yield). An analytical sample was isolated by preparative GLC (see Table I for NMR data): ir (neat) 3080 (w), 3020 (m), 2970 (m), 2930 (s), 1455 (m), 740 (s), 718 (m), and 700 cm^{-1} (m); mass spectrum *m/e* 144 (molecular ion). Anal. Calcd for $C_{11}H_{12}$: C, 91.61; H, 8.39. Found: C, 91.47; H, 8.43.

Generation of Benzyne in the Presence of *trans*-1,3-Pentadiene. When the above procedure was applied using the trans diene, a mixture of 1 and 2 was isolated (62% yield combined). The ratio 1:2 was 3.9:1 (GLC). The isomers were separated by preparative GLC.

1: NMR ($CDCl_3$) 1.31 (d, J = 6.8 Hz, 3 H, methyl), 3.38 (broad s, 3 H, benzylic), 5.88 (m, 2 H, olefinic), and 7.16 ppm (m, 4 H, aromatic); ir (neat) 3035 (w), 3026 (m), 2970 (m), 2930 (m), 2880 (m), 1581 (w), 1492 (m), 1450 (m), 747 cm^{-1} (s); mass spectrum *m/e* 144 (molecular ion). Anal. Calcd for $C_{11}H_{12}$: C, 91.61; H, 8.39. Found: C, 91.46; H, 8.43.

2: NMR, see Table I; ir 3080 (w), 3030 (m), 2970 (m), 2930 (w), 1460 (m), 965 (s), 745 cm^{-1} (s); mass spectrum *m/e* 144 (molecular ion). Anal. Calcd for $C_{11}H_{12}$: c, 91.61; H, 8.39. Found: C, 91.61; H, 8.33.

Oxidation of 3.[17] To 29 ml of a $NaIO_4$–$KMnO_4$ solution (0.38 M $NaIO_4$ and 0.0064 M $KMnO_4$) was added 20 ml of *t*-BuOH and enough K_2CO_3 to achieve a pH of 8. To this was added 20 mg of **3.** The solution was stirred at room temperature for 5 hr. After acidification with 2 M HCl, the solution was extracted five times with a 1:1 mixture of ether and pentane. The combined organic extracts were dried over anhydrous $MgSO_4$. The solvent was removed by distillation. The acetic acid in this residue was removed by vapor transfer and identified by comparing its NMR spectrum with that of authentic material. The mass spectrum of the residue showed a molecular ion (*m/e* 148) consistent with $C_9H_8O_2$. The NMR spectrum was identical with that of independently prepared benzocyclobutene-1-carboxylic acid.

Oxidation of 1. A mixture of 40 mg of **1,** 63.5 mg of dichlorodicyanoquinone, and 1 ml of benzene was brought to reflux for 15 min. After cooling, 50 ml of pentane was added and the mixture was filtered. The filtrate was then passed through a short column of alumina using pentane as the eluent. The solvent was removed under vacuum. The NMR spectrum was identical with that of commercial 1-methylnaphthalene.

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Registry No.—**1,** 21564-70-5; **2,** 54384-63-3; **3,** 54384-64-4; benzyne, 462-80-6; *cis*-1,3-pentadiene, 1574-41-0; *trans*-1,3-pentadiene, 2004-70-8; benzenediazonium 2-carboxylate, 1608-42-0; benzocyclobutene-1-carboxylic acid, 14381-41-0; dichlorodicyanoquinone, 84-58-2; 1-methylnaphthalene, 90-12-0.

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(4) A few exceptions to this generalization are found in the addition of benzyne to 1,3-cycloheptadiene,[5] 1,3,5-cycloheptatriene,[5] and *trans*-cyclooctene.[2b] The conformational peculiarities of these ring systems[6] apparently prevent the appropriate geometry for what is probably a concerted ene reaction.[1b]

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(6) P. Crews, *J. Chem. Soc. D,* 583 (1971); M. Traetteberg, *J. Am. Chem. Soc.*, **86,** 4265 (1964); P. C. Manor, D. P. Shoemaker, and A. S. Parkes, ibid., **92,** 5260 (1970).

(7) (a) Crews' modification[1b] of Friedman's procedure[7b] was used. (b) F. M. Logullo, A. H. Seitz, and L. Friedman, *Org. Synth.*, **48,** 12 (1969).

(8) A similar oxidation of **2** was not possible owing to insufficient material. From their NMR spectra, it is apparent that **2** and **3** are geometric isomers. Furthermore, **2** has a strong band at 965 cm^{-1} in its ir spectrum, indicating the trans propenyl group. This band was absent in **3.**

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(10) D. Craig, *J. Am. Chem. Soc.*, **72,** 1678 (1950); D. Craig, J. J. Shipman, and R. B. Fowler, ibid., **83,** 2885 (1961).

