propenyl)benzene was followed, except that the tellurium reagent was prepared with different proportions of Super-Hydride (1 M, 2.6 mL, 2.6 mmol) and tellurium powder (255 mg, 2.00 mmol). after the mixture was stirred at room temperature for 6 h all of the tellurium had dissolved, and the mixture was dark crimson. (3-Chloro-1-propenyl)benzene (306 mg, 2.00 mmol) in dry dioxane (2.0 mL plus a 2.0 mL rinse) was added, causing an immediate deposition of tellurium. The mixture was lowered into an oil bath, preheated to 110 °C, and refluxed for 1 h. A workup as before followed by chromatography over silica gel (60 × 1 cm) with 99:1 hexane–ethyl acetate gave the same (^1H NMR, 400 MHz) isomer ratio of 4–7 (207 mg, 88%) as obtained by the previous couplings of (3-chloro-1-propenyl)benzene and (3-bromo-1-propenyl)benzene.

Detection of Bis(2-cyclohexenyl) Telluride by ^{13}C NMR. 3-Bromocyclohexene (644 mg, 4.00 mmol) in dry THF (4.0 mL plus a 4.0-mL rinse) was added to the tellurium reagent (2.00 mmol) prepared in the usual manner in a septum-stoppered centrifuge tube. The tube contained a magnetic stirring bar and was filled with argon. The mixture was stirred at room temperature for 15 min and then centrifuged for 10 min to remove a small amount of particulate matter. A portion of the supernatant (2.0 mL) was transferred to a septum-stoppered, argon-filled ^{13}C NMR tube. THF-d_8 (1.0 mL) was added, and the ^{13}C NMR spectrum of the mixture was recorded (22.6 MHz). The diagnostically significant features of the spectrum were resonances at δ 125.8, 125.9, 130.6, and 130.7 and the absence of resonances between δ 30.0 and 65.0. The NMR sample remained unchanged on being allowed to stand under argon for longer than 10 days. However, upon exposure of air, the mixture rapidly deposited black tellurium. ^{13}C NMR spectra were also recorded for 3-bromocyclohexene and 2,2′-bicyclohexenyl (1) in the presence of 1 and 2 equiv, respectively, of triethylborane. The former had ^{13}C NMR (THF-d_8, 22.6 MHz) values of δ 19.5, 25.4, 33.7, 49.1, 130.0, and 131.2.[44] The latter had ^{13}C NMR (THF-d_8, 22.6 MHz) values of δ 23.2, 26.2, 26.8, 41.2, 128.2, 128.6, 131.2, and 131.3.[44]

Attempted Coupling of 3-Bromocyclohexene by Using Se^{2-}. A suspension of lithium selenide in THF was prepared by the literature procedure:[7c] Under argon, gray selenium powder (158 mg, 2.00 mmol) was added portionwise to Super-Hydride (1 M, 4.2 mL, 4.2 mmol) with magnetic stirring. The milky, white suspension was stirred for a further 20 min, and then 3-bromocyclohexene (645 mg, 4.00 mmol) and dry *tert*-butyl alcohol (0.37 mL, 0.29 g, 3.9 mmol) in dry dioxane (4.0 mL plus a 4.0-mL rinse) were added by syringe. Within 1 h, all of the halide had reacted (TLC). After a further 2.5 h at room temperature, the mixture was lowered into an oil bath (110 °C) and refluxed for 3.5 h. No metallic selenium was deposited, and VPC analysis of the reaction mixture indicated less than a 2% yield of the coupled product (1).

In a preparative experiment, gray selenium powder (154 mg, 1.95 mmol) was added portionwise under nitrogen to Super-Hydride (1 M, 4.0 mL, 4.0 mmol). After the mixture had been stirred for 20 min, 3-bromocyclohexene (647 mg, 4.02 mmol) and dry *tert*-butyl alcohol (0.37 mL, 0.29 g, 3.9 mmol) in dry THF (4.0 mL plus a 2.0-mL rinse) was added by syringe. After 3 h of stirring at room temperature, the reaction was complete (TLC), and the mixture was taken up in ether (40 mL) and washed with water (3 × 20 mL). The combined aqueous extracts were back-extracted with ether (30 mL). The combined ether extracts were dried (Na_2SO_4), filtered, and concentrated to an oily solid. The crude product was chromatographed over silica gel (40 × 1.5 cm) with 9:1 hexane–ethyl acetate and then again over silica gel (66 × 1.5 cm) with hexane to give **21** (306 mg, 65%) as a homogeneous (TLC, silica, 9:1 hexane–ethyl acetate) oil. Compound **21**: NMR ($CDCl_3$, 100 MHz) δ 1.31–2.31 (m, 12 H), 3.52–3.77 (m, 2 H), 5.52–5.96 (m, 4 H); ^{13}C NMR ($CDCl_3$, 22.6 MHz) δ 20.0, 20.1, 24.9, 30.7, 31.0, 36.6, 128.4, 128.6, 128.9, 129.0; exact mass, *m/e* 242.0571 (calcd for $C_{12}H_{18}Se$, *m/e* 242.0574). A satisfactory combustion analysis could not be obtained for this compound.

Acknowledgment is made to the Natural Sciences and Engineering Research Council of Canada and Research Corp. (Cottrell Grant) for financial support. We thank William A. Kiel for preliminary experiments.

