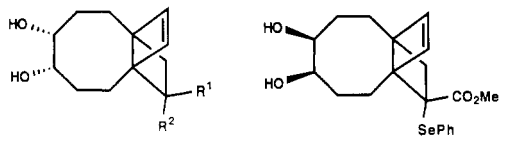
up to room temperature slowly. The solution was diluted with water and ether and the organic layer was separated. The aqueous layer was extracted with ether and the combined organic phase was washed with 1 N HCl and $NaHCO_3$ solution and dried ($MgSO_4$). Evaporation of the solvent followed by chromatography on silica gel with ether/petroleum ether (25:75) as eluent gave 1.87 g (44%) of **8an** and 2.04 g (48%) of a mixture of **8an** and **8ax** as a colorless solid. A sample of **8an** was recrystallized from petroleum ether: mp 118–119 °C; IR (KBr) 1720, 1240, 1040, 760 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.2–2.4 (m, 14 H), 2.4–2.9 (m, 2 H), 3.56 (s, 3 H), 4.0–4.4 (m, 2 H), 6.04 (d, J = 2 Hz, 1 H), 6.34 (d, J = 2 Hz, 1 H), 7.2–7.7 (m, 5 H). A mixture of **8an** and **8ax** in THF (8 mL) was treated with 3 N HCl at room temperature for 3 h. The mixture was neutralized with $NaHCO_3$ solution and extracted with dichloromethane. The extract was dried ($MgSO_4$) and the solvent was evaporated. Chromatography of the residue on silica gel with ether/methanol (97:3) as eluent gave the diol **10an** (69 mg, 23%), **10ax** (127 mg, 42%), and their mixture (92 mg, 30%) as colorless oil. **10an**: IR (neat) 3400, 1720, 1260 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.6–3.0 (m, 12 H), 3.57 (s, 3 H), 3.8–4.2 (m, 2 H), 6.12 (d, J = 2 Hz, 1 H), 6.40 (d, J = 2 Hz, 1 H), 7.2–7.6 (m, 5 H). **10ax**: IR (neat) 3400, 1720, 1260 cm^{-1}; ^1H NMR ($CDCl_3$) 1.6–3.1 (m, 12 H), 3.58 (s, 3 H), 3.7–4.1 (m, 2 H), 6.42 (s, 2 H), 7.2–7.6 (m, 5 H). To a mixture of 3.83 g (9.41 mmol) of **10an** and **10ax** and 1.35 g (17.1 mmol) of pyridine in 23 mL of dichloromethane was added 3.9 mL of 15% hydrogen peroxide (17.1 mmol) at room temperature. The mixture was stirred vigorously for 1.5 h and diluted with water, and the organic layer was separated. The aqueous layer was extracted with dichloromethane and the combined organic phase was washed with 5% HCl, $NaHCO_3$ solution, and water. After being dried ($MgSO_4$), the solvent was evaporated and the residue chromatographed quickly on silica gel (ether/methanol (97:3) as eluent) to give 1.29 g (55%) of **9a** as a colorless oil: IR (neat) 3400, 1710, 1600, 1270, 780 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.5–2.5 (m, 10 H), 3.69 (s, 3 H), 3.5–4.0 (m, 2 H), 6.46 (d, J = 2 Hz, 1 H), 6.63 (d, J = 2 Hz, 1 H), 7.13 (s, 1 H).

