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C(9)-C Bonds of 10-Methyl-9-alkyl-9,10-dihydroacridines Acting Like Metal-Carbon Bonds in the Reactions with Electrophiles

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The C(9)-C bonds of 10-methyl-9-alkyl-9,10-dihydroacridines (AcrHR: R = CMe_2COOMe, CMe(H)COOEt, Bu^t, $CHPh_2$) are readily cleaved by electrophiles (perchloric acid, oxygen, and iodine) in acetonitrile at 298 K, acting like metal-carbon bonds to yield the corresponding alkane, alkyl hydroperoxide, and alkyl iodide, respectively.

The metal-carbon bonds of many metal alkyls (RM) are susceptible to cleavage by Brönsted acids (Eq.1).[1)]

$$RM + H^+ \longrightarrow RH + M^+ \tag{1}$$

In the presence of oxygen the cleavage of RM is often accompanied by the oxygenation of the alkyl group to yield the corresponding alkyl hydroperoxide (Eq. 2).[2,3)] The metal-carbon bonds are also cleaved by other

$$RM + O_2 + H^+ \longrightarrow ROOH + M^+ \tag{2}$$

electrophiles such as molecular iodine (Eq. 3).[1)] Such lability of metal-carbon bonds has widely been utilized as

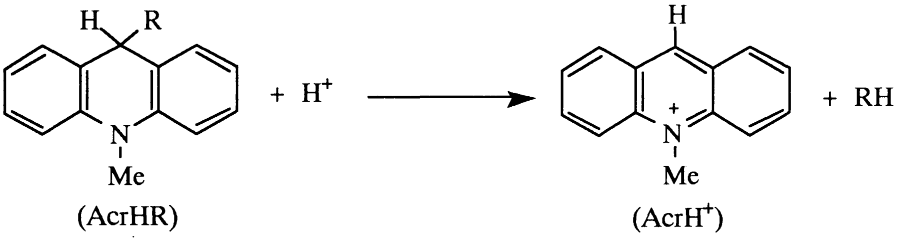
$$RM + I_2 \longrightarrow RI + MI \tag{3}$$

basic chemical transformations of great synthetic utility. In contrast, the carbon-carbon bonds are normally stable toward acids as well as other electrophiles under mild conditions.[4)] Thus, no electrophilic cleavage of the C-C bonds of diamagnetic neutral organic compounds has so far been reported, although cleavage of C-C bonds in organic radical cations has recently attracted considerable attention.[5,6)]

We wish to report herein that the C(9)-C bonds of alkyl-substituted 10-methyl-9,10-dihydroacridines (AcrHR) are susceptible to cleavage by electrophiles to undergo the same type of the reactions as metal-carbon bonds (Eqs. 1-3).

To our surprise, the C(9)-C bond of AcrHR (R = CMe_2COOMe), formed by the reduction of 10-

methylacridinium ion with a ketene silyl acetal ($Me_2C{=}C(OMe)OSiMe_3$),[7] is readily cleaved by $HClO_4$ in deaerated MeCN at 298 K to yield the corresponding alkane (Eq. 4).[8] The susceptibility of the C-C bond of



(4)

AcrHR to electrophilic cleavage by $HClO_4$ (Eq. 4) is diminished with a monomethyl-substituted derivative (R = CMe(H)COOEt), and disappears completely with an unsubstituted one (R = CH_2COOEt) as shown in Table 1. The C-C bonds of other alkylated acridine (AcrHR: R = Bu^t, $CHPh_2$)[9] are also stable toward $HClO_4$.

When the reaction of AcrHR (R = CMe_2COOMe and Bu^t) is carried out in the presence of $HClO_4$ and oxygen, the oxygenation of the alkyl group of AcrHR takes place to yield the corresponding alkyl hydroperoxide (Eq. 5), together with RH (Eq. 4), as shown in Table 1.[8] In the case of R = $CHPh_2$, Ph_2CHOOH may be

$$\mathrm{AcrHR} + \mathrm{O_2} + \mathrm{H^+} \longrightarrow \mathrm{ROOH} + \mathrm{AcrH^+} \qquad (5)$$

initially formed, but decomposes in the presence of $HClO_4$ to yield PhCHO and Ph_2CO, since secondary alkyl

Table 1. Electrophilic Cleavage of the C(9)-C Bond of AcrHR (4.0×10^{-2} mol dm^{-3}) in MeCN at 298 K

AcrHR	Electrophile	Time / h	Product (yield / %)
R =			
CMe_2COOMe	$HClO_4$[a]	10	$HCMe_2COOMe$ (100), AcrH$^+$ (100)
CMe(H)COOEt	$HClO_4$[a]	23	$H_2CMeCOOEt$ (40), AcrH$^+$ (40)
CH_2COOEt	$HClO_4$[a]	10	no reaction
CMe_2COOMe	$O_2/HClO_4$[b]	1	$HOOCMe_2COOMe$ (85), AcrH$^+$ (100) $HCMe_2COOMe$ (15)
CMe_2COOMe	I_2[c]	1	$ICMe_2COOMe$ (45), AcrH$^+$ (50) $HOCMe_2COOMe$ (5)
Bu^t	$HClO_4$[a]	10	no reaction
Bu^t	$O_2/HClO_4$[b]	1.5	Bu^{t}OOH (100) AcrH$^+$ (100)
$CHPh_2$	$HClO_4$[a]	10	no reaction
	$O_2/HClO_4$[b]	2.3	PhCHO (98), AcrH$^+$ (100) Ph_2CO (2)
Me	$HClO_4$[a]	10	no reaction
	$O_2/HClO_4$[b]	10	no reaction

a) 0.90 mol dm^{-3} in deaerated MeCN. b) In the presence of 0.90 mol dm^{-3} $HClO_4$ in oxygen-saturated MeCN. c) 4.0×10^{-2} mol dm^{-3}.