Registry No. 1 (isomer I), 42347-45-5; **1** (isomer II), 57705-09-6; **2**, 55759-30-3; **3** (isomer I), 80794-91-8; **3** (isomer II), 80794-92-9; **4**, 58463-02-8; **5**, 74120-63-1; **6**, 33788-14-6; **7**, 80754-12-7; **8**, 80754-13-8; **9**, 80754-14-9; **10**, 18476-57-8; **11**, 16736-42-8; **12**, 35387-63-4; **13**, 3047-21-0; **14**, 26907-85-7; **15**, 38926-02-2; **16**, 80754-15-0; **17**, 26907-84-6; **18** (isomer I), 80754-16-1; **18** (isomer II), 80754-17-2; **19**, 80754-18-3; **20**, 103-29-7; **21**, 80754-19-4; **22**, 80754-20-7; Te^{2-}, 22541-49-7; Te_2^{2-}, 25778-65-8; Se^{2-}, 22541-48-6; 3-bromocyclohexene, 1521-51-3; 3-chlorocyclohexene, 2441-97-6; 3-bromocycloheptene, 36291-49-3; 3-bromocyclooctene, 7422-06-2; (3-bromo-1-propenyl)benzene, 4392-24-9; (3-chloro-1-propenyl)benzene, 2687-12-9; (*E*)-5-chloro-1,3-pentadiene, 28070-18-0; (*E*)-4-chloro-2-pentene, 18610-33-8; 1-bromo-3-methyl-2-butene, 870-63-3; (*E*)-1-bromo-2-hexene, 73881-10-4; (*Z*)-1-bromo-2-hexene, 79930-19-1; (bromomethyl)benzene, 100-39-0.

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(44) Signals due to triethylborane are not reported here.

Indirect Electrooxidation (an Ex-Cell Method) of Alkylbenzenes by Recycle Use of $(NH_4)_2Ce(NO_3)_6$ in Various Solvent Systems

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Indirect electrooxidation (an ex-cell method) of the side chain of alkylbenzenes has been performed by recycle use of $(NH_4)_2Ce(NO_3)_6$ (CAN) in various solvent systems. The side-chain oxidation of *p*-methoxytoluene (1) with CAN in methanol proceeds smoothly, yielding anisaldehyde (3, 94%), while use of aqueous methanol or acetic acid resulted in a mixture of 3 and the dimeric product 4 (19–35%) along with complex products (28–47%). Electrooxidation of the recovered cerium(III) salts was performed smoothly in methanol by passing 1.1–1.2 F/mol of electricity to give a reddish methanol solution of CAN, which can be used for the next oxidation of 1. The repeated use of CAN over 10 times produced the desired 3 in over 90% yields. Similarly, the oxidation of alkylbenzenes, bearing a *p*-methoxy group, gave the corresponding side-chain-oxidized products. In contrast, *p-tert*-butyltoluene (**9e**) could be oxidized by heating with CAN in aqueous 50% acetic acid at 85–90 °C to give *p-tert*-butylbenzaldehyde in over 90% yield. The regeneration of CAN after the oxidation of **9e** was also accomplished by electrolysis in the aqueous 50% acetic acid system. The reaction mechanisms in connection with the nature of CAN in various solvent systems are discussed.

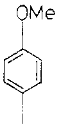
Recently, much attention has been paid to the four-electron oxidation of the side chain of alkylbenzenes. Among the various kinds of approaches, electrooxidation[1] seems attractive in view of its simple operation, nonpol-

Table I. Oxidation of *p*-Methoxytoluene (1) with $(NH_4)_2Ce(NO_3)_6$

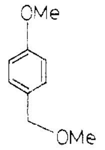
entry	solvent (v/v)	temp, °C	time, h	product yields,[a] % 3	4	others[b]
1	AcOH-H_2O (9/1)	1-2	7	21	32	35
2	AcOH-H_2O (9/1)	15-17	7	43	17	20
3	AcOH-H_2O (9/1)	60	1.5	53	19	23
4	AcOH-H_2O (1/1)	60	1.5	49	20	19
5	MeOH	23-25	0.5	93		
6	MeOH-H_2O (4/1)	25-27	0.5	76	13	

[a] Isolated yield after column chromatography. [b] Unknown products.

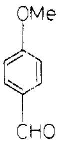
luting nature, and economy. However, the reported results obtained by the electrooxidation of *p*-methoxytoluene (1)[2]



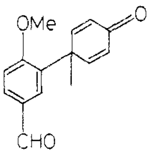
1



2



3



4

and its homologues[3] are insufficient in terms of yields and product selectivity. Most recently, the indirect electrooxidation (an ex-cell method)[4] of toluene and *o*-chlorotoluene in an aqueous $HClO_4$–$Ce(ClO_4)_4$ system is reported to give the corresponding aldehydes in 82–79% yields.[5]

Our continuing efforts on searching electrolysis conditions for this purpose led us to develop highly efficient indirect electroxidation (an ex-cell method) procedures.[6] Thus, the oxidation of 1 and its homologues **9a–d** provided the corresponding side-chain-oxidized products **3** and **10a–d** in excellent yields by recycle use of ammonium hexanitratocerate(IV) [$(NH_4)_2Ce(NO_3)_6$, common name ceric ammonium nitrate, CAN] as an electron carrier in methanol. In contrast, the indirect electrooxidation (an ex-cell method) of the methyl group of *p-tert*-butyltoluene (**9e**) could be realized with CAN in aqueous acetic acid.

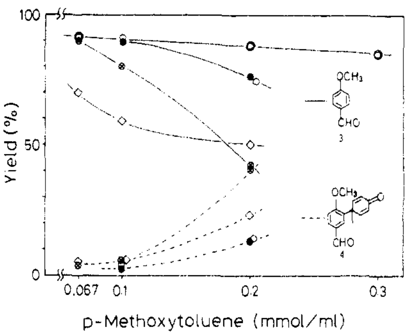
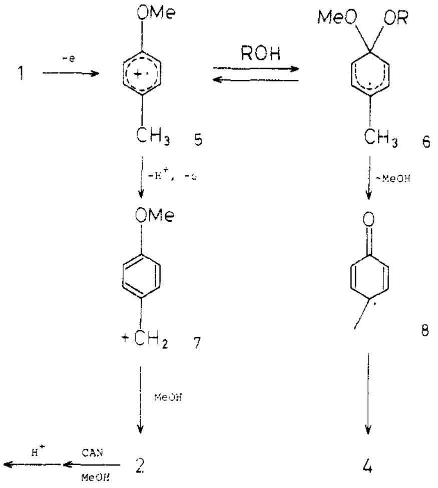


Figure 1. Yields of 3 and 4 for the concentration of 1 in methanol and aqueous methanol systems: MeOH (concentric circles); MeOH-H_2O, 4/1 (●), 2/1 (○), 1/1 (⊗), 1/2 (◇).

