LAH Reduction of 10 to 13. A solution of 0.5 g (0.0017 mol) of **10** in THF (10 mL) was added to a gently refluxing suspension of 0.1 g (0.0026 mol) of LAH in THF (10 mL). After the addition the reaction mixture was refluxed for 1 h and then cooled in an ice bath. Saturated sodium sulfate solution was added dropwise slowly and carefully until a white granular precipitate was formed. The mixture was diluted with ethyl acetate (25 mL) and filtered through a Celite pad. The residue was washed thoroughly with ethyl acetate. The combined filtrate was dried over $MgSO_4$ and concentrated to obtain 0.46 g (96%) of **13** as a thick oil: ^{13}C NMR ($CDCl_3$) 138.08, 128.50, 128.06, 126.77, 64.11, 62.46, 59.17, 58.73, 43.34, 42.49, 33.14, 31.72, 31.61, 26.31, and 25.99.

Acknowledgment. We thank Dr. C. M. Cimarusti for his interest and encouragement in this work and C. Przybyla for making some of the early intermediates. We acknowledge the efforts of our colleagues in the Kilolab and Pilot Plant in further developing these procedures to the multikilogram level. We thank Dr. M. A. Porubcan and the Squibb Institute Analytical Department for assistance during the course of this work.

Electrogenerated Base (EG Base) Induced Hydroxymethylation of the Side Chain of Nitroalkylbenzenes with Paraformaldehyde

Sigeru Torii,* Yasuo Murakami, Hideo Tanaka, and Koichi Okamoto

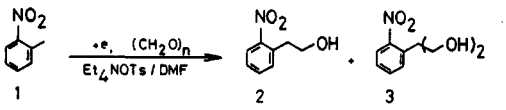
Department of Industrial Chemistry, School of Engineering, Okayama University, Okayama 700, Japan

Received December 30, 1985

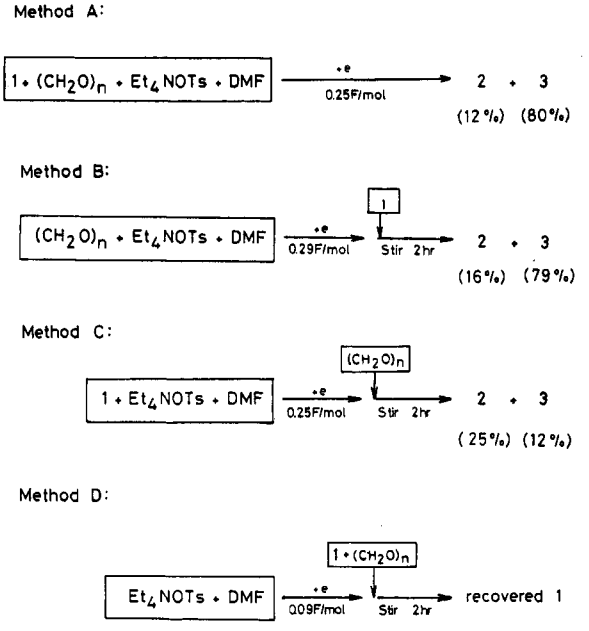
Hydroxymethylation of nitroalkylbenzenes with paraformaldehyde was accomplished by electrolysis in a $(CH_2O)_n$–DMF–Et_4NOTs–(Pt electrode) system. The reaction was found to be catalytic (0.25 faraday/mol) and dependent on the electroreduction of formaldehyde and/or nitroalkylbenzene. A variety of nitroalkylbenzenes were transformed to their corresponding mono- and/or bishydroxymethylated derivatives in good yield. The product yield and selectivity were shown to depend on the order of reagent addition, solvent, supporting electrolyte, and structure of the starting nitroalkylbenzenes. A plausible mechanism of the generation of base catalysts (EG base) in electroreductive media is discussed.

Homologation of the alkyl chain of nitroalkylbenzenes is an essential procedure for derivatization of readily accessible nitroalkylbenzenes into useful intermediates.[1] Among various kinds of approaches, hydroxymethylation of nitroalkylbenzenes with paraformaldehyde is a powerful procedure for this purpose and has been extensively investigated by use of a variety of bases, such as KO-*t*-Bu,[2] NaOMe,[3] KOH,[4] NaOH,[4] KOH- or NaOH-crown ether,[5] alkali phenolate,[6] tetraalkylammonium hydroxide,[7] DBU,[7] and NaCN.[8] However, due to the low conversion of the starting materials and/or the lack of the product selectivity, there still remain difficulties in obtaining mono- or bishydroxymethylation products from the nitroalkylbenzenes in satisfactory yields.