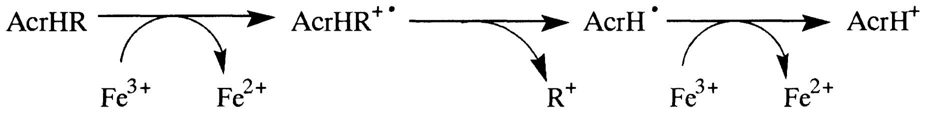
hydroperoxides such as Ph_2CHOOH are generally unstable in the presence of acid, compared to the tertiary alkyl hydroperoxides such as Bu^tOOH.[10] On the other hand, no C-C bond cleavage of AcrHR has occurred with R = Me[11] by $HClO_4$ or O_2 (Table 1).

The C(9)-C bond is also cleaved by molecular iodine to yield the corresponding alkyl iodide (Table 1).[8] The stoichiometry of the reaction is given by Eq. 6, where I_2 is reduced to I_3^-. Such behavior of the C-C bonds

$$\mathrm{AcrHR} + 2\mathrm{I_2} \longrightarrow \mathrm{RI} + \mathrm{AcrH^+} + \mathrm{I_3^-} \qquad (6)$$

of AcrHR (Eqs. 4-6) are essentially the same as observed for metal alkyls (Eqs. 1-3).

On the other hand, the C(9)-C bond of AcrHR (R = CMe_2COOMe and Bu^t) is readily cleaved upon the electron transfer oxidation by $Fe(ClO_4)_3$ in MeCN to yield $AcrH^+$ and R^+ (Eq. 7).[8] The carbonium ions R^+ formed primarily react with H_2O contained in MeCN to yield mainly the corresponding alcohols (ROH). In the case of AcrHR (R = Me), however, the C(9)-H bond is cleaved exclusively to yield 9,10-dimethylacridinium ion ($AcrMe^+$) and H^+. The radical cation ($AcrHR^{+\bullet}$; R = CMe_2COOMe, Bu^t, and Me) were detected by using a stopped flow spectrophotometer (λ_{max} = 710, 710, and 660 nm, respectively).[12] The much shorter lifetimes of $AcrHR^{+\bullet}$ (14 ms and 91 ms for R = CMe_2COOMe and Bu^t) than that of $AcrHMe^{+\bullet}$ (1.2 s) indicate the facile cleavage of the C(9)-C bond of $AcrHR^{+\bullet}$ as compared with the C(9)-H cleavage of $AcrHMe^{+\bullet}$. The PM3 molecular orbital calculation[13] reveals that the C(9)-C bond of AcrHR (R = CMe_2COOMe, Bu^t) is lengthened by the one-electron oxidation from 1.56 Å in AcrHR to 1.57 Å in $AcrHR^{+\bullet}$, while little is changed in AcrHMe and $AcrHMe^{+\bullet}$ (1.53 Å). Thus, the C(9)-C bond of AcrHR with bulky substituents such as CMe_2COOMe and Bu^t may be susceptible to cleavage upon the oxidation as is the case of metal-carbon bonds.[1,14]



$$\mathrm{AcrHR} \xrightarrow[\mathrm{Fe^{3+}}\quad\mathrm{Fe^{2+}}]{} \mathrm{AcrHR^{+\bullet}} \xrightarrow[\mathrm{R^{+}}]{} \mathrm{AcrH^{\bullet}} \xrightarrow[\mathrm{Fe^{3+}}\quad\mathrm{Fe^{2+}}]{} \mathrm{AcrH^{+}} \qquad (7)$$

The PM3 calculation is also carried out for the protonated form in which H^+ is attached to the carbonyl oxygen. The C(9)-C bond of the protonated form of AcrHR (R = CMe_2COOMe) is also lengthened as is the case of the radical cation in which the C-C bond is readily cleaved in MeCN (Eq. 7). The C-C bond length of the protonated AcrHR becomes shorter in order R = CMe_2COOMe (1.58 Å) > R = CMe(H)COOMe (1.57 Å) > R = CH_2COOMe (1.55 Å), in agreement with the diminished reactivity of AcrHR with R = CMe(H)COOEt and no reactivity with R = CH_2COOEt toward $HClO_4$. Thus, the bizarre susceptibility of the C-C bond of AcrHR (R = CMe_2COOMe) to electrophilic cleavage by $HClO_4$ (Table 1) may be ascribed to the protonation on the carbonyl oxygen, which significantly weakens the C-C bond, as well as the conformational factor that allows the appropriate stereoelectronic disposition of the C-C bond to be cleaved. We are currently studying the detailed mechanisms of electrophilic cleavage of these novel C-C bonds acting like metal-carbon bonds.

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