the volume of sample injected, nor the solvent employed was found to affect the magnitude of the molar responses obtained from monitoring either of the two constituents.) When compared to the RMR's of the peaks obtained from injection of the free bases or maleic acid itself, all four salts yielded eluates which exhibited optimum quantitative response (RMR's of 102–104% of theoretical) at IPT 200–230 °C. At temperatures below (down to 160 °C) and above (up to 280 °C) this range, the salt eluate RMR's decreased to 70–80% of the injected free base or acid responses. Lower IPT's apparently result in such slow rates of dissociation kinetically that yields of the products in chromatographically detectable amounts under the dynamic conditions of the GLC system are diminished. At temperatures higher than the optimum, on the other hand, reduced peak response is most likely due to partial thermal degradation of the salts to nonvolatile species, as evidenced by the appearance of black involatile residues and <100% weight-loss plateaus (Figure 3) in the TGA experiments. The narrow optimum IPT range over which most efficient thermal dissociation is achieved represents a potential limitation of the technique of injecting salts directly into "unmodified" GLC systems as a method for the determination of these types of analytes.

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Identification and Determination of 16-Carbon 2,5-Dialkyloxolanes in Autoxidized *n*-Hexadecane Samples by Capillary Gas Chromatography and Mass Spectrometry

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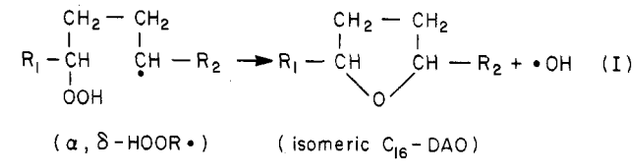
Identification and determination of isomeric 16-carbon (C_{16}) 2,5-dialkyloxolanes, formed during the autoxidation of *n*-hexadecane under reduced oxygen pressures, by gas chromatography/mass spectrometry (GC/MS) and capillary GC are described. A bonded phase fused silica capillary column and a "reduced pressure" on-column injection technique have been utilized for the quantitative GC analysis. Nine chromatographic peaks have been identified and assigned to six pairs of geometric isomers of C_{16} 2,5-dialkyloxolanes based on relative retention times, stereochemistry of cis and trans isomers, and formation of characteristic five-membered ring oxonium ions formed by electron-impact fragmentation. Relative standard deviations (RSDs) obtained from the GC analyses of 1-alkanol standards and isomeric C_{16} 2,5-dialkyloxolanes in acetone solutions were between 1.5 and 3.5% at concentrations ranging from 20 to 100 ng/μL with 1.0-μL injections.

In the liquid-phase autoxidation of *n*-hexadecane with pure oxygen at 100 to 110 kPa and 120 to 180 °C, α,δ-hydroperoxyhexadecyl radicals (α,δ-HOOR·), which are formed from hexadecylperoxy radicals by intramolecular hydrogen abstraction reaction, react predominantly with oxygen to form α,δ-hydroperoxyhexadecylperoxy radicals. The latter radicals are precursors to the formation of α,δ-hexadecanedihydroperoxides and hydroperoxyhexadecanones (*1*). At low oxygen pressures, however, isomerization and cyclization reactions of α,δ-HOOR· also become important (*2*). The cyclization reaction leads to the formation of C_{16} 2,5-dialkyloxolanes (C_{16}-DAO) or 2-dodecyloxolane (for brevity, isomeric C_{16}-DAO include 2-dodecyloxolane in this paper), i.e.



where R_1 is $-(CH_2)_xCH_3$ or $-H$, R_2 is $-(CH_2)_yCH_3$ or $-H$, and $x + y = 10$ or either x or $y = 11$.

This paper describes the identification and determination of isomeric C_{16}-DAO in autoxidized *n*-hexadecane samples by capillary GC/MS and capillary GC, using bonded phase fused silica capillary columns.