Scheme I



Scheme II



Incidentally, electrochemically generated bases (EG base) in the electroreductive media have received much attention from both the mechanistic and synthetic points

(1) For example, see: (a) Garcia, E. E.; Fryer, R. I. *J. Heterocycl. Chem.* **1974**, *11*, 219. (b) Hengartner, U.; Batcho, A. D.; Blount, J. F.; Leimgruber, W.; Larscheid, M. E.; Scott, J. W. *J. Org. Chem.* **1979**, *44*, 3748. (c) Biere, H.; Russe, R. *Tetrahedron Lett.* **1979**, 1361. (d) Kozikowski, A. P.; Ishida, H.; Chen, Y.-Y. *J. Org. Chem.* **1980**, *45*, 3350. (e) Kozikowski, A. P.; Ishida, H. *J. Am. Chem. Soc.* **1980**, *102*, 4265. (f) Gupton, J. T.; Lizzi, M. J.; Pork, D. *Synth. Commun.* **1982**, *12*, 939. (g) Maehr, H.; Smallheer, J. M. *J. Org. Chem.* **1984**, *49*, 1549. (h) Somei, M.; Shoda, T. *Heterocycles* **1981**, *16*, 1523. (i) Rebek, J., Jr.; Tai, D. F.; Shue, Y.-K. *J. Am. Chem. Soc.* **1984**, *106*, 1813. (j) Kupchan, S. M.; Kameswaren, V.; Findlay, J. W. A. *J. Org. Chem.* **1973**, *37*, 405. (k) Lloyd, D. H.; Nichols, D. E. *Tetrahedron Lett.* **1983**, *24*, 4561. (l) Haefliger, W.; Knecht, H. *Tetrahedron Lett.* **1984**, *25*, 285 and references cited therein.

(2) Wesslen, B. *Acta Chem. Scand.* **1967**, *21*, 718.

(3) (a) Bakke, J. *Acta Chem. Scand.* **1967**, *21*, 1967. (b) Bakke, J. Fr. Pat. 1 568 656, 1969; *Chem. Abstr.* **1970**, *72*, 78643.

(4) (a) Tungler, A.; Mathe, T.; Petro, J.; Bende, Z. Ger. Offen. 3 020 236, 1980; *Chem. Abstr.* **1981**, *95*, 6783. (b) Morimoto, T.; Hashimoto, I.; Yamaoka, H. Japanese Patent 77 122 330, 1977; *Chem. Abstr.* **1978**, *88*, 104880.

(5) Shinoda, K.; Tokuda, T. Japanese Patent 77 156 825, 1977; *Chem. Abstr.* **1978**, *88*, 152219.

(6) Morimoto, T.; Hashimoto, I.; Yamaoka, H. Japanese Patent 77 108 941, 1977; *Chem. Abstr.* **1978**, *88*, 104875.

(7) Morimoto, T.; Hashimoto, I.; Yamaoka, H. Japanese Patent 77 139 035, 1977; *Chem. Abstr.* **1978**, *88*, 104876.

(8) Tungler, A.; Bende, Z.; Petro, J.; Mathe, T. Hung, Pat. 30 628, 1984; *Chem. Abstr.* **1984**, *101*, 90566.

0022-3263/86/1951-3143$01.50/0

Table I. Effect of Supporting Electrolyte on Electrochemical Hydroxymethylation of 2-Nitrotoluene (1) with Paraformaldehyde[a]

entry	supporting electrolyte	product yield, %[b] 2	product yield, %[b] 3	recovered starting material, %[b]
1	Et_4NOTs	12	80	5
2	Et_4NClO_4	11	70	4
3	Et_4NBr	20	55	5
4	Bu_4NBr	18	59	4
5	$KClO_4$	34	23	30
6	KI	31	30	20
7	$NaClO_4$	10		73
8	NaI	9		79
9	$LiClO_4$	1		84
10	LiI	2		75
11	NH_4ClO_4			74
12	NH_4Br			90

[a] Carried out under a constant current of 3.3 mA/cm^2 (0.25 faraday/mol) at 20–25 °C with an H-shaped divided cell fitted with two platinum electrodes (1.5 cm^2). DMF was used as solvent. [b] Isolated yield based on 2-nitrotoluene (1).

of view, and the unique properties of EG base in several base-induced reactions have been demonstrated.[9] This prompted us to investigate a possibility of using of EG base as a catalyst to promote the hydroxymethylation of nitroalkylbenzenes with paraformaldehyde.

In this paper, we describe the results of the hydroxymethylation of 2-nitrotoluene (1) as well as its analogues with paraformaldehyde by the aid of EG base generated in electroreductive media.

