

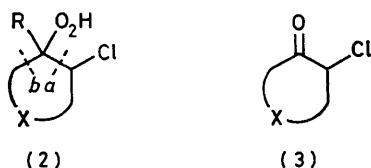
Selective Bond Cleavage in the Iron(III) Chloride-catalysed Photo-oxidation of Olefins

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Summary Iron(III) chloride-catalysed photo-oxidation of substituted olefins gave either *gem*-dichloro-ketones or α,ω -dichloro-ketones selectively, depending upon the substitution pattern of the substrates.

We reported previously¹ that iron(III) chloride had a characteristic effect on the photo-oxidation of olefins in pyridine. The reaction was postulated to take place *via* a long-range electron transfer mechanism to produce a β -chloro-hydroperoxide intermediate (**2**).² It was shown that the intermediate from cyclohexene is the secondary hydroperoxide



(**2**, R = H), which undergoes dehydration to produce the α -chloro-ketone (**3**), while the intermediate from 1-methylcyclohexene (**1a**) is the tertiary hydroperoxide (**2**, R = Me), which undergoes C-C bond cleavage at either the *a* or the *b* bond to produce (**4a**) or (**5a**), respectively, after trapping another chlorine atom. We have called the reaction involving the dehydration to give the α -chloro-ketone a type A reaction, and the reaction involving C-C bond cleavage type B. However, since it became obvious that the direction of the bond cleavage depended very much on the substitution pattern of the olefin substrate, we now wish to amend the classification as follows: type A reactions involve no C-C bond cleavage as in the case of cyclohexene; type B reactions involve bond cleavage at the double bond (*a*-position) to produce the *gem*-dichloro-ketone (**4**); type C reactions involve bond cleavage at the position adjacent to the double bond (*b*-position) to produce the α,ω -dichloro-ketone (**5**).

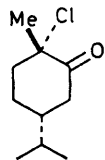
Although the yields and selectivity for the type B and C reactions are not high with simple mono-substituted cycloalkenes as shown in entry (i) of the Table, we have found now that an extra alkyl group in an appropriate position of the cycloalkenes dramatically enhances the yields and the selectivity for the reaction. As shown in entries (ii) and (iii) of the Table, the introduction of an alkyl group (R²) on C-2 of the cycloalkene (**6**) promoted the type B reaction producing (**7**), while introduction on the ω -C atom (**8**) promoted the type C reaction producing (**9**). The reaction conditions were as reported previously,¹ and the products were identified by spectroscopic analysis. The selectivity is quite high, and no products from the alternative types of reaction were identified. It is notable that the alkyl groups are more effective in directing the bond cleavage as compared with the chlorine atom in the hydroperoxide intermediate.

TABLE. Photo-oxidation of the cycloalkenes (**1**), (**6**), and (**8**).

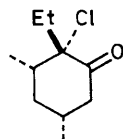
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(i)	<table border="0"> <tr> <td></td> <td>X</td> <td></td> <td></td> </tr> <tr> <td>a;</td> <td>-[CH₂]₂-</td> <td>47</td> <td>7</td> </tr> <tr> <td>b;</td> <td>-[CH₂]₃-</td> <td>6^a</td> <td>0</td> </tr> <tr> <td>c;</td> <td>-[CH₂]₄-</td> <td>35</td> <td>33</td> </tr> <tr> <td>d;</td> <td>-CH₂CHPr^{1-b}</td> <td>26</td> <td>12</td> </tr> </table>		X			a;	-[CH ₂] ₂ -	47	7	b;	-[CH ₂] ₃ -	6 ^a	0	c;	-[CH ₂] ₄ -	35	33	d;	-CH ₂ CHPr ^{1-b}	26	12												
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	 (6)	Type B	 (7)																														
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^a Identified as the ethylene acetal. ^b (+)-Menthene. The product (**10**) was the major product (43%). ^c Both methyl groups are *cis*. (**11**) was the major product (35%).

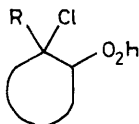
The formation of the α -chloro-ketones (**10**) and (**11**) from the olefins (**1d**) and (**8d**), respectively, presumably occurs *via* the β -chloro-hydroperoxide (**12**), followed by dehydration, which is typical of type A reactions. The intermediates (**12**) are alternative regioisomers of the normal type of



(10)



(11)



(12)

chloro-hydroperoxides (2). Their formation and stereochemistry were discussed elsewhere³ in terms of the steric effect of an isopropyl group or two *cis*-methyl groups, respectively, on the ring.

Both type B and type C reactions have potential in organic synthesis because the products possess alkyl ketone or α -chloro-ketone functions on one end, and *gem*-dichloro- or monochloro-functions on the other end of a carbon chain of any length. The type C reaction seems particularly valuable because a wide variety of compounds are accessible starting from cycloalkenes of any size appropriately substituted with two different alkyl groups, which are in turn available from cyclic ketones by the modified Shapiro reaction.⁴

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¹ A. Kohda, K. Ueda, and T. Sato, *J. Org. Chem.*, 1981, **46**, 509.

² E. Murayama, A. Kohda, and T. Sato, *J. Chem. Soc., Perkin Trans. 1*, 1980, 947.

³ A. Kohda and T. Sato, Abstracts of papers presented at the Annual Meeting of the Chemical Society of Japan, Tokyo, April 1981, Vol. II, p. 1068.

⁴ F. T. Bond and R. A. DiPietro, *J. Org. Chem.*, 1981, **46**, 1315.