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 crown 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. Previous evidence for this arrangement includes steric effects of substituents in solubilization and spectra of 1 and 2. The proposed diazonium ion-crown ether complex involving the 19F NMR spectra was prepared by the thermal decomposition of solid p-tert-butylbenzenediazonium hexafluorophosphate (2) was prepared from p-tert-butylaniline in 80% yield by the procedure of Rutherford, Redmond, and Rigamonti. 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; 1H 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 (PF6) 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. Product analysis in thermolysis reactions was accomplished by gas chromatography on a 10 ft × 1/4 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.

**Acknowledgement** is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research. Mr. Richard A. Wolcott is thanked for his assistance in obtaining the 19F NMR spectra.

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

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**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, we required large quantities of (−)-camphor. This substance can be obtained from relatively inexpensive (−)-borneol by oxidation with an almost bewildering array of reagents. However, the need for repeated large-scale work forced us to consider factors such as cost, ease of operation, and total reaction volume in the selection of an oxidation procedure. In our previous work we had employed tert-butyl hypochlorite. However, the somewhat tedious preparation of this reagent and its potentially explosive nature, especially during large-scale preparations, led us to consider alternative methods.

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New compounds were characterized by their ability to oxidize secondary alcohols to ketones; reportedly, no attempts to consider alternate sources of positive chlorine which might affect the same transformation. Sodium hypochlorite has been used indirectly with ruthenium tetroxide to oxidize secondary alcohols to ketones, and succeeded in a future paper. We have made use of this dif- formed reaction will be the subject of a future paper.

Experimental Section

General Procedures. Sodium hypochlorite solutions 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 CP-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, \([\alpha]_D^0\) = +12.1° (CHCl₃) = +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 then poured into 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 then 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 then removed by high-vacuum rotary evaporation with the condenser 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, \([\alpha]_D^0\) (CHCl₃) = –42.1°. The \(^1H\) NMR and IR spectra and VPC retention time of this product were identical with those of an authentic sample. The remainder of the petroleum ether was then removed by high-vacuum rotary evaporation with the condenser 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, \([\alpha]_D^0\) (CHCl₃) = –42.1°. The \(^1H\) NMR and IR spectra and VPC retention time of this product were identical with those of an authentic sample.

Oxidation of Cyclohexanol. Cyclohexanol (99.9 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 solution (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).

### Table I. Oxidation of Alcohols with NaOCl

| entry | alcohol          | product           | % yield
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>(–)-borneol</td>
<td>(–)-camphor</td>
<td>95</td>
</tr>
<tr>
<td>2</td>
<td>(+)-isoborneol</td>
<td>(+)-camphor</td>
<td>91</td>
</tr>
<tr>
<td>3</td>
<td>(–)-menthol</td>
<td>(–)-menthone</td>
<td>94</td>
</tr>
<tr>
<td>4</td>
<td>cyclohexanol</td>
<td>cyclohexanone</td>
<td>96</td>
</tr>
<tr>
<td>5</td>
<td>2,2,5-trimethylcyclohexanol</td>
<td>2,2,5-trimethylcyclohexanone</td>
<td>95</td>
</tr>
<tr>
<td>6</td>
<td>5a-endoisoborneol</td>
<td>5a-endoisoborneol</td>
<td>94</td>
</tr>
<tr>
<td>7</td>
<td>5a-androstan-3,17-diol</td>
<td>5a-androstan-3,17-dione</td>
<td>96</td>
</tr>
<tr>
<td>8</td>
<td>norborneol</td>
<td>norcamphor</td>
<td>92</td>
</tr>
<tr>
<td>9</td>
<td>2-octanol</td>
<td>2-octanone</td>
<td>94</td>
</tr>
<tr>
<td>10</td>
<td>1-dodecyl alcohol</td>
<td>decyl decanoate</td>
<td>89</td>
</tr>
<tr>
<td>11</td>
<td>2-ethyl-1,3-hexanediol</td>
<td>2-ethyl-1-hydroxy-3-hexanone</td>
<td>85</td>
</tr>
</tbody>
</table>

\(a\) All yields represent isolated pure products. Known products were identified by comparison with authentic samples.


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Notes


(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. \(^1H\) NMR and IR spectra and VPC retention time of this product were identical with those of an authentic sample.


(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.

The aqueous washes were then combined and extracted five times with ether. The ether layers were combined and dried over anhydrous magnesium sulfate. The ether was distilled through a 30-in. Vigreux column until less than 300 mL of solution remained. The aqueous washes were then combined and extracted five times with ether. The ether layers were combined and dried over anhydrous magnesium sulfate, and concentrated by rotary evaporation to give a colorless oil (9.6 g). Vacuum distillation in a short-path apparatus gave 92.9 g.

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 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 cooled to 0 °C. The mixture of product and excess hypochlorite 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% 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 then 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 liquid which had 1H NMR and IR spectra and VPC retention time identical with those of an authentic sample.

Acknowledgment. We gratefully acknowledge to the National Science Foundation (NSF CHE78-27084) and the National Institutes of Health (AM 20398) for generous financial support of this work. We are also grateful to the National Institutes of Health for a National Research Service Award (1 F32 CA 06455 01) to H.N.W. We thank Dr. M. E. Jung for kindly providing samples of the diols used in this work.

Registry No. (--)=Borneol, 464-45-9; (--)=isoborneol, 24393-70-2; (--)=menthol, 227-24-9; cyclohexanol, 108-93-0; 2,5,5-trimethyl-1-cyclohexanol, 72210-25-5; (--)=isocamphor, 72310-28-1; 5a-androstene-3,17-diol, 571-20-0; norbornol, 1362-88-4; 2-octanol, 123-96-6; 1-decy1 alcohol, 112-30-1; 2-ethyl-1,3-hexanediol, 94-96-2; (-)=menthone, 10407-97-9; cyclohexanol, 108-94-1; 2,2,5-trimethyl-1-cyclohexanol, 933-36-8; 9-cyanocamphor, 70696-71-5; 5a-androstene-3,17-dione, 846-46-8; norcamphor, 497-38-1; 2-octanone, 111-13-7; decyl deca-noate, 1654-86-0; 2-ethyl-1-hydroxy-3-hexanone, 29790-80-5.


Oligonuclear Ruthenocene Complexes

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In continuation of our studies of oligo- and polymeric metallocones as precursors of mixed-valence systems, 1 we wished to prepare oligoruthenocenoylenes of type 3 (n = 2-4). The availability of the 1,1′-diido derivative 1, 2 coupled with the observed ease of lithiation of the ruthenocene complex, 3, 4 suggested a ready synthetic pathway to 3 (eq 1) via coupling of 1 with the 1,1′-dilithiocyclohexane 2 (chelated with TMEDA = N,N,N′,N′-tetramethylethlenediamine).

$$\text{2} \rightarrow \text{3}$$

The analogous reaction involving the diido and (TMEDA-chelated) dilithium derivatives of the iron generator, ferrocene, had previously been found to proceed smoothly in ether solvents, giving up to 85% yields of coupling products including higher polymers. 5

In the present investigation, 1 was allowed to react with 2 in a molar ratio of 2:5 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 1,2 ferrocene polymerization studies, including the use of tetrhydrofurane 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 nucleophile attack than the corresponding diidoferrocene because of reduced electron density on the rings in the ruthenium complex, 6, 7 our failure to attain, or at least approach, the high coupling yields achieved in dilithioferrocene/diidoferrocene 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 1) 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.


