the aid of thin-layer chromatography using precoated silica gel GF plates (Analtech).

tert-Butylamine–borane was purchased from Callery Chemical Co., Ltd., and was used without purification. Dichloromethane and aluminum chloride were used without purification. Most of the compounds used in this study were commercial products, and some compounds were prepared from known procedures. The products obtained were readily available materials in most cases. Otherwise, identification was based on ^{1}H NMR, IR, mass spectral data and elemental analyses.

Since the reactions performed are all similar in many aspects, a typical reaction is described as a specific example.

Preparation of *p*-Methoxyphenethyl Bromide. To a cold (0 °C), stirred suspension of aluminum chloride (4.02 g, 30 mmol) in dichloromethane (100 mL) was added *tert*-butylamine–borane (5.17 g, 60 mmol). The resulting mixture was allowed to stir at 0 °C for 10 min. A clear solution resulted (premixing the two reagents is recommended for reproducible results). A solution of 4′-methoxy-2-bromoacetophenone (2.14 g, 10 mmol) in dichloromethane (10 mL) was added. The resulting mixture was stirred at 0 °C for 2 h. Cold dilute HCl (0.1 N, 50 mL) was added dropwise to the reaction mixture. The product was extracted with ethyl acetate. The combined organic extracts were washed with 50 mL of 0.1 N HCl twice and then with brine. Concentration of the organic extracts gave an oil, which was purified by flash chromatography on silica gel (eluted with 5% ethyl acetate in hexane). The chromatographed material was distilled at 10 mm (Kugelrohr) to give 1.73 g of *p*-methoxyphenethyl bromide (86% yield, bp 240 °C/10 mm). ^{1}H NMR and mass spectral data of this material were identical with authentic material.

Registry No. *tert*-Butylamine–borane, 7337-45-3; 1-(4-chlorophenyl)ethanone, 99-91-2; 1-(3,4-dichlorophenyl)ethanone, 2642-63-9; 1-(2,4-dichlorophenyl)ethanone, 2234-16-4; (3,4-dichlorophenyl)phenylmethanone, 6284-79-3; 2,4-dichlorobenzaldehyde, 874-42-0; 2-naphthalenecarboxaldehyde, 66-99-9; 1-[1,1′-biphenyl]-4-ylethanone, 92-91-1; 4-acetylbenzoic acid, methyl ester, 3609-53-8; 4-(4-chlorophenyl)-4-oxobutanoic acid, 3984-34-7; 1-[2-[(acetyloxy)methyl]-4-(3-bromopropoxy)phenyl]ethanone, 117526-93-9; 1-[2-bromo-4-(methylthio)phenyl]-1-propanone, 102831-33-4; 2-bromo-1-(4-methoxyphenyl)ethanone, 2632-13-5; 1-(4-nitrophenyl)ethanone, 100-19-6; 1-chloro-4-ethylbenzene, 622-98-0; 1,2-dichloro-4-ethylbenzene, 6623-59-2; 2,4-dichloro-1-ethylbenzene, 54484-62-7; 1,2-dichloro-4-(phenylmethyl)benzene, 64543-53-9; 2,4-dichlorobenzenemethanol, 1777-82-8; 2-methylnaphthalene, 91-57-6; 4-ethyl-1,1′-biphenyl, 5707-44-8; 4-ethylbenzoic acid, methyl ester, 7364-20-7; 4-ethylbenzenemethanol, 768-59-2; 4-(1-hydroxyethyl)benzoic acid, methyl ester, 84851-56-9; 4-chlorobenzenebutanol, 19967-22-7; 5-(3-bromopropoxy)-2-ethylbenzenemethanol, 117526-94-0; 2-bromo-4-(methylthio)-1-propylbenzene, 102831-34-5; 1-(2-bromoethyl)-4-methoxybenzene, 14425-64-0; 1-(1-chloroethyl)-4-nitrobenzene, 19935-75-2; 4-ethylbenzenamine, 589-16-2; α-methyl-4-nitrobenzenemethanol, 6531-13-1.

