generated and Recycled in Situ[a]

run	alcohol	precursor	alcohol/ X[b]	conversion, %[c]	product	yield, %[d]
1		1	3.1	87		98
2		1[e]	3.1	85		93
3		1[f]	3.1	79		97
4		1	3.1	100[g]		81[h]
5		IRA-400 (Br)[i]	3.5	63		94
6		IRA-94 (HBr)[j]	4.2	80		95
7		HBr(aq)[k]	3.4	46		74
8		HBr-pyridine[l]	3.3	38		100
9		PVP·HCl[m]	3.2	51[n]		35
10		1	3.5	88		91
11		1	3.3	96		90
12		1	3.7	79		91
13		1	0.6[o]	76		82
14		1	3.5	49		90
15	n-$C_8H_{17}OH$	1	3.9	58	n-$C_7H_{15}COOH$[p] n-$C_7H_{15}COOC_8H_{17}$-n	59 40
16		1	4.3	92[q]	n-$C_7H_{15}COOH$[p] n-$C_7H_{15}COOC_8H_{17}$-n	57 36
17		1	3.5	56		71

[a] Reactions were carried out with 20.0 mmol of alcohol in 3.0 mL of acetonitrile at 50 °C. The passed electricity was 2.4 F/mol based upon the alcohol unless otherwise stated. [b] The molar ratio of alcohol to the halide ion contained in the precursor. [c] Amount of consumed starting material, determined by GLC analysis. [d] These yields were based on the consumed starting material and were determined by GLC analysis. The yields based on the total amount of starting material are obtained by multiplication of the percent conversion and yield given in the table. [e] The polymeric reagent recovered from the reaction mixture of the experiment (run 1) was used as the precursor. [f] The polymeric reagent recovered from the reaction mixture of the experiment (run 2) was used as the precursor. [g] The passed electricity was 3.0 F/mol. [h] Isolated yield. [i] A strong base anion-exchange resin, Amberlite IRA-400, in the bromide form. [j] Hydrobromide of a weak base anion-exchange resin, Amberlite IRA-94. [k] A mixture of 4 N aqueous hydrobromic acid (1.5 mL) and acetonitrile (3.0 mL) was used. [l] Pyridine–HBr (6.0 mmol), water (1.2 mL), and acetonitrile (4.0 mL) were used. [m] Crosslinked poly-4-vinylpyridine hydrochloride. [n] Enough current to perform the reaction did not flow under the usual conditions. The passed electricity was 1.6 F/mol. [o] Because of the low solubility, 3.2 mmol of cyclododecanol was used. [p] n-$C_7H_{15}CHO$ was not detected in the reaction mixture. [q] The passed electricity was 4.5 F/mol.

current (60 mA) was passed through the cell with slow stirring. After 2.4 mF/mol of electricity (based on the alcohol) was passed (ca. 21.5 h), the reaction mixture was analyzed by GLC. (See the Experimental Section for details.) Results are summarized in Table I.

The exhausted polymeric reagent was regenerated by continuous electrochemical oxidation in situ, and only a catalytic amount of 1 (based on the alcohol) was required for the reaction. No chemical oxidant was consumed during the reaction. No contaminating reduced product was formed.

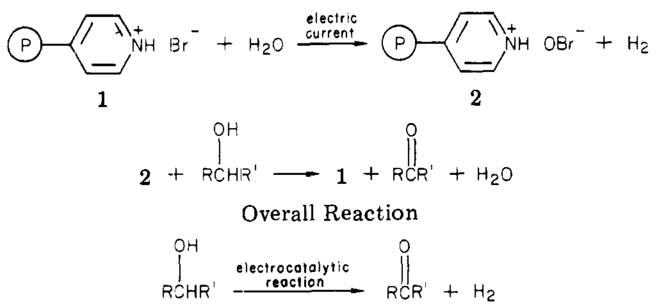
Successful applications to various secondary alcohols proved that the present reaction is useful in organic synthesis. From cyclic and acyclic secondary alcohols were obtained the corresponding ketones in high yields. It is noteworthy that the current efficiency of the present reaction was very high, and only a slight excess of electricity was required to obtain the ketones in satisfactory yields.