Similarly, phenylselenenylation of 2.00 g (6.86 mmol) of a mixture of **7bn** and **7bx** (1:3) gave **8bn** (2.12 g, 79%) as a colorless oil. The corresponding stereoisomer was not obtained in pure state. **8bn**: IR (neat) 1720, 1250, 1050, 720 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.0–2.2 (m, 15 H), 2.56 (d, J = 14 Hz, 1 H), 3.53 (s, 3 H), 3.9–4.4 (m, 2 H), 6.03 (d, J = 2 Hz, 1 H), 6.30 (d, J = 2 Hz, 1 H), 7.3–7.6 (m, 5 H). Hydrolysis of 2.10 g (4.70 mmol) of **8bn** as described above gave 1.91 g (100%) of the diol **10bn** as a colorless oil: IR (neat) 3400, 1720, 1260, 1060, 740 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.4–2.7 (m, 11 H), 2.47 (d, J = 14 Hz, 1 H), 3.53 (s, 3 H), 3.8–4.1 (m, 2 H), 5.95 (d, J = 2 Hz, 1 H), 6.27 (d, J = 2 Hz, 1 H), 7.3–7.6 (m, 5 H). Oxidation of 1.91 g (4.70 mmol) of **10bn** afforded 208 mg (18%) of **9b** as a colorless oil: IR (neat) 3400, 1710, 1600, 1280, 790 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.5–2.3 (m, 10 H), 3.71 (s, 3 H), 3.8–4.0 (m, 2 H), 6.39 (d, J = 2 Hz, 1 H), 6.55 (d, J = 2 Hz, 1 H), 7.22 (s, 1 H).



10ax R^1=SePh, R^2=CO_2Me
10an R^1=CO_2Me, R^2=SePh

10bn

8-(Methoxycarbonyl)[6]paracyclophane-3,4-dione (3). To a solution of 1.97 g (15.5 mmol) of oxalyl chloride in 31 mL of dichloromethane was added 1.61 g (20.6 mmol) of dimethyl sulfoxide in 4.1 mL of the same solvent at −78 °C. The mixture was stirred there for 40 min and then a solution of 1.29 g (5.16 mmol) of **9a** in 25 mL of dichloromethane was added. The mixture was stirred for 1 h before 5.20 g (51.6 mmol) of triethylamine was added. The mixture was warmed up slowly to ca. −5 °C, where water was added. The organic layer was separated and the aqueous layer was extracted with dichloromethane. The combined organic phase was washed with 5% HCl, $NaHCO_3$ solution, and water and dried ($MgSO_4$). Evaporation of the solvent followed by quick chromatography on silica gel (ether/petroleum ether (40:60) as eluent) gave 439 mg (35%) of **4** as a yellow oil: IR (neat) 1710, 1700, 1600, 1260, 790 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.8–2.4 (m, 4 H), 2.5–2.7 (m, 4 H), 3.70 (s, 3 H), 6.44 (d, J = 2 Hz, 1 H), 6.60 (d, J = 2 Hz, 1 H), 7.12 (s, 1 H). A similar reaction of **9b** gave **4** in 14% yield. A solution of **4** (439 mg, 1.78 mmol) in hexane (200 mL) was heated under nitrogen at 50 °C for 12 h. The solvent was evaporated and the residue chromatographed on silica gel (ether/petroleum ether (25:75) eluent) to afford 269 mg (61%) of **3** as a yellow solid. Recrystallization from hexane gave an analytical sample: mp 123–125 °C; IR (KBr) 1700, 1580, 1540, 1260, 1060, 690 cm^{-1}; MS, m/e (relative intensity) 246 (M^+) was not observed, 228 (100), 176 (66), 158 (70); ^1H NMR ($CDCl_3$) δ 1.8–2.5 (m, 2 H), 2.4–3.1 (m, 5 H), 3.90 (m + s, 4 H), 7.17 (d, J = 10 Hz, 1 H), 7.35 (dd, J = 10, 1 Hz, 1 H), 7.77 (d, J = 1 Hz, 1 H); UV (EtOH) λ_{max} (log ϵ) 405 (1.01), 322 (2.99), 251 (3.73), 223 (4.31) nm. Anal. Calcd for $C_{14}H_{14}O_4$: C, 68.28; H, 5.73. Found: C, 68.11; H, 5.69. The rates of isomerization of **4** to **3** were measured as described before[4e,f,7a] to give the following data: k(25 °C) = (5.55 ± 0.14) × 10^{-6}, k(33 °C) = (1.58 ± 0.06) × 10^{-5}, k(40 °C) = (3.52 ± 0.12) × 10^{-5} s^{-1}.

