Table V. ^{1}H NMR Data for *p-tert*-Butylbenzenediazonium Salts 1 and 2 in Deuterated Dimethyl Sulfoxide in the Absence and Presence of 18-Crown-6

counter-ion	equiv of crown ether	chemical shift, ppm^{a,b}	proton
BF_4^-	0	1.37	$C(CH_3)_3$
	1.0	1.37	
	0	8.60	aromatic (2,6)
	1.0	8.53	
	0	8.04	aromatic (3,5)
	1.0	8.04	
PF_6^-	0	1.37	$C(CH_3)_3$
	1.0	1.37	
	0	8.60	aromatic (2,6)
	1.0	8.52	
	0	8.04	aromatic (3,5)
	1.0	8.04	

[a] Relative to Me_4Si. [b] Chemical shifts for the aromatic protons refer to the center of the doublet in each leg of the A_2B_2 pattern.

ether became symmetrical in the presence of 5 equiv of 18-crown-6.

Comparison of the chemical shift data for the anions of 1 and 2 in the absence and presence of 5 equiv of 18-crown-6 reveals a change of 257 Hz for 1 and 144 Hz for 2. The smaller chemical shift change observed for 2 is again consistent with a lesser degree of ion pairing when the counterion is hexafluorophosphate.

Central to this argument is the formulation of the crown ether–diazonium salt complex 5 as resulting from insertion of the neck of the arenediazonium cation into a crown ether collar.[6,13,14] Previous evidence for this arrangement includes steric effects of substituents in solubilization[6,13] and titration calorimetric[14] studies and ^{1}H NMR spectral changes of certain macrocyclic polyethers in the presence of arenediazonium salts.[6,13]

Because of insufficient solubility of uncomplexed 2 it was not possible to probe for changes in the ^{1}H NMR spectra of 1 and 2 in 1,2-dichloroethane upon addition of 18-crown-6. However, such measurements could be made in dimethyl sulfoxide and are summarized in Table V.

Although the chemical shifts of the *tert*-butyl group hydrogens and the 3,5 aromatic ring hydrogens of 1 and 2 are unaffected by the presence of 18-crown-6, the 2,6 aromatic ring hydrogens are shifted upfield by 7–8 Hz in the presence of 18-crown-6. This chemical shift change for only the ortho hydrogens provides further evidence for the proposed diazonium ion–crown ether complex 5.

Experimental Section

General Methods. Melting points were measured with a Mel-Temp melting point apparatus and are uncorrected. Infrared spectra were recorded on a Perkin-Elmer Model 457 infrared spectrophotometer, using sodium chloride plates. NMR spectra were measured with either a Varian A-60 or XL-100 spectrometer. Abbreviations used in identifying signal multiplicities are s (singlet) and m (multiplet). Gas chromatographic analysis was performed on an Antek 400 or a Varian 2400 flame-ionization gas chromatograph.

Materials. The compounds 1,2-dichloroethane (Aldrich, Gold Label), 18-crown-6 (4, PCR Research Chemicals), *tert*-butylbenzene (Aldrich), and *N*,*N*-dimethylaniline (Mallinckrodt, reagent grade) were obtained from the indicated sources and used directly. *p-tert*-Butylbenzenediazonium tetrafluoroborate[4] (1), 4-*tert*-butyl-4′-(dimethylamino)azobenzene,[7] and *p-tert*-butylchlorobenzene[15] were prepared according to the cited literature procedures. An authentic sample of *p-tert*-butylfluorobenzene was prepared by the thermal decomposition of solid *p-tert*-butylbenzenediazonium tetrafluoroborate by using a standard procedure.[16]

p-tert-Butylbenzenediazonium hexafluorophosphate (2) was prepared from *p-tert*-butylaniline[4] in 80% yield by the procedure of Rutherford, Redmond, and Rigamonti.[17] The crude salt was washed with cold anhydrous diethyl ether, dissolved in a minimum amount of acetone, precipitated by adding pentane, and then dried in vacuo. The resulting white solid had the following: mp 125 °C dec; ^{1}H NMR δ 7.8–8.6 (m, 4 H), 1.34 (s, 9 H); IR (Nujol mull), characteristic bands at 2289 (NN stretch) and 820 (PF_6^-) cm^{-1}.

