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METAL-CATALYZED ORGANIC PHOTOREACTIONS
ONE-STEP SYNTHESIS OF CHLORINATED KETONES FROM OLEFINS BY THE PHOTO-OXIDATION IN THE PRESENCE OF IRON(III) CHLORIDE

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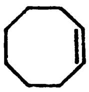
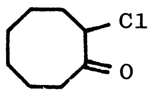
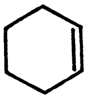
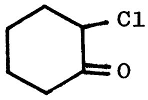
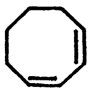
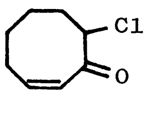
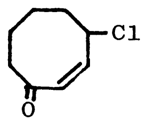
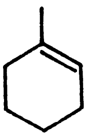
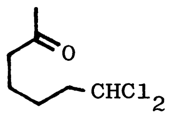
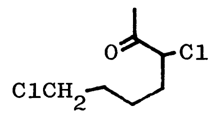
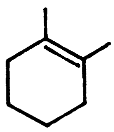
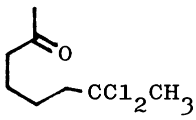
Under the photo-oxidation in pyridine in the presence of iron(III) chloride, mono- and di-substituted olefins gave α-chloroketones, while tri- and tetra-substituted olefins gave dichloroketones involving C-C bond cleavage.

In the preceding paper,[1] we described a regioselective hydroxyhydroperoxidation of olefins by the uranyl compounds-catalyzed photo-oxidation. We observed now that the photo-oxidation in the presence of iron(III) chloride afforded either α-chloroketones or C-C bond-cleavage products, depending upon the types of olefins.

When solutions of mono- and di-substituted olefins 1 - 7 (0.5 mmol, 0.025 M) in pyridine, containing an equivalent amount of iron(III) chloride, were irradiated with Pyrex-filtered light (high-pressure mercury vapor lamp, Ushio UM 452 (450 W)) for 30 - 120 min while oxygen gas was bubbled through, α-chloroketones 10 - 17 and vinylog 18 were obtained as the almost exclusive products (Type A). Under the same reaction conditions, tri- and tetra-substituted olefins 8 and 9 afforded products 19 - 21 (Type B). The results are summarized in Table 1. It was confirmed in the reaction of cyclooctene (1) that the lack of oxygen under the otherwise same conditions (under nitrogen) resulted in the formation of 1,2-dichlorocyclooctane (cis + trans) in 16% yield, while the dark reaction in the presence of iron(III) chloride and oxygen resulted in the recovery of the starting material. The relative positions of hydroxyl group and chlorine in the

Table 1. Products and yields of the photo-oxidation of olefins in pyridine in the presence of an equivalent amount of $FeCl_3$

Types	Olefins	Products	Yields[a]
A	 1	 10[b]	57% (40%)
	 2	 11	33%
	1-octene 3	$C_6H_{13}COCH_2Cl$ 12	10%
	2-octene 4	$C_5H_{11}COCH(Cl)CH_3$ + $C_5H_{11}CH(Cl)COCH_3$ 13 (1 : 1.3) 14	43% 50%[c]
	$CH_3CH = CHCH_2OH$ 5	$CH_3COCH(Cl)CH_2OH$ 15[d]	28%
	oleyl alcohol 6	$C_8H_{17}C(=O)—C(H)(Cl)(CH_2)_8OH$ 16	33%[c]
	 7	 +  17 (1 : 2.4) 18	29%[e]
B	 8	 +  19 (6 : 1) 20	29% 19: (16%) 20: (3%)
	 9	 21	26%

a) Yields were determined by NMR analyses using an internal reference on the crude materials. Values in the parentheses refer to the isolated yields. The amounts of the unreacted starting materials were not determined.

b) Cyclooctene oxide (3%) and cis- and trans-1,2-dichlorocyclooctane (2%) were identified as by-products.

c) In the presence of tri-t-butylphenol.

d) 2,3-Dichloro-1-butanol (5%) was identified as by-product.

e) Reaction in pyridine-CCl_4 (1 : 1 by volume).

product 16 has not been elucidated. The hydroxyl group was intact under the present reaction conditions. The isolation of 17 and 18 in the reaction of diene 7 reflects the inertness of the double bond conjugated with the carbonyl group. Actually, 3-methyl-2-cyclohexenone was recovered unchanged under the present reaction conditions.