Reductive Deoxygenation of Aryl Aldehydes and Ketones by *tert*-Butylamine–Borane and Aluminum Chloride

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Reductive deoxygenation of aryl ketones is an important and valuable procedure in organic synthesis.[1] Recently, we reported a mild and selective method for the reductive deoxygenation of aryl aldehydes and ketones using sodium cyanoborohydride in the presence of zinc iodide.[2] Although the method works well with most substrates, it does not deoxygenate aryl ketones having a *p*-chloro substituent. It was found that even lithium aluminum hydride in combination with aluminum chloride does not readily reduce *p*-chloroacetophenones to *p*-(chloroethyl)benzene. Recently, Ono et al. reported that sodium borohydride and aluminum chloride also hydrogenolyzed *p*-chloroacetophenone to the corresponding hydrocarbon.[3] Meanwhile, in our continuous search for better reducing agents for reductive deoxygenation of aryl ketones, we have found that *tert*-butylamine–borane in the presence of aluminum chloride in dichloromethane can reduce not only *p*-chloroacetophenone but also dichloroaryl ketone to the corresponding hydrocarbon. The reagent is also quite mild and selective. *tert*-Butylamine–borane is a very mild reducing agent and is used in the selective reduction of aldehydes and ketones to the corresponding alcohol.[4-7] The reagent as well as other amine–boranes has been used in the presence of a Lewis acid like boron trifluoride etherate and aluminum chloride to reduce alicyclic and aryl ketones to the corresponding alcohols only.[8,9] The increase in

(1) (a) *Reduction*; Augustine, R. L., Ed.; Marcel Dekker: New York, 1968. (b) House, H. O. *Modern Synthetic Reactions*, 2nd ed.; W. A. Benjamin: Menlo Park, CA, 1972; Chapter 4. For a recent review of various methods of reductive deoxygenation of arylketones, see the references cited in ref 2.

(2) Lau, C. K.; Dufresne, C.; Belanger, P. C.; Piétré, S.; Scheigetz, J. *J. Org. Chem.* **1986**, *51*, 3038–3043.

(3) Ono, A.; Suzuki, N.; Kamimura, J. *Synthesis* **1987**, 736–738.

(4) Paquette, L. A. *J. Org. Chem.* **1981**, *46*, 3768.

(5) Chang, F. C. *Synth. Commun.* **1981**, *11*, 875–879.

(6) Andrews, G. C. *Tetrahedron Lett.* **1980**, *21*, 693–696.

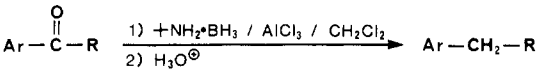
(7) Andrews, G. C.; Crawford, T. C. *Tetrahedron Lett.* **1980**, *21*, 697–700.

(8) Jones, W. M. *J. Am. Chem. Soc.* **1960**, *82*, 2528–2532.

(9) Grundon, M. F.; McCleery, D. G.; Wilson, J. W. *Tetrahedron Lett.* **1976**, 295–296.

0022-3263/89/1954-0491$01.50/0

Table I. Reductive Deoxygenation of Aryl Carbonyls with *tert*-Butylamine-Borane/Aluminum Chloride in Dichloromethane