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The development of bonded phase fused silica capillary columns has made it possible to employ liquid on-column injection techniques without loss of column performance (*3–5*). The silicon rubber bonded phase columns have been regenerated from the deposition of high boiling and nonvolatile sample components by rinsing the columns with organic solvents without phase displacement, phase stripping, and loss of resolution (*3, 6*). Sample injection, however, still remains the most critical aspect of capillary column GC quantitation. The on-column injection technique has been advanced significantly since the Grob on-column injector (*7*). It generally gives better quantitative accuracy and precision than conventional vaporizing injection techniques. "Cold" on-column injection, however, could lead to peak distortion or splitting due to liquid sample flooding of the column inlet, which occurs more readily with polar solvents (*8, 9*). Some new approaches, which have been reported recently to overcome this problem, are the "retention gap" method (*8, 10*), the "hot" on-column injection (*11, 12*), and the "solvent focusing" technique (*13, 14*).

The present capillary GC work which we report in this paper utilizes a "reduced pressure" technique for on-column injection to eliminate the peak splitting problem.

EXPERIMENTAL SECTION

Reagents. All organic solvents used were "distilled-in-glass" grade from Burdick & Jackson Laboratories, Inc. (Muskegon, MI). Other analytical reagents used were ACS reagent grade. GC calibration standards of 1-alkanols (C_{10}, C_{12}, C_{14}, C_{16}, and C_{18}; 99.8+%) were purchased from Applied Sciences Laboratoires, Inc. (State College, PA). An isomeric mixture of 2-ethyl-5-decyloxolane was synthesized via a methane sulfonic ester in the presence of pyridine (*15*) from 3,6-hexadecanediol (*1*).

Reduced Oxy Fractions. Autoxidized *n*-hexadecane samples (oxidates) were prepared at conversions of 0.1–2.3% in a stirred-flow microreactor (*1*) at the temperatures, *T*, of 160–200 °C and partial oxygen pressures, P_{O_2}, of 4–120 kPa (*2*). The oxidates were reduced by sodium borohydride ($NaBH_4$) using a procedure described elsewhere (*1*). Oxy fractions in the reduced oxidates were separated from unreacted *n*-hexadecane using Waters Sep-PAK silica cartridges (Milford, MA) as follows. A reduced oxidate (1 to 10 mL) and 5 mL of hexane were introduced on a silica cartridge, which was then washed twice with 10 mL of hexane to remove unreacted *n*-hexadecane. The reduced oxy fraction was quantitatively eluted from the cartridge into a 5-mL volumetric flask with acetone (ca. 5 mL). The sample size of a reduced oxidate was determined by the concentration of oxygenated C_{16} compounds (ca. 1×10^{-4} mol/cartridge) to avoid overloading of the cartridge. More than 99% of the unreacted *n*-hexadecane was eliminated from the reduced oxidates by the oxy fraction separation procedure described above.

Isomeric C_{16}-DAO Enrichment. A $NaBH_4$ reduced oxidate (14.6 g) obtained from the autoxidation of *n*-hexadecane at 200 °C (P_{O_2} = 4.8 kPa; reaction time t = 111 s) was dissolved in 20 mL of *n*-hexane. The mixture was passed through a first Sep-PAK silica cartridge and the cartridge was washed twice with 10 mL of *n*-hexane. The volume of eluate (ca. 60 mL) was reduced to ca. 40 mL under dry nitrogen flow. The condensed sample solution was passed through a second Sep-PAK silica cartridge, which was then washed twice with 5 mL of *n*-hexane. The eluate, which only contained unreacted *n*-hexadecane and *n*-hexane, was discarded. The oxy fraction enriched with isomeric C_{16}-DAO was collected into a 5-mL volumetric flask by washing the second cartridge with acetone (ca. 5 mL).

Gas Chromatography. On-column injection capillary GC analyses of the reduced oxy fraction samples were performed on a modified Perkin-Elmer Sigma 3B gas chromatograph/Sigma 10 data station system equipped with a flame ionization detector (FID) and J & W Scientific Model II on-column injector (Rancho Cordova, CA).