(11) The necessary presence of picric acid in the maleic anhydride [2 + 4] addition to *cis*-1,3-pentadiene[10] obfuscates this comparison. The acid reportedly retards polymerization of the diene, but may also exert some catalytic effect.

(12) Stewart[13] has placed a relative rate limit on the addition of tetracyanoethylene to the cis and trans dienes. The ratio $k_{cis}/k_{trans} = 10^{-5}$ was based on the rate of color fading of the complex formed between the cis diene and TCNE. No adduct was isolated.

(13) C. A. Stewart, Jr., *J. Org. Chem.*, **28,** 3320 (1963).

(14) This is not the case for monoolefins. Stepwise [2 + 2] addition[2b] to simple olefins does not result in an allylic intermediate, which is the case when a diene is the benzyne acceptor.

(15) A reviewer commented on the observed [2 + 2] addition of benzyne to disubstituted double bonds in 2,3-dimethyl-1,3-butadiene[2a] and *trans,trans*-2,3-hexadiene.[2c] Although [2 + 2] addition was found in these systems, ene addition still predominated (although slightly with the 2,4-hexadiene). It is obviously a delicate balance of steric and electronic factors that determines the ene/[2 + 2] ratio. We thank the reviewer for his comments.

(16) In a recent publication, M. Jones, Jr., and coworkers report the thermolysis of **2** and **3,** which were prepared by the addition of benzyne (generated from the photolysis of phthaloyl peroxide) to *trans*- and *cis*-1,3-pentadiene: M. R. DeCamp, R. H. Levin, and M. Jones, Jr., *Tetrahedron Lett.*, 3575 (1974).

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Efficacious Cleavage of the Benzyl Ether Protecting Group by Electrochemical Oxidation

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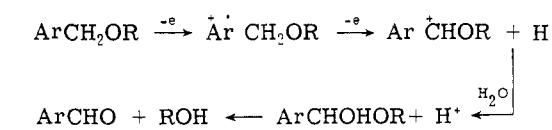
An effective way to protect an alcohol is via its benzyl ether.[2] However, the common ways used to remove this blocking group (i.e., catalytic hydrogenation or alkali metal reduction) involve conditions which may not be applied to molecules where other easily reduced functional groups are present. We wish to report a straightforward procedure whereby a benzyl group can be cleanly removed electrochemically under mild, *oxidative* conditions.[3] This provides a complementary alternative to the presently used reductive methods.

Early work by Lund[4] revealed that the oxidation potential for the benzyloxy group was low enough to allow electrochemical oxidation. This work was followed by other studies[5-7] which indicated that the oxidation of benzylic ethers, esters, or alcohols will proceed to form benzaldehyde. The probable mechanism of this reaction is as shown in Scheme I. Even though previous workers have focused

Scheme I



attention on the formation of the aromatic aldehyde, concomitant formation of the alcohol in the above sequence has been confirmed by Miller,[5] who, in fact, suggested the possible usefulness of this reaction as a method of cleaving benzyl protecting groups. However, the generality and utility of this reaction apparently have not been tested, possibly because of Miller's observation that constant "pulsing" of the electrode potential was necessary in order to obtain reasonable yields. Without this pulsing, Miller reports that under his conditions (anhydrous acetonitrile with added

Table I
Isolated Yields of Alcohols from Electrolyses of Their p-Anisyl Ethers at 1.65 V (SCE)

Alcohol	Yield, %	Alcohol	Yield, %
1-Octanol	98		74[a]
2-Octanol	90		
l-Borneol	93	$PhCH_2OH$	75
Cholesterol	89	2,6-Dichlorobenzyl alcohol	88
$PhOCH_2CH_2OH$	74	Cyclododecanol	89

[a] The dianisyl ether was used.

sodium carbonate) the anode becomes fouled, causing a significant drop in the current.

Viewing the above reaction in terms of its potential usefulness in the synthesis of complex molecules, we have sought to test the generality of the reaction on a variety of compounds, and to develop a simple methodology whereby consistently high yields would be possible.

Consideration of the mechanism in Scheme I would lead one to expect that an electron-supplying substituent on the aromatic ring would make the initial oxidation step easier. This is in fact observed;[4] so we have concentrated our efforts on the study of *p*-methoxy substituted benzyl ethers, thus enabling us to work at a potential lower than is necessary for the oxidation of most other substituted benzyl ethers, or simpled unsubstituted benzyl ethers. Although acids have been protected as their *p*-anisyl esters,[8,9] *p*-anisyl ethers have not been widely used previously, probably because no particular advantage over benzyl ethers was envisaged. We anticipate no problems in using them, however, and they are easily prepared.