Scheme I



Oxidation of 1 with $(NH_4)_2Ce(NO_3)_6$. The oxidation of 1 with CAN in aqueous 90% acetic acid in homogeneous medium has been reported to give anisaldehyde 3 in a quantitative yield.[7] However, the results of our careful reinvestigations clearly indicate that the reaction products consist of 3 (21–53%), dimeric product 4 (32–19%), and complex products (28–47%) (Table I, entries 1–3). The dimer 4 was also obtained in aqueous 50% acetic acid (entry 4). After examining a variety of solvent systems, we found methanol to be a suitable solvent for the selective oxidation of 1 to 3 with CAN and for the electrochemical regeneration of cerium(IV).

Treatment of 1 with 4.6 molar equiv of CAN in methanol at room temperature for a few minutes afforded the aldehyde 3 exclusively (Table I, entry 5). But the oxidation of 1 with CAN in aqueous methanol produced 3 together with the dimer 4 (entry 6). As shown in Figure 1, the yields of 3 and 4 varied depending upon the concentration of 1 as well as the amount of water in methanol. When the concentration of 1 was less than 0.1 M, only 3 could be obtained in each solvent system. In aqueous methanol, concentrations 1 higher than 0.1 M facilitate the formation of the dimeric product 4. Obviously, the presence of water in the media affects product selectivity.

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(1) The anodic oxidation of the side chain of alkylbenzenes are well documented in the following references: (a) Weinberg, N. L. "Technique of Electroorganic Chemistry"; Wiley: New York, 1974; Vol. I, p 235. (b) Bard, A. J.; Lund, H. "Encyclopedia of Electroorganic Chemistry of the Elements"; Marcel Dekker: New York, 1978; Vol. XI.

(2) The direct electrooxidation of *p*-methoxytoluene has been carried out in MeOH–CH_2Cl_2–H_2SO_4–(Pt electrode)[2a] and MeOH–MeONa–(C electrode)[2b] systems. The former electrolysis system provides a mixture of the side-chain-oxidized products 2 (22%) and 3 (32%), and the latter provides *p*-methoxybenzaldehyde dimethyl acetal in 66% yield. (a) Rakoutz, M.; Michelet, D.; Brossard, B.; Varagnat, J. *Tetrahedron Lett.* **1978**, 3723. (b) Nilsson, A.; Palmiquist, U.; Patterson, T.; Ronlan, A. *J. Chem. Soc., Perkin Trans. 1* **1978**, 708.

(3) The direct electrooxidation of *p*-chloro-[3a] and *p*-phenoxytoluenes[3b] has been reported. (a) Chidambaran, S.; Pathy, M. S. V.; Udupa, H. V. K. *J. Electrochem. Soc. India* **1968**, *17*, 95; *Chem. Abstr.* **1969**, *70*, 25168; (b) Torii, S.; Wake, Y; Okamoto, T. Japanese Patent 125137, 1977. Two-electron oxidation of *p-tert*-butyltoluene has been performed by electrolysis in a AcOH–Bu_4NBF_4–(C electrodes) system, but no attempts have been made to produce *tert*-butylbenzaldehyde: (c) Cedheim, L.; Eberson, L.; Helgee, B.; Nyberg, K.; Servin, R.; Sternerup, H. *Acta Chem. Scand., Ser. B* **1975**, *B29*, 617.

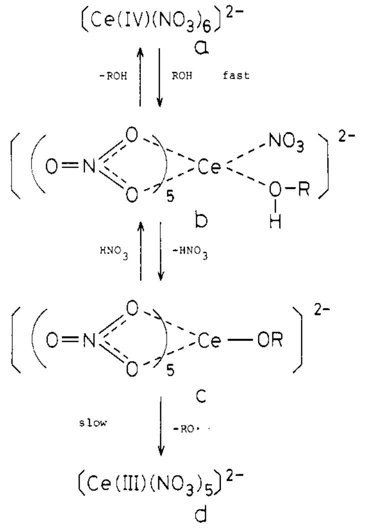
(4) Recent development of indirect electrooxidation of in-cell and ex-cell methods has been reviewed: Clarke, R.; Kuhn, A.; Okoh, E. *Chem. Br.* **1975**, *11*, 59.

(5) Kramer, K.; Robertson, P. M.; Ibl, N. *J. Appl. Electrochem.* **1980**, *10*, 29.

(6) The oral presentation of this investigation has been done by S.T. before the journal of ref 4 had been mailed: "Abstracts of Papers" 157th Spring Meeting of the Electrochemical Society, St. Louis, MO, May 11–[illegible], 1980; p 1090.

(7) Syper, L. *Tetrahedron Lett.* **1966**, 4493.

Scheme II



A plausible mechanism of the formation of the aldehyde **3** and the dimer **4** is illustrated in Scheme I.[8] The cation radical intermediate **5**, derived from **1** after a one-electron oxidation with CAN, may equilibrate with ROH (R = H or Me) in the media, providing a radical intermediate, **6**. If R = H, **6** yields the radical intermediate **8** by the acid-catalyzed elimination of MeOH. The dimerization of **8** leads to **4**. However, the conversion of **6** (R = Me) into **8** can not be expected to arise in anhydrous methanol due to the difficulty of cleavage of the R–O bonds in **6**. In this case, loss of a proton from **5** followed by further one-electron transfer with CAN would provide the benzyl cation intermediate **7**, a precursor of **2**. Independently, the treatment of **2** with CAN (2.2 equiv) in methanol afforded **3** in 97% yield.

