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Acenaphthylene was recrystallized from petroleum ether (bp 60–80°). Maleic anhydride and dichloromaleic anhydride were recrystallized from chloroform and ligroin (bp 80–100°). Chloro- and methylmaleic anhydride were fractionally distilled, crystallized at −40° from ether–petroleum ether, and again distilled. All solvents were distilled prior to use.

Photochlorination of Alcohols

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Three limiting conditions have been found for the photochlorination of 1-pentanol. In 70% H_2SO_4, chlorination is the exclusive reaction. Polar effects lead to mild selectivity for remote attack. In 20–40% H_2SO_4 and in CCl_4, oxidation and chlorination compete, but conditions can be chosen to make chlorination >90%. In aqueous acetate buffer, chlorination can predominate over oxidation though both compete. There is good selectivity for δ-chlorination, and the chlorination proceeds *via* the alkyl hypochlorite. Photochlorination of cyclopentanol at pH 5 forms 5-chloropentanal quantitatively.

In the many reviews that cover photochlorination by Cl_2,[2-7] data on alcohols are conspicuously absent. The situation is summarized by Poutsma:[8] "alcohols react rapidly with chlorine by a series of steps which ultimately lead to oxidation and formation of carbonyl compounds and chlorinated carbonyl compounds and radical chlorination is not a generally useful route to chloro alcohols." Reports on photochlorination of ethanol[9] and 1-propanol[10] supported this view.

It was conceived that primary and secondary alcohols might be successfully photochlorinated if the hydroxy group were protected by protonation. Kollonitsch and coworkers[11] had already shown that Cl_2 photochlorinations in H_2SO_4 were successful, and they photochlorinated amino acids and peptides in this way. Since alcohols are half-protonated in ~50% H_2SO_4[12-15] and are converted to hydrogen sulfates in 96% H_2SO_4,[16] an intermediate 70% H_2SO_4 was chosen to give extensive protonation without hydrogen sulfate formation.

1-Pentanol is quantitatively photochlorinated in 70% H_2SO_4 with no detectable oxidation (Table I). Products were converted to acetates for both gc analysis and material balance distillation. For the gc analyses, conversion was limited to 50% by using 0.5 mol of Cl_2/mol of 1-pentanol. For the material balance studies, it was more convenient to use equimolar Cl_2 and 1-pentanol. The distilled products consisted of 1-pentyl acetate, monochloro-1-pentyl acetates, and material characterized as dichloro-1-pentyl acetates from the boiling point. The recovery was 87% of theoretical. The gc bands were identified by exact superposition on bands of authentic samples.

The pattern of the chlorination is typical for alkane chains containing a terminal electronegative substituent. These have been extensively investigated and show avoidance of the α position, partial avoidance of the β position, and near-random attack at the γ position and more remote methylenes.[2-7]

The results with 2-hexanol are similar (Table II) and show that the method is equally successful with secondary alcohols. However, the method may be limited to those alcohols which are small enough to be soluble in 70% H_2SO_4, yet are large enough to have γ and more remote hydrogens. The products from such alcohols typically separate on dilution and this facilitates their isolation.

This accomplished the initial objective and the study could have been terminated at this point. However, we were curious about photochlorination of alcohols in less acidic conditions such as CCl_4, dilute H_2SO_4, and aqueous acetate buffers. The results were unexpected.

