Oxidation of 10-Chlorotricyclene, *exo*-6-Chlorocamphene, and *trans*-8-Chlorocamphene

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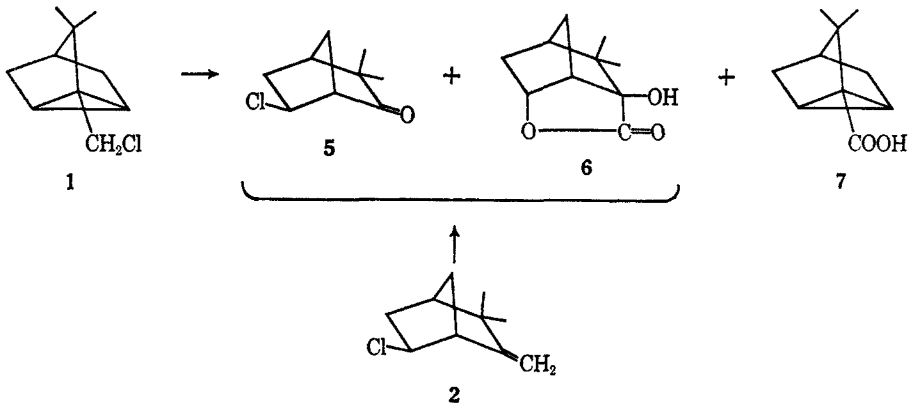
Neutral permanganate oxidation of 10-chlorotricyclene (1) produces *exo*-6-chlorocamphenilone (5) and *exo*-2-hydroxycamphene-*endo*-2-carboxylic acid lactone (6) in addition to the major product, tricyclenic acid (7). The same ketone and lactone (5 and 6) are the principle materials isolated from the oxidation of *exo*-6-chlorocamphene (2). *trans*-8-Chlorocamphene (4) forms camphenilone (8) as the only product, whereas the *cis* isomer (3) is inert to oxidation. This behavior can be understood by considering the steric requirements for the formation of the necessary reaction intermediate.

In a recent report on the chlorination of camphene,[1] we noted that two unidentified compounds were found among the oxidation products of 10-chlorotricyclene (1) and *exo*-6-chlorocamphene (2). We have since characterized these compounds and have studied the oxidation of *cis*- and *trans*-8-chlorocamphene (3 and 4). The results of our investigations are of interest because two new bicyclo[2.2.1]heptane derivatives (5 and 6) were produced and also because we found that *cis*-8-chlorocamphene (3) was resistant to oxidation. This latter peculiarity can be explained by invoking a novel kind of steric hindrance.

The Oxidation Reactions.—Equations 1 and 2 represent permanganate reactions in 75% aqueous acetone to which magnesium sulfate was added to maintain neutral conditions.

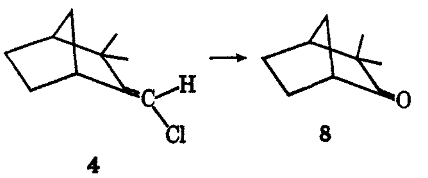


(1)

Tricyclenic acid (7) could be obtained from 1 in yields as high as 95%; the per cent conversion to the acid was erratic, however, and sometimes dropped below 50%. Two new compounds, *exo*-6-chlorocamphenilone (5) and *exo*-2-hydroxycamphene-*endo*-2-carboxylic acid lactone (6), were also isolated. These same materials (5 and 6) were found in about equal amounts as the only important products from neutral oxidation of 2 (eq 1) and probably their appearance as oxidation products of 1 is the result of rearrangement of 1 to 2 prior to oxidation. We demonstrated that such a conversion takes place with ease at room temperature in the presence of manganese dioxide when no permanganate is present. The observed fluctuations in yield of acid 7 may be traceable to variation in the amount of 1 converted into 2 during oxidation, a process dependent on the rate of precipitation of manganese dioxide which, in turn, was not controlled from run to run.