The complex of tetravalent cerium having 12 coordinates coupled with six bidentate nitrate ions as ligands has been shown to be a divalent hexanitratocerate ion (a, Scheme II).[9] The divalent anion a can easily associate with methanol (or water) to provide intermediate b.[10] Elimination of nitric acid from b would provide reactive species c.[10] Accordingly, it can be postulated that the oxidation of **1** with CAN proceeds by either one-electorn transfer from **1** to c, producing the cation radical **5** (Y = Me or H) along with the ten-coordinated Ce(III)[11] ion d, or the direct coupling of **1** with RO· derived from d, giving the radical intermediate **6**.[8]

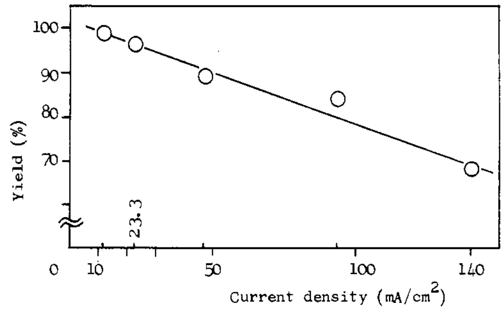


Figure 2. Relationship of the conversion yields [Ce(III) → Ce(IV)] vs. current density: the anolyte was 10% $(NH_4)_2Ce^{III}(NO_3)_5$ in aqueous 1 M HNO_3; the catholyte was aqueous 2% HNO_3; Pt electrodes, after passing 1.5 F/mol of electricity at 25 °C.

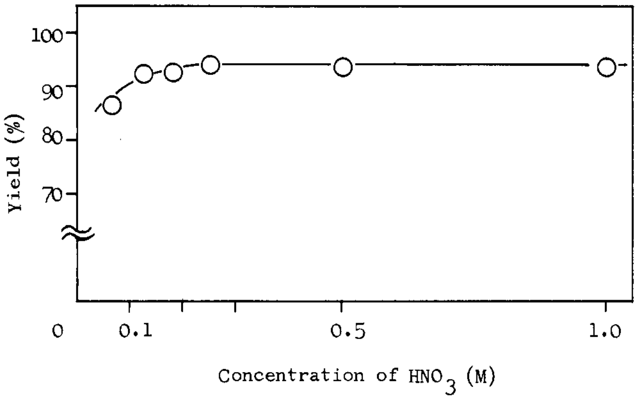


Figure 3. Relationship of the conversion yields [Ce(III) → Ce(IV)] vs. HNO_3 concentration: the anolyte was aqueous 10% $(NH_4)_2Ce^{III}(NO_3)_5$; the catholyte was aqueous 2% HNO_3; Pt electrodes, after passing 1.2 F/mol of electricity at 23.3 mA/cm² at 25 °C.

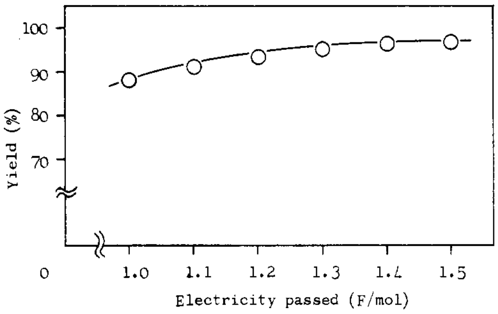


Figure 4. Relationship of the conversion yields [Ce(III) → Ce(IV)] vs. the electricity passed: the anolyte was 10% $(NH_4)_2Ce^{III}(NO_3)_5$ in aqueous 1 M HNO_3; the catholyte was aqueous 2% HNO_3; Pt electrodes at 23 mA/cm².

Indirect Electrooxidation (an In-Cell Method) of 1. The indirect electrooxidation (an in-cell method) of **1** with a Ce(IV)/Ce(III) redox system was also examined. Thus, electrolysis of **1** in CAN (0.2 molar equiv)–Et_4NOTs–MeOH (carbon anode and Cu cathode) system afforded the aldehyde **3** (77%) along with an unidentified complex mixture after passage of 5 F/mol of electricity. The considerable formation of byproducts is presumably due to the exposure of the substrate and/or products to the oxidizing electrode. By contrast, in the ex-cell method, the oxidation of **1** with CAN and the regeneration of CAN are accomplished in different reactors.

Electroregeneration of $(NH_4)_2Ce(NO_3)_6$ (an Ex-Cell Method). The cerium(III) complex was recovered as pale yellow crystals from the reaction mixture after evaporation of the solvents and subsequent removal of **3** by extraction with benzene. In order to establish the optimum conditions for the anodic regeneration of cerium(IV), we examined the effects of the current density, the concentration

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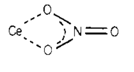
(8) In connection with the mechanism of the side-chain oxidation of alkylbenzenes with CAN, two different mechanisms have been criticized: one involves a radical cation mechanism, initiated by the direct electron transfer from alkylbenzenes to cerium(IV),[8a,b] and the other deals with a hydrogen atom abstraction mechanism by the metal ligands.[8c] (a) Baciocchi, E.; Mandolini, L.; Rol, C. *J. Org. Chem.* **1980**, *45*, 3906. (b) Baciocchi, E.; Rol, C.; Mandolini, L. *J. Am. Chem. Soc.* **1980**, *102*, 7597. (c) Eberson, L.; Oberrauch, E. *Acta Chem. Scand., Ser B* **1979**, *B33*, 343 and references cited therein.