Utilizing controlled-potential electrolysis, we have obtained good yields in a variety of functionalized systems when the electrolysis is performed in 60–85% aqueous acetonitrile[10] with lithium perchlorate (0.1 *M*) as the supporting electrolyte. The presence of water (as an available nucleophile capable of attacking the intermediate benzyloxy carbonium ion) produces a much cleaner reactions and obviates the need for electrode "pulsing", thus simplifying the experimental technique.[5] The electrolyses were performed at +1.65 V relative to SCE. Table I summarizes the results.

Since convenience in the isolation of the free alcohol is an important criterion, it should be pointed out that the other product of this reaction, anisaldehyde, is readily removed from the reaction mixture by extraction with saturated aqueous sodium bisulfite solution. In each case the product was appropriately purified (usually by distillation) to give the isolated yields listed in Table I. In some of the compounds studied it is not possible to remove the protecting group using standard reductive techniques without concomitant reduction of other functionality.

Although we have concentrated mainly on anisyl ethers owing to their low oxidation potential, benzyl ethers (or other types of substituted benzyl ethers) may also be removed in this manner by raising the oxidation potential to 2.0 V. The results of the oxidation of the benzyl ether of *l*-borneol is an illustrative example (68% yield). Since the oxidation potentials of *p*-anisyl and benzyl are substantially different, it should be possible[11] to have two different alcohol groups in the same molecule protected, one perhaps as the *p*-anisyl ether and the other as the benzyl ether, and to selectively remove first the anisyl protecting group by electrolysis at +1.65 V, and at a later time to remove the benzyl by electrolysis at +2.0 V. This high degree of selectivity is illustrated by the electrolyses of the *p*-anisyl ethers of benzyl alcohol and 2,6-dichlorobenzyl alcohol, which electrolyzed to produce benzyl alcohol and 2,6-dichlorobenzyl alcohol, respectively, uncontaminated with any anisyl alcohol.

Experimental Section

p-Anisyl chloride was prepared by treating anisyl alcohol with thionyl chloride in ether containing a catalytic amount of pyridine. Distillation gave the chloride in 86% yield, bp 85–90° (2 mm) [lit.[12] bp 101–103° (8–10 mm)].

Preparation of Anisyl Ethers. The ethers were prepared via a Williamson synthesis. The general procedure involved stirring the required alcohol with sodium hydride in anhydrous DMF until gas evolution had ceased. The resulting solution was treated with an equimolar amount of anisyl chloride. After 1 hr an additional amount of anisyl chloride was added so that it was present in a 20% excess. After stirring overnight, the solution was poured over ice and the resulting suspension was extracted with chloroform. The organic phase was washed with sodium hydroxide solution and with water, dried with magnesium sulfate, and concentrated to give the desired ether. Before electrolysis the crude ethers were distilled, recrystallized, or chromatographed.

Electrochemical Apparatus. A simple electrochemical cell was constructed from a beaker and a glass tube of about 75-ml capacity which was sealed at one end with a sintered glass frit of medium porosity. The frit was covered with a gel[13] of 0.1 *M* lithium perchlorate in DMF and methyl cellulose. This isolates the cathode and anode, while maintaining electrical conductivity between the two. The tube was suspended in the beaker and the inside of the tube was utilized as the anodic chamber. A platinum wire cathode and a platinum mesh anode were used. The power source was a Wenking 70HVI potentiostat (Brinkmann Instruments).

Electrochemical Oxidation. General Procedure. A solution of 60–85% aqueous acetonitrile was made 0.1 *M* in lithium perchlorate.[10] This solution was placed in the electrochemical cell. To the anode chamber was added 4 mmol of the compound to be electrolyzed, and the solution was electrolyzed at +1.65 V (SCE) until the initial current of ca. 200 mA had dropped to less than 3 mA. The anolyte was concentrated in vacuo with minimal heating until the acetonitrile was removed. (The solution may be neutralized before concentration to minimize any reaction under the acidic conditions of the concentrated solution, but for the compounds listed in Table I we observed no undesirable reactions when this neutralization was omitted. *Caution: Under no circumstances should the solution be evaporated to dryness.*) The resulting aqueous suspension was saturated with sodium chloride and extracted with ether. The combined ether extract was washed with saturated sodium bisulfite solution, dried, and concentrated to yield products which were essentially pure by NMR analysis. The residue was then appropriately purified. The yields of the purified materials are listed in Table I.