Electrochemical Hydroxymethylation of 1 with Paraformaldehyde. Transformation of readily available 2-nitrotoluene (1) into useful indole derivatives has been a current subject in an industrial chemistry sense.[10] Apparently, the key step of this transformation involves the homologation of the methyl group of 1. As a potential procedure for this purpose, we investigated the hydroxymethylation of 1 with paraformaldehyde in electroreductive media, leading to 2-(2-nitrophenyl)-1,3-propanediol (3) which is an important precursor of indole synthesis (Scheme I).

Electrolysis was carried out in an H-shaped divided cell fitted with platinum electrodes[11] (1.5 cm^2 each). A mixture of 1 and paraformaldehyde in *N,N*-dimethylformamide (DMF) containing Et_4NOTs as a supporting electrolyte was charged into the cathode compartment and regulated dc power at 3.3 mA/cm^2 was supplied at ambient temperature. After passage of 0.25 faraday/mol of electricity, workup of the catholytes gave 80% yield of 2-(2-nitrophenyl)-1,3-propanediol (3) along with 12% yield of 2-(2-nitrophenyl)ethanol (2) (method A in Scheme II).

The effect of the supporting electrolyte was significant for the successful hydroxymethylation of 1. Some results obtained with various electrolytes are given in Table I.

It is of interest to note that tetraalkylammonium salts effected the hydroxymethylation of 1 affording 2 and/or 3 in sufficient yields (entries 1–4 in Table I), while potassium and sodium salts were less effective for this purpose (entries 5–8) and lithium and ammonium salts are not feasible for base-catalyzed reactions (entries 9–12). These results indicate that the cations from supporting electrolytes play a significant role as a counterion for electrogenerating anionic species in electroreductive media. On the other hand, the effect of solvent is also important. DMF and hexamethylphosphoramide (HMPA) can be successfully used, yielding the hydroxymethylation products 2 (12–16%) and 3 (65–80%) (entries 1 and 2 in Table II). In contrast, MeCN and dioxane were less effective (entries 3 and 4), and no appreciable amounts of 2 and 3 were obtained in MeOH (entry 5).

Table II. Effect of Solvent on Electrochemical Hydroxymethylation of 2-Nitrotoluene (1) with Paraformaldehyde[a]

entry	solvent	applied voltage, V	product yield, %[b] 2	product yield, %[b] 3	recovered starting material, %[b]
1	DMF	7	12	80	5
2	HMPA	36–40	16	65	1
3	MeCN	5–6	26	31	34
4	dioxane	35	31	11	42
5	MeOH	6–7	0	0	94

[a] Carried out under a constant current of 3.3 mA/cm^2 (0.25 faraday/mol) at 20–25 °C with an H-shaped divided cell fitted with two platinum electrodes (1.5 cm^2). Et_4NOTs was ussed as a supporting electrolyte. [b] Isolated yield based on 2-nitrotoluene (1).

Above all, it is evident that proper choice of both electrolyte and solvent is indispensable for this purpose. An Et_4NOTs–DMF system is the most efficient combination, in which a powerful base catalyst (EG base) can be generated under the electrolysis conditions. In order to obtain some information on generation of EG base in the electroreductive media, we conducted the electrolysis in different modes, i.e., methods B–D as illustrated in Scheme II. In Method B, a catalytic amount of electricity (0.29 faraday/mol) was supplied to a mixture of paraformaldehyde and Et_4NOTs in DMF under the same conditions as those described for method A, and then, 1 was added into the catholytes. After the mixture was stirred for additional 2 h at ambient temperature without passing current, workup of the catholytes gave 2 (16%) and 3 (79%), respectively. In method C, paraformaldehyde was added into the deep wine-red cathode solution prepared by electrolysis of a DMF solution of 1 and Et_4NOTs (0.25 faraday/mol), and the mixture was stirred for 2 h, affording 2 (25%) and 3 (12%) along with recovered 1 (53%). On the other hand, in method D, a DMF solution of Et_4NOTs was electrolyzed (0.09 faraday/mol), then 1 and paraformaldehyde were added to the cathode solution, and the mixture was stirred for additional 2 h. Workup of the catholytes afforded no appreciable amounts of 2 and/or 3 but only recovered 1 (91%).