(9) Beineke, T. A.; Delgaudio, J. *Inorg. Chem.* **1968**, *7*, 715.

(10) Ammonium hexanitraocerate(IV) has been used as a colorimetric reagent for the analysis of alcohols, giving a cerium(IV)–alcoholl complex based on the following equilibrium: $[Ce^{IV}(NO_3)_6]^{2-} + n\,ROH \rightleftarrows [Ce^{IV}(NO_3)_{6-n}(OR)_n]^{2-} + nHNO_3$. The structure of the complex c has not yet been clarified, but it is likely that in the initial stage, one of the coordinated bonds of cerium(IV) (see below) with a bidentate nitrate would replace with a new Ce–O bond as the cerium(IV)–alcohol complex via the intermediate b: Doyle, M. P. *J. Chem. Educ.* **1974**, *51*, 131.



(11) Al-Karaghouli, A. L.; Wood, J. S. *J. Chem. Soc. D* **1970**, 135.

Table II. Indirect Electrooxidation of *p*-Methoxytoluene by Recycle Use of $(NH_4)_2Ce(NO_3)_6$ in a MeOH System (an Ex-Cell Method)[a]

entry	electrodes,[b] anode-cathode	additive[c] in cathode	electricity,[d] F/mol	product yields,[e] % 3	2	1
1[f]	Pt			94		
2	Pt-Pt	NH_4NO_3	1.2	93		
3	Pt-Pt	NH_4NO_3	1.2	88		
4	Pt-Pt	NH_4NO_3	1.2	90		
5	Pt-Pt	NH_4NO_3	1.2	92		
6	Pt-Pt	NH_4NO_3	1.0	85	4	
7	Pt-Pt	65% HNO_3	1.2	91		
8	Pt-Pt	65% HNO_3	1.2	90		
9	Pt-Pt	65% HNO_3	1.0	85	5	
10	C-Sus	NH_4NO_3	1.2	74	7	
11	C-Sus	NH_4NO_3	2.0	24	24	20
12	C-Pt	NH_4NO_3	1.5	90		

[a] The recovered Ce(III) salt was subjected to the electrolysis at 10 mA/cm^2 at room temperature, and the following oxidation of 1 with the regenerated Ce(IV) was carried out at room temperature for 30 min. [b] Pt = platinum foil, C = carbon plate; SUS = stainless steel SUS 27 (1.5 × 2 cm^2). [c] Either NH_4NO_3 (600 mg)-MeOH (30 mL) or aqueous 65% HNO_3 (1 mL)-H_2O (30 mL) was used. [d] Referring to the amount of CAN used in entry 1. [e] Isolated yields. [f] Oxidation of 1 (1.01 mmol) in a MeOH solution of CAN (4.1 mmol) was carried out at room temperature for 20 min.

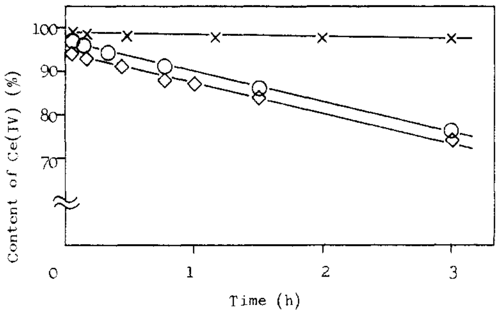


Figure 5. Relationship between the initial concentration of Ce(IV) vs. time. A 12% solution of $(NH_4)_2Ce^{IV}(NO_3)_6$ in H_2O (×), MeOH (○), or 1 M HNO_3–MeOH (◇) was allowed to stand at 25 °C.

of nitric acid, and the amount of electricity in aqueous 10% $(NH_4)_2Ce(NO_3)_5$. The conversion yield vs. the current density plotted in Figure 2 shows that a current density less than ca. 23 mA/cm^2 is favorable in producing the cerium(IV) in over 95% yield. A plot of the concentration of nitric acid in the anolyte vs. the conversion yield of Ce(III) → Ce(IV) at 23.3 mA/cm^2 after passage of 1.2 F/mol of electricity is shown in Figure 3, indicating that it is necessary to maintain the concentration of nitric acid at more than 0.2 M in the anodic media. As shown in Figure 4, an oversupply of electricity of more than 1.2 F/mol did not improve the conversion yield of Ce(III) → Ce(IV).

The method used for the regeneration of CAN in methanol from the cerium(III) complex was similar to that in aqueous systems,[12] except that we isolated a clean red methanol solution of the cerium(IV) complex. The electrolysis of the cerium(III) complex was carried out in a divided cell, into which the MeOH–cerium(III) complex (used as an anolyte) and MeOH–NH_4NO_3 (used as a catholyte) were charged, by passing 1.2 F/mol of electricity at room temperature. The results of the repeating use of the regenerated cerium(IV) for the oxidation of 1 in the presence of either NH_4NO_3 or aqueous 65% HNO_3 are shown in Table II (entries 2–5, 7, and 8). When we used the cerium(IV) prepared by passage of 1.0 F/mol of electricity, the intermediate 2 was isolated in 4–5% yield along with the desired 3 (85%, entries 6 and 9, Table II), indicating that the regeneration of cerium(IV) complex requires 1.1–1.2 F/mol of electricity. For the present purpose, the carbon–platinum electrodes system could be used successfully in contrast to the cases of carbon or stainless (SUS 27) electrodes (entries 10 and 11).