The original GC injection port was modified to install the on-column injector by replacing the flash vaporizing heating block with a custom built aluminum heating block (50 × 70 × 35 mm). This block had a capillary column passage hole (35 mm × 5 mm i.d.) with graphite ferrule inserts at the both ends and the heater transferred from the replaced injection port. The base plate of the injector was mounted on the GC cabinet front wall. The spaces between the injector-base plate and GC oven wall were well insulated with glass wool (*16*).

The reduced oxy fractions were separated on a J & W DB-5 (SE-54) fused silica capillary column (60 m × 0.32 mm i.d.) with a film thickness of 0.25 μm. The linear velocity of hydrogen carrier gas was 40 cm/s at 105 °C under a gauge pressure of 124 kPa, initial injector heating block temperature of 75 °C, and detector temperature 185 °C. The column oven temperature was programmed from 95 to 180 °C with a heating rate of 2 °C/min and held at 180 °C for 15 min.

GC Sample Introduction. A J & W 10-μL syringe with a fused-silica needle (20 cm × 0.19 mm o.d.) was utilized for this work. The syringe cleaning and loading procedures were basically similar to those suggested by the manufacturer (*16*). The filled length of a 1-μL solution in the needle was ca. 64 mm at ambient temperature. The syringe ready for on-column injection contained ca. 0.03 μL (2 mm long at the needle tip) of air, 1.0 μL of acetone solution in the front end of the needle, ca. 2.1 μL of acetone in the rest of the needle, and 1.0 μL of acetone in the syringe barrel.

To reduce the column pressure during the syringe-needle insertion for the elimination of peak distortion or splitting, a Whitey toggle operated vent valve (SS-OGS2-A; Cleveland, OH) was installed at the end of the on-column injector purge line next to a Nupro ultrafine metering valve (Willoughby, OH), which was set at 20 mL/min (*16*).

The sample introduction into the capillary column was performed as follows: The sample deposition area of the column, which was ca. 5–7 cm outside of the GC cabinet wall, was equilibrated at ambient temperature. The toggle-vent valve was opened to reduce the column pressure. The tip of the needle was then inserted into the restricted glass arm in front of the injector stopcock. The stopcock was opened and the needle was advanced ca. 13 cm inside of the column. The toggle-vent valve was closed and the sample solution was deposited within a 2 cm length of the column by simultaneous needle retraction and plunger insertion to avoid the formation of a liquid plug. The syringe was withdrawn until the needle tip just cleared the stopcock and the stopcock was closed. The needle was withdrawn completely from the injector. Finally, the sample deposition area of the column was placed 2–3 cm inside of the GC oven and temperature programming was initiated.

Capillary Column Regeneration. The fused silica capillary column was gradually contaminated by the deposition of sodium borate, which was in the $NaBH_4$ reduced, silica cartridge separated oxy fraction sample solutions in trace quantity. After 20–25 sample injections, the contaminated column was regenerated by washing in succession with 3 mL each of methanol–10% water, methanol, acetone, dichloromethane, and *n*-hexane. During the course of this work, the column was successfully regenerated five times without any loss of its original resolution.

Gas Chromatography/Mass Spectrometry. GC/MS analysis was performed on a Perkin-Elmer Model 900 gas chromatograph using a J & W DB-5 fused silica capillary column (30 m × 0.25 mm i.d.; 0.25 μm film thickness) interfaced directly to the ionization source of a Vacuum Generators Micromass MM-16 mass spectrometer, which was equipped with a Finnigan INCOS 2000 data system. The mass spectrometer source and GC interface temperatures were maintained at 230 and 280 °C, respectively. The mass spectrometer was operated at a resolution of approximately 1000. All measurements were made in the EI mode at 70 eV.