In contrast with the stoichiometric reactions of iron(III) chloride mentioned thus far, we found that it functioned as catalyst when an appropriate chlorine source was present. Carbon tetrachloride and chloroform were found to be suitable for this purpose, as revealed from the results shown in Table 2.

Table 2. Concentration effect of $FeCl_3$ upon the product yields from 4.[a)]

$FeCl_3$ Mol equiv to 4	Combined yields of 13 and 14	
	in Pyridine-CCl_4	in Pyridine-$CHCl_3$
0	13%	
1/10	46%	
1/2	64%	60%
1	73%	

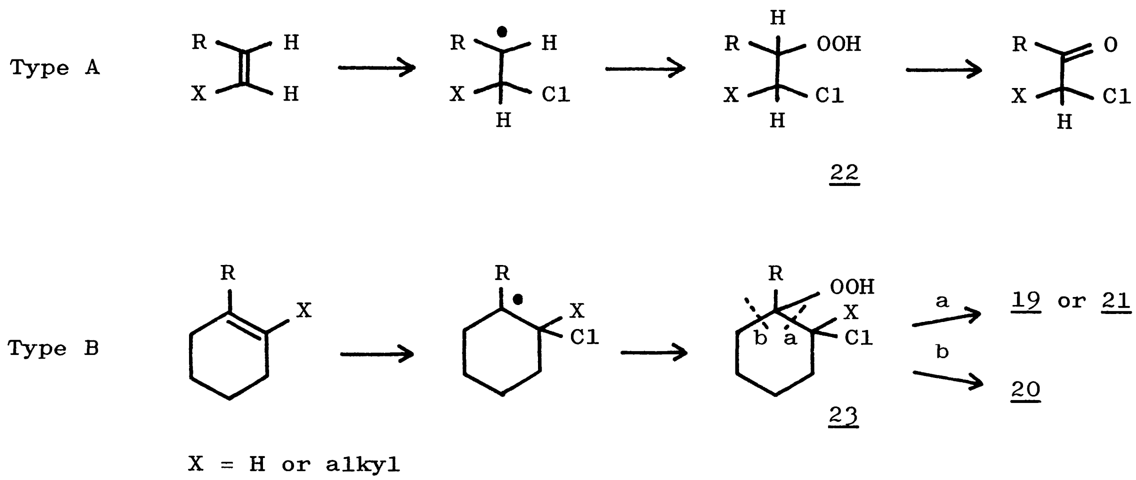
a) Solutions of 4 (0.025 M) and varying amounts of $FeCl_3$ in pyridine-CCl_4 (1 : 1 by volume) or in pyridine-$CHCl_3$ (1 : 10 by volume) were irradiated for 1 h under oxygen.

In the table, the combined yields of 13 and 14 from 2-octene are shown with varying amounts of iron(III) chloride in the mixture solvents of pyridine-carbon tetrachloride or pyridine-chloroform. Thirteen percent yield of the products (13 + 14) was obtained in the absence of the catalyst, but the reaction in this case was complex and the products were accompanied by several by-products. It is notable that the yield of the products in the reaction of 2-octene was large in pyridine-carbon tetrachloride (73%) as compared with that in pyridine alone (43%, see Table 1), while no effect of carbon tetrachloride was found in case of 1-methylcyclohexene (8).

It was revealed from the experiments with 2-octene in pyridine-carbon tetrachloride that other metal salts (Fe(II), Cu(I), or Cu(II), chlorides or sulfates) exhibited weaker catalytic activities (19 - 42% yields of 13 + 14, as compared with 73% yield by iron(III) chloride), but cobalt(II) chloride showed no effect.

We postulate the scheme of the present reaction as (1) the formation of chlorine atom by the irradiation, (2) the anti-Markownikoff addition of the chlorine atom to the double bond, and (3) the combination of the radical thus formed with molecular oxygen to produce chlorohydroperoxides 22 and 23 (Scheme 1). In the Type A reactions, the hydroperoxides 22 are secondary, and they would give α-chloroketones by the dehydration, while in the Type B reactions, the hydroperoxides 23 are tertiary and C-C bond cleavage would become the main reaction path. Tri-t-butylphenol retarded the Type B reactions, while it had generally no influence on the Type A reactions. This scheme is essentially the same as that proposed for the uranyl acetate-catalyzed photo-oxidation of olefins.[1)]

Scheme 1.



Reference

1) E. Murayama and T. Sato, Tetrahedron Letters, 1977, 4079.

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