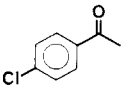
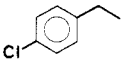
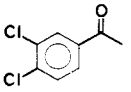
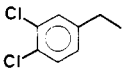
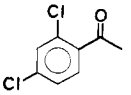
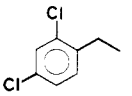
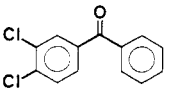
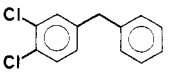
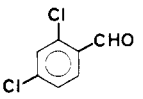
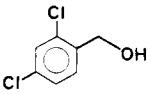
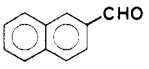
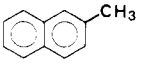
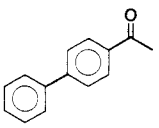
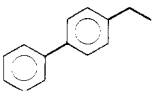
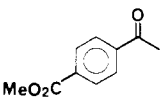
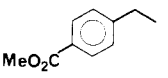
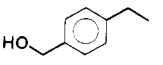
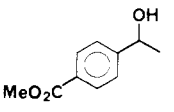
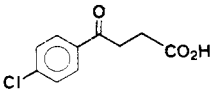
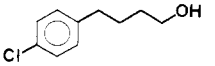
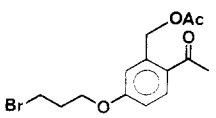
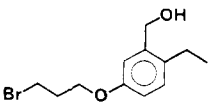
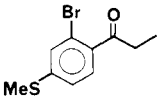
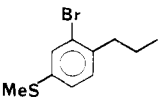
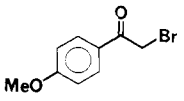
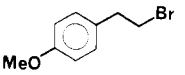
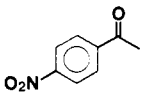
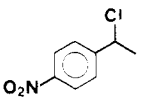
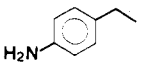
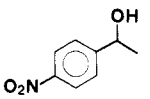
ENTRY	COMPOUND	SOLVENT	RATIO[a] A:B:C	TIME (HOURS)	TEMP. °C	PRODUCTS	YIELDS %[b]	b.p°C (mm)[c]
1		CH_2Cl_2	1:3:6	20	22		77	195°(160 mm)
2		CH_2Cl_2	1:3:6	4	22		62	120°(10 mm)
3		CH_2Cl_2	1:3:3	2	22		56	128°(10 mm)
4		CH_2Cl_2	1:3:6	4	22		76	180°(0.6 mm)
5		CH_2Cl_2	1:3:6	20	22		78[d]	Oil
6		CH_2Cl_2	1:3:6	20	22		64[d]	Oil
7		CH_2Cl_2	1:3:6	1	20		91[d]	Oil
8		CH_2Cl_2	1:3:6	2	0		58[d]	Oil
							16[d]	Oil
							7[d]	Oil
9		CH_2Cl_2	1:3:6	20	22		62[d]	Oil
10		CH_2Cl_2	1:3:6	20	22		63[d]	Oil

Table I (Continued)

ENTRY	COMPOUND	SOLVENT	RATIO[a] A:B:C	TIME (HOURS)	TEMP. °C	PRODUCTS	YIELDS %[b]	b.p°C (mm)[c]
11		CH_2Cl_2	1:3:6	1	22		57[d]	Oil
12		CH_2Cl_2	1:3:6	2	0		86	240°(10mm)
13		CH_2Cl_2	1:3:6	20	22		39[d]	Oil
							9[d]	Oil
							9[d]	Oil

[a] A:B:C = substrate:aluminum chloride:*tert*-butylamine–borane. [b] Yields are isolated by distillation except where otherwise stated. [c] All values are in accord with those found in the literature. [d] Yields are isolated by chromatography on silica gel.

reactivity of the present method is probably due to the choice of dichloromethane as solvent, which also gives a homogeneous solution when the two reagents are mixed.

Results and Discussion

The optimum solvent and ratio of reagents were investigated by using 4-phenylacetophenone as substrate. Dichloromethane was found to be the solvent of choice. Reduction of 4-phenylacetophenone to 4-ethylbiphenyl was complete in 1 h at room temperature. The optimum ratio of reagents was found to be 1:3:6, substrate to aluminum chloride to *tert*-butylamine–borane, respectively. Although a ratio of 1:1:3 also gave similar results with this particular substrate, it was found that the ratio 1:3:6 is generally better and faster. At least a stoichiometric amount of aluminum chloride and 3 molar equiv of *tert*-butylamine–borane is needed for the reaction to proceed at a reasonable rate. Toluene is an acceptable solvent in some cases, but the reaction is slower in this medium. In tetrahydrofuran, only the corresponding alcohol was obtained. Other Lewis acid catalysts were investigated. Boron trifluoride etherate or zinc iodide in combination with *tert*-butylamine–borane reduces *p*-chloroacetophenone to the corresponding alcohol after 20 h under the same reaction conditions.