A 1.0-μL aliquot was introduced into the capillary column using a J & W Model I fixed position on-column injector at ambient temperature. The GC column temperature was then raised to 95 °C and programmed to 180 °C at the rate of 2 °C/min. The linear velocity of helium carrier gas was 20 cm/s at 95 °C.

RESULTS AND DISCUSSION

Capillary GC separations of two representative reduced oxy fraction samples utilizing the "reduced pressure" on-column injection technique to eliminate peak distortion or splitting are shown in Figure 1. Prior to the development of this injection technique, the incidence of peak distortion or

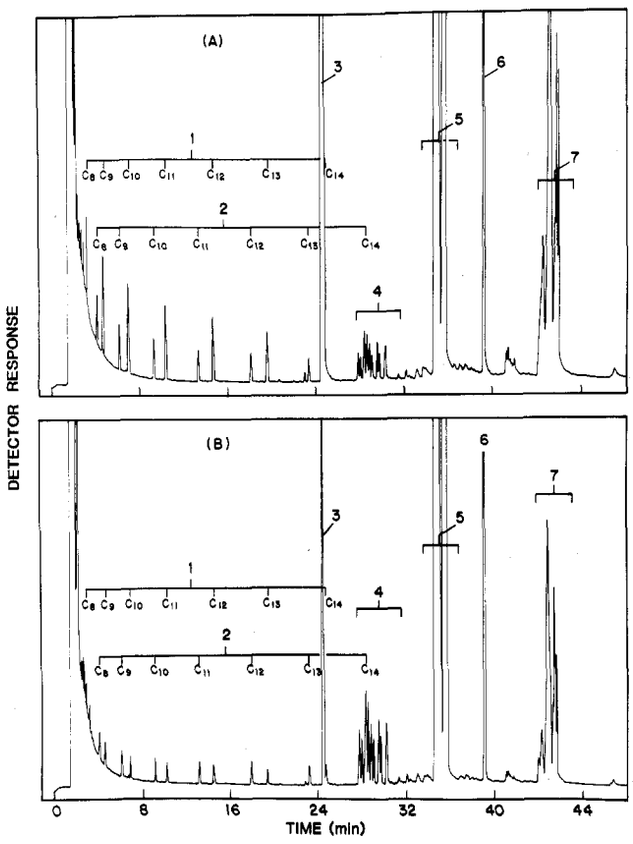


Figure 1. Gas chromatograms of oxy fractions (A) and (B) obtained from $NaBH_4$ reduced oxidates: reactions conditions, T = 190 °C, t = 68.8 s, P_{O_2} = 20.4 kPa for (A) and T = 190 °C, t = 69.3 s, P_{O_2} = 5.0 kPa for (B); silica cartridge separation, collected in 5 mL of acetone from 5.43 g (A) and 12.21 g (B) of reduced oxidates, respectively; column, 60 m × 0.32 mm i.d. DB-5, 0.25 μm; injection size, 1.0 μL; hydrogen flow rate, 40 cm/s at 105 °C; detector, FID; oven-temperature program, 95–180 °C with a heating rate of 2 °C/min; (peak identity) (1) C_8–C_{14} 2-alkanols, (2) C_8–C_{14} 1-alkanols, (3) *n*-hexadecane, (4) isomeric C_{16}-DAO, (5) isomeric 2- to 8-hexadecanols, (6) 1-hexadecanol, and (7) isomeric α,γ- and α,δ-hexadecanediols.

splitting with the on-column injector was about 90% under the GC conditions. Identification of major oxygenated compounds formed in the autoxidation of *n*-hexadecane at high oxygen pressures and GC peak assignments of the $NaBH_4$ reduced compounds corresponding to peaks 1, 2, and 5–7 in the figures have been previously reported (*1*, *17*). Peak 4, which consists of 10 GC peaks, has been tentatively identified as C_{16}-DAO isomers based on the retention times of a mixture of geometric isomers of synthesized 2-ethyl-5-decyloxolane (*2*).