These latter results will be better understood if the facts regarding the dark ionic oxidation are presented first. In an air atmosphere and in an aqueous media from acetate buffers at pH 5 to 40% H_2SO_4, Cl_2 rapidly oxidizes 1-pentanol to pentyl pentanoate. Analysis by gc of ether-extractable products showed pentyl pentanoate as the only product and specifically pentanal and pentanoic acid were not detected by gc or by nmr of aqueous Na_2CO_3 extracts. The reaction is complete in several

Table I
Photochlorination of 1-Pentanol (0.90 *M*) with Cl_2 at 25° under N_2

	Relative yields at 50% conversion, %				
Solvent	2-Cl	3-Cl	4-Cl	5-Cl	Pentyl pentanoate
70% H_2SO_4	6	25	51	18	0
60% H_2SO_4	9	26	41	24	0
50% H_2SO_4	9	26	40	22	3
40% H_2SO_4	8	24	39	19	19
30% H_2SO_4	12	26	34	17	11
20% H_2SO_4	10	26	38	18	8
CCl_4	11	27	37	20	5
Aqueous acetate buffer	0	9	86	1	4

Table II
Photochlorination of 2-Hexanol (0.90 *M*) with Cl_2 at 25° under N_2

	Relative yields at 50% conversion, %					
Solvent	3-Cl	4-Cl[a]	5-Cl	6-Cl	2-Hexanone	Chloro-2-hexanones
70% H_2SO_4	13	24	41	22	0	0
50% H_2SO_4	15	27	36	16	6	0
30% H_2SO_4	3	7	6	2	77	5
CH_2Cl_2	14	28	31	20	7	0
Aqueous acetate buffer	3	5	75	5	12	0

[a] The gc bands of 1-Cl and 4-Cl were not resolved. However, 4-Cl should predominate over 1-Cl because of photochlorination of a secondary hydrogen relative to a primary hydrogen.

hours at 25°. Protonation of the alcohol stops the oxidation and 1-pentanol in 70% H_2SO_4 saturated with Cl_2 was unchanged after 24 hr at 25° as shown by the nmr spectrum and by gc of ether extracts of diluted reaction mixtures.

The formation of pentyl pentanoate rather than pentanoic acid may seem curious. However, there is much precedent for this predominance of ester products. Such a predominance has been reported for chromic acid oxidation of alcohols,[17] hypochlorite oxidations,[18] and photodecomposition of 1-butyl hypochlorite.[19]

In 20–50% H_2SO_4 and in CCl_4, use of N_2 (O_2-free) atmosphere and 300-W sun lamp irradiation caused photochlorination of 1-pentanol to predominate over oxidation (Table I). The ether-extractable products were distilled and a satisfactory material balance was obtained (Experimental Section). Since the chlorination pattern resembles that in 70% H_2SO_4 and since photochlorination in 70% H_2SO_4 gave no oxidation (*via* α-chlorination), α-chlorination is believed to be absent likewise from the 20–50% H_2SO_4 runs. If so, the 0–11% oxidation arises from competing ionic oxidation.

With 2-hexanol, it was more difficult to overcome the competing ionic oxidation, and the latter predominated in 30% H_2SO_4 despite the O_2-free atmosphere and 300-W irradiation (Table II).

With small alcohols like ethanol and 1-propanol, even though primary, it will be more difficult to prevent predominance of ionic oxidation because the hydrogens are deactivated toward photochlorination by proximity to the hydroxyl substituent and/or being primary. It is suspected that this coupled with use of air atmospheres accounts for the earlier reports that ethanol and 1-propanol oxidize on photochlorination.[9,10]

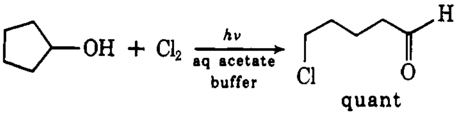
In aqueous acetate buffer, a different pattern of photochlorination emerged with selectivity for δ-chlorination as shown for 1-pentanol in Table I and 2-hexanol in Table II. This selectivity is the same as that reported for photodecomposition of alkyl hypochlorites[19-25] and it is reasonable to presume that hypochlorites are intermediates in these aqueous acetate reactions.