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Registry No.—*p*-Anisyl chloride, 824-94-2; *p*-anisyl alcohol, 105-13-5; thionyl chloride, 7719-09-7; 1-octanol, 111-87-5; 2-octanol, 123-96-6; *l*-borneol, 464-45-9; cholesterol, 57-88-5; 2-phenoxyethanol, 122-99-6; 2,5-dimethyl-3-hexyne-2,5-diol, 142-30-3; benzyl alcohol, 100-51-6; 2,6-dichlorobenzyl alcohol, 15258-73-8; cyclododecanol, 1724-39-6; 1-octanol *p*-anisyl ether, 54384-75-7; 2-octanol *p*-anisyl ether, 54384-76-8; *l*-borneol *p*-anisyl ether, 54384-77-9; cholesterol *p*-anisyl ether, 33999-75-6; 2-phenoxyethanol *p*-anisyl ether, 54384-78-0; 2,5-dimethyl-3-hexyne-2,5-diol di-*p*-anisyl ether, 54384-79-1; benzyl alcohol *p*-anisyl ether, 3613-53-4; 2,6-dichlorobenzyl alcohol *p*-anisyl ether, 54384-80-4; cyclododecanol *p*-anisyl ether, 54384-81-5.

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Reactions of Molecular Bromine Chloride and Amine–Bromine Chloride Complexes with Cyclopentadiene

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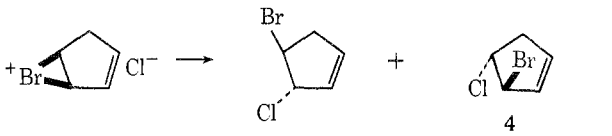
A survey of the literature reveals that there has been one study of the addition of bromine chloride to an allene,[1] and many investigations of the addition of this electrophile to olefins,[2a-e] but that no studies on the addition of bromine chloride to conjugated dienes have been undertaken. Earlier studies[2b-e] established that molecular bromine chloride adds to olefins via a bromonium ion–chloride ion ion pair, in which the rate-determining step involves formation of this ion pair. In the most recent investigation,[2a] Bellucci et al. compared the addition of bromine chloride with that of pyridine–bromine chloride complex, and concluded that the second, product-determining step is rate determining in the case of the complex.[3]

It seemed to us that it would be of interest to investigate the reaction of these halogenating agents with the conjugated diene cyclopentadiene. We chose cyclopentadiene because it offered the possibility of both cis and trans 1,2 and 1,4 addition, and because we had recently studied the additions of chlorine[4] and bromine[5] to this diene. In the present study we were particularly interested in comparing the addition of bromine chloride with amine–bromine chloride complexes, since if these reagents do involve different rate-determining steps they would likely produce a different mixture of stereoisomeric bromochlorocyclopentenes.

The possibility of anti-Markovnikov addition was also considered, since chloride ion could add to either of the carbons (bonded to bromine) as illustrated in the following reaction.



1 Markovnikov 4 anti-Markovnikov

Delocalization of the charge (resulting in unsymmetrical bridging, i.e., weaker bonding between carbon 3 and bromine) is probable here since a secondary carbonium ion would result.[6] Extensive delocalization should favor cis attack of chloride ion (as in the case of the chlorination of cyclopentadiene[4]) to give cis 1,2 addition as shown below.

5

Results and Discussion

The addition of bromine chloride and amine–bromine chloride complexes to cyclopentadiene resulted in the formation of only three isomeric bromochlorocyclopentenes: *trans*-4-bromo-3-chlorocyclopentene (**1**), *trans*-3-bromo-5-chlorocyclopentene (**2**), and *cis*-3-bromo-5-chlorocyclopentene (**3**). The ratios and yields of these isomers formed under various conditions are shown in Table I.

2 3

The data in Table I show that all of the amine–bromine chloride complexes react with cyclopentadiene to give very similar mixtures of bromochlorocyclopentenes, and that the product composition from the complexes is considerably different from that of bromine chloride. In particular, bromine chloride gives significantly more cis 1,4 addition

Table I
Addition of Bromine Chloride and Amine–Bromine Chloride Complexes to Cyclopentadiene

Halogenating agent	Solvent	Temp, °C	Bromochlorocyclopentenes 1	2	3	Yield, %
BrCl	C_5H_{12}	−15	34	18	48	78
BrCl	CH_2Cl_2	−15	22	15	63	68
BrCl	CCl_4	−15	25	12	63	76
			27	15	58	
Pyridine–BrCl	C_5H_{12}	−15	53	21	26	81
Pyridine–BrCl	CH_2Cl_2	−15	90	4	6	78
Pyridine–BrCl	CCl_4	−15	51	22	27	86
BrCl	CH_2Cl_2	25	25	15	60	64
Pyridine–BrCl	CH_2Cl_2	25	79	10	11	72
Quinoline–BrCl	CH_2Cl_2	25	63	16	21	83
3,5-Lutidine–BrCl	CH_2Cl_2	25	83	9	8	74
2,6-Lutidine–BrCl	CH_2Cl_2	25	73	13	14	108