Compound 5 is the expected product from normal oxidative cleavage of the olefinic linkage in 2. Compound 6 would result from an intermediate analogous to the α-hydroxy ketones which are formed by permanganate oxidation of olefins in neutral or slightly basic aqueous solution (Scheme I).[2-4] The same mechanism explains the permanganate oxidation of camphene to form camphenylic acid, observed by Wagner as long as 70 years ago.[5] Scheme I clearly requires *exo* attack of the permanganate ion as would be expected from consideration of the hydroboration of camphene;[6] the preferred approach of both reagents to the camphene double bond is from the less hindered bridge side of the molecule.

When 1 was treated with permanganate in refluxing 85% aqueous acetone, with no attempt to prevent accumulation of hydroxide ion, approximately equal amounts of 10-hydroxytricyclene (9) and *exo*-6-hydroxycamphene (10) were isolated. The tricyclenol (9), formed by hydrolysis of 1, is a likely precursor



(2)

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(1) B. H. Jennings and G. B. Herschbach, *J. Org. Chem.*, **30**, 3902 (1965).

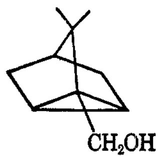
(2) K. B. Wiberg and K. A. Saegebarth, *J. Amer. Chem. Soc.*, **79**, 2822 (1957), and references cited therein.

(3) R. Stewart in "Oxidation in Organic Chemistry," Part A, K. B. Wiberg, Ed.,Academic Press Inc., New York, N. Y., 1965, pp 41–46.

(4) R. Stewart, "Oxidation Mechanisms," W. A. Benjamin, Inc., New York, N. Y., 1964, pp 62–63.

(5) G. Wagner, *J. Russ. Phys. Chem. Soc.*, **28**, 73 (1896); *Bull. Soc. Chim. Fr.*, **16**, 1836 (1896).

(6) H. C. Brown, "Hydroboration," W. A. Benjamin, Inc., New York, N. Y., 1962, p 126 ff.



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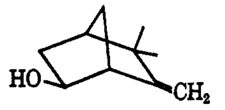

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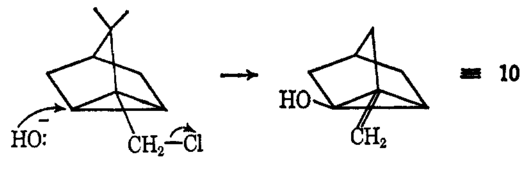
of 7. The hydroxycamphene (10) could arise from 2, formed by the rearrangement of 1 in the presence of manganese dioxide (see above). Alternatively it could be formed directly from 1 by a pseudo-S$_N$2′ mechanism which is able to successfully compete with the nonrearranging mechanism because of release of the steric strain present in all tricyclene derivatives (eq 3).



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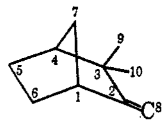
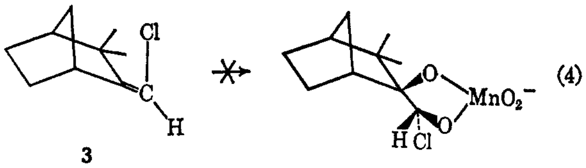
(3)

The response of the *cis*- and *trans*-8-chlorocamphenes (3 and 4) to treatment with potassium permanganate has interesting mechanistic implications. Because we were never successful in separating the *cis* from the *trans* isomer,[1] we oxidized mixtures of the pair (ratio of *cis/trans*, 1:2). The reaction proceeded to camphenilone (8) as the only product but despite the use of a large excess of potassium permanganate some unoxidized 8-chlorocamphene always remained (glpc). The nmr spectrum of this unreacted material, isolated by preparative glpc, was assignable to the *cis* isomer alone (see Table I in ref 1). Moreover, the mole ratio (glpc) of unreacted 3 to product 8 was approximately 1:2 as would be expected for clean oxidation of the *trans* isomer accompanied by no reaction of the *cis*. Selective oxidation of 4 had clearly occurred. This difference in the sensitivity of the isomers to potassium permanganate must be steric in origin. Examination of Fisher–Taylor–Herschfelder models[7] shows that the