As shown above, method B gave a quite similar result to that of method A, while method D failed in conversion of 1 to 2 and 3. These facts suggested that the generation of EG base would be mainly concerned with the electroreduction of formaldehyde.[9b] On the other hand, in method A, the electrolysis was conducted at −1.1 to −1.4 V vs. Ag/AgCl, negative enough to promote the reduction of 2-nitrotoluene (1).[12] Actually, during the course of the electrolysis (method A) a solution at the vicinity of the

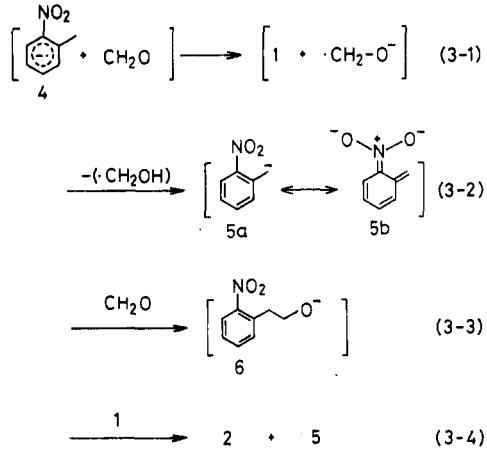
(9) (a) Baizer, M. M. *Tetrahedron* **1984**, *40*, 935. (b) Shono, T.; Kashimura, S.; Ishizaki, K. *Electrochim. Acta* **1984**, *29*, 603. (c) Baizer, M. M. *Organic Electrochemistry*, 2nd ed.; Baizer, M. M., Lund, H., Eds.; Marcel Dekker: New York, 1983; p 1038 and references cited therein.

(10) (a) Bakke, J. *Acta Chem. Scand.* **1970**, *24*, 2650. (b) Morimoto, T.; Hashimoto, I. Japanese Patent 77 85 165, 1977; *Chem. Abstr.* **1978**, *88*, 22619. (c) Bakke, J.; Heikman, H.; Hellgren, E. B. *Acta Chem. Scand., Ser. B* **1974**, *B28*, 393. (d) Bakke, J. *Acta Chem. Scand., Ser. B* **1974**, *B28*, 134. See also ref 1.

(11) In place of Pt cathode, the conventional cathode, such as carbon, Pb, stainless steel, Al, Ni, Zn, and Cu were used without significant change of the efficiency.

(12) Half-peak potential of 1 has been reported. −1.18 V vs. SCE; Meites, L.; Zuman, P. *CRC Handbook Series in Organic Electrochemistry*; CRC: Cleveland, OH, 1976; Vol. I, p 290. −1.23 V. *vs.* Ag/AgCl–1 N KCl; Sagae, H.; Fujihira, M.; Lund, H.; Osa, T. *Bull. Chem. Soc. Jpn.* **1980**, *53*, 1537.

Scheme III



cathode turned deep wine-red, characteristic color for the anion radical 4 arising from one-electron reduction of 1. This color disappeared with the diffusion into the bulk solution. Thus, we thought that 2-nitrotoluene (1) must be reduced under the electrolysis conditions of method A. In this connection, it is noteworthy that no detectable reduction products of 2-nitrotoluene (1) were isolated in the electrolysis media. These contradictory results might be explained by assuming that electron transfer of initially formed anion radical 4 with formaldehyde proceeds smoothly to afford a kind of anion radical ($^{\bullet}CH_2O^-$), which subsequently abstracts a proton of the methyl group of 1, affording carbanion 5 (Scheme III). Furthermore, the above electron-transfer mechanism (eq 3-1) would be supported by the observation in method C that the deep wine-red solution prepared in the initial electroreduction of 1 turned dark yellow immediately after paraformaldehyde was added. Apparently, the anionic species ($^{\bullet}CH_2O^-$) can be expected to arise from direct electroreduction of formaldehyde even in the presence of 1. Thus, in method A, both direct electroreduction of formaldehyde and electron transfer from anion radical of 1 to formaldehyde would be involved in the generation of EG base ($^{\bullet}CH_2O^-$). The anion 5 thus obtained would react with formaldehyde to afford anion 6, which would probably behave as a base to abstract a proton of the methyl group of 1, leading to 2. By repeating a similar reaction sequence, 1 would be transformed into 2 and the analogous base-induced hydroxymethylation of 2 in the electroreductive media would cause further transformation into 3.

In order to compare the property of EG base ($^{\bullet}CH_2O^-$) with those of conventional base catalysts, hydroxymethylation of 1 with various base catalysts (0.25 equiv) was carried out. Some of the results along with a typical electrochemical hydroxymethylation of 1 (entry 5) are summarized in Table III. These results clearly indicate that EG base is superior to any other base catalysts listed in Table III, since the predominant formation of 3 is only achieved by the electrochemical procedure. Although the structure and the role of EG base have not been clarified yet, EG base in electroreductive media is enough basic for the double hydroxymethylation of 1.