Kinetic methods for studying the thermal decomposition of the arenediazonium salts and their coupling reactions with *N*,*N*-dimethylaniline were the same as those previously reported.[7,10]

Product analysis in thermolysis reactions was accomplished by gas chromatography on a 10 ft × $^1/_8$ in. column of 15% Carbowax 20-M on Chromosorb W at temperatures of 90–110 °C. Anisole was used as the internal standard, and molar response corrections were made. In all cases, quantitative yields of *p-tert*-butylchlorobenzene and *p-tert*-butylfluorobenzene resulted from the thermolysis of 0.01 M solutions of 1 and 2 in 1,2-dichloroethane at 50.0 °C.

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Registry No. 1, 52436-75-6; 2, 73286-45-0; 3, 121-69-7.

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(15) Lerer, M.; Fabre, C. *Bull. Soc. Chim. Fr.* **1956**, 199.

(16) Vogel, A. I. "A Textbook of Practical Organic Chemistry", 3rd ed.; Longman: London, 1956; pp 609–12.

(17) Rutherford, K. G.; Redmond, W.; Rigamonti, J. *J. Org. Chem.* **1961**, *26*, 5194.

Convenient and Inexpensive Procedure for Oxidation of Secondary Alcohols to Ketones

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In connection with certain studies concerned with the total synthesis of chirally pure natural products,[1] we required large quantities of (–)-camphor. This substance can be obtained from relatively inexpensive (–)-borneol by oxidation with an almost bewildering array of reagents.[2] However, the need for repeated large-scale work forced us to consider fractors such as cost, ease of operation, and total reaction volume in the selection of an oxidation procedure. In our previous work[1] we had employed *tert*-butyl hypochlorite. However, the somewhat tedious preparation[3] of this reagent and its potentially explosive nature,[3] especially during large-scale preparations, led us

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(1) R. V. Stevens and F. C. A. Gaeta, *J. Am. Chem. Soc.*, **99**, 6105 (1977).

(2) For leading references, see "Compendium of Organic Synthetic Methods", (I. T. Harrison and S. Harrison, Vol. I and II; L. G. Wade, Vol. III), Wiley-Interscience, New York.

(3) Preparation: (a) "Organic Syntheses", Wiley, New York: Collect. Vol. 4, 1963, p 125; Collect. Vol. 5, 1973, p 184. Use as an oxidant: (a) C. A. Grob and H. J. Schmid, *Helv. Chim. Acta*, **36**, 1763 (1953); D. Ginsburg, *J. Am. Chem. Soc.*, **75**, 5489 (1953); G. S. Fonken, J. L. Thompson and R. H. Levin, *ibid.*, **77**, 172 (1955).

Table I. Oxidation of Alcohols with NaOCl

entry	alcohol	product	% yield[a]
1	(−)-borneol	(−)-camphor	95
2	(±)-isoborneol	(±)-camphor	91
3	(−)-menthol	(−)-menthone	94
4	cyclohexanol	cyclohexanone	96
5	2,2,5-trimethylcyclohexanol	2,2,5-trimethylcyclohexanone	90
6	9-cyanoisoborneol[b]	9-cyanocamphor	94
7	5α-androstane-3β,17β-diol	5α-androstane-3,17-dione	96
8	norborneol	norcamphor	92
9	2-octanol	2-octanone	96
10	1-decyl alcohol	decyl decanoate	89
11	2-ethyl-1,3-hexanediol	2-ethyl-1-hydroxy-3-hexanone	85

[a] All yields represent isolated, pure products. Known products were identified by comparison with authentic samples. New compounds were characterized by their ^{1}H and ^{13}C NMR, IR, and exact mass spectra. [b] The synthesis of this compound will be described in a future paper.

to consider alternate sources of positive chlorine which might effect the same transformation. Sodium hypochlorite has been used indirectly with ruthenium tetroxide to oxidize secondary alcohols to ketones;[4] reportedly, no reaction occurs in the absence of catalyst. Sodium hypochlorite has also been used in a two-phase system with a phase-transfer catalyst to oxidize secondary alcohols to ketones in moderate yield.[5] In our hands this procedure failed to oxidize borneol to camphor and led to a complex mixture of polymeric products.

We now report that secondary alcohols are cleanly oxidized to ketones with sodium hypochlorite in acetic acid in the absence of catalyst. Inexpensive concentrated solutions of sodium hypochlorite are sold commercially as "swimming pool chlorine".[6] Dropwise addition of this reagent to a solution of the alcohol in acetic acid at room temperature leads to an exothermic reaction which is usually complete 15 min after the end of the addition. Ketones are isolated in excellent yield (see Table I) by diluting the mixture with water and collecting the products by filtration (solids) or extraction (liquids). We have repeatedly used this procedure for the oxidation of borneol to camphor without incident.[8]

Other secondary alcohols are oxidized equally efficiently (see Table I). The reaction appears to be relatively insensitive to geometric or steric constraints (e.g., compare Table I entries 1 and 2, 4 and 5). Methyl ketones are formed without undergoing a subsequent haloform reaction (entry 9). Primary aliphatic alcohols react sluggishly, leading to dimeric esters, presumably via hemiacetal intermediates (entry 10).[9] We have made use of this difference in reactivity to oxidize a secondary alcohol in the presence of a primary alcohol (entry 11). The use of this reagent as a selective oxidant and applications of the ester-forming reaction will be the subject of a future paper.