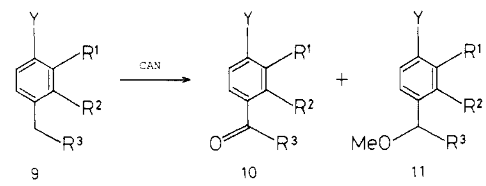
Table III. Oxidation of Alkylbenzenes 9 by $(NH_4)_2Ce(NO_3)_6$

entry	alkyl-benzenes	time,[a] min	product yields,[b] % 10	11
1	9a	5	86	
2	9b	5	83	
3	9c	60	80	
4	9d	5	63	19
5	9e	60[c]		10[d]

[a] Unless otherwise noted, the reaction was carried out at room temperature. [b] Isolated yield. [c] Carried out at reflux. [d] 9e was recovered (50%).

The stability of the cerium(IV) complex in various solvent systems is shown in Figure 5. It should be noted that the cerium(IV) complex is very stable in water (×) but not in methanol solutions (○, ◇). Under the latter conditions, about 20–25% of the cerium(IV) was consumed in 3 h. Fortunately, the oxidation of *p*-methoxytoluene with cerium(IV) in methanol could be performed within a few minutes, thereby avoiding complications due to the competitive oxidation of methanol.

Oxidation of 9a–d with $(NH_4)_2Ce(NO_3)_6$. The yields of the side-chain-oxidized alkylbenzenes 10 and 11 formed by treatment of 9a–d with CAN in methanol at room temperature are summarized in Table III (entries 1–4). However, the oxidation of *p-tert*-butyltoluene (9e) with CAN under refluxing conditions resulted in the formation of 11e (10%) along with the recovered 9e (50%). Happily



9-11	Y	R1	R2	R3
a	OMe	H	Me	H
b	OMe	Me	H	H
c	OMe	H	H	Me
d	OMe	H	-(CH$_2$)$_3$-	
e	*tert*-Bu	H	H	H

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Table IV. Indirect Electrooxidation of *p*-*tert*-Butyltoluene by Recycle Use of $(NH_4)_2Ce(NO_3)_6$ in Aqueous 50% AcOH (an Ex-Cell Method)

entry	electrodes[b] anode	electrodes[b] cathode	electricity,[c] F/mol	yield of 10e,[d] %
1[e]				84
2	C	SUS	2.0	87
3	C	SUS	2.0	94
4	C	SUS	2.0	91
5	C	SUS	1.2	94
6	C	SUS	1.2	92
7	C	SUS	1.2	92
8	Pt	SUS	4.5	93
9	PbO_2	SUS	2.0	92
10	Pt	Pt	1.2	85

[a] The recovered aqueous 50% AcOH–Ce(III) salts was submitted to electrolysis at 23 mA/cm^2 at room temperature, and the following oxidation of **9e** with the regenerated Ce(IV) was carried out at 85–95 °C for 1.5 h. [b] C = carbon plate (1.5 × 2 cm^2); SUS = stainless steel SUS 27 (1.5 × 2 cm^2); Pt = platinum foil (1.5 × 2 cm^2); PbO_2 (1.5 × 2 cm^2). [c] Referring to the amount of CAN used in entry 1. [d] Isolated yields. [e] Treatment of **9e** (0.68 mmol) with CAN (2.97 mmol) in aqueous 50% AcOH at 85–95 °C for 1.5 h.

enough, the oxidation of **9e** was accomplished by treatment with CAN in aqueous 50% acetic acid at 85–95 °C for 1.5 h, yielding 90% of **10e** (Table IV, entry 1). The results of the repeating use of CAN for the oxidation of **9e** are shown in Table IV (entries 2–7). The carbon–stainless steel (SUS 27) electrode systems could be used successfully with less than 0.5% loss in [Ce(IV)] in the course of the unit operation.

Experimental Section

Melting points are uncorrected. The IR spectra were recorded on a JASCO IRA-1 spectrometer. ^1H NMR spectra were determined at 60 MHz with Hitachi R-24 spectrometer. Polarographic analyses were carried out with a Kowa Electronics Model PGS-1550 potentiogalvanostat and a FG-102A function generator. The concentration of cerium(IV) was determined by titration with a standard solution (0.1 N) of iron(II) ammonium sulfate. Elemental analysis were performed in our laboratory. Commercially available **1** and **9a–e** were used.

Oxidation of *p*-Methoxytoluene (1) with CAN in AcOH–H_2O. To a solution of **1** (122 mg, 1 mmol) in AcOH–H_2O (9:1, 5 mL) was added dropwise a solution of CAN (2.4 g, 4.1 mmol) in AcOH–H_2O (9:1, 10 mL). After being stirred at 15–17 °C for 7 h, the mixture was diluted with water (15 mL) and extracted with Et_2O–hexane (1:2, 10 mL × 3 times). The extracts were washed with aqueous $NaHCO_3$ and brine, dried (Na_2SO_4), and concentrated in vacuo. The residue was chromatographed [SiO_2, hexane–benzene–AcOEt (10:10:1)] to give **3** (58 mg, 43%).

The aqueous solution was concentrated to ca. 5 mL, extracted with AcOEt, washed with aqueous $NaHCO_3$ and brine, and dried (Na_2SO_4). Evaporation of the solvents followed by column chromatography [SiO_2, hexane–benzene–AcOEt (5:5:1)] gave pale yellow crystals of **4**: 20 mg (17%); mp 132–133 °C; IR (Nujol) 1679, 1659, 1620, 1600, 1380, 1268, 1222 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.73 (s, 3, CH_3), 3.86 (s, 3, CH_3O), 6.32 (d, J = 10 Hz, 2, HC=C—C=O), 6.99 (d, J = 10 Hz, 2, C=CHC=O), 7.03 (d, J = 7 Hz, 1, Ar H), 7.81 (dd, J = 2, 7 Hz, 1, Ar H), 7.88 (d, J = 2 Hz, 1, Ar H), 9.87 (s, 1, CHO).

Anal. Calcd for $C_{15}H_{14}O_3$: C, 74.36; H, 5.82. Found: C, 74.57; H, 6.06.