In order to confirm the identification of peak 4 compounds by a GC/MS method, an enrichment procedure for isomeric C_{16}-DAO has been devised. The procedure is based on the loading capacity of a silica cartridge and difference in affinity toward silica surfaces between alcohols and ethers (see Experimental Section). The GC separation of a C_{16}-DAO enriched oxy fraction is shown in Figure 2. Identification of six pairs of C_{16}-DAO geometric isomers and assignments of 13 C_{16}-DAO isomers to ten GC peaks (a–j) (peak 4 in Figure 1) are discussed below.

A GC separation of synthesized 2-ethyl-5-decyloxolane showed two peaks at the retention times of 29.81 and 30.36 min, which corresponded to peaks f and g in Figure 2, respectively, indicating the existence of geometric isomers. The product ratio between the first and second isomers of synthesized 2-ethyl-5-decyloxolane was 0.6:1.00.

On the basis of the conformational analysis of a pair of geometric isomers of 2-ethyl-5-decyloxolane, the second GC

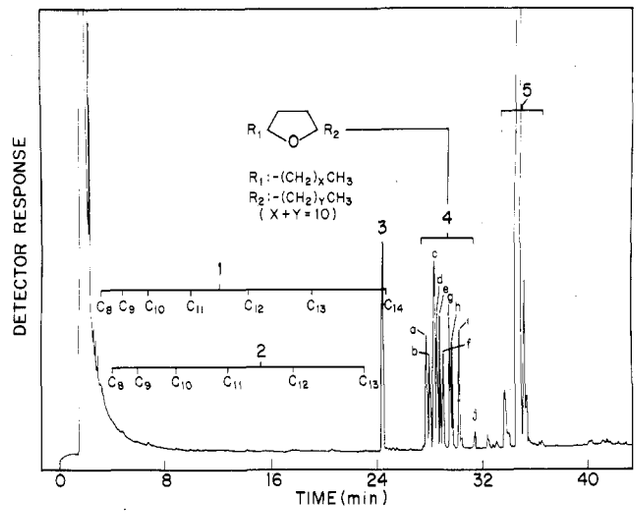
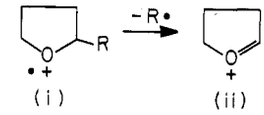


Figure 2. Gas chromatogram of isomeric C_{16}DAO enriched oxy fraction obtained by two-stage silica cartridge separation: GC conditions, same as in Figure 1; (peak identity) (a) a mixture of *cis*-2,5-dihexyloxolane and *cis*-2-pentyl-5-heptyloxolane, (b) *cis*-2-butyl-5-octyloxolane, (*c*) a mixture of *trans*-2,5-dihexyloxolane, *trans*-2-pentyl-5-heptyloxolane, and *cis*-2-propyl-5-nonyloxolane, (d) *trans*-2-butyl-5-octyloxolane, (e) *trans*-2-propyl-5-nonyloxolane, (f) *cis*-2-ethyl-5-decyloxolane, (g) *trans*-2-ethyl-5-decyloxolane, (h) *cis*-2-methyl-5-undecyloxolane, (I) *trans*-2-methyl-5-undecyloxolane, (j) 2-dodecyloxolane, and remaining peaks see Figure 1.

peak has been assigned to the trans configuration, which is likely to possess slightly higher boiling point and stronger affinity toward the SE-54 liquid phase than the cis configurations; i.e., the trans isomer is less hindered at the ring oxygen than the cis isomer. The observed isomer ratio of synthesized 2-ethyl-5-decyloxolane also supports the GC peak assignments, since the stereochemistry of cyclic ether formation predicts a more stable transition state for the trans isomer than for the cis isomer.