Table III
Photochlorination of Alcohols (0.90 *M*) in Aqueous Acetate Buffer (4.7 *M*, pH 5) at 25° under N_2 with Stirring and 0.5 Equiv of Cl_2

	Relative gc band areas, %							
Alcohol	1-Cl	2-Cl	3-Cl	4-Cl	5-Cl	6-Cl	RCOOR	Ketone
1-Butanol		20	30	50			0	
1-Hexanol		1	4	77	8	0	10	
2-Pentanol[a]	5		6	21	53			16
2-Octanol[a]	0		0	8	83	3[b]		0

[a] In the absence of irradiation, the products were 50% recovered alcohols, 48% ketone, and ~2% chloro ketones. [b] No gc bands could be detected in the region expected for the 7-Cl and 8-Cl derivatives.

The photochlorination of cyclopentanol in aqueous acetate buffer gave 20% recovered cyclopentanol and 80% 5-chloropentanal (eq 1). This predominance of ring opening



(1)

in cyclopentyl radicals has been reported before in the decomposition of tertiary cyclopentyl hypochlorites to δ-chloro ketones.[23,26]

Four other alcohols were photochlorinated in a stirred aqueous acetate buffer. These studies were less complete in that no material balance was attempted, only relative gc band areas were recorded, and only a limited number of the gc bands were identified by direct comparison with authentic samples (the remaining bands were identified on the basis that retention times increase with increasing separation of polar groups). These preliminary data are summarized in Table III and show the selectivity for δ-chlorination under these conditions. It is remarkable that the photochlorinations proceed so completely *via* the hypochlorite, and this method offers some advantages over methods involving isolation of the unstable primary and secondary alkyl hypochlorites.

The photochlorination of *tert*-butyl alcohol in acetate buffer was monitored by nmr. The only products were chloromethane and acetone, which are the decomposition products to be expected from *tert*-butyl hypochlorite.[26] Evidently they arose from decomposition of the hypochlorite, and photodecomposition of tertiary hypochlorites can be achieved by photolyzing a mixture of the tertiary alcohol and Cl_2 in an acetate buffer.

Experimental Section

Photochlorination of Alcohols. The alcohol (0.15 mol) was added to 150 ml of solvent and the air was swept out by a stream of N_2. While the mixture was magnetically stirred and while it

Table IV
Material Balance from the Photochlorination of 0.15 Mol of 1-Pentanol with 0.15 Mol of Cl_2

	Yield, %			
Solvent	$C_5H_{11}OAc$	C_5H_{10}-ClOAc	$C_5H_9Cl_2$-OAc	Total
70% H_2SO_4	24	48	15	87
30% H_2SO_4	35	28	16	79
CCl_4	35	29	21	85
Aqueous acetate	24	52	10	86
buffer	37	42	13	92

was irradiated with a 300-W tungsten bulb equipped with parallel reflector, 0.075 mol of weighed liquid Cl_2 was allowed to vaporize into the reaction flask. Addition required about 20 min and stirring and irradiation were continued until a KI test (on an aliquot) was negative.

The mixture was extracted with diethyl ether (after dilution to 20% H_2SO_4 in the cases of more concentrated acids). The extract was washed with 5% Na_2CO_3 and dried over $MgSO_4$. The solvent was removed by aspiration and the residue was refluxed for 1 hr with 30 g of acetic anhydride. The acetylated mixture was diluted with ether, washed with 5% Na_2CO_3, dried over $MgSO_4$, and concentrated by aspiration.

The aqueous acetate buffer (solvent in certain runs) was prepared by dissolving 408 g of sodium acetate trihydrate and 102 g of acetic acid in water and diluting to 1 l.

Gas Chromatography. All gas chromatograms were obtained on a Barber-Colman Series 5000 equipped with flame ionization detector. The fuel gas was an air-H_2 mixture and the carrier gas was N_2. A 6 ft × 0.25 in. glass U column was packed with 10% silanated polyethylene glycol succinate (EGSS-X) on 100-200 mesh Chromosorb Q.[27] The injector temperature was 220°, the detector temperature was 250°, and the flow rate was 21 ml min^{-1}.