Similarly, oxidation of **1** with CAN in aqueous AcOH at 1–60 °C was carried out with the results listed in Table I (entries 1–4).

Oxidation of *p*-Methoxytoluene (1) with CAN in MeOH. To a solution of **1** (123 mg, 1.01 mmol) in MeOH (5 mL) was added dropwise a solution of CAN (2.37 g, 4.23 mmol) in MeOH (10 mL), and the mixture was stirred for 5 min at room temperature. After evaporation of the solvent, the organic substances were extracted with benzene. The usual workup and the following chromatography (SiO_2; benzene–AcOEt, 10:1) of the crude product gave **3** (129 mg, 94%), whose IR and ^1H NMR spectra were identical with those of the authentic sample. The residual cerium(III) as a solid was subjected to anodic oxidation in the manner as shown in the following paragraph.

Oxidation of **1** with CAN in aqueous MeOH was carried out in the manner as described above. The results are summarized in Figure 1.

Electroregeneration of Cerium(IV) from Cerium(III). Apparatus. Electrolysis was performed in an H-type cell with a sintered-glass disk separating the anode and cathode compartments. Two platinum foils (1.5 × 2 cm^2) were used as working and auxiliary electrodes. The regurated dc power was supplied by a Metronix Model 543B instrument.

Electrolysis (Entry 2 in Table II). The recovered cerium(III) as described in the above paragraph was dissolved in MeOH (15 mL) and charged into the anode compartment of an H-type cell. Into the cathode compartment was charged a solution of NH_4NO_3 (600 mg) in MeOH (30 mL). Electrolysis was carried out under a constant current of 20 mA/cm^2 at room temperature. After passage of 1.2 F/mol (based on CAN added in entry 1) of electricity, a deep red solution of methanolic CAN was obtained. The solution was immediately used for the oxidation of **1**. Thus, **1** (123 mg, 1.01 mmol) was treated with the regenerated cerium(IV) in the same manner as described in the above paragraph. The electrolysis conditions and the results of the recycle use of the cerium(IV) are summarized in Table II.

Oxidation of 1,2-Dimethyl-4-methoxybenzene (9a) with CAN in MeOH (Entry 1 in Table III). To a solution of **9a** (93 mg, 0.69 mmol) in MeOH (3 mL) was added in a few minutes a solution of CAN (1.59 g, 2.90 mmol) in MeOH (5 mL). After an additional 5 min at 27–28 °C, the mixture was diluted with water (15 mL), extracted with CH_2Cl_2, washed with brine, and dried (Na_2SO_4). Evaporation of the solvents followed by column chromatography (SiO_2; hexane–AcOEt, 20:1) gave **10a** (86%).[13]

Similarly, the oxidation of **9b–e** with CAN was carried out, and the reaction conditions and results are listed in Table III. The physical properties and the spectral data of **10b**,[14] **10c**,[15] **10d**,[16] **10e**,[17] **11d**,[18] and **11e**[19] were identical with those of the authentic samples.

Indirect Electrooxidation of *p*-*tert*-Butyltoluene (9e) with Recycle Use of CAN in Aqueous 50% AcOH (an Ex-Cell Method). To a solution of CAN (1.75 g, 2.97 mmol) in aqueous 50% AcOH (15 mL) was added **9e** (100 mg, 0.68 mmol). After 1.5 h at 85–95 °C, the mixture was extracted with hexane–benzene (1:1, 3 × 10 mL). The usual workup and the following chromatography (SiO_2; benzene–AcOEt, 10:1) gave **10e** (94%).[19] For regeneration of the cerium(IV), the cerium(III)–H_2O–AcOH solution was electrolyzed in the anode compartment fitted with a carbon plate electrode (1.5 × 2 cm^2). The cathode compartment was fitted with stainless-steel electrode (1.5 × 2 cm^2) and charged with a solution of 200 mg of NH_4NO_3 in 30 mL of H_2O–AcOH (1:1). After passage of 1.2 F/mol of electricity, based on the initially added CAN (entry 1), under a constant current of 23 mA/cm^2 at room temperature, an orange cerium(IV) solution was obtained.

The recycle use of the cerium(IV) solution for the oxidation of **9e** was carried out in a similar manner as described above. The reaction conditions and results are shown in Table IV.

Indirect Electrooxidation of 1 with CAN (an In-Cell Method). A mixture of **1** (61 mg, 0.5 mmol), CAN (56 mg, 0.1 mmol), and Et_4NOTs (100 mg) in MeOH (10 mL) was electrolyzed by using a carbon anode and a Cu cathode (1.5 × 2 cm^2 each) at a constant current of 10 mA/cm^2 at room temperature. After passage of 5 F/mol of electricity (2.2 h), the mixture was concentrated, and the residue was chromatographed [SiO_2; hex-

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(14) Gattermann, L.; Frenzel, C. *Ber.* **1898**, *31*, 1150.

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(17) Chichibabin, A. E.; Elgazine, S.; Lengold, V. A.; Russ, J. *Bull. Soc. Chim. Fr.* **1928**, 238; *Chem. Abstr.* **1928**, *22*, 2744.

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(19) Huang, R. L.; Lee, H. H. *J. Chem. Soc.* **1964**, 5963.

ane–benzene–AcOEt (5:5:1)] to give **3** (53 mg, 77%).

Oxidation of (*p*-Methoxyphenyl)methyl Methyl Ether (2) with CAN in MeOH. To a solution of **2** (154 mg, 1.01 mmol) in MeOH (5 mL) was added a solution of CAN (1.23 g, 2.2 mmol) in MeOH (10 mL). After being stirred at room temperature for 5 min, the concentrated mixture was extracted with benzene. Workup of the extracts gave **3** (133 mg, 97%), whose spectral data were identical in all respects with those of the authentic sample.