Mass spectra of synthesized *cis*- and *trans*-2-ethyl-5-decyloxolanes are shown in Figure 3. The two spectra are very similar and exhibit $(M - 1)^+$ ion at m/z 239. This confirms that synthesized 2-ethyl-5-decyloxolane exists in cis and trans configurations. It should be noted that the principal features of the spectra are the most abundant ions at m/z 99 and the relatively abundant ions at m/z 211 corresponding to $(M - R_1)^+$ and $(M - R_2)^+$ oxonium ions, respectively. This is consistent with previously reported findings that the most important cleavage reaction of simple 2-substituted tetrahydrofuran derivatives (i) is the loss of the 2-substituent with the formation of an oxonium ion (ii) of m/z 71 (*18*).



(II)

On the basis of the expected 2-substituent cleavage reactions of isomeric C_{16}-DAO, a series of mass fragmentograms was obtained for $(M - R_1)^+$ and $(M - R_2)^+$ oxonium ions by scanning through the mass spectral data of GC peaks (a–i) (see Figure 2). The results are summarized in Figure 4, which positively identify the presence of six pairs of geometric isomers of C_{16}-DAO. From the scan numbers at their mass response maxima, the six pairs of the isomers have been also assigned to GC peaks (a–i). GC peak j is tentatively identified as 2-dodecyloxolane, which is a very minor product formed in the autoxidation of *n*-hexadecane under reduced oxygen pressures.

The identified-oxygenated compounds which interfere with GC determination of isomeric C_{16}-DAO are 1-tetradecanol and 2-pentadecanol, however, both of which are very minor com-

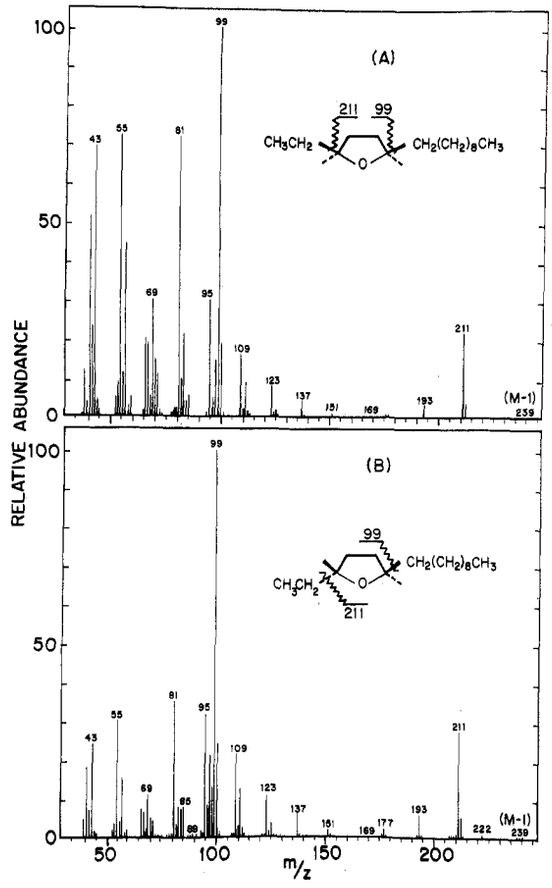


Figure 3. Mass spectra of a synthesized mixture of (A) *cis*- and (B) *trans*-2-ethyl-5-decyloxolanes (see the GC/MS conditions in the Experimental Section).

Table I. GC Analysis of 1-Alkanol Standards[a]

standard	concn, ng/μL ($\hat{X}$)	mean concn,[b] ng/μL ($\bar{X}$)	RSD $100(s/\bar{X})$	rel accuracy $100(\bar{X} - \hat{X})/\hat{X}$
1-dodecanol	82.83	83.27	2.6	+0.53
1-tetradecanol	66.17	66.23	2.3	+0.09
1-hexadecanol	68.36	68.26	3.3	−0.15
1-octadecanol	95.55	95.15	2.6	−0.42

[a] GC conditions are the same as those given in Figure 1. [b] Ten replicate measurements (n = 10).

ponents in $NaBH_4$-reduced oxidates obtained from the autoxidation of *n*-hexadecane (*2*, *19*). Since C_{16}-DAO standards were not available in sufficient purity to permit their use for GC calibration, the quantitative determination of isomeric C_{16}-DAO was based on a calibration curve obtained with 1-tetradecanol. Linear regression analysis of the alkanol calibration data obtained at four concentrations ranging from 20 to 95 ng/μL (n = 2 at each concentration) gives a linear relationship with a slope of 0.973 (detector response per 10 ng of 1-tetradecanol), a correlation coefficient of 0.9996, and a standard error of estimate of 0.193.