A primary alcohol was oxidized to give a mixture of the corresponding carboxylic acid and ester, but aldehyde was not formed in an appreciable amount (runs 15 and 16). A secondary hydroxyl group was oxidized in preference to the primary one, and butan-1,3-diol was oxidized to give 1-hydroxybutan-3-one in 71% yield (run 17).

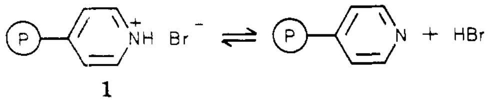
As the precursor of the polymeric oxidizing reagent, 1 was the most suitable among those examined and was reused several times with little loss of activity (runs 2 and 3). When the crosslinked poly-4-vinylpyridine hydrochloride was used instead of 1, the reaction gave substantial amounts of other products together with the expected ketone (run 9). In the case with a strong base anion-exchange resin in the bromide form as the precursor (run 5), the current did not flow smoothly, and the current efficiency was much lower. The hydrobromide of a weak base anion-exchange resin was effective as the precursor (run 6), but its mechanical stability was not enough for the present purpose, and most of the resin beads were broken into fine particles in the first cycle of use.

Although the reaction mechanism has not been elucidated as yet, it is reasonable to consider that HBr bound to the polymer played an important role in the present reaction, because the use of crosslinked poly-4-vinylpyridine instead of 1 resulted in conspicuous reductions of the electric current and yields of ketones.

Scheme I



The precursor 1 may participate in the equilibrium shown in eq 2. Therefore, there is a possibility that this


(2)
1

free HBr played an important role. However, when the reaction was carried out with aqueous hydrobromic acid or hydrobromic acid–pyridine salt instead of 1, the conversion was low (runs 7 and 8), indicating that the polymer effect was very important.

Although there is no evidence that the polymer reacted directly at the electrodes, it is noteworthy that the electric current was negligibly small when the electrodes were dipped in the solution but were not in contact with the layer of resin beads.

Electrolyte is necessary in usual electrochemical reactions, and it seems possible that free HBr liberated from the resin functioned as the electrolyte. However, as we have mentioned above, free HBr liberated from the resin did not appear to play an important role in the reaction, and direct contact of the resin with the electrodes seemed to be necessary for the reaction. These experimental observations suggest that the bromide ions on the surface of the resin beads released the electrons when the beads contacted the anode, and protons on the resin accepted the electrons when the beads contacted the cathode. Since the layer of the resin beads was stirred during the reaction, both the anode and the cathode successively contacted the fresh beads. When the resin beads contact each other, the electron-transfer might also occur. Thus it would be a reasonable speculation that HBr bound to the resin played a role as the electrolyte and that the electricity passed through the layer of resin beads.

On the basis of these and other experimental observations, we propose Scheme I for an understanding of the experimental results. Since the present reaction did not proceed in the absence of water, we assumed that 1 was electrochemically oxidized in the presence of water to give 2 and gaseous hydrogen in the first step of the reaction.[3] Here 2 is the hypobromous ion with the associated pyridinium cation bound to the resin, which is the oxidized form of 1, though its structure is hypothetical.[4] In the second step, we assumed that 2 reacted with the alcohol to produce the ketone and 1 which was again oxidized by the electrochemical reaction. The oxidized form of 1 was shown to be capable of converting secondary alcohols to ketones even in the absence of electric current as has been mentioned above. We also determined the amount of evolved gaseous hydrogen. During the reaction with 18.9 mmol of 2-octanol in the presence of 1 containing 7.5 mmol of HBr, 12.0 mmol of the corresponding ketone and 15.8 mmol of gaseous hydrogen were obtained. This result is consistent with the scheme on the assumption that about half of the polymeric reagent was in the oxidized form at the end of the reaction and if the amount of hydrogen that arose from the electrolysis of water was negligible under the conditions.