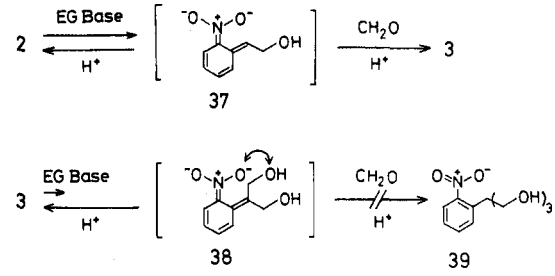
Electrochemical Hydroxymethylation of Nitroalkylbenzenes. The present electrochemical procedure was successfully applied to the hydroxymethylation of a variety of nitroalkylbenzenes (Table IV). Hydroxymethylation of methyl or methylene groups at the 2- and 4-position to nitro group of nitroalkylbenzenes **7**, **9**, **12**, **15**, **17**, **19**, **24**, **32**, and **35** took place smoothly under similar electroreduction conditions to those described above, yielding mono- and/or bishydroxymethylation products

Table III. Hydroxymethylation of 2-Nitrotoluene (1) with Bases[a]

entry	base	products yield, %[b] 2	products yield, %[b] 3	recovered starting material, %[b]
1	KO-*t*-Bu	27	43	16
2	KOH	24	57	7
3	MeONa	20	3	63
4	DBU	0	0	86
5	electrolysis[c]	12	80	5

[a] A mixture of 1 (2.2 mmol), $(CH_2O)_n$ (66 mg), and base (0.25 equiv) in DMF was stirred at room temperature for 3 h. [b] Isolated yield based on 2-nitrotoluene (1). [c] Electrolysis was carried out according to method A.

Scheme IV



except for **28**, while methyl or methylene groups located at the 3-position to the nitro group remained intact (entries 3–5 and 10).

It is of interest to note that the product selectivity was highly dependent on the structure of the starting nitroalkylbenzenes, monohydroxymethylation products **16**, **18**, and **36** were predominantly obtained in entries 5, 6, and 12, while bishydroxymethylation products **3**, **8**, **11**, **14**, and **34** were exclusively obtained in entries 1–4 and 11. The dramatical change of the products would be explained on account of the ortho effects of the anion intermediates as exemplified in Scheme IV.

Thus, in the case of the reaction of 1 (entry 1 in Table IV), bishydroxymethylation product **3** was obtained predominantly via anion **37**, while trishydroxymethylation product **39** derived from further reaction of **3** with EG base (**3** → **38** → **39**) was not isolated at all. This fact suggested that the interaction of ortho substituents of **38** caused almost complete shift of the equilibrium (**3** ⇄ **38**) to the left-hand side. A similar ortho effect can be assumed for the other entries and well in accordance with the product yields and selectivity (Table IV).

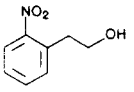
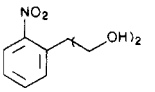
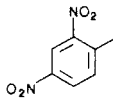
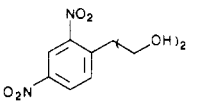
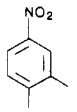
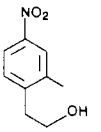
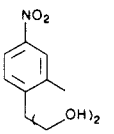
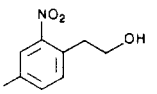
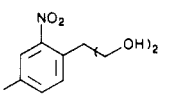
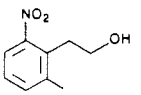
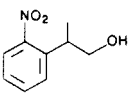
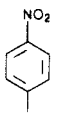
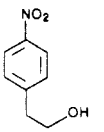
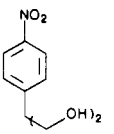
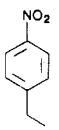
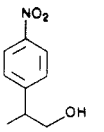
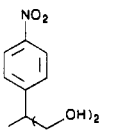
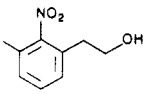
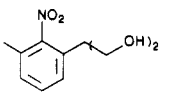
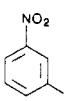
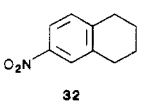
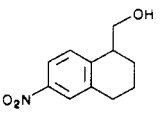
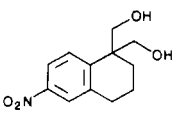
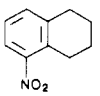
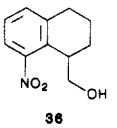
The high product selectivity coupled with reasonable product yields makes us believe that EG base induced hydroxymethylation possesses high potentiality in organic synthesis. Further application of the EG base induced reaction and the utilization of hydroxymethylation products in synthesis of indole-related compounds will be reported in due course.