The measures of precision and accuracy of the present GC analysis procedure were determined with a standard 1-alkanol mixture containing 1-dodecanol, 1-tetradecanol, 1-hexadecanol, and 1-octadecanol in acetone. Results obtained for this mixture are summarized in Table I. The RSDs obtained for the 1-alkanol standards are comparable to those (i.e., 1.3 to 2.2%) obtained for C_9–C_{34} *n*-alkanes in acetone with 1-μL injections by a "nonvaporizing" on-column injection (*20*).

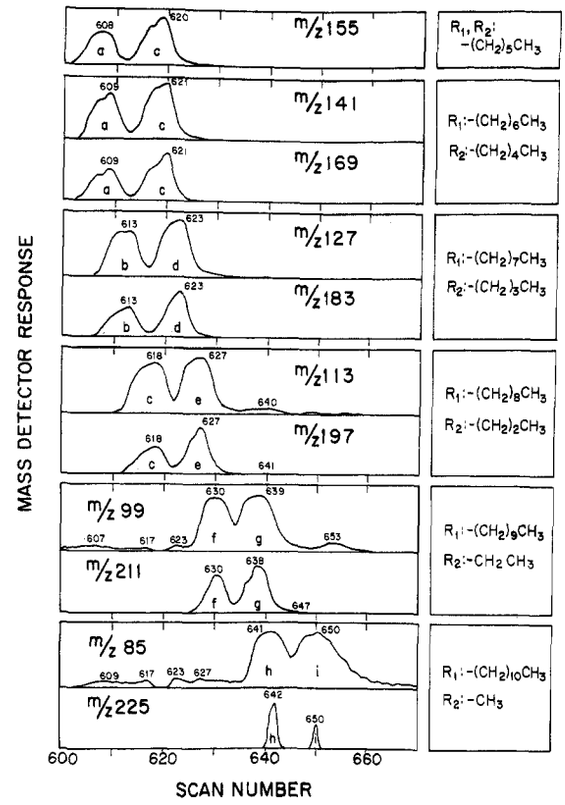


Figure 4. Mass fragmentograms of $(M - R_1)^+$ and $(M - R_2)^+$ oxonium ions obtained for the six pairs of isomeric C_{16}-DAO: (peak intensity) peaks (a–i) correspond to those in Figure 2.

Table II. GC Analysis of Isomeric C_{16}-DAO[a]

GC peak ID[b]	mean concn,[c] ng/μL ($\bar{X}$)	std dev (s)	RSD $100(s/\bar{X})$
a	37.76	0.92	2.4
b	24.75	0.54	2.2
c	74.12	1.58	2.1
d	33.92	0.57	1.7
e	33.24	0.75	2.3
f	25.35	0.64	2.5
g	33.90	0.50	1.5
h	25.03	0.54	2.2
i	34.29	1.19	3.5[d]
j	4.31	0.12	2.8

[a] GC conditions are the same as those given in Figure 1. [b] See Figure 2. [c] Seven replicate injections (n = 7). [d] Interfered by a shouder peak.

One-microliter aliquots of reduced oxy fraction samples (A) and (B) in Figure 1 were found to contain 91.5 and 159.3 ng of isomeric C_{16}-DAO, respectively. These amounts originate from 1.09 and 2.44 mg of the corresponding oxidates. Some of the results of quantitative GC analysis of total isomeric C_{16}-DAO formed in the autoxidation of *n*-hexadecane at elevated temperatures and under reduced oxygen pressures have been reported elsewhere (*2*).