A polymeric reagent prepared by treatment of crosslinked polyvinylpyridine with aqueous bromine was also found to be capable of converting secondary alcohols to ketones. For example, 1.60 g (dry) of crosslinked polyvinylpyridine was treated with 2.15 mmol of aqueous bromine. The polymeric reagent thus obtained (3.06 g, wet) was allowed to react with 5.17 mmol of 2-octanol to give 1.30 mmol of 2-octanone during 15 h at 50 °C. Since it is well-known that the hypobromite is formed by treatment of bromine with aqueous alkaline solution, the action of aqueous bromine on the polyvinylpyridine containing the basic pyridyl group could afford 2, the hypobromite bound to the resin, which oxidized secondary alcohols to give ketones.

The current efficiency of the "in situ" process was much higher than that of the "batch" process. The reason for this result is not clear at present, but a possible explanation can be made as follows. The importance of direct contact of the resin beads with the electrodes implies that only the bromide ions on the surface of the resin were oxidized and that those on the deep inside of the resin matrix were hardly used for the electrochemical reaction. In the "in situ" process, electricity was passed in the presence of the alcohol. Therefore, the oxidized form of 1 presumably reacted with the alcohol immediately after the generation, producing the ketone and the revivified 1 which was again oxidized by the electrochemical reaction. Accordingly, bromide ions on the surface of the resin would be recycled efficiently, and most of the electricity was effectively used for the oxidation of the alcohol. In the "batch" process, however, electricity was passed in the absence of the alcohol. Therefore after the bromide ions on the surface of the resin were oxidized, the electricity would be consumed mainly in side reactions such as electrolysis of the solvent or water. The oxidized form of 1 thus generated was separated and was allowed to react with the alcohol in the absence of electric current. Consequently the current efficiency of the "batch" process would become very low. The low current efficiency of the "batch" process can also be ascribable to instability of the oxidized form of 1 which may partly decompose during the electrochemical generation or separation.

Since oxidation of alcohols to the corresponding carbonyl compounds is a basic synthetic process, several procedures using insoluble polymeric reagents have been applied. For example, a reagent prepared from polymeric thioanisole and chlorine has been reported to be an excellent reagent for the oxidation of alcohols.[5] Chromic acid on anion-exchange resins[6] and polyvinylpyridinium chlorochromate[7] were also reported to be quite effective for the oxidation of alcohols. In comparison with these published procedures, the following features and advantages of the present

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[3] The use of electrochemically generated hypobromite for the phase-transfer-catalyzed oxidation of benzyl alcohols has been reported: Pletcher, D.; Tomov, N. *J. Appl. Electrochem.* **1977**, *7*, 501–504; *Chem. Abstr.* **1978**, *88*, 29562.

[4] Polyvinylpyridine–Br_2 and polyvinylpyridine–HBr_3 are known, and the possibility cannot be ruled out that the oxidized form of 1 has such structures. See: Ohkawara, S.; Oiji, Y.; Imoto, E. *Kogyo Kagaku Zasshi* **1962**, *65*, 1658–1664. See also ref 2.

[5] Crosby, G. A.; Weinshenker, N. M.; Uh, H.-S. *J. Am. Chem. Soc.* **1975**, *97*, 2232–2235.

[6] Cainelli, G.; Cardillo, G.; Orena, M.; Sandri, S. *J. Am. Chem. Soc.* **1976**, *98*, 6737–6738.

[7] Fréchet, J. M. J.; Warnock, J.; Farrall, M. J. *J. Org. Chem.* **1978**, *43*, 2618–2621.

procedure should be stressed. (a) The polymeric reagent was regenerated by electrochemical reaction in situ. No chemical oxidants were required for the regeneration of the reagent. (b) Since the polymeric reagent was recycled in situ, only a catalytic amount of it was sufficient for the reaction. (c) Clean and valuable hydrogen was formed quantitatively as a second product.

