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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 combined use of $TiCl_4$, methanol and water. Various vinyl chlorides, such as α-chlorostilbene, 1-phenyl-1-chloro-1-propene and 2,6-dimethyl-4-chloro-3-heptene, were hydrolyzed to corresponding ketones in high yields at room temperature. Steroid I was smoothly converted to testosterone propionate II in 96% yield by this method.

The hydrolysis of substituted vinyl chlorides to corresponding ketones is usually performed in excess concentrated sulfuric acid.[1] Under these drastic conditions, undesirable side reactions such as polymerization are not negligible, and, in some cases, these reactions prevail over the hydrolysis.

In the previous communication, we reported that vinyl chlorides were hydrolyzed to corresponding ketones in fairly good yields at room temperature by the action of $TiCl_4$ and ethanethiol in methylene chloride.[2] However, this method was not successfully applied to the hydrolysis of vinyl chlorides having an ethylenic double bond in the same molecules.

In order to establish a widely applicable method, we have further examined various reaction conditions using α-chlorostilbene as a representative vinyl chloride. Finally, it was found that the combined use of $TiCl_4$, methanol and water in methylene chloride led to a smooth hydrolysis of α-chlorostilbene giving deoxybenzoin in 94% yield. This method, however, was not sufficient for the hydrolysis of 1-phenyl-1-chloro-1-propene, which afforded hydrolyzed product, propiophenone, only in 31% yield because of an undesirable polymerization of the vinyl chloride. The polymerization was assumed to proceed at the initial stage of the reaction in heterogeneous reaction medium where a considerable amount of $TiCl_4$-H_2O complex is not dissolved in methylene chloride. After a number of experiments, it was found that the $TiCl_4$-H_2O complex could be completely dissolved in methylene chloride by the addition of a small amount of acetone. The hydrolysis of vinyl chloride in the resulted homogeneous solution afforded ketone in high yield. The reaction was carried out as follows: 3.04 g (16 mmol) of $TiCl_4$ in 4.0 ml of methylene chloride was added dropwise to a mixture of 190 mg (6.0 mmol) of methanol, 520 mg (9.0 mmol) of acetone and 110 mg (6.0 mmol) of water in 4.0 ml of methylene chloride at 0°C during 10 min. Into the resulted clear yellow solution, a solution containing 610 mg (4.0 mmol) of 1-phenyl-1-chloro-1-propene in 4.0 ml of methylene chloride was added drop by drop with stirring at room temperature over a period of 2 hr, and the stirring was continued for an additional 1 hr. Then the usual work-up afforded propiophenone in 85% yield.

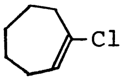
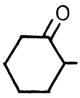
In a similar manner, various vinyl chlorides, α-chlorostilbene, 1,3-diphenyl-1-chloro-1-propene, α-chloro-p-bromostyrene, 2,6-dimethyl-4-chloro-3-heptene, 1-chlorocycloheptene, and 2-(3-chloro-2-butenyl)cyclohexanone, were hydrolyzed to corresponding ketones in high yields as are summarized in Table I.

As is shown in Table I, the yields of the hydrolysis of vinyl chlorides considerably depended on the amount of methanol or acetone. For example, the use of a large excess of methanol or acetone rather resulted in the formation of ketones in quite low yields.

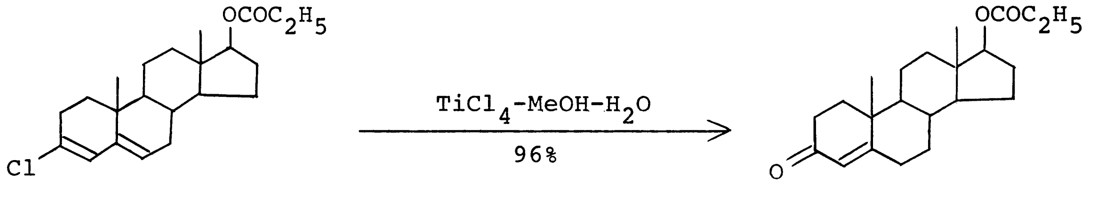
It is noted that the hydrolysis of 2-(3-chloro-2-butenyl)cyclohexanone afforded 2-(3-oxobutyl)cyclohexanone in 59% yield along with a small amount of bicycloketones, $\Delta^{1,9}$-2-octalone and 2-methylbicyclo[3.3.1]non-2-ene-9-one. This fact provides a remarkable contrast with the results obtained in the case of the hydrolysis in concentrated sulfuric acid, where the latter bicycloketones are produced as main products via intramolecular aldol condensation, followed by dehydration of initially formed 2-(3-oxobutyl)cyclohexanone.[3]

In addition, it should be noted that steroid I[4] was quite smoothly converted into testosterone propionate II in 96% yield without accompanying both the hydrolysis of the ester function and the addition reaction of methanol or water to the ethylenic double bond.

Table I.

Vinyl chloride	Mole ratio per vinyl chloride				Time,hr	Yield,%
	H_2O	CH_3OH	$TiCl_4$	CH_3COCH_3		
PhCCl=CHPh	1	1	2	——	24	94
	1.5	1.5	4	2.3	24	94
	1.5	10	4	2.3	24	5
	1.5	1.5	4	10	24	trace
$PhCCl=CHCH_3$	1	1	2	——	3	31
	1.5	1.5	4	2.3	3	85
$PhCCl=CHCH_2Ph$	1.5	1.5	4	2.3	5	87
$p\text{-}BrC_6H_4CCl=CH_2$	1.5	1.5	4	2.3	3	90
$(CH_3)_2CHCH_2CCl=CHCH(CH_3)_2$	1.5	1.5	5	2.3	24	76[a]
	1.5	1.5	5	2.3	24	87[a]
 $-CH_2CH=CClCH_3$	2	1	4	3	20	59[b]+8[c]

a Isolated as 2,4-dinitrophenylhydrazone. b 2-(3-Oxobutyl)cyclohexanone.
c A mixture of 2-methyl[3.3.1]non-2-ene-9-one and $\Delta^{1,9}$-2-octalone.



I II

On the basis of above results, we tentatively suggest that the hydrolysis proceeds through a following pathway similar to that proposed for the reaction in the presence of $TiCl_4$ and ethanethiol. An intermediate III is formed by the addition of methanol to the vinyl chloride activated by $TiCl_4$, and then it is hydrolyzed to ketone.

$$R^1R^2C=CClR^3 \xrightarrow[MeOH]{TiCl_4} \underset{III}{[R^1R^2CH\text{-}CCl(OMe)R^3]} \longrightarrow R^1R^2CHCOR^3$$

References

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3. J. A. Marshall and D. J. Schaeffer, J. Org. Chem., 30, 3642 (1965).
4. The authors wish to express their thanks to the Takeda Chemical Industries Co. Ltd., for furnishing this sample.

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