accessibility of the π-electron system is approximately the same in both compounds. It is notable, however, that the chlorine atom in the *cis* isomer is held rigidly between the two methyl groups attached to C$_3$. This arrangement could have inhibitory effects on the oxidation because of the obstruction it offers to the formation of the intermediate cyclic manganese ester. The necessary rehybridization of C$_8$ in compound 3 (sp^2 to sp^3) requires that the chlorine atom be dislodged from its position between the methyl groups (eq 4). Such a process is severely hindered. There is, on the other hand, no corresponding steric restriction to conversion of the unsaturated system of the *trans* isomer to the properly oriented spiro system. To our knowledge no other example of this type of steric hindrance has been reported in the literature.



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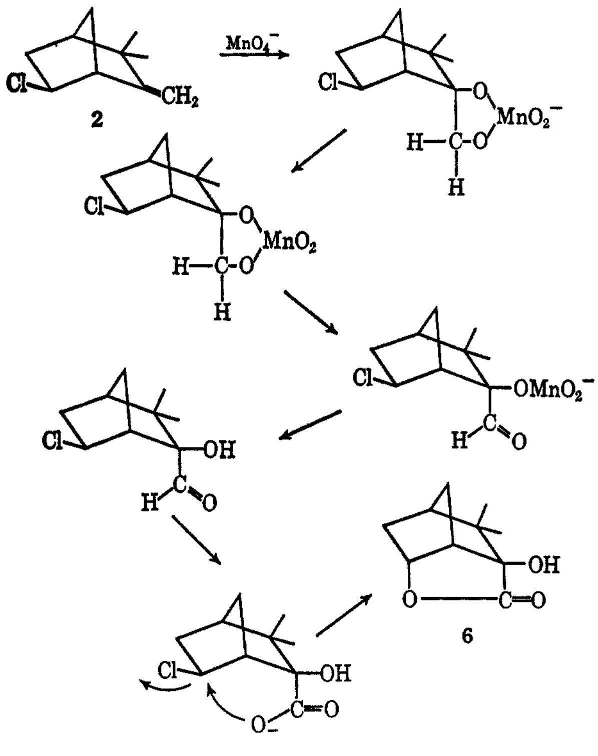
(4)

SCHEME I



Structure of Compound 5.—The fact that *exo*-6-chlorocamphenilone is the expected product from the oxidation of 2 constitutes chemical evidence for the assignment of structure 5 to the ketone. All the physical data obtained for the liquid support this formulation. Elemental analysis and the weight of the molecular ion (172), obtained from the mass spectrum (Figure 1), establish the molecular formula as $C_9H_{13}ClO$. The ir spectrum of the compound shows the presence of a ketonic carbonyl group (5.70 μ) and *gem*-dimethyl groups (7.20 and 7.32 μ).

The nmr spectrum (Table I) resembles that of *exo*-6-chlorocamphene[1,8] and shows the resonances expected for *exo*-6-chlorocamphenilone. The deshielded proton giving rise to the quartet at δ 3.99 must be the one attached to the carbon which bears the chlorine. *endo* trientation of this H is demanded by the fact that the C$_1$ proton (δ 2.88) is not appreciably split. The multiplicity of this C$_6$ hydrogen derives from its coupling with the *endo* (J = 7.5 cps) and *exo* (J = 4 cps) protons on C$_5$.[9] The resonances of the remaining nuclei are superimposed on each other to an extent which precludes further analysis.

The electron impact fragmentation pattern of 5 (Figure 1) is strikingly similar to that of camphenilone (8)[10] and is thus confirmatory evidence for the structure of 5. The peak at m/e 109 in the spectrum of the

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[7] These models cannot accommodate the entire bicyclic system but it is possible to construct the part of the system of interest here (C$_2$–C$_3$–C$_8$–C$_9$–C$_{10}$).