Structure Elucidation of Naturally Occurring Long-Chain Mono- and Dienes

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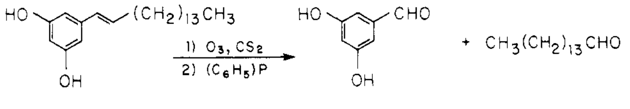
Recently, we isolated from *Hakea trifurcata* and *Hakea amplexicaulis* several 5-alkenylresorcinols capable of mediating DNA strand scission.[1] The compounds were isolated initially as complex mixtures of resorcinols, which differed solely in the lengths of individual alkenyl substituents and in the positions of double bonds. Separation of these air-sensitive compounds could be effected by C_{18} reverse-phase HPLC but only on a modest scale. In order to determine the position of unsaturation on a microscale, we developed a technique whereby individual 5-alkenylresorcinols were subjected to oxidative cleavage with O_3 and the products of cleavage were identified directly by CI mass spectrometric analysis of the product mixture. The details of this analytical method are reported herein and constitute a useful supplement to currently available methods.[2,3]

Results and Discussion

Due to the limited amounts of naturally derived 5-alkenylresorcinols available, initial studies were carried out with use of synthetic model compounds. Successive treatments of a CS_2 solution of 1,3-dihydroxy-5-hexadec-*trans*-1′-enylbenzene (1) with O_3 at −78 °C, and then with triphenylphosphine, afforded a product mixture whose chemical ionization mass spectrum (supplementary material, Figure 1) reflected the presence of the expected aldehydes (**2** and **3**, pseudomolecular ions at *m/z* 139 and 227, respectively) as well as peaks derived from triphenylphosphine and its oxide (*m/z* 185, 263, 279, and 307). Verification of the origin of the peaks attributed to triphenylphosphine and its oxide was achieved by repetition of the ozonolysis experiment in the absence of olefin; the resulting mass spectrum (supplementary material, Figure 2) contained peaks at *m/z* 185, 263, 279, and 447 (attributed to $[(C_6H_5)_3P - (C_6H_5)_2P + H]^+$). While the mass spectrum contained the information needed to assign the position of unsaturation, the peak corresponding to 3,5-dihydroxybenzaldehyde was relatively small, presumably indicating decomposition either during ozonolysis or



1 M_r 332

2 M_r 138

3 M_r 226

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[1] (a) Scannell, R. T.; Barr, J. R.; Murty, V. S.; Reddy, K. S.; Hecht, S. M. *J. Am. Chem. Soc.* **1988**, *110*, 3650. (b) Barr, J. R.; Murty, V. S.; Yamaguchi, K.; Hecht, S. M. *Chem. Res. Toxicol.* **1988**, *1*, 204.

[2] (a) Ferrer-Correia, A. J. V.; Jennings, K. R.; Sen Sharma, D. K. *J. Chem. Soc., Chem. Commun.* **1975**, 973. (b) Ferrer-Correia, A. J. V.; Jennings, K. R.; Sen Sharma, D. K. *Org. Mass Spectrom.* **1976**, *11*, 867. (c) Chi, R.; Harrison, A. G. *Anal. Chem.* **1981**, *53*, 34. (d) Ghaderi, S.; Kulkarni, P. S.; Ledford, E. B.; Wilkins, C. L.; Gross, M. L. *Anal. Chem.* **1981**, *53*, 428. (e) Tomer, K. B.; Crow, F. W.; Gross, M. L. *J. Am. Chem. Soc.* **1983**, *105*, 5487. (f) Peake, D. A.; Gross, M. L. *Anal. Chem.* **1985**, *57*, 115 and references therein. (g) Jensen, N. J.; Tomer, K. B.; Gross, M. L. *Anal. Chem.* **1985**, *57*, 2018.