Experimental Section

General Procedures. Sodium hypochlorite solutions[6] and glacial acetic acid (Mallinckrodt, analytical reagent) were used as received. Starting alcohols were purified by distillation or crystallization, as appropriate; purity was established by vapor-phase or thin-layer chromatography prior to use. Infrared spectra were recorded on a Beckman IR 4210 infrared spectrophotometer. NMR spectra were taken on Varian T-60, Bruker WP-200, and Varian CFT-20 spectrometers in dilute deuteriochloroform solutions with tetramethylsilane as internal standard. Mass spectra were recorded on an AEI-MS 9 mass spectrometer. Optical rotations were measured with a Perkin-Elmer Model 141 polarimeter.

Oxidation of (−)-Borneol. (−)-Borneol (502 g, 3.26 mol, $[\alpha]^{25}_{D}$ ($CHCl_3$) −35.3°) was dissolved in glacial acetic acid (1.5 L) in a 5-L 3-neck flask fitted with a mechanical-stirring apparatus and thermometer. Aqueous sodium hypochlorite solution (2 L of 2.0 M solution, 4.0 mol) was added dropwise over 2.5 h. The mixture was cooled in an ice bath as necessary to keep the internal temperature in the range 15–25 °C. The mixture was stirred for 1 h after completion of the addition, at which time a positive potassium iodide–starch test was obtained. Saturated aqueous sodium bisulfite solution (200 mL) was added until the color of the mixture changed from yellow to white and the potassium iodide–starch test was negative. The mixture was then poured over an ice–brine mixture (10 L), and the resulting white solid was collected on a Buchner funnel and washed with saturated aqueous sodium carbonate solution until foaming was no longer evident. The solid product was pressed as dry as possible and dissolved in petroleum ether (2 L, bp 20–60 °C), and the aqueous and organic layers were separated. The aqueous layer was extracted twice with petroleum ether and discarded. The organic layers were combined and dried over anhydrous calcium chloride. The mixture was concentrated by rotary evaporation until most of the petroleum ether was removed and a white slurry remained. The remainder of the petroleum ether was then removed by high-vacuum rotary evaporation with the condensor cooled to −78 °C to prevent sublimation of camphor, leaving 475 g (95.8%) of (−)-camphor as a free-flowing white powder, mp 175.5–176.5 °C, $[\alpha]^{25}_{D}$ ($CHCl_3$) −42.1°. The ^{1}H NMR and IR spectra and VPC retention time of this product were identical with those of an authentic sample.

Oxidation of Cyclohexanol. Cyclohexanol (99.0 g, 0.988 mol) was dissolved in glacial acetic acid (660 mL) in a 2-L 3-neck flask fitted with a mechanical-stirring apparatus and thermometer. Aqueous sodium hypochlorite (660 mL of 1.80 M solution, 1.19 mol) was added dropwise over 1 h. The reaction was cooled in an ice bath to maintain the temperature in the 15–25 °C range. The mixture was stirred for 1 h after the addition was complete. A potassium iodide–starch test was positive. Saturated aqueous sodium bisulfite solution (3 mL) was added until the color of the reaction mixture changed from yellow to white and the potassium iodide–starch test was negative. The mixture was then poured into an ice–brine mixture (2 L) and extracted six times with ether. The organic layer was washed with aqueous sodium hydroxide (5% by weight) until the aqueous layer was basic (pH test paper).

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(4) S. Wolfe, S. K. Hasan, and J. R. Campbell, *J. Chem. Soc. D*, 1420 (1970).

(5) G. A. Lee and H. H. Freedman, *Tetrahedron Lett.*, 1041 (1976); S. L. Regen, *J. Org. Chem.*, **42**, 875 (1977).

