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INTRA- AND INTER-MOLECULAR CARBON-CARBON BOND FORMATION BY PHOTOSENSITIZED OXYGENATION OF VINYLFERROCENES[1,2]

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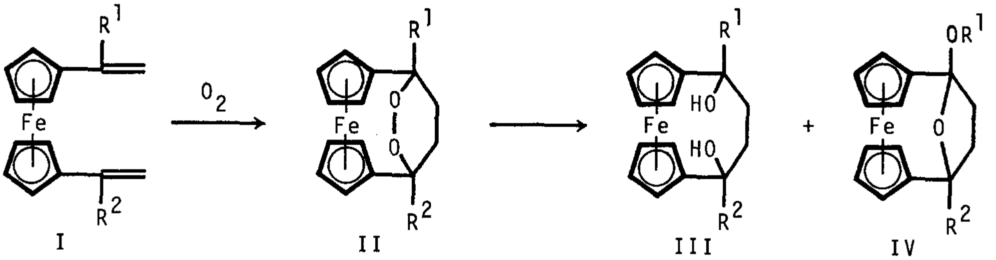
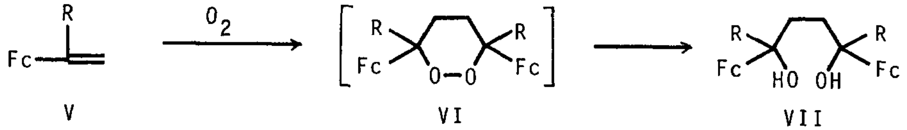
In the series of the study on the reaction of ferrocene derivatives with molecular oxygen, we have reported[3-5] that vinylferrocenes (I, V) were oxidized with oxygen gas in the presence of mineral acids, Lewis acids or silica gel in the dark to give six-membered cyclic peroxides (II) and/or their derivatives (III, IV, VII and others) through intra- and inter-molecular cyclizations. The vinylferrocenes were autoxidized neither under the basic condition nor on alumina. This communication describes that the same oxidative cyclization as in the acid-catalyzed autoxidation resulted from photosensitized oxygenation of the vinylferrocenes under the basic condition.

Irradiation of 1,1'-divinylferrocene derivatives (I) in the presence of sodium copper-chlorophillin (sensitizer) while bubbling through dry O_2 gas produced various [4]ferrocenophane derivatives; peroxide (IIa), diols (IIIa-c), ketals (IVa, IVc) and others.[6] The diols (III) and ketals (IV) are chemical transformation products of the peroxides (II) in the reaction system or in the work-up, as shown in the previous reports.[4] Since all other [4]ferrocenophane derivatives are evidently those derived from the diols (III) or ketals (IV),[4] the yields of those derivatives are included into the ones of the diols (III) and ketals (IV), respectively, in Table 1.

When sodium copper-chlorophillin was absent, irradiation of divinylferrocene (Ia) gave only trace amount of ketal (IVa). The oxidation was dramatically inhibited by addition of 1,4-diazabicyclo[2.2.2]octane (DABCO), an efficient quencher of singlet molecular oxygen ($^1\Delta$).[7] Therefore, involvement of



a: $R^1 = R^2 = C_6H_5$
b: $R^1 = R^2 = CH_3$
c: $R^1 = C_6H_5$, $R^2 = CH_3$



a: R = C_6H_5

(Fc: Ferrocenyl group)

singlet oxygen in the oxygenation was secured. The reactivity in the photosensitized oxidative cyclization of I in CH_2Cl_2 indicated the same tendency as the acid-catalyzed autoxidation; decreasing in the total yields in the order of Ia > Ic > Ib.

Irradiation of vinylferrocene (Va) in the absence of both alumina[8] and sensitizer gave no dimerization product (VII). Since the oxygenation in hexane or other solvents afforded only a slight amount of dimerization products even in the presence of alumina, the vinylferrocene (Va) and sensitizer absorbed on alumina were directly irradiated under an O_2 atmosphere. In the reaction system without solvent, the total yield of the diol (VII) and its dehydrated compounds[3,5] increased with prolong of reaction time.

Intramolecular carbon-carbon bond formation in photosensitized oxygenation of quadricyclane and norbornadiene, conformationally rigid compounds, was described by Itô et al.[9] as a new type reaction with singlet oxygen. However, there has been no report that two independent olefin molecules and a singlet molecular oxygen formed intermolecularly a carbon-carbon bond to give oxidative

Table 1 Photosensitized oxygenation and acid-catalyzed autoxidation of vinylferrocenes.

Starting material[a]	Conditions[b] Additions	Solvent	Time (hr)	Recovered olefin(%) I or V	Products(%)[c] Peroxide II	Diol III or VII	Ketal IV	Total
(Photosensitized oxygenation)								
Ia	Sensitizer	CH_2Cl_2	1	1.2	88.4		0.8	89.2
Ia	Sensitizer	CH_3OH	1		trace	22.8	18.4	41.2
Ia	No-sensitizer, CH_3COONa[d]	CH_2Cl_2	1	75.0			trace	trace
Ia	Sensitizer and DABCO[e]	CH_2Cl_2	1	69.5	trace	1.2	4.3	5.5
Ib	Sensitizer	CH_2Cl_2	1	85.5		7.2		7.2
Ib	Sensitizer	CH_2Cl_2	14	9.2		24.5		24.5
Ib	Sensitizer	CH_2Cl_2-CH_3OH	1	56.7		15.5		15.5
Ib	Sensitizer	CH_2Cl_2-CH_3OH	5	31.3		44.2		44.2
Ic	Sensitizer	CH_2Cl_2	1	89.4		8.2	trace	8.2
Ic	Sensitizer	CH_2Cl_2	14			26.8	7.2	34.0
Va	Sensitizer and alumina		6	91.6		7.3		7.3
Va	Sensitizer and alumina		24	76.2		14.1		14.1
Va	Sensitizer and alumina	Hexane	5	62.5		0.8		0.8
(Acid-catalyzed autoxidation)								
Ia[f]	WCl_6	CH_2Cl_2	0.25		59.0	34.0	trace	93.0
Ib[f]	WCl_6	CCl_4	1	5.4		14.0		14.0
Ic[f]	7N-HCl	Benzene	1			19.0	4.5	23.5
Va[g]	Silica gel	Hexane	5	47.8		36.4		36.4

a. The vinylferrocenes were used as starting materials immediately after preparations. *b*. Irradiation in solution was carried out by an internal method with sodium vapor lamp (Toshiba SL-Na-50). Sensitizer: sodium copper-chlorophillin. *c*. A small amount of the corresponding acylferrocene was produced in each reaction besides cyclization products. *d*. Since the sensitizer is a base, CH_3COONa was added in order to make the blank experimental system basic. *e*. 1,4-Diazabicyclo[2.2.2]octane. *f*. The unpublished results obtained so far in the highest yields. *g*. The result in References and Notes 3.

dimerization products.[10] It is also interesting that the photosensitized oxygenation produced the same products as in the acid-catalyzed autoxidation.[3-5] These results seem to suggest activation of triplet molecular oxygen in ground state ($^3\Sigma$) into singlet state ($^1\Delta$) in the autoxidation system.[12]

REFERENCES AND NOTES

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