January, 1983] © 1983 The Chemical Society of Japan Bull. Chem. Soc. Jpn., 56, 285—286 (1983)

Metal-catalyzed Organic Photoreactions. The Photooxidation of Vinylsilanes and Vinyl Sulfides in the Presence of Iron(III) Chloride, and the Regioselective Synthesis of α-Chloro Ketones

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(Received June 26, 1982)

The irradiation of a pyridine solution of vinylsilanes or vinyl sulfides in the presence of iron(III) chloride under oxygen produced α-chloro ketones, with a carbonyl group at the olefinic carbon originally bearing a silicon or sulfur atom.

We have previously reported that the iron(III) chloride-catalyzed photooxidation of mono- or disubstituted olefin gives an α-chloro ketone (Type A), while that of tri- or tetrasubstituted olefin gives a *gem*-dichloro ketone (Type B) or an α,ω-dichloro ketone (Type C), depending upon the substitution pattern of the starting olefins.1) The selectivity of the reaction type is generally excellent, and no products from the alternative reaction type are observed. In the Type-A reaction of unsymmetrical olefin, however, the regioselectivity is poor, and a 1:1 mixture of 2-chloro-3-octanone (**2**) and 3-chloro-2-octanone (**3**) has been obtained from 2-octene (**1**) in a total yield of 58%. In the present study, we investigated the photooxidation of vinylsilane and vinyl sulfide in order to find a way to control the regioselectivity.

Results and Discussion

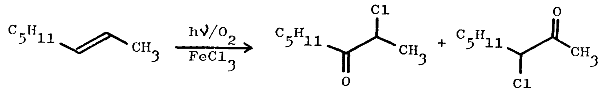
Pyridine solutions of vinylsilanes or vinyl sulfides **4**—**12** containing an equivalent amount of iron(III) chloride were irradiated with Pyrex-filtered light for 1 h while oxygen was being bubbled through. The subsequent evaporation of the solvent, followed by extraction, gave α-chloro ketones or aldehyde **13**—**21** as almost exclusive products. The results are summarized in the table. The structures of the products were determined by comparison with authentic samples prepared by known methods. It is evident from the table that the carbonyl group is introduced regioselectively at the olefinic carbon originally bearing a silicon or sulfur atom in every case except the reaction from **4**, which has the trimethylsilyl group at the terminal position. The steric effect caused by the presence of the alkyl group on the ring system is not sufficient to induce the regioselectivity, as exemplified by the reaction of 3-methylcyclohexene. The product was assumed from NMR analysis to be a mixture of *cis*- and *trans*-2-chloro-3-methylcyclohexanone (**18**) and 2-chloro-6-methylcyclohexanone (**21**). The assumption was confirmed by the dehydrochlorination of the mixture with lithium chloride in *N,N*-dimethylformamide to afford a 1:1 mixture of 2- and 3-methyl-2-cyclohexenone. It was confirmed that **21** produced 2-methyl-2-cyclohexenone under dehydrochlorination conditions, presumably because of the isomerization of the primary product, 6-methyl-2-cyclohexenone.

The usefulness of these reactions as a synthetic method is demonstrated by the regioselective preparation of alkyl-substituted 2-chlorocyclohexanones from appropriate vinylsilanes or vinyl sulfides. The requisite vinyl compounds have been conveniently prepared from the appropriate ketones either by an acid-actalyzed reaction with thiols2) or by a modified Shapiro reaction.3) These alkyl-substituted 2-chlorocyclohexanones have also been prepared by other methods,4,5) but the regioselectivity is not as high as that observed in the present study. The diastereoselectivity concerning the alkyl group and chlorine atom was not attained because the α-chloro ketones underwent a *cis-trans* isomerization under the present reaction conditions.