[3] (a) Wolff, R. E.; Wolff, G.; McCloskey, J. A. *Tetrahedron* **1966**, *22*, 3093. (b) Alpin, R. T.; Coles, L. *Chem. Commun.* **1967**, 858. (c) Beroza, M.; Bierl, B. A. *Anal. Chem.* **1967**, *39*, 1131. (d) Niehaus, W. G.; Ryhage, R. *Tetrahedron Lett.* **1967**, *49*, 5021. (e) Capella, P.; Zorzut, C. M. *Anal. Chem.* **1968**, *40*, 1458. (f) Eglinton, G.; Hunneman, D. H. *Org. Mass Spectrom.* **1968**, *1*, 593. (g) Niehaus, W. G.; Ryhage, R. *Anal. Chem.* **1968**, *40*, 1840. (h) Tumlinson, J. H.; Heath, R. R.; Doolittle, R. E. *Anal. Chem.* **1974**, *46*, 1309. (i) Minniken, D. E. *Lipids* **1975**, *10*, 55. (j) Dommes, V.; Wirtz-Peitz, F.; Kunau, W.-H. *J. Chromatogr. Sci.* **1976**, *14*, 361. (k) Ariga, T.; Araki, E.; Murata, T. *Anal. Biochem.* **1977**, *83*, 474. (l) Ariga, T.; Araki, E.; Murata, T. *Chem. Phys. Lipids* **1977**, *19*, 14. (m) Francis, G. W.; Tande, T. *J. Chromatogr.* **1978**, *150*, 139. (n) Janssen, G., Parmentier, G. *Biomed. Mass Spectrom.* **1978**, *5*, 439. (o) Murata, T.; Ariga, T.; Araki, E. *J. Lipid Res.* **1978**, *19*, 172. (p) Bierl-Leonhardt, B. A.; DeVilbiss, E. D.; Plimmer, J. R. *J. Chromatogr. Sci.* **1980**, *18*, 364. (q) Blomquist, G. J.; Howard, R. W.; McDaniel, C. A.; Remaley, S.; Dwyer, L. A.; Nelson, D. R. *J. Chem. Ecol.* **1980**, *6*, 257. (r) Horiike, M.; Miyata, N.; Hirano, C. *Biomed. Mass Spectrom.* **1981**, *8*, 41. (s) Suzuki, M.; Ariga, T.; Sekine, M.; Araki, E.; Miyatake, T. *Anal. Chem.* **1981**, *53*, 985. (t) Kidwell, D. A.; Biemann, K. *Anal. Chem.* **1982**, *54*, 2462. (u) Buser, H.-R.; Arn, H.; Guerin, P.; Rauscher, S. *Anal. Chem.* **1983**, *55*, 818. (v) Cervilla, M.; Puzo, G. *Anal. Chem.* **1983**, *55*, 2100.

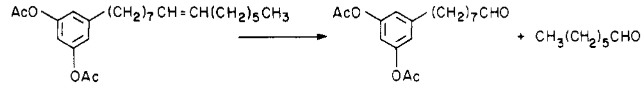
0022-3263/89/1954-0494$01.50/0

mass spectral analysis. In an effort to obtain a more easily interpreted mass spectrum, the phenolic hydroxyl groups in 1 were protected by methylation or acetylation prior to analysis.

As anticipated, ozonolysis of 1,3-dimethoxy-5-hexadec-*trans*-1′-enylbenzene (**4**) in carbon disulfide followed by decomposition of the formed ozonide with triphenylphosphine afforded a product mixture whose mass spectrum more clearly reflected the chemical conversion of interest. Strong pseudomolecular ions were observed at *m*/*z* 167 (corresponding to 3,5-dimethoxybenzaldehyde (**5**)) and *m*/*z* 227 (for pentadecanal (**3**)). The acetylated resorcinol derivative, 1,3-diacetoxy-5-hexadec-*trans*-1′-enylbenzene (**6**), also afforded a product mixture that gave an easily interpreted mass spectrum (supplementary material, Figure 3); in addition to the ion at *m*/*z* 227 corresponding to pentadecanal, a strong peak was also observed at *m*/*z* 223 (for 1,3-diacetoxybenzaldehyde). Because acetylation of the naturally derived alkenylresorcinol derivatives proved more convenient than methylation, all subsequent work was carried out with resorcinol *O*-acetyl derivatives.

The solvent used for the ozonolysis reaction and the reducing agent employed to cleave the ozonide were found to be important. Treatment of 1,3-dimethoxy-5-hexadec-*trans*-1′-enylbenzene with ozone in methanol followed by reduction of the ozonide with dimethyl sulfide produced reaction mixtures that yielded very complicated positive and negative ion CI mass spectra. Ozonolysis reactions run in dichloromethane utilizing either dimethyl sulfide or zinc dust and acetic acid also yielded very complicated mass spectra, which made identification of the derived aldehydes tedious. Stabilization of the aldehydes was attempted by in situ derivatization with (2,4-dinitrophenyl)hydrazine, but the presence of many peaks again made facile identification of the formed aldehydes difficult. The simplest and most easily interpreted spectra arose from reactions that were run in CS_2 and from ozonides that were reduced with triphenylphosphine.[4]

The first natural product analyzed for position of unsaturation was 1,3-dihydroxy-5-pentadec-*cis*-8′-enylbenzene, which had been isolated both from *Hakea trifurcata* and *Hakea amplexicaulis*.[1] Ozonolysis of the corresponding di-*O*-acetyl derivative (**8**; M_r 402) in CS_2, followed by treatment with $(C_5H_6)_3P$, afforded a product mixture that was analyzed directly by chemical ionization mass spectrometry (Figure 1). The positive ion mass spectrum contained MH^+ ions at *m*/*z* 321 and 115; these were assigned as pseudomolecular ions for 8-(1,3-diacetoxyphenyl)octanal and heptanal, respectively.[5] This assignment established the position of unsaturation unambiguously, allowing the structure of the natural product to be specified completely.[8] The structure established for this natural product was verified by total synthesis,[1a] which also serves to support the validity of the analytical method described here.