(6) We used Sani-Chlor Pool Sanitizer (General Pool Supply, Los Angeles, CA 90045) which is sold as a 12.5% solution by weight. As sold, these solutions were found to be 1.8–2.0 M by means of a simple titration procedure.[7] On standing at room temperature in their original containers, these solutions decreased in concentration by about 20% per month. For most applications an excess of the reagent can be used with the stated concentration as a guide. For more precise work the simple titration procedure[7] is recommended. Our cost was $0.95/gal or about 13¢/mol.

(7) I. M. Kolthoff and R. Belcher, "Volumetric Analysis", Interscience, New York, 1957, pp 262–6.

(8) We have experienced no difficulties in working with this reagent. However, as with all strong oxidants, care should be taken due to the potential for formation of peroxides.

(9) (a) Preparation of esters from aldehydes via hemiacetals has been described previously: P. Sundararaman, E. C. Walker, and C. Djerassi, *Tetrahedron Lett.*, 1627, (1978). (b) Oxidation of primary benzylic alcohols by hypochlorites has been described previously: C. Y. Meyers, *J. Org. Chem.*, **26**, 1046 (1961).

The aqueous washes were then combined and extracted five times with ether. The ether layers were combined and dried over magnesium sulfate. The ether was distilled through a 30-in. Vigreux column until less than 300 mL of solution remained. The remainder was fractionally distilled through a 12-in. Vigreux column. After a forerun of ether, cyclohexanone (bp 155 °C) was distilled to give 92.9 g (95.8%) of a colorless liquid which had ^{1}H NMR and IR spectra and VPC retention time identical with those of an authentic sample.

Oxidation of 2-Ethyl-1,3-hexanediol. 2-Ethyl-1,3-hexanediol (Eastman, 10.12 g, 0.068 mol) was dissolved in glacial acetic acid (50 mL) in a 250-mL 3-neck flask equipped with a thermometer and magnetic stirring bar. Aqueous sodium hypochlorite (49 mL of 1.48 M solution, 0.072 mol) was added dropwise over 1 h. The reaction was cooled in an ice–water bath as necessary to maintain the temperature between 20 and 25 °C. The mixture was stirred for 30 min after completion of the addition, after which a potassium iodide–starch test was negative. The reaction mixture was poured into ice-brine (300 mL), and the resulting mixture was extracted five times with ether. The combined ether extract was washed three times with saturated aqueous sodium carbonate solution and twice with aqueous sodium hydroxide solution (5% by weight). The aqueous washes were combined and extracted three times with ether. The ether extracts were then combined, dried over anhydrous magnesium sulfate, and concentrated by rotary evaporation to give a colorless oil (9.64 g). Vacuum distillation in a short-path apparatus gave 8.42 g (85%) of 2-ethyl-1-hydroxy-3-hexanone as a colorless oil:[10] ^{1}H NMR (200 MHz) δ 3.73 (2 H, ddd, J = 6, 11, 11 Hz, CH_2OH), 2.65 (1 H, m, $O{=}CHEt$), 2.49 (2 H, t, J = 7 Hz, $CH_2CH_2C{=}O$), 2.12 (1 H, t, J = 6 Hz, CH_2OH, exchanges with D_2O), 1.40–1.80 (4 H, m, CH_2), 0.85–1.05 (6 H, superimposed t, CH_2CH_3); ^{13}C NMR δ 215.0 ($C{=}O$), 62.9, 55.8, 45.2, 21.5, 16.8, 13.8, 11.8; IR (CCl_4) 3450 (br, OH), 2950 (s, CH), 2920 (m, CH), 2864 (m, CH), 1703 cm^{-1} (s, $C{=}O$); exact mass, m/e found 144.1146, calculated for $C_8H_{16}O_2$ 144.1151.

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Registry No. (−)-Borneol, 464-45-9; (±)-isoborneol, 24393-70-2; (−)-menthol, 2216-51-5; cyclohexanol, 108-93-0; 2,2,5-trimethylcyclohexanol, 73210-25-0; 9-cyanoisoborneol, 73210-26-1; 5α-androstane-3β,17β-diol, 571-20-0; norborneol, 1632-68-4; 2-octanol, 123-96-6; 1-decyl alcohol, 112-30-1; 2-ethyl-1,3-hexanediol, 94-96-2; (−)-camphor, 464-48-2; (±)-camphor, 21368-68-3; (−)-menthone, 14073-97-3; cyclohexanone, 108-94-1; 2,2,5-trimethylcyclohexanone, 933-36-8; 9-cyanocamphor, 56906-71-9; 5α-androstane-3,17-dione, 846-46-8; norcamphor, 497-38-1; 2-octanone, 111-13-7; decyl decanoate, 1654-86-0; 2-ethyl-1-hydroxy-3-hexanone, 27970-80-5.