As for the reaction mechanism of the iron(III) chloride-catalyzed photooxidation of olefin, we have proposed a reaction scheme involving a photoinduced interligand electron transfer (long-range electron transfer), followed by a chlorine and oxygen attack on the double bond.1a) We assumed that the same type of reaction proceeds in the present case and that the chlorine atom produced by the long-range electron transfer attacks the double bond in such a way as to produce a radical stabilized by a silicon or sulfur atom. The succeeding attack by the oxygen-radical anion, followed by protonation, produces a hydroperoxide **23**, which then affords the observed product. The isolated byproduct was either *S*-methyl methanethiosulfonate, *S*-ethyl ethanethiosulfonate, or diphenyl disulfide, depending on the substituent (methyl, ethyl, or phenyl respectively) on the sulfur atom of the starting vinyl sulfide. The poor regioselectivity in the case of vinylsilane **4** suggests that the stabilizing effect of the trimethylsilyl group for the α-radical is comparable to that of the alkyl group. However, it seems that the sulfur atom stabilizes the α-radical more effectively than the methyl group, as is indicated by the formation of a single product **17** from vinyl sulfide **8**.

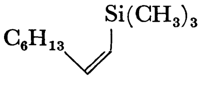
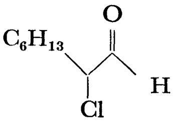
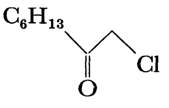
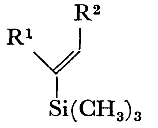
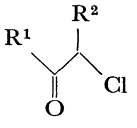
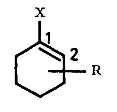
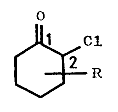
Experimental

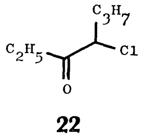
Starting Materials. 1-Trimethylsilyl-(*Z*)-1-octene (**4**) was prepared from 1-trimethylsilyl-1-octyne by hydroboration, followed by protonolysis.6) Vinylsilanes **5**, **6**, **7a**, and **12a** were prepared from the corresponding tosylhydrazones and chlorotrimethylsilane according to the reported method.7) In a similar way, vinyl sulfide **12b** was prepared from 2-methylcyclohexanone tosylhydrazone and dimethyl disulfide in a 51% yield. **12b**: IR, 3040, 2920, 1620, 1435, 1335, 995, and 790 cm^{-1}; NMR, δ 1.22 (3H, d, J=8 Hz), 1.5—2.0 (4H, m), 2.31 (3H, s), 2.0—2.6 (3H, m), and 5.60 (1H, t, J=4 Hz). Vinyl sulfides **7b**, **7c**, **8**, and **10b** were prepared from the corresponding cyclohexanones and thiols, using *p*-toluenesulfonic acid or titanium(IV) chloride–triethylamine as a catalyst, according to the previously reported method.2) Vinyl sulfides **9** and **11** were prepared from the tosylhydrazone of 2-methylcyclohexanone or of 4-methylcyclohexanone respectively by utilizing a modified Shapiro reaction, according to the previously reported method.3)



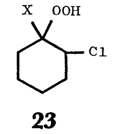
1 **2** **3**

TABLE 1. PRODUCTS AND YIELDS OF THE PHOTOOXIDATION OF VINYL SILANES OR VINYL SULFIDES

Starting material	Product	Yield/%
 **4**	 **13**	6
	 **14**	9
		
5 $R^1=C_6H_{13}$, $R^2=H$	**14**	41
6 $R^1=C_3H_7$, $R^2=C_2H_5$	**15**	67
		
7 $R=H$, a: $X=Si(CH_3)_3$	**16**	72
b: $X=SC_6H_5$		58
c: $X=SC_2H_5$		53
8 $R=2\text{-}CH_3$, $X=SC_6H_5$	**17**	50
9 $R=3\text{-}CH_3$, $X=SCH_3$	**18**	*cis* 32 *trans* 13
10 $R=4\text{-}CH_3$, a: $X=Si(CH_3)_3$	**19**	*cis* 28 *trans* 36
b: $X=SC_2H_5$		*cis* 3 *trans* 31
11 $R=5\text{-}CH_3$, $X=SCH_3$	**20**	*cis* 32 *trans* 8
12 $R=6\text{-}CH_3$, a: $X=Si(CH_3)_3$	**21**	*cis* 38 *trans* 38
b: $X=SCH_3$		*cis* 22 *trans* 22