Registry No. 1, 104-93-8; **2**, 1515-81-7; **3**, 123-11-5; **4**, 80866-06-4; **9a**, 4685-47-6; **9b**, 6738-23-4; **9c**, 1515-95-3; **9d**, 1730-48-9; **9e**, 98-51-1; **10a**, 52289-54-0; **10b**, 32723-67-4; **10c**, 100-06-1; **10d**, 1078-19-9; **10e**, 939-97-9; **11d**, 16821-24-2; **11e**, 3395-87-7; diammonium hexanitratocerate, 16774-21-3.

Cyclization of Conjugated Azines. Synthesis and Thermal Rearrangements of 1,8-Diaryl-4,5-diaza-3-methyl- and -3-phenyl-1,3,5,7-octatetraenes (α,β-Unsaturated Azines) to 1-(1-Methyl-3-phenyl- and -1,3-diphenyl-1-propenyl)-5-arylpyrazoles

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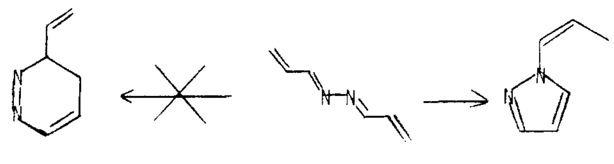
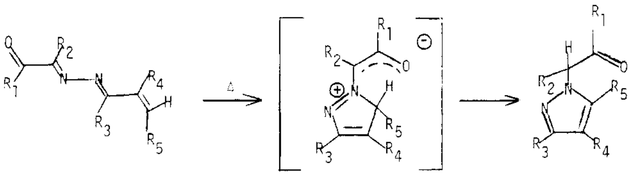
Methyl- (**20**) and phenyl-substituted (**29**) α,β-unsaturated azines were prepared and subjected to thermolyses. In all cases the thermolyses reaction produced two pyrazoles (**23**, **24** and **32**, **33**, respectively), except where the azine had a terminal methylene grouping. The ratios of the pyrazoles were determined from the ^{1}H NMR. The steric and electronic effects of the azine substituents on the ratios of the pyrazoles formed are discussed. The ^{13}C NMR of the isolated azines and pyrazoles are reported.

Symmetrical azines **1** derived from α,β-unsaturated carbonyl species and hydrazine yield *N*-propenylpyrazoles[1,2] **2** rather than the dihydropyridazines **3** which one would have anticipated if the cyclization reaction were to proceed in the manner expected[3] for an all carbon 1,3,5-unsaturated system. This type of reaction is quite common to azine chemistry and is termed a "criss-cross" cycloaddition reaction.[4]


3 1 2

It has been shown in our laboratories that a variety of simple N-substituted pyrazoles as well as tetrahydroindazoles, pyrazolopyrans, and cyclopentapyrazoles may be prepared from α,β-unsaturated α-oxoazines **4**[5] by thermolysis.



4 5 6

We have also shown[6] that α-oxo-α-allenylazines **7** readily form pyrazolo[1,5-*b*]isoquinolines **8** and pyrazolo[5,1-*c*]-1,4-oxazines **9** apart from monocyclic N-substituted pyrazoles (Scheme I).

We propose that unsaturated azines with cumulated double bonds in conjugation with the azine moiety will prove to be versatile synthons for a large variety of fused pyrazolo-substituted species as shown in Scheme II.

In order to explore further the scope of the reaction of allenylazine species related to **7**, we wished to prepare these compounds without the carbonyl moiety. We chose to start this work by examining the reactions of simple unsymmetrical unsaturated azines, related to **4**, with no carbonyl groups.

It has been shown[5] that the azine **4** may be prepared readily from the monohydrazone of a diketone, **11** and (2-propynyl)triphenylphosphonium bromide (**12**). However, our attempts to make the hyrazone of cinnamaldehyde, **15**, directly always resulted in the formation of

$$\underset{\mathbf{11}}{R^1C(O)C(R^2){=}NNH_2} + \underset{\mathbf{12}}{HC{\equiv}CCH_2P^+(Ph)_3Br^-} \rightarrow\ \rightarrow \mathbf{4}$$

$$\underset{\mathbf{13}}{PhCH{=}CHCHO} + \underset{\mathbf{14}}{H_2NNH_2} \rightarrow$$

$$[\underset{\mathbf{15}}{PhCH{=}CHCH{=}NNH_2}] \rightarrow \underset{\mathbf{16}}{(PhCH{=}CHCH{=}N{-})_2}$$

the symmetrical cinnamaldehyde azine **16**, thus thwarting our ability to prepare **17** from **15** and the salt **12**. We found, however, that **17** may be obtained readily (89% yield) by allowing (2-propynyl)triphenylphosphonium bromide (**12**) to react initially with an equivalent amount

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[2] Stern, R. L.; Krause, J. G. *J. Heterocycl. Chem.* **1968**, *5*, 263.

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[5] Albright, T. A.; Evans, S.; Kim, C. S.; Labaw, C. S.; Russiello, A. B.; Schweizer, E. E. *J. Org. Chem.* **1977**, *42*, 3691–3697.

[6] Schweizer, E. E.; Evans, S. *J. Org. Chem.* **1978**, *43*, 4328–4334.

[7] Y is normally more electronegative than X or is able to stabilize a negative charge. For example: X = N, Y = O; X = C, Y = CE$_2$, NR, O (E = aromatic, O=CR, PR$_3$$^+$); Z = CR$_2$, NR, O. This is not meant to be an exhaustive list. Apart from the examples mentioned above[2,3,6] where X = Y = Z = C, X = Z = C, and Y = O, we have also prepared X = C, Y = O, and Z = N.[8]

[8] Schweizer, E. E.; Lee, K. J., unpublished results.

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