Experimental Section

IR spectra were recorded on a JASCO IRA-1 grating spectrometer, and ^1H NMR spectra were measured at 60 MHz with a Hitachi R-24 spectrometer. Chemical shifts are in parts per million downfield from Me_4Si used as an internal reference. Melting and boiling points are uncorrected. Column chromatography was carried out with Wako gel C-200 (silica gel) with hexane–EtOAc as an eluent. Elemental analyses were performed in our laboratory.

Materials. 2-Nitrotoluene (1), 2,4-dinitrotoluene (7), 3,4-dimethylnitrobenzene (9), 2,5-dimethylnitrobenzene (12), 2,3-dimethylnitrobenzene (15), 2-ethylnitrobenzene (17), 4-nitrotoluene (19), 4-ethylnitrobenzene (24), 2,6-dimethylnitrobenzene (28), and

Table IV. Electrochemical Hydroxymethylation of Nitroalkylbenzenes with Paraformaldehyde

entry	starting material	electricity,[a] faraday/mol	products, % yield[b]				recovered starting material, %[b]
1	 1	0.25 (0.25)	 2	12 (16)	 3	80 (79)	5 (3)
2	 7	0.11 (0.11)			 8	99 (97)	
3	 9	0.25 (0.25)	 10	4 (15)	 11	80 (50)	6 (15)
4	 12	0.50 (0.50)	 13	13 (36)	 14	71 (37)	7 (15)
5	 15	0.26 (0.27)	 16	98 (94)			
6	 17	0.57 (0.53)	 18	88 (49)			(39)
7[c]	 19	0.25 (0.25)	 20	5 (17)	 21	26 (34)	5 (21)
8[d]	 24	0.48 (0.48)	 25	15 (30)	 26	63 (6)	(4)
9	 28	0.25 (0.26)	 29	13 (7)	 30	3 (4)	73 (84)
10	 31	0.25					90
11	 32	0.34 (0.50)	 33	6 (17)	 34	83 (57)	5 (12)
12	 35	0.50 (0.50)	 36	61 (62)			34 (29)

[a] Electricity passed in method A; the numbers in parentheses indicate that of method B. [b] Yields of products based on starting nitroalkylbenzenes (method A); the numbers in parentheses indicate isolated yields obtained in method B. [c] 2-(4-Nitrophenyl)allyl alcohol (**22**), 22% (2%), and 2-(hydroxymethyl)-2-(4-nitrophenyl)-1,3-propanediol (**23**), 17%, were also isolated. [d] α-Methyl-4-nitrosytyrene (**27**), 4%, was isolated.

3-nitrotoluene (31) were purchased from Nippon Kayaku Co., Ltd. and/or Tokyo Kasei kogyo Co., Ltd. 6-Nitro-1,2,3,4-tetrahydronaphthalene (32) and 5-nitro-1,2,3,4-tetrahydronaphthalene (35) were prepared by nitration of 1,2,3,4-tetrahydronaphthalene according to the procedure of Kobe and Doumane.[13] DMF was dried over CaH_2 and distilled before use.

Apparatus. An H-shaped cell divided with a sintered-glass frit was used, which was equipped with two platinum foil electrodes (1.5 cm^2, 10 mm apart), gas lead pipes, stirring bars, and a thermometer. A vessel was immersed in a water bath at 20–25 °C, and regulated dc power was supplied by a Metronix Model 543B.

General Procedure: Electrochemical Hydroxymethylation of 2-Nitrotoluene (1) with Paraformaldehyde. Method A. Into both the anode and cathode compartments was placed a DMF solution of Et_2NOTs (6 mL, 400 mg each). To the catholytes were added 2-nitrotoluene (1: 370 mg, 2.7 mmol) and $(CH_2O)_n$ (172 mg, 5.7 mmol on the basis of formaldehyde). The mixture was electrolyzed under a constant current of 3.3 mA/cm^2 at room temperature for 3.6 h (0.25 faraday/mol). The catholytes were poured into brine, and then the mixture was acidified with cold 5% aqueous HCl and extracted with EtOAc. The extracts were washed with brine, dried (Na_2SO_4), and concentrated in vacuo. The residue was chromatographed on SiO_2 (3:1 hexane–ethyl acetate), yielding 2-(2-nitrophenyl)ethanol (2; 56 mg, 12%), and 2-(2-nitrophenyl)-1,3-propanediol (3; 425 mg, 80%) along with 18 mg (5%) of starting material 1.

Compound 2:[2,15] IR (neat) 3340, 1610, 1525, 1350, 1045 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.75 (br s, 1 H, OH), 3.10 (t, J = 6.4 Hz, 2 H, $ArCH_2$), 3.86 (t, J = 6.4 Hz, 2 H, CH_2O), 7.14–7.95 (m, 4 H, Ar H).