[8] H. G. Richey, Jr., J. E. Grant, T. J. Garbacik, and D. L. Dull, *J. Org. Chem.*, **30**, 3909 (1965).

[9] These J values are in good agreement with literature values for *endo–endo* and *exo–endo* coupling constants; see P. Laszlo and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **86**, 1176 (1964).

[10] E. von Sydow, *Acta Chem. Scand.*, **18**, 1099 (1964).

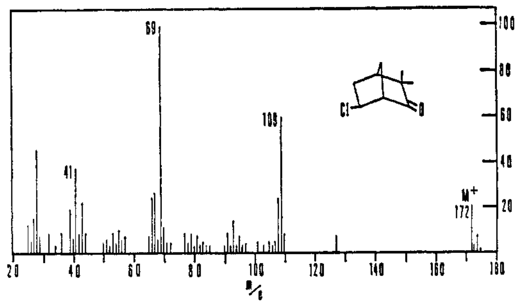


Figure 1.—Mass spectrum of *exo*-6-chlorocamphenilone (5) at 70 eV. Metastable peaks appear at $m^* = 41 = (67)^2/109$ and $m^* = 80 = (93)^2/108$.

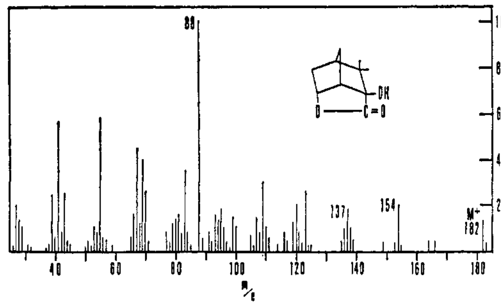


Figure 2.—Mass spectrum of *exo*-2-hydroxycamphene-*endo*-2-carboxylic acid lactone (6) at 70 eV. Metastable peaks appear at $m^* = 36.5 = (55)^2/83$ and $m^* = 130.5 = (154)^2/182$.

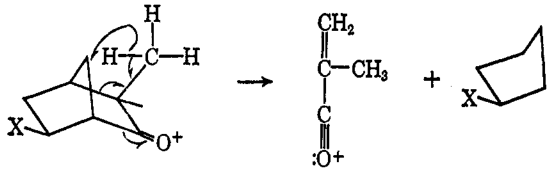
Table I

Nmr Spectra

	Chemical shift values[a]	Multiplicity and coupling constant[b]	Assignment
exo-6-Chlorocamphenilone (5) (in CCl_4)	0.92 (3)	s	Methyl
	1.06 (3)	s	Methyl
	1.75–2.52 (6)	Overlapping peaks	
	2.68 (1)	s, b	C_1
	3.99 (1)	q, d of d, (1:1:1:1) J = 7.5, 4.0 cps	*endo*-C_6
exo-2-Hydroxycamphene-*endo*-2-carboxylic acid lactone (6) (in $DCCl_3$)	1.04 (3)	s	Methyl
	1.12 (3)	s	Methyl
	1.29–2.30 (5)	Overlapping peaks	
	2.95 (1)	d (1:1), J = 6.0 cps	C_1
	3.34[c] (1)	s	Hydroxyl
	4.75 (1)	t, b, d of d, (1:2:1) J = 6.0, 6.0 cps	C_6

[a] Resonances are given in δ units relative to tetramethylsilane internal standard (δ 0). The values given for multiplets designate the positions of the centers of the groups. Numbers in parentheses refer to the relative values of the areas of the peaks. [b] s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, b = broad. [c] This resonance shifts position with changes in solvent, temperature, and concentration; it disappears on addition of D_2O.

chloro ketone can result from the loss of both Cl and CO from the parent ion and corresponds to the peak at *m/e* 110 (loss of CO) in the spectrum of **8**. The base peak for both compounds is at *m/e* 69 and could arise from the scission given in eq **5**. The moderately intense peak exhibited by both **5** and **8** at *m/e* 41 could result from loss of CO from fragment **11**.