Relative Gc Retention Times. Times for products derived from 1-butanol (column temperature 125°) follow: butyl acetate, 1.00; butyl butanoate, 1.31; 2-chloro-, 2.72; 3-chloro-, 3.44; and 4-chloro-1-butyl acetate, 5.47. Times for products derived from 1-pentanol (column temperature 125°) follow: pentyl acetate, 1.00; pentyl pentanoate, 1.60; 2-chloro-, 2.43; 3-chloro-, 3.23; 4-chloro-, 3.90; and 5-chloro-1-pentyl acetate, 5.60. Times for products derived from 1-hexanol (column temperature 135°) follow: hexyl acetate, 1.00; hexyl hexanoate, 2.17; 2-chloro-, 2.52; 3-chloro-, 3.09; 4-chloro-, 3.89; 5-chloro-, 4.28; and 6-chloro-1-hexyl acetate, 5.60. Times for products derived from 1-octanol (column temperature 165°) follow: octyl acetate, 1.00; octyl octanoate, 3.45; 2-chloro-, 2.33; 3-chloro-, 2.80; 4-chloro-, 3.18; 5-chloro-, 3.45; 6-chloro-, 3.82; 7-chloro-, 3.96; and 8-chloro-1-octyl acetate, 5.18.

Relative retention times for products derived from 2-pentanol (column temperature 90°) follow: 2-pentanol, 1.00; 2-pentanone, 0.813; 3-chloro-, 1.70; and 1-chloro-2-pentanone, 3.12. At a column temperature of 125° they were as follows: 2-pentyl acetate, 1.00; 2-pentanone, 1.00; 1-chloro-, 3.77; 3-chloro-, 2.48; 4-chloro-, 3.06; and 5-chloro-2-pentyl acetate, 4.85.

Times for products derived from 2-hexanol (column temperature 100°) follow: 2-hexanol, 1.00; 2-hexanone, 0.830; 3-chloro-, 1.64; and 1-chloro-2-hexanone, 3.58. At a column temperature of 115° times were as follows: 2-hexyl acetate, 1.00; 2-hexanone, 0.814; 1-chloro-, 3.50; 3-chloro-, 2.67 and 2.91; 4-chloro-, 3.40 and 3.63; 5-chloro-, 4.05 and 4.42; and 6-chloro-2-hexyl acetate, 6.47. Where two times are given, this represents erythro and threo isomers. They were easily paired because each erythro-threo pair always gave equal gc band areas despite variations in the other product ratios.

Times for products derived from 2-octanol (column temperature 135°) follow: 2-octanol, 1.00; 2-octanone, 0.870; 3-chloro-, 1.46; and 1-chloro-2-octanone, 2.83. At a column temperature of 125° the times were as follows: 2-octyl acetate, 1.00; and 2-octanone, 0.800. At a column temperature of 150° the times were as follows: 2-octyl acetate, 1.00; 2-octanone, 1.00; 4-chloro-, 2.34 and 2.61; 5-chloro-, 2.89 and 3.16; and 6-chloro-2-octyl acetate, 3.47 and 3.76. Again, two times represents an erythro-threo pair. A minor gc band at 5.11 consistently appeared in this last set of gc bands.

Times for products derived from cyclopentanol (column temperature 150°) follow: cyclopentyl acetate, 1.00; cyclopentanone, 1.10; 5-chloropentanal, 2.26; 2-chlorocyclopentyl acetate, 2.69; 3-chlorocyclopentyl acetate, 3.08; and 2-chlorocyclopentanone, 3.23.

The compounds listed above represent either identified products, or potential products for which a search was made.