Compound 3:[2] IR (neat) 3340, 1610, 1525, 1355 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.15 (br s, 2 H, OH), 3.45–3.70 (m, 1 H, CH), 3.91 (d, J = 6.0 Hz, 4 H, CH_2), 7.16–7.78 (m, 4 H, Ar H).

Method B. Into both the anode and cathode compartments was placed a DMF (6 mL) solution of Et_4NOTs (400 mg). To the catholytes was added $(CH_2O)_n$ (158 mg). After regulated dc power (3.3 mA/cm^2) was supplied (0.29 faraday/mol) at room temperature for 2.0 h, 2-nitrotoluene (1; 175 mg, 1.3 mmol) was added to the catholytes. The mixture was stirred at room temperature for additional 2 h without passing current and the catholytes were worked up in the same manner as described above, affording 2 (34 mg, 16%) and 3 (198 mg, 79%) along with 1 (6 mg, 3%).

Method C. Into both the anode and cathode compartments was placed a DMF (6 mL) solution of Et_4NOTs (400 mg). 2-Nitrotoluene (1; 291 mg, 2.1 mmol) was added to the catholytes. After the solution was electrolyzed (3.3 mA/cm^2, 0.25 faraday/mol), $(CH_2O)_n$ (152 mg) was added to the catholytes, and the mixture was stirred at room temperature (2 h). Workup of the catholytes afforded 2 (88 mg, 25%), 3 (50 mg, 12%) and 1 (154 mg, 53%).

Method D. Into both the anode and cathode compartments was placed a DMF solution of Et_4NOTs (6 mL, 400 mg each). After 0.09 faraday/mol of electricity (3.3 mA/cm^2) were passed, 2-nitrotoluene (1; 302 mg, 2.2 mmol) and $(CH_2O)_n$ (158 mg, 4.9 mmol) were added to the catholytes. The mixture was stirred at room temperature for the additional 2 h. Workup of the catholytes afforded 276 mg (91%) of recovered 1.

In a similar manner, hydroxymethylation of nitroalkylbenzene derivatives was performed according to method A and/or method B as described above. The reaction conditions along with yields of products are listed in Table IV. Analytical samples were obtained by column chromatography on SiO_2 with hexane–ethyl acetate (3:1). Physical and analytical data of the products 10,[17] 11,[20] 13,[6] 16,[8] 18,[14] 20,[3a,16] 21,[2,17] 22,[2] 23,[17] 25,[14] 26,[19] and 27[18] were identified with those of the authentic samples. All new compounds 8, 14, 29, 30, 33, 34, and 36 were characterized by correct elemental analysis, ^1H NMR, and IR spectra.

2-(2,4-Dinitrophenyl)-1,3-propanediol (8): mp 92.5–93.5 °C (hexane/$CHCl_3$); IR (Nujol) 3240, 1535, 1360, 1050 cm^{-1}; ^1H NMR (acetone-d_6) δ 3.00 (br s, 2 H, OH), 3.40–3.85 (m, 1 H, ArCH), 3.98 (d, J = 5.6 Hz, 4 H, CH_2O), 7.90–8.58 (m, 3 H, Ar H). Anal. Calcd for $C_9H_{10}N_2O_6$: C, 44.63; H, 4.16. Found: C, 44.52, H, 4.13.

2-(4-Methyl-2-nitrophenyl)-1,3-propanediol (14): mp 73–74 °C (hexane/$CHCl_3$); IR (Nujol) 3300, 1530, 1350 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.35 (s, 3 H, CH_3), 3.30–4.00 (m, 1 H, ArCH), 3.56 (br s, 2 H, OH), 3.83 (d, J = 6.0 Hz, CH_2), 7.25–7.50 (m, 3 H, Ar H). Anal. Calcd for $C_{10}H_{13}NO_4$: C, 56.87; H, 6.20. Found: C, 56.79; H, 6.24.

2-(3-Methyl-2-nitrophenyl)ethanol (29): bp 95–97 °C (0.015 mmHg); IR (neat) 3330, 1530, 1375, 1045 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.03 (br s, 1 H, OH), 2.29 (s, 3 H, CH_3), 2.79 (t, J = 6.4 Hz, 2 H, $ArCH_2$), 3.80 (t, J = 6.4 Hz, 2 H, CH_2O), 7.10–7.31 (m, 3 H, Ar H). Anal. Calcd for $C_9H_{11}NO_3$: C, 59.66; H, 6.12. Found: C, 59.75; H, 6.11.