22



23
$X=SR$ or SiR_3

Photooxidation. The irradiation was carried out on a solution of vinylsilane or vinyl sulfide (10 ml, 0.025 M)† containing an equivalent molar amount of iron(III) chloride; it was done in Pyrex tubes for 30 min or 60 min while oxygen gas was being bubbled through. A high-pressure mercury lamp [Ushio UM 452 (450 W)] was used as the light source. The irradiated solution was worked up by either of the following two ways. Work-up I: The solvent was removed *in vacuo*, and the reaction product was extracted with carbon tetrachloride or dichloromethane from the residue. The extract was passed through a short colunm of Florisil, and the eluate was concentrated *in vacuo*. The material thus obtained was analyzed directly by GLC or NMR techniques. 1,1,2,2-Tetrachloroethane was used as an internal reference for the NMR analysis. Work-up II: The pyridine solution after the irradiation was neutralized with 4 M hydrochloric acid and shaken with chloroform or dichloromethane. The extract was dried over sodium sulfate, and the solvent was removed *in vacuo*. The residue was analyzed as above.

In all cases except the reaction of **10**, each product was isolated in a pure form on preparative GLC or TLC; the spectroscopic data and retention time on a GLC were compared with those of authentic samples prepared by known methods: **13**,8) **14**,1b) **15**,9) **16**,1b) **17**,5b) **18**,5a) **19**,4) **20**,5a) and **21**.5b) The spectroscopic data of **13** and **15** are as follows: **13**: IR, 2950, 2925, 2855, 2710, 1733, 1470, 1380, and 785 cm^{-1}; NMR δ 0.88 (3H, dist. t), 1.1—1.6 (8H, m), 1.7—2.0 (2H, m), 4.03 (1H, dt, J=6 and 2 Hz), and 9.48 (1H, d, J=2 Hz); **15**: IR, 2960, 2875, 1715, 1460, and 785 cm^{-1}; NMR δ 0.95 (3H, t, J=8 Hz), 1.03 (3H, t, J=8 Hz), 1.4—2.1 (4H, m), 2.62 (2H, t, J=7 Hz), and 3.93 (1H, t, J=7 Hz).

The spectroscopic and GLC analyses of **19** were carried out and the results compared with those of an authentic sample as a mixture of *cis*- and *trans*-isomers.4)

References

1) a) E. Murayama, A. Kohda, and T. Sato, *J. Chem. Soc., Perkin Trans. 1*, **1980**, 947; b) A. Kohda, K. Ueda, and T. Sato, *J. Org. Chem.*, **46**, 509 (1981); c) A. Kohda and T. Sato, *J. Chem. Soc., Chem., Commun.*, **1981**, 951; d) T. Sato, K. Maemoto, and A. Kohda, *ibid.*, **1981**, 1116.

2) T. Mukaiyama and K. Saigo, *Chem. Lett.*, **1973**, 479.

3) T. Nakai and T. Mimura, *Tetrahedron Lett.*, **1979**, 531.

4) R. MacDonald and T. E. Tabor, *J. Am. Chem. Soc.*, **89**, 6573 (1967).

5) a) F. M. Lasdovics and E. M. Schulman, *J. Am. Chem. Soc.*, **99**, 6672 (1977); b) F. M. Laskovics and E. M. Schulman, *Tetrahedron Lett.*, **1977**, 759.

6) E. C. Ashby and S. R. Noding, *J. Organomet. Chem.*, **177**, 117 (1979).

7) L. A. Paquette, W. E. Fristad, D. S. Dime, and T. R. Bailey, *J. Org. Chem.*, **45**, 3017 (1980).

8) E. Elkik, *Bull. Soc. Chim. Fr.*, **1968**, 283.

9) J. Metzger and B. Koether, *Ann. Univ. Saraviensis I*, **1952**, 151; *Chem. Abstr.*, **47**, 10524 (1953).

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† 1 M=1 mol dm^{-3}.