Authentic Samples. Pentanal, pentanoic acid, alcohols, ketones, and butyl butanoate were commercial samples. Pentyl pentanoate and octyl octanoate were prepared from the acid chloride plus the alcohol. The nmr spectra and boiling points were recorded.[28] α-Chloro ketones were prepared by addition of 0.5 equiv of Cl_2 to a solution of the ketone in 30% H_2SO_4. The gc of the ether extract showed only two other bands in the region of the starting ketone and these were assigned to the two possible α-chloro ketones. The longer retention time was assigned to the 1-chloro-2-alkanone and the shorter retention time to the 3-chloro-2-alkanone on the basis that the latter generally have lower boiling points (3-chloro- and 1-chloro-2-pentanone, bp 136[29] and 158°;[30] 3-chloro- and 1-chloro-2-hexanone, bp 60 (23 mm),[31] 70° (15 mm).[32]

For the monochloro primary alcohols, mixtures of known composition were available from a previous study.[33] For the monochloro-2-pentanols and -2-hexanols, gc bands were assigned on two bases. First was that retention times increase with increasing separation of the chloro and acetoxy functional groups. Second, the known mixtures of the α-chloro ketones and ketone (from 2-pentanone and 2-hexanone) were reduced to the α-chloro-2-alkanols and alkanol with $NaBH_4$ in 95% ethanol (18 hr at 25°). The gc analysis gave three bands in the same ratio of areas and in the same order of retention times as the ketones. This served to identify the gc bands of the 1-chloro-2-alkanol, 3-chloro-2-alkanol, and unsubstituted 2-alkanol.

For the monochloro-2-octanols, identification of the gc bands rested on analogies to the results with 2-pentanol and 2-hexanol.

Material Balances in the Photochlorination of 1-Pentanol. The ether-extractable products from photochlorinations of 1-pentanol were converted to acetates as described above and distilled. Three fractions were obtained: bp 140-150° (1-pentyl acetate), bp 108-110° (33 mm) (monochloro-1-pentyl acetates plus 0-11% of pentyl pentanoate), and bp 135-145° (33 mm) (presumed to be dichloro-1-pentyl acetates). Table IV summarizes the yields of these three fractions and shows that 79-87% of the starting 1-pentanol is accounted.

5-Chloropentanal. A mixture of 17.6 g (0.200 mol) of cyclopentanol and 200 ml of acetate buffer (described above) was introduced into a 500-ml flask equipped with a Dry Ice-acetone condensor and a cooling bath at 15°. After sweeping with N_2, 17.8 g (0.250 mol) of Cl_2 was introduced over 30 min with stirring and irradiation (300-W tungsten sun lamp). Stirring and irradiation were continued until a KI test for Cl_2 was negative (1-2 hr). During the reaction, a slow stream of N_2 was maintained and this accounts for the loss of some Cl_2.

The mixture was extracted with diethyl ether. The extract was washed with 5% Na_2CO_3, dried over $MgSO_4$, and concentrated under vacuum to give 22.2 g of ether-free product. The nmr spectrum in CCl_4 indicated 80% 5-chloropentanal [δ 1.75 (m, 4 H), 2.45 (m, 2 H), 3.55 (t, 2 H), and 9.60 (s, 1 H)] and 20% cyclopentanol [δ 1.55 (m, 8 H) and 4.20 (m, 1 H)]. The yield was confirmed by treating 0.50 g of product with 2.00 g of 2,4-dinitrophenylhydrazine by the method of Ban[34] to give 0.85 g of the dinitrophenylhydrazone (79% yield based on cyclopentanol consumed), mp 104-105° (lit. mp 108°).[34]

A gc analysis of the product and the acetylated product confirmed that only cyclopentanol and 5-chloropentanal were present and that specifically cyclopentanone, 2-chlorocyclopentanone, and 2- and 3-chlorocyclopentanol were absent. Attempts to distil the acetylated product gave 5-chloropentanal, bp 81-85° (23 mm) (lit. [35] bp 52° (12 mm[35]), but there was considerable loss due to polymerization.

This would appear to be the most attractive method for preparing 5-chloropentanal.