8 M_r 402 **9** M_r 320 **10** M_r 114

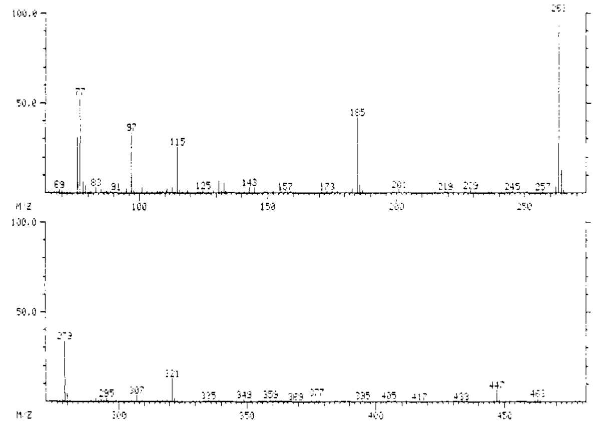


Figure 1. Chemical ionization mass spectrum of the products resulting from ozonolysis of 1,3-diacetoxy-5-pentadec-*cis*-8′-enylbenzene (**8**); peaks for aldehydes **9** and **10** were present at *m*/*z* 321 and 115, respectively. The peak at *m*/*z* 97 was shown to result from dehydration of heptanal.

The second natural product analyzed was 1,3-dihydroxy-5-heptadec-*cis*-8′-enylbenzene, which had been isolated from *Hakea amplexicaulis*.[1b] Ozonolysis of the corresponding diacetate (**11**) afforded a product mixture whose CI mass spectrum contained peaks at *m*/*z* 321 and 143 (supplementary material, Figure 4). Assignment of these peaks as MH^+ ions of 8-(1,3-diacetoxy-5-phenyl)octanal (**9**) and nonanal (**12**) established the position of unsaturation for the natural product.[8]

Also isolated from *Hakea trifurcata* was a resorcinol derivative having M_r 412. This compound was shown to contain two dihydroxybenzene groups linked through an unbranched alkene. Acetylation afforded a tetraacetate (**13**), which was subjected to ozonolysis and subsequent analysis of the crude product mixture by CI mass spectrometry (supplementary material, Figure 5). As shown in the figure, both 8-(1,3-diacetoxy-5-phenyl)octanal (**9**) and 6-(1,3-diacetoxy-5-phenyl)hexanal (**14**) could be identified by the appearance of MH^+ ions at *m*/*z* 321 and 293, respectively. Although not as strong as the spectra obtained from the first two natural products (vide supra), the relevant aldehydes could still be identified readily, permitting the structure of this resorcinol derivative to be established as 1,3-dihydroxy-5-(14′-(3″,5″-dihydroxyphenyl)tetradec-*cis*-6′-enyl)benzene.[1a,8]

Of special interest in the context of development of methodology for locating position of unsaturation was a 5-alkenylresorcinol derivative from *Hakea amplexicaulis* found to have two double bonds. Ozonolysis of the diacetate (**15**; M_r 428) gave a product mixture whose CI mass spectrum is shown in Figure 6 (supplementary material). As anticipated, this spectrum reflected the presence of two aldehydes, **9** (*m*/*z* 321) and hexanal (**16**; *m*/*z* 101), as well as a dialdehyde (malonodialdehyde, **17**; *m*/*z* 73). This spectrum permitted the structure of the natural product to be assigned as 1,3-dihydroxy-5-heptadeca-8′,11′-dienylbenzene.[1b]

The foregoing examples establish the utility of the ozonolysis–mass spectrometry procedure for location of the

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[4] An analogous observation has been made by Beroza and Bierl; they analyzed aldehydes derived from alkenes by gas chromatography and found that the chromatographic analyses were optimal when the aldehydes were produced by successive treatments with O_3/CS_2 and then with $(C_6H_5)_3P$ (Beroza, M.; Bierl, B. *Anal. Chem.* **1967**, *39*, 1131).

