CHEMISTRY LETTERS, pp. 261-264, 1973. Published by the Chemical Society of Japan

A CONVENIENT METHOD FOR THE HYDROLYSIS OF VINYL CHLORIDES TO KETONES

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A new and useful method for the hydrolysis of vinyl chlorides was investigated by the use of EtSH and $TiCl_4$. Various vinyl chlorides, such as α-chlorostilbene, 1,3-diphenyl-1-chloro-1-propene and 2,6-dimethyl-4-chloro-3-heptene, were hydrolyzed to corresponding ketones in good yields at room temperature.

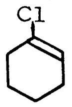
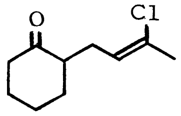
It is generally known that the hydrolysis of vinyl chlorides is performed only under rather drastic conditions such as in excess concentrated sulfuric acid or in the mixture of sulfuric acid and acetic acid.1) In this communication, a new and useful method for the hydrolysis of vinyl chlorides to ketones by the use of $TiCl_4$ under mild conditions is reported.

In the previous communication2), we reported that vinyl sulfides were hydrolyzed very rapidly at room temperature in acetic acid, methylene chloride or benzene in the presence of 2 molar amounts of $TiCl_4$ and 4 molar amounts of water. In connection with the results, the activation of vinyl chlorides with $TiCl_4$ toward hydrolysis was now examined. In the first place, α-chlorostilbene was treated with $TiCl_4$ in various solvents containing 2 molar amounts of water, however, no reaction occurred in polar solvents or only a small amount of polymerized products resulted in nonpolar solvents such as methylene chloride. On the other hand, when α-chlorostilbene was treated with 1 molar amount of EtSH and 2 molar amounts of $TiCl_4$ in methylene chloride containing a small amount of water at room temperature for 5 hr, deoxybenzoin was produced in 40% yield and, at the same time, α-ethylthiostilbene was obtained in 42% yield.3)

This reaction is not sufficient for the preparative method of ketones from vinyl chlorides because of the undesirable formation of vinyl sulfide by a side reaction. This difficulty was overcome by the further treatment of the reaction mixture in AcOH, by which the vinyl sulfide was hydrolyzed to ketone as described in the previous communication.2) In a typical experiment, 676 mg (3.14 mmol) of α-chlorostilbene was added to the mixture of 195 mg (3.14 mmol) of EtSH and 1.19 g (6.28 mmol) of $TiCl_4$ in methylene chloride (9.4 ml) at room temperature. After stirring for 5 hr, 9.4 ml of acetic acid and 226 mg (12.5 mmol) of water were added and stirring was continued for 3 hr. Then usual work-up afforded deoxybenzoin in the total yield of 72%.

In the similar manner, following vinyl chlorides were hydrolyzed to the corresponding ketones. The results are shown in Table 1.

Table 1

Vinyl chloride	Reaction time (hr)	Yield (%)
$C_6H_5CCl{=}CHC_6H_5$	5	40 [42]2)
	40	42 [53]2)
	5 [3]1)	72
	40 [3]1)	93
$C_6H_5CCl{=}CHCH_2C_6H_5$	5 [3]1)	96
$C_6H_5CCl{=}CHCH_3$	2 [1]1)	91
β-Naph-$CCl{=}CH_2$	1 [1]1)	60
$C_6H_5CH_2CH_2CCl{=}CHCH_2C_6H_5$	5 [3]1)	16
$(CH_3)_2CH\text{-}CH_2CCl{=}CH\text{-}CH(CH_3)_2$	5 [3]1)	63³⁾
	24	343)
	24	50

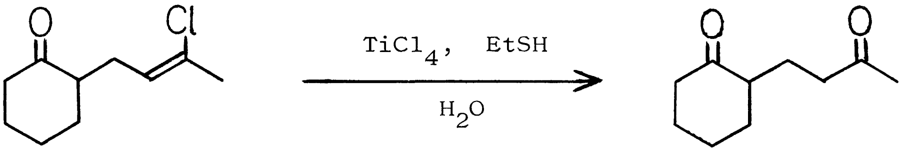
1) Brackets indicate the reaction time after the addition of AcOH and H_2O.

2) Brackets indicate the yield of α-ethylthiostilbene.

3) Isolated as 2,4-dinitrophenylhydrazone.

It is noted that the reaction proceeded smoothly in the cases of vinyl chlorides having an aromatic group conjugated with the vinyl group. The hydrolysis of non-conjugated vinyl chloride, however, was accompanied with a few by-products and the yields of the corresponding ketones decreased.

It should be further noted that the hydrolysis of 2-(3-chloro-2-butenyl)-cyclohexanone 1 afforded diketone 2 as a main product and bicycloketones, $\Delta^{1,9}$-2-octalone and 2-methylbicyclo[3.3.1]non-2-en-9-one, were not detected. This fact provides a remarkable contrast with the results obtained in the case of the hydrolysis of 1 in concentrated sulfuric acid.[4)] In strongly acidic medium, diketone 2 is easily converted to bicycloketones *via* intramolecular aldol condensation, followed by dehydration.



1 2

It was found that this reaction was considerably affected by solvents. Remarkable rate retardation was observed in carbon tetrachloride, cyclohexane and benzene. This retardation is perhaps due to a smaller polarity of the solvent and/or to low solubility of $TiCl_4$-EtSH complex in these solvents. No reaction occurred in acetic acid and dioxane, probably because of the formation of stable complexes with $TiCl_4$ to decrease the concentration of the active species, $TiCl_4$-vinyl chlorides complexes.

From these facts, the reaction may be explained by assuming an initial formation of an intermediate 3 by the addition of EtSH to $TiCl_4$-activated double bond. There are two possible pathways of the hydrolysis of 3 to ketone. Namely, ketone is produced by direct hydrolysis of 3 or by the hydrolysis of 4 which is formed by the elimination of hydrogen chloride from 3.

$$\begin{tikzcd}
 & & \underset{4}{R_1R_2C{=}C(SEt)R_3} \arrow[dd, "H_2O,\ TiCl_4"] \\
R_1R_2C{=}CClR_3 \arrow[r, "EtSH,\ TiCl_4"] & \underset{3}{[R_1R_2HC\text{-}CCl(SEt)R_3]} \arrow[ur] \arrow[dr, "H_2O"'] & \\
 & & R_1R_2HC\text{-}COR_3
\end{tikzcd}$$

Acknowledgment. The authors wish to express their thanks to Dr. Hisashi Takei for his helpful discussion.

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2) T. Mukaiyama, K. Kamio, and S. Kobayashi, Bull. Chem. Soc. Japan, 45, 3723 (1972).
3) Deoxybenzoin was produced in fair yield without addition of water. The hydrolysis is perhaps caused by a small amount of water contained in the reaction system. It was found that the reaction rate had been rather retarded by the addition of one or two molar amounts of water.
4) S. Julia, Bull. Soc. Chim. Fr., 21, 780 (1954); V. Prelog, P. Barmann, and M. Zimmermann, Helv. Chim. Acta, 32, 1284 (1949); J. A. Marshall and D. J. Schaeffer, J. Org. Chem., 30, 3642 (1965).

(Received December 27, 1972)