In Table II are capillary GC analysis data of peaks (a–j) (see Figure 2) obtained from seven measurements on the acetone solution of a C_{16}-DAO enriched oxy fraction using the on-column injection technique. The RSDs obtained are similar to those obtained for the 1-alkanol standards (cf. Table I).

By use of the mean concentrations, $\bar{X}$, obtained for peaks a–i in Table II, the cis/trans ratios of six pairs of geometric C_{16}-DAO isomers have been estimated and are presented in Table III. GC peaks a and c contained more than one isomer. Peak a was resolved by an assumption based on statistical

Table III. Relative Amounts and Cis/Trans Ratios of Isomeric C_{16}-DAO Formed in the Autoxidation of *n*-Hexadecane

isomeric C_{16}-DAO	GC peaks[a] (cis, trans)	rel amt formed, %	cis/trans ratio
2,5-dihexyl	a, c	8.90[b]	0.76
2-pentyl-5-heptyl	a, c	17.82	0.76
2-butyl-5-octyl	b, d	17.96	0.73
2-propyl-5-nonyl	c, e	17.70	0.74[c]
2-ethyl-5-decyl	f, g	18.13	0.75
2-methyl-5-undecyl	h, i	18.16	0.73
2-dodecyl[d]	j	1.32	

[a] Corresponding GC peaks to cis and trans isomers except peak (j); cf. Figures 2 and 4. [b] Obtained by assuming that the amounts of *cis*- and *trans*-2,5-dihexyloxolanes formed are half of the formed amounts of *cis*- and *trans*-2-pentyl-5-heptyloxolanes, respectively. [c] Estimated from the cis/trans ratios of geometric isomers of 2-butyl-5-octyloxolane and 2-ethyl-5-decyloxolane. [d] No geometric isomer.

considerations of the formation of α,δ-HOOR·; namely, the amount of *cis*-2,5-dihexyloxolane formed was half of the formed amount of *cis*-2-pentyl-5-heptyloxolane. Similarly, peak c was resolved assuming that the amount of *trans*-2,5-dihexyloxolane formed was half of the formed amount of *trans*-2-pentyl-5-heptyloxolane and that the cis/trans ratio of geometric isomers of 2-propyl-5-nonyloxolane would be 0.74, which was estimated from those ratios of geometric isomers of 2-butyl-5-octyloxolane and 2-ethyl-5-decyloxolane.

The cis/trans ratios obtained reflect steric effects in the cyclization reaction of α,δ-HOOR· at elevated temperatures; similarly as those observed in the synthesis of a mixture of *cis*- and *trans*-2-ethyl-5-decyloxolanes by a direct displacement reaction of sulfonate groups with hydroxyl groups at a low temperature.

The precision and accuracy of data obtained by the present GC analysis procedure have been very satisfactory for the kinetic studies of *n*-hexadecane autoxidation at elevated temperatures and reduced oxygen pressures. Detailed results of those studies will be reported elsewhere (*21*).

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Registry No. *n*-Hexadecane, 544-76-3; *cis*-2,5-dihexyloxolane, 92957-51-2; *trans*-2,5-dihexyloxolane, 92957-52-3; *cis*-2-pentyl-5-heptyloxolane, 92957-53-4; *trans*-2-pentyl-5-heptyloxolane, 92957-54-5; *cis*-2-butyl-5-octyloxolane, 92957-55-6; *trans*-2-butyl-5-octyloxolane, 92957-56-7; *cis*-2-propyl-5-nonyloxolane, 92957-57-8; *trans*-2-propyl-5-nonyloxolane, 92957-58-9; *cis*-2-ethyl-5-decyloxolane, 92957-59-0; *trans*-2-ethyl-5-decyloxolane, 92957-60-3; *cis*-2-methyl-5-undecyloxolane, 92957-61-4; *trans*-2-methyl-5-undecyloxolane, 92957-62-5; 2-dodecyloxolane, 92957-63-6.

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