1-(Hydroxymethyl)-6-nitro-1,2,3,4-tetrahydronaphthalene (33): mp 59–60 °C (hexane/$CHCl_3$); IR (Nujol) 3300, 1520, 1355 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.60–2.10 (m, 4 H, CH_2CH_2), 2.46 (br s, 1 H, OH), 2.50–3.25 (m, 3 H, ArCH, $ArCH_2$), 3.79 (d, J = 6.0 Hz, 2 H, CH_2O), 7.27–7.98 (m, 3 H, Ar H). Anal. Calcd for $C_{11}H_{13}NO_3$: C, 63.76; H, 6.32. Found: C, 63.51; H, 6.18.

1,1-Bis(hydroxymethyl)-6-nitro-1,2,3,4-tetrahydronaphthalene (34): mp 112–114 °C ($CHCl_3$); IR (Nujol) 3340, 1515, 1355 cm^{-1}; ^1H NMR (acetone-d_6) δ 1.70–2.10 (m, 4 H, CH_2CH_2), 2.75–3.00 (m, 2 H, $ArCH_2$), 3.65–3.99 (m, 6 H, CH_2OH), 7.62–7.95 (m, 3 H, Ar H). Anal. Calcd for $C_{12}H_{15}NO_4$: C, 60.75; H, 6.37. Found: C, 60.83; H, 6.41.

4-(Hydroxymethyl)-5-nitro-1,2,3,4-tetrahydronaphthalene (36): bp 105–107 °C (0.01 mmHg); IR (neat) 3340, 1530, 1360 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.72–2.00 (m, 4 H, CH_2CH_2), 2.25 (br s, 1 H, OH), 2.76–2.97 (m, 2 H, $ArCH_2$), 3.50–3.77 (m, 3 H, $CHCH_2O$), 7.04–7.67 (m, 3 H, Ar H). Anal. Calcd for $C_{11}H_{13}NO_3$: C, 63.76; H, 6.32. Found: C, 64.05; H, 5.98.

Reaction of 2-Nitrotoluene (1) with $(CH_2O)_n$ in the Presence of Various Base Catalysts. A mixture of 1 (302 mg, 2.2 mmol) and $(CH_2O)_n$ (132 mg, 2 mmol on the basis of formaldehyde) in DMF containing base catalysts (0.55 mmol) was stirred for 3 h at ambient temperature. The mixture was poured into brine, acidified with cold 5% aqueous HCl, and extracted with EtOAc. The extracts were washed with brine, dried (Na_2SO_4), and concentrated in vacuo. The residue was chromatographed on SiO_2 (3:1 hexane–ethyl acetate), affording 2 and 3. Results and conditions are summarized in Table III.

Registry No. 1, 88-72-2; 2, 15121-84-3; 3, 15121-85-4; 7, 121-14-2; 8, 101212-87-7; 9, 99-51-4; 10, 91748-02-6; 11, 89729-73-7; 12, 89-58-7; 13, 65813-72-1; 14, 102781-38-4; 15, 83-41-0; 16, 91413-89-7; 17, 612-22-6; 18, 64987-77-5; 19, 99-99-0; 20, 100-27-6; 21, 91748-03-7; 24, 100-12-9; 25, 63489-72-5; 26, 29740-75-8; 28, 81-20-9; 29, 102781-39-5; 30, 102781-40-8; 31, 99-08-1; 32, 19353-86-7; 33, 102781-41-9; 34, 102781-42-0; 35, 29809-14-1; 36, 102781-43-1.

(13) Kobe, K. A.; Doumane, T. F. *Organic Syntheses*; Wiley: New York, 1955; Collect. Vol. III, p 653.
(14) Bakke, J. *Acta Chem. Scand.* **1971**, *25*, 1201.
(15) *1984–1985 Aldrich Catalog Handbook of Fine Chemicals*; Aldrich: Milwaukee, 1984; p 816.
(16) Reference 15, p 817.
(17) Van Helden, R.; Kramer, P. A. Eur. Pat. 106 375, 1984; *Chem. Abstr.* **1984**, *101*, 110512.
(18) Deno, N. C.; Kish, F. A.; Peterson, H. J. *J. Am. Chem. Soc.* **1965**, *87*, 2157.
(19) Gilbert, C.; Roux-Schmidt, M. C.; Seyden-Penne, J. *Bull. Soc. Chim. Fr.* **1970**, 2405.
(20) Van Helden, R.; Syrier, J. L. M.; Baardman, F. Eur. Pat. 97 980, 1984; *Chem. Abstr.* **1984**, *100*, 174469.