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[10] I. I. Lapkin and F. G. Saitkulova, *Zh. Org. Khim.*, 6, 450, (1970).

Oligonuclear Ruthenocene Complexes[1]

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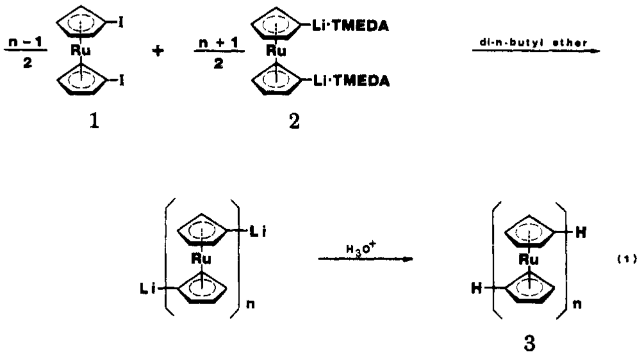
In continuation of our studies of oligo- and polynuclear metallocenes as precursors of mixed-valence systems,[1] we wished to prepare oligoruthenocenylenes of type **3** (n = 2–4). The availability of the 1,1′-diiodo derivative **1**,[2] coupled with the observed ease of lithiation of the ruthenocene complex,[2,3] suggested a ready synthetic pathway to **3** (eq 1) via coupling of **1** with the 1,1′-dilithioruthenocene **2** (chelated with TMEDA = *N,N,N′,N′*-tetramethylethylenediamine).



The analogous reaction involving the diiodo and (TMEDA-chelated) dilithium derivatives of the iron congener, ferrocene, had previously been found to proceed smoothly in ether solvents, giving up to 85% yields of coupling products including higher polymers.[1]

In the present investigation, **1** was allowed to react with **2** in a molar ratio of 2:3 in a di-n-butyl ether medium (0.034 M in **1**) at 25–85 °C, and the hydrolyzed product mixture, after reductive elimination of any iodo groups present and removal of regenerated ruthenocene by sublimation (20% recovery), constituted crude coupling products (24% overall yield). Further workup by chromatography produced dimer (**3**, n = 2; 7.0%), trimer (**3**, n = 3; 3.5%), and tetramer (**3**, n = 4; 2.2%). In addition, a small polymeric fraction (**3**, $n > 4$; 5.5%) was extracted from the top of the column but was not further investigated at this time.

Other experiments conducted under a variety of conditions similar to those employed in the earlier[1,4,5] ferrocene polymerization studies, including the use of tetrahydrofuran or dimethoxyethane solvents, failed to proceed with any higher efficiency; overall yields of coupling products did not exceed 25%, although in all instances unreacted starting materials could be recovered in appreciable quantities (20–50%) after conversion to ruthenocene. Since **1** should be a more suitable substrate for nucleophilic attack than the corresponding diiodoferrocene because of reduced electron density on the rings in the ruthenium complex,[3,6] our failure to attain, or at least approach, the high coupling yields achieved in dilithioferrocene/diiodoferrocene polycondensations[1] must be traced to the low anion nucleophilicity of **2** despite the assistance given by the chelating agent. This problem requires further investigation.

Oligomers **3** (n = 2–4) possess melting points (Table I) in the same range as those of the respective oligonuclear ferrocenes but show reduced solubility relative to their ferrocene counterparts. All three homologues are colorless

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[1] Metallocene Polymers. 38. For part 37, see E. W. Neuse and L. Bednarik, *Macromolecules*, 12, 187 (1979). This work was supported by the South African Council for Scientific and Industrial Research. A generous gift of cyclopentadiene dimer from Esso Chemical Supply Co. is gratefully acknowledged.

[2] L. Bednarik and E. W. Neuse, *J. Organomet. Chem.*, 168, C8 (1979). We are grateful to one of the referees for drawing our attention to a previous, undetailed publication on halo- and lithioruthenocenes: H. Rosenberg and R. A. Ference, Abstracts, 160th National Meeting of the American Chemical Society, Chicago, IL, Sept 1970, No INOR 158.

[3] M. D. Rausch, E. O Fischer, and H. Grubert, *J. Am. Chem. Soc.*, 82, 76 (1960).

[4] E. W. Neuse and L. Bednarik, *Transition Met. Chem.*, 4, 87 (1979).

[5] E. W. Neuse and L. Bednarik, *Transition Met. Chem.*, 4, 104 (1979).

[6] S. P. Gubin and A. A. Lubovich, *J. Organomet. Chem.*, 22, 183 (1970).

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