Indirect electrochemical oxidation of organic compounds has received increasing attention.[8] Direct electrochemical oxidation of alcohols is usually difficult due to the relatively high oxidation potential of alcohols. Recently an elegant electrochemical oxidation of alcohols using iodonium ions[8d] and thioanisole[8e] as a catalytic electron carrier has been reported. From this point of view, the present methodology has a high potential, since it may remove defects of the conventional electroorganic process such as difficulty in separation and recovery of the electrolyte.

Apparently the oxidation of alcohols is a well-established process in organic synthesis, but reconsideration from the environmental point of view seems to be necessary at present. The conventional procedures involve the use of stoichiometric amounts of organic or inorganic oxidants, causing a disposal problem of toxic wastes. The development of the present methodology may shed light on the solution of the problem and further study must be continued in the direction of "pollution-free" organic synthesis.

Registry No. 1, 65993-03-5; 2-octanol, 123-96-6; α-methylbenzenemethanol, 98-85-1; 5-nonanol, 623-93-8; cyclohexanol, 108-93-0; cyclododecanol, 1724-39-6; 2-(1-methylethyl)-5-methylcyclohexanol, 1490-04-6; 1-octanol, 111-87-5; 1,3-butanediol, 107-88-0; 2-octanone, 111-13-7; 1-phenylethanone, 98-86-2; 5-nonanone, 502-56-7; cyclohexanone, 108-94-1; cyclododecanone, 830-13-7; 2-(1-methylethyl)-5-methylcyclohexanone, 10458-14-7; octanoic acid, 124-07-2; octyl octanoate, 2306-88-9; 4-hydroxy-2-butanone, 590-90-9; PVP·HCl, 54907-32-3; HBr-pyridine, 18820-82-1; HBr, 10035-10-6.

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Observation in the Periselective Photoadditions of Electron-Donating or Electron-Accepting Anthracenes to Cyclohepta-1,3,5-triene by Orbital and Steric Interaction Controls

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Irradiations (I_2-CCl_4 filter solution, 340-420 nm) of substituted anthracenes with a large excess of cyclohepta-1,3,5-triene in various solvents afforded a variety of photoaddition products in moderate yields. These periselective formations are explained in terms of the following controlling factors: (1) orbital interactions, (2) steric interactions.

Since pericyclic syntheses are very valuable for stereo-, regio-, and periselective controls, they could provide for a logical assembling of molecules. Especially in the past decade, the thermal pericyclic reactions of conjugated medium-ring polyenes have aroused considerable interest, and much effort has been made to establish their capability for cycloadditions, and the donor-acceptor relationships of the cycloaddends in the reactions were pointed out to be important.[1-3] The recognition of the donor-acceptor relationships of the cycloaddends also leads to a description of the entire spectrum of photochemical cycloadditions.[4]

As a continuation of our previous reports,[5] we have examined the photoadditions of substituted anthracenes to cyclohepta-1,3,5-triene. These results are discussed here in detail in comparison with the previous work.

Theoretical Background.

A number of pericyclic reactions take place photochemically, usually with consequences different from those of analogous thermal reactions.[1,2] Epiotis[6] has reported that the effect of configuration interaction can reverse the stereoselectivity of the cycloadditions when the two cycloaddends have widely different polarities. On the other hand, Inagaki et al.[7] have pointed out the possible importance of an abnormal orbital interaction in excited-state reactions between electron donors and acceptors: the photochemical reactions between powerful electron donors and acceptors are likely controlled by the $(HOMO)_D$-$(LUMO)_A$ interaction involved in the D^*A-$D^{+*}A^-$ or DA^*-D^+A^{-*} interaction, the frontier orbital interaction being the same as one in the usual thermal reaction by the stereoselection rules. For example, *trans,trans*-2,4-hexa-

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