(5)

5, X = Cl
8, X = H

11
m/e 69

Structure of Compound 6.—The molecular formula for solid **6** (mp 214°), deduced from carbon–hydrogen analysis and molecular weight (182, Figure 2), is $C_{10}H_{14}O_3$. It is clear from the ir spectrum that a lactone group (5.61 μ) accounts for two of the oxygens; the third is incorporated in an intramolecularly hydrogen bonded tertiary hydroxyl group (2.73 μ with a shoulder at 2.82 μ, and 7.37 μ). *gem*-Dimethyl groups are also present (7.19 and 7.30 μ). This information, combined with a knowledge of the source of the material, prompted the formulation of its structure as hydroxylactone **6** (see Scheme I).

The nmr spectrum is compatible with the assigned structure. Peaks are present for two nonequivalent methyl groups and a hydroxyl group (Table I). Since the C_1 proton is split (J = 6 cps), the hydrogen at C_6 must be *exo*. Appearance of this *exo* proton as a triplet results from its interactions with the proton at C_1 and also with the *exo* hydrogen at C_5, both coupling constants being the same and equal to 6 cps.[11,12] Little if any interaction between the *exo* H at C_6 and the *endo* H at C_5 is discernible, in agreement with the observations of Ramey, *et al.*,[12] on similar systems.

The mass spectrum of **6** (Figure 2) shows the loss of water (*m/e* 164), CO (*m/e* 154), CO_2 (*m/e* 138), and HOCO (*m/e* 137). The base peak at *m/e* 88 must result from extensive rearrangements of the molecular ion to yield either the $C_3H_4O_3$ or the $C_4H_8O_2$ ion. The spectrum is impossible to interpret in the absence of deuterium labeling and serves as a good illustration of Djerassi's thesis[13] that relatively simple bicyclic compounds undergo complex rearrangements and fragmentations on electron bombardment.

Experimental Section

Preparation of the Chloro Compounds.—10-Chlorotricyclene (1) was prepared by chlorination of camphene[1] in a carbon tetrachloride solution containing pyridine to prevent formation of camphene hydrochloride, a deleterious by-product because it decomposes to hydrogen chloride, a catalyst for the rearrangement of **1** to **2**. The final yield of 96% pure **1** (glpc), entirely free of unsaturated contaminants, was only 1%. ***exo*-6-Chlorocamphene (2)** was prepared by rearrangement of **1**. Copper pellets, shown to accelerate rearrangement, were added to the crude chlorinated solution (no pyridine)[1] and the mixture was heated in an open beaker on a steam bath for several hours during which time camphene and hydrogen chloride (decomposition of camphene hydrochloride) evaporated and **1** rearranged to **2**. Infrared bands at 14.12 and 14.52 μ (**1**) were replaced by a band at 14.33 μ (**2**). The resultant oil was vacuum distilled using a spinning-band column (Nester–Faust); the fraction collected between 85 and 90° (20 mm) was found by ir and glpc to be 85% pure **2**. A 95% pure isomeric mixture of ***cis*- and *trans*-8-chlorocamphene** (1:2, glpc) was prepared by treating *exo*-2,10-dichlorobornane with dimethylaniline.[1] The isomers were inseparable on DC-11, 10% Bentone, 20% Carbowax M20, and FFAP glpc columns (Varian Aerograph).

General Procedure for Oxidations.—The general method for oxidation and work-up was the same for all compounds. A

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[11] This *exo–exo* coupling constant (J = 6 cps) is low compared with 8.9–11.4 cps found in norbornanes; see ref 9 and 12.

[12] K. C. Ramey, D. C. Lini, R. M. Moriarty, H. Gopal, and H. G. Welsh, *J. Amer. Chem. Soc.*, **89**, 2401 (1967).