[5] The peak at *m*/*z* 97 was attributed to loss of water from heptanal. The elimination of water from heptanal has been observed[6] and studied mechanistically by several investigators.[7] A chemical ionization mass spectrum of heptanal was also taken under the same conditions used for analysis of the ozonolysis reaction mixture. Again, loss of water was seen and the $MH^+/(MH - H_2O)^+$ ratios for the two spectra were very similar.

[6] Harrison, A. G. *Chemical Ionization Mass Spectrometry*; CRC Press: Boca Raton, FL, 1983.

[7] (a) Meyerson, S.; Fenselau, C.; Young, J. L; Landis, W. R.; Selke, E.; Leitch, L. C. *Org. Mass Spectrom.* **1970**, *3*, 689. (b) Jardine, I.; Fenselau, C. *Org. Mass Spectrom.* **1975**, *10*, 748. (c) Fales, H. M.; Fenselau, C.; Duncan, J. H. *Org. Mass Spectrom.* **1976**, *11*, 669.

[8] The cis configuration of the olefin was determined by ¹H NMR spectroscopy.

position of unsaturation within long-chain alkenes and the successful application of this technique for the structure elucidation of natural products. In each case, the number of cleavage products expected were seen, and unambiguous identification could be made since summation of the carbon atoms in the cleavage products always yielded the number of carbons known to be in the alkenyl chain, based on mass spectrometric analysis of the parent compound.

Relative to previous methods that involved initial separation of the ozonolysis products prior to mass spectral analysis, direct analysis by CI mass spectrometry obviates the need to define conditions useful for product purification and avoids the potential destruction of unstable products. The method requires no adaptation of the source or reagent gases required for CI mass spectral analysis.

Experimental Section

Materials. All chemical ionization mass spectrometry experiments were performed on a Finnigan 4600 gas chromatograph–mass spectrometer. Methane was used as the reagent gas for all positive ion spectra. Pulsed positive ion negative ion chemical ionization (PPINICI)[9] employed a mixture of methane–nitrous oxide (95:5). A standard direct exposure probe was utilized for all spectra with a program of 0.050–0.650 V at 0.020 V/s. The pressure of the source was 0.35 Torr.

The acetylation and ozonolysis reactions were performed in the same manner for all of the 5-alkenylresorcinols studied. These are illustrated here for 1,3-dihydroxy-5-hexadec-*cis*-8′enylbenzene.

Acetylation of 1,3-Dihydroxy-5-heptadec-*cis*-8′-enylbenzene. A solution containing 1.2 mg (3.5 μmol) of 1,3-dihydroxy-5-heptadec-*cis*-8′-enylbenzene in 500 μL of dry pyridine under argon was cooled to 0 °C and treated dropwise with 200 μL (216 mg; 2.1 mmol) of acetic anhydride. The combined solution was stirred under argon at 25 °C for 3 h. The reaction mixture was quenched by the addition of an ice chip and extracted with $CHCl_3$. The chloroform extract was washed with water, dried over $MgSO_4$, and concentrated to afford 1,3-diacetoxy-5-heptadec-*cis*-8′-enylbenzene (11) as an oily product: yield $\sim$1.5 mg; silica gel HPTLC (9:1 $CHCl_3$–CH_3OH) R_f 0.78; CI mass spectrum (positive ion), m/z 431 (M + H)$^+$.

Ozonolysis of 1,3-Diacetoxy-5-hexadec-*cis*-8′-enylbenzene (11). A solution containing 1.6 mg (3.7 μmol) of 1,3-diacetoxy-5-hexadec-*cis*-8′-enylbenzene in 250 μL of CS_2 was cooled to −78 °C and saturated with O_3. Excess O_3 was removed with a stream of argon, and the reaction mixture was treated with solid triphenylphosphine (1.0 mg; 3.8 μmol). The resulting solution was allowed to warm to room temperature and was employed directly for mass spectrometric analysis.