Reduction of Aryl Ketones. Table I summarizes the reduction of various aryl ketones and aldehydes. The reaction conditions and ratio of reagents for best results are also listed. In general, the reduction of *p*-chloroaryl ketones gave reasonable yield of the corresponding hydrocarbons (entries 1–4). However, the reagent reduces 2,4-dichlorobenzaldehyde (entry 5) only to the corresponding alcohol with no further reduction to the corresponding toluene. Not all aldehydes behave the same way. 2-Naphthaldehyde (entry 6) was reduced to 2-methylnaphthalene in 64% yield. Methyl 4-acetylbenzoate (entry 8) was reduced to methyl 4-ethylbenzoate in 58% yield; some reduction (16%) of the ester also occurred. In the case of aryl ketones bearing an alkyl acid or acetate functionality (entry 9, 10), no selectivity was observed, and the corresponding methylene alcohol was obtained. Primary as well as aromatic bromides were not reduced by this reagent (entries 10–12). Most interestingly, the very reactive 4′-methoxy-2-bromoacetophenone (entry 12) was reduced to 4-methoxyphenethyl bromide in 84% yield without losing the bromide. Aliphatic ketones, for example, methyl 2-phenylethyl ketone, were reduced to the corresponding alcohols only. No trace of deoxygenation was observed. In the case of *p*-nitroacetophenone, it is interesting to find that the major product is the 1-(α-chloroethyl)-4-nitrobenzene (39%). Two minor products, 4-(aminoethyl)benzene (9%) and 1-(α-hydroxyethyl)-4-nitrobenzene (9%) were also isolated. It is also of interest to note that dimethylbenzamide was not reduced at room temperature overnight while benzyl nitrile was reduced to benzyl amine at 0 °C in 3 h.

tert-Butylamine–borane is a very mild reducing agent by itself. It has been used to selectivly reduce an aldehyde in the presence of both a ketone and a lactone.[4] However, when combined with aluminum chloride in dichloromethane, it becomes a very powerful reductive deoxygenation reagent for aryl ketones, and yet some of its selective character remains. *tert*-Butylamine–borane is a white solid, relatively nonpyrophoric and nonhygroscopic, and hence it is very easy to handle on a large scale. The reduction is also very easy to perform. Thus the combination of *tert*-butylamine–borane with aluminum chloride provides a useful alternative to the arsenal of reductive deoxygenation of aryl ketones.

Experimental Section

Proton nuclear magnetic resonance spectra were obtained on a Bruker AM250 spectrometer, and infrared spectra were measured on a Perkin-Elmer 681 spectrophotometer. Boiling points reported are those observed during distillation with a Kugelrohr apparatus and are uncorrected. Melting points were measured on a Büchi 510 melting point apparatus. Low-resolution mass spectral analyses were performed by the Morgan-Schaffer Corporation, Montreal, and elemental analyses were performed by Guelph Chemical Laboratories Ltd, Guelph, Ontario. All reactions as well as column chromatography were monitored routinely with

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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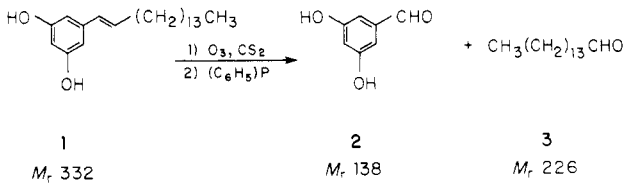
Recently, we isolated from *Hakea trifurcata* and *Hakea amplexicaulis* several 5-alkenylresorcinols capable of mediating DNA strand scission.[1] The compounds were isolated initially as complex mixtures of resorcinols, which differed solely in the lengths of individual alkenyl substituents and in the 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) (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