[13] D. S. Weinberg and C. Djerassi, *J. Org. Chem.*, **31**, 115 (1966).

stirred solution of chloro compound was refluxed with excess potassium permanganate until completion of oxidation was ascertained by glpc analysis of a small sample (see below for conditions). When the reaction was finished, the heavy inorganic precipitate was suction filtered, the filter cake leached with ether and 10% sodium bicarbonate, and then Soxhlet extracted with ether. Solid sodium chloride was added to the filtrate, layers were separated, and each layer was washed with the alternate solvent. The chilled combined aqueous portions were acidified with sulfuric acid and any precipitated organic acid was filtered, washed, dried, and identified as tricyclenic acid (**7**) by its melting point and ir spectrum (compared with that of authentic acid prepared from camphene[14]). The combined dried crude ether layers were routinely analyzed by glpc in order to determine the relative amounts of the neutral products. After solvent was evaporated the oil was distilled using suitably located traps held at −50° (Dry Ice–alcohol) to prevent loss of the typically volatile bicyclic ketones. All fractions were examined by ir and glpc. Results for each individual compound are given below.

Oxidation of 10-Chlorotricyclene (1).—When the reaction was carried out in 75% aqueous acetone with magnesium sulfate added (equivalent to the amount of potassium permanganate used) tricyclenic acid was isolated from the aqueous layer in yields ranging from 10 to 95%. Analysis (glpc areas and ir of eluates) of the ether layer demonstrated the presence of **5** and **6** in approximately equal amounts as well as three other unknown materials in trace amounts. Similar analysis of the ether layers from oxidations conducted in 85% aqueous acetone in the absence of magnesium sulfate showed approximately equal amounts of 10-hydroxytricyclene (**9**) and *exo*-6-hydroxycamphene (**10**) (interconversion of these two alcohols did not occur under glpc conditions used[1]), and a carbonyl compound (5.73 and 5.89 μ; possibly 6-oxocamphenilone) having a retention time between the alcohols and the lactone, but no ketone or lactone.

In order to test whether **1** can isomerize to **2** in the oxidizing medium, a few drops of **1**, bp 89° (20 mm), was dissolved in spectrograde carbon tetrachloride and placed over manganese dioxide at room temperature for 18 hr. The solution was filtered from the oxide; its ir spectrum showed complete disappearance of peaks at 11.41, 11.75, 14.12, and 14.52 μ (**2**). All peaks assignable to **2**[1] were present.

Oxidation of *exo*-6-Chlorocamphene (2).—For reactions in 75% aqueous acetone with added magnesium sulfate analyses (glpc areas and ir of eluates) of the crude ether layers showed approximately equal amounts of lactone and ketone. Vacuum distillation gave a fraction (0.5 g from 3.8 g starting material), bp 93° (16 mm), shown by glpc and ir to be mostly **5**, slightly contaminated with **6** and an unknown. The residue (0.8 g) contained both **5** and **6** in a 1:6 ratio. The lactone (**6**) was purified by recrystallization from alcohol, mp 214°. No acid was isolated from oxidation of samples of **2** known to be free of **1**. Our previous report[1] of a 5% yield of acid from **2** is in error, presumably because of our earlier use of starting material slightly contaminated with **1**. The ether layers obtained from oxidations in the absence of magnesium sulfate contained **6**, **9**, and **10** (glpc areas, ir of eluates) in a ratio of approximately 2:1:1; two other unidentified alcohols (2.76 and 2.90 μ) were found in nearly the same amounts as **9** and **10**; **5** was not detected.