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Registry No. 1-Butanol, 71-36-3; 1-pentanol, 71-41-0; 1-hexanol, 111-27-3; 1-octanol, 111-87-5; 2-pentanol, 6032-29-7; 2-hexanol, 626-93-7; 2-octanol, 123-96-6; cyclopentanol, 96-41-3; 1-pentyl acetate, 628-63-7; 2-chloro-1-pentyl acetate, 49633-67-2; 3-chloro-1-pentyl acetate, 49633-68-3; 4-chloro-1-pentyl acetate, 36978-15-1; 5-chloro-1-pentyl acetate, 20395-28-2; pentyl pentanoate, 2173-56-0; dichloro-1-pentyl acetate, 49694-02-2; 5-chloropentanal, 20074-80-0.

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Mechanistic Studies Regarding the Oxidation of Alcohols by Silver Carbonate on Celite

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The mechanism of the oxidation of alcohols by silver carbonate on Celite was thoroughly investigated to ascertain the nature of the transition state and the possible intervention of reaction intermediates. Kinetic, stereochemical, and isotopic labeling techniques were used to differentiate among the various theoretically plausible mechanistic alternatives. The effects of surface adsorption and solvent composition on the outcome of the reaction were also studied. The data were consistent with a concerted process for which a model is proposed.

Although silver carbonate precipitated on Celite is a relatively new[1] oxidizing agent, it has already gained wide acceptance. The chief advantages of this reagent lie in its selectivity, the mild conditions necessary to carry out the oxidation, and the ease with which the products can be isolated. These factors have been extensively reviewed in a recent report.[2] It can be seen from this review that silver carbonate is an efficient and convenient reagent for the oxidation of not only alcohols but a variety of other substrates.

In view of the wide scope of this reaction and its ever-increasing applications in organic synthesis, we thought that it would be of considerable theoretical as well as practical interest to undertake a comprehensive study of the mechanism of the oxidation of alcohols. Some preliminary findings of this investigation were reported in an earlier communication.[3] We now wish to present the final data which bear on the mechanism. For convenience we have chosen to present and discuss our findings under seven different headings: stoichiometry, intermediates, surface phenomena, isotope effects, steric effects, kinetics, and postulated models.

Results and Discussion

I. Stoichiometry. Since the usual procedure for carrying out silver carbonate oxidations utilizes a large excess of silver carbonate, the mole ratios of reactants and products are not immediately apparent. To ascertain the exact stoichiometry of the reaction we have conducted two independent experiments. The first was a gravimetric method which consisted of trapping the carbon dioxide produced during the course of the reaction in a suitable absorption tube. It was found that the moles of carbon dioxide produced were approximately equal to the moles of alcohol oxidized and independent of the amount of silver carbonate used. The second experiment involved the oxidation of standard solutions of benzhydrol with varying amounts of silver carbonate which had been previously analyzed to obtain its exact composition. Quantitative analyses of the product (benzophenone) were carried out by comparing the ultraviolet absorption of the mixtures against a standard Beer's law curve. These data are summarized in Tables I and II. It was generally found that the mole ratio of alcohol to silver carbonate was 1:1.

The above data allowed us to establish the exact stoichiometry of the reaction, which can be summarized by the following equation.

$$R_2CHOH + Ag_2CO_3 \longrightarrow R_2C{=}O + H_2O + 2Ag + CO_2$$

The stoichiometric relationships defined by the above equation are consistent with the mechanistic model proposed in the last section.[4]

II. Intermediates. The oxidation of alcohols to carbonyl compounds necessarily involves the removal of two hydrogens. In principle, unless the process is concerted, each of these hydrogens may come off as a free radical, a hydrogen ion, or a hydride ion. This leads to six theoretically possible reaction intermediates.


$-\dot{C}-OH$
1


$-\ddot{C}-OH$
2


$-\overset{+}{C}-OH$
3


$-CH-O\cdot$
4


$-CH-O^-$
5


$-CH-O^+$
6