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Registry No. **1**, 117940-45-1; **2**, 26153-38-8; **3**, 2765-11-9; **4**, 117940-46-2; **5**, 7311-34-4; **6**, 117940-47-3; **7**, 57179-37-0; **8**, 111047-32-6; **9**, 117940-48-4; **10**, 111-71-7; **11**, 117940-49-5; **12**, 124-19-6; **13**, 117940-50-8; **14**, 117940-51-9; **15**, 114679-03-7; **15** (diacetate), 117940-52-0; **16**, 66-25-1; **17**, 542-78-9; trifurcatal A2, 22910-86-7; 1,3-dihydroxy-5-heptadec-*cis*-8′-enylbenzene, 52483-19-9; 1,3-dihydroxy-5-(14′-(3″,5″-dihydroxyphenyl)tetradec-*cis*-6′-enyl)benzene, 52483-24-6.

Supplementary Material Available: Chemical ionization mass spectra of the products resulting from ozonolysis of **1**, **6**, **11**, **13**, and **15** and from a control reaction in which a solution of CS_2 alone was treated with O_3 and then with $(C_6H_5)_3P$ (7 pages). Ordering information is given on any current masthead page.

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(9) Hunt, D. F.; Stafford, G. C., Jr.; Crow, F. W.; Russell, J. W. *Anal. Chem.* **1976**, *48*, 2098.

Observation of Diazonium Ion–Crown Ether Molecular Complexes in the Gas Phase by Field Desorption and Fast Atom Bombardment Mass Spectrometry

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Although host–guest complexation between diazonium salts and crown ethers is quite well documented in solution through kinetic, thermodynamic, and spectroscopic studies,[1–4] the extent and mode of this interaction in the gas phase has not been addressed.

We have recently shown that fragile carbocation and carbodication salts as well as onium ions can be ejected and intact monocations observed by desorption–ionization techniques.[5] Intact dication ejection was also achieved with several dication salts.[6] In relation to these studies we have utilized field desorption (FD) and fast atom bombardment (FAB) mass spectrometry to examine diazonium/crown complexation and to provide the first comparison with solution studies. The results are summarized in Table I.

In solution, the stability of the diazonium/crown complex is strongly dependent on both electronic and steric factors.[2] Electron-donating substituents increase the diazo character and weaken complexation, whereas electron-withdrawing groups increase the positive charge at nitrogens and favor complexation. ^{15}N NMR studies are also in accord with this view.[7]

The steric requirement for the formation of a diazonium/crown complex is more stringent than that for an anilinium/crown complex.[2] The accepted host–guest model in solution is an insertion-type complex (IC) for the diazonium ion,[8] for which one X-ray structure is already available, and a charge-transfer complex (CT) for the anilinium ion (Scheme I).[2]

Just how general is the IC model for diazonium ions? (a) In a detailed study, Zollinger et al.[9] investigated the kinetics of dediazoniation of crown-complexed diazonium ions for comparison with uncomplexed ArN_2^+. It was found that the kinetics were essentially the same. This means that the same intermediate, i.e., a tight aryl cation/nitrogen molecule pair, has to be involved. However,

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(1) Nakazumi, H.; Szele, I.; Zollinger, H. *Tetrahedron Lett.* **1981**, *22*, 3053.

(2) Izatt, R. M.; Lamb, J. D.; Swain, C. S.; Christensen, J. J.; Haymore, B. L. *J. Am. Chem. Soc.* **1980**, *102*, 3032 and references therein.

(3) Korzeniowski, S. H.; Petcavich, R. J.; Coleman, M. M.; Gokel, G. W. *Tetraheddron Lett.* **1977**, 2647.

(4) Beadle, J. R.; Khanna, R. K.; Gokel, G. W. *J. Org. Chem.* **1983**, *48*, 2142.

(5) Laali, K.; Fishel, D. L.; Lattimer, R. P.; Hunt, J. B. *Org. Mass. Spectrom.* **1988**, *23*, 705.

(6) Laali, K.; Maas, G.; Hunt, J. E.; Wagner, A.; Lattimer, R. P. *Tetrahedron, Lett.* **1988**, *29*, 3463.

(7) Casewit, C.; Roberts, J. D.; Bartsche, R. A. *J. Org. Chem.* **1982**, *47*, 2875.

(8) Kyba, E. P.; Helgeson, R. C.; Madan, K.; Gokel, G. W.; Tarnowski, T. L.; Moore, S. S.; Cram, D. J. *J. Org. Chem.* **1977**, *99* 2564.

(9) Nakazumi, H.; Szele, I.; Yoshida, K.; Zollinger, H. *Helv. Chim. Acta* **1983**, *66*, 1721.

(10) Laali, K.; Szele, I.; Zollinger, H. *Helv. Chim. Acta* **1983**, *66*, 1737 and references therein.

0022-3263/89/1954-0496$01.50/0