Oxidation of *cis*- and *trans*-8-Chlorocamphene (3 and 4).—Mixtures of isomers (**3**/**4**, 1:2) were oxidized in either 75% aqueous acetone or 75% aqueous *t*-butyl alcohol, with or without added magnesium sulfate, to camphenilone as the only product (glpc and ir of eluate as compared with authentic material from oxidation of camphene). A peak which appeared at the same retention time as the starting material could not be eliminated by refluxing with additional permanganate. The ir spectrum of the eluate from this peak was different from that of the *cis–trans* mixture: the relative intensity of the peak at 7.60 μ was much less whereas absorption at 5.69 μ was far more pronounced; peaks were missing at 6.30, 9.45, 12.86, 14.58 (weak), 11.84, and 13.83 μ (strong). In the nmr spectrum peaks were missing at δ 1.06 (methyl for *trans*), 3.17 (H at C_1 for *trans*), 4.50 (vinyl for *trans*), and the resonances present, at 1.23, 1.27, 2.67, and 5.75, were those previously assigned[1,8] to the *cis* isomer. Area analysis of the gas chromatograms of the crude product mixtures revealed that the ratio of **3** to **8** was in most cases approximately 1:2. *cis*-8-Chlorocamphene (**3**) and camphenilone (**8**) were not effectively separated by vacuum distillation and almost equal amounts of each were found (glpc areas, ir of eluates) in fractions whose boiling points ranged between 68 and 80° (12 mm). No acid was ever isolated from the aqueous fraction.

Analytical Information.—Gas chromatographic analyses were carried out on an Aerograph Model A-90-P (formerly Wilkens Instrument and Research Inc., now Varian Aerograph). Perkin-Elmer ir spectrophotometers (Model 137-B Infracord and Model 337), a Varian A-60 nmr spectrometer, and a Consolidated Electrodynamics mass spectrometer (Model 21-103 C) were used. Carbon–hydrogen analyses were performed at Schwartzkopf Microanalytical Laboratory, Woodside, N. Y. All analytical data were obtained from materials purified by preparative glpc.

A. Elemental Analyses.—Qualitative analysis (sodium fusion) established the presence of chlorine in compound **5**.

Anal. Calcd for $C_9H_{13}OCl$ (**5**): C, 62.62; H, 7.59. Found: C, 62.53; H, 7.72.

Anal. Calcd for $C_{10}H_{14}O_3$ (**6**): C, 65.91; H, 7.74. Found: C, 65.94; H, 7.99.

B. Gas Chromatographic Analyses.—Columns were made of 0.25 × 60 in. copper tubing packed with DC-11 or 10% Bentone 34 on Chromosorb W, DMCS, 60–80 mesh (Varian Aerograph). A wide range of temperatures and carrier gas flow rates gave satisfactory operating conditions. Typically both chlorinated and oxidized mixtures were examined at t_{col} 105°, t_{det} 144°, t_{inj} 154°; helium flow rates were 25–80 ml/min. The sequence of retention times under all conditions was $\mathbf{8} < \mathbf{2} < \mathbf{3} \approx \mathbf{4} \approx \mathbf{9} < \mathbf{10} \approx \mathbf{5} < \mathbf{6}$.

C. Infrared Absorptions.—Listed below are important peaks (given in microns) in the ir spectra of new compounds **5** and **6**. (characteristic peaks for other compounds are recorded elsewhere):[1] **compound 5** (neat), 2.85 (overtone of C=O), 5.70 with shoulder at 5.80 (C=O), 7.21, 7.32 (*gem*-dimethyl), 2.70, 9.33, 10.30, 10.44, 10.92, 11.19, 11.88, 12.43, 13.18, 14.90; **compound 6** ($HCCl_3$), 2.73 with shoulder at 2.82 (OH), 5.61 (lactone), 7.19, 7.30 (*gem*-dimethyl), 7.37 (*t*-OH), 7.83, 8.43, 8.64, 8.85, 9.03, 9.68, 9.95.

Registry No.—**1**, 4017-69-0; **2**, 4031-63-4; **3**, 4031-61-2; **4**, 4031-62-3; **5**, 16205-79-1; **6**, 16205-80-4; **8**, 13211-15-9.

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(14) M. Hanack and H. Eggensperger, *Ann.*, 648, 3 (1961).