Tetrahedron Letters No.43, pp. 4281-4284, 1967. Pergamon Press Ltd. Printed in Great Britain.

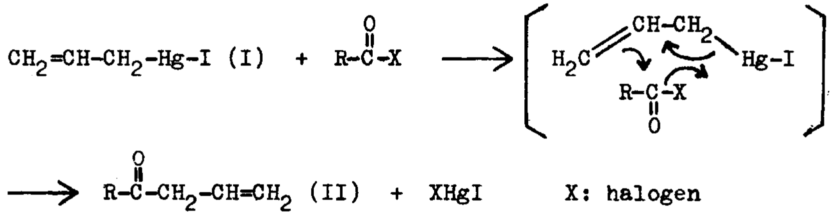
THE REACTION OF ALLYLMERCURIC IODIDE WITH ACYL HALIDE

Isao Kuwajima, Koichi Narasaka and Teruaki Mukaiyama
Laboratory of Organic Chemistry, Tokyo Institute of Technology
Ookayama, Tokyo

(Received in Japan 10 July 1967)

It is known that chloromercuriacetaldehyde reacts with acyl halides to give the corresponding vinyl esters.[1)] Recently it was reported that 1-butene is obtained exclusively along with mercuric chloride bromide by the reaction of crotylmercuric bromide with hydrogen chloride.[2)]

Based on these reports, the reaction of allylmercuric iodide(I) with acyl halide was examined with the assumption that allyl ketone(II) would result according to the following equation.



$$CH_2{=}CH{-}CH_2{-}Hg{-}I \text{ (I)} + R{-}\overset{O}{\overset{\|}{C}}{-}X \longrightarrow \left[\cdots \right] \longrightarrow R{-}\overset{O}{\overset{\|}{C}}{-}CH_2{-}CH{=}CH_2 \text{ (II)} + XHgI$$

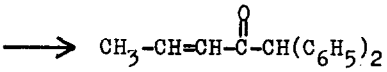
X: halogen

When equimolar amounts of diphenylacetyl chloride(III) and allylmercuric iodide(I) were refluxed in dioxane for 8 hr in a dark, mercuric chloride iodide precipitated almost quantitatively. Separation with alumina column chromatography and further purification by distillation afforded an oily liquid (132-4°/0.10 mmHg). The infrared spectrum of this liquid has an intense peak at 1695 cm^{-1} attributable to ketone carbonyl group and its nmr spectrum has the peaks at τ 8.33(quartet, 3 protons), 4.88(singlet, 1 proton) 3.10-4.13(multiplet, 2 protons) and 2.88(10 aromatic protons). This compound was confirmed to be diphenylmethyl propenyl ketone(IV) by the above mentioned spectroscopic data and elemental analysis. The infrared spectrum of the crude reaction mixture, however, had a different picture from the purified one, showing characteristic peaks for carbonyl group at 1720 cm^{-1} and for vinyl group at 1635, 990 and 917

cm^{-1}. These results show that the reaction of diphenylacetyl chloride(III) with allylmercuric iodide(I) affords allyl ketone, as expected, which changes readily into diphenylmethyl propenyl ketone(IV) during the purification procedure.

$$(I) + (C_6H_5)_2CH-\overset{O}{\overset{\|}{C}}-Cl \longrightarrow ClHgI + \left[CH_2{=}CH-CH_2-\overset{O}{\overset{\|}{C}}-CH(C_6H_5)_2 \right]$$

(III)



$$\longrightarrow CH_3-CH{=}CH-\overset{O}{\overset{\|}{C}}-CH(C_6H_5)_2$$

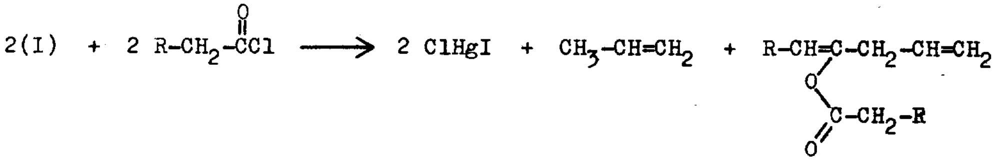
(IV)

(IV) yield 73%

analysis

	found	calcd.
C	86.47	86.40
H	7.06	6.83

On the other hand, when acyl chloride having two hydrogen atoms on α-carbon was allowed to react with allylmercuric iodide(I) under the similar condition, propylene was evolved and enol ester(V) was obtained along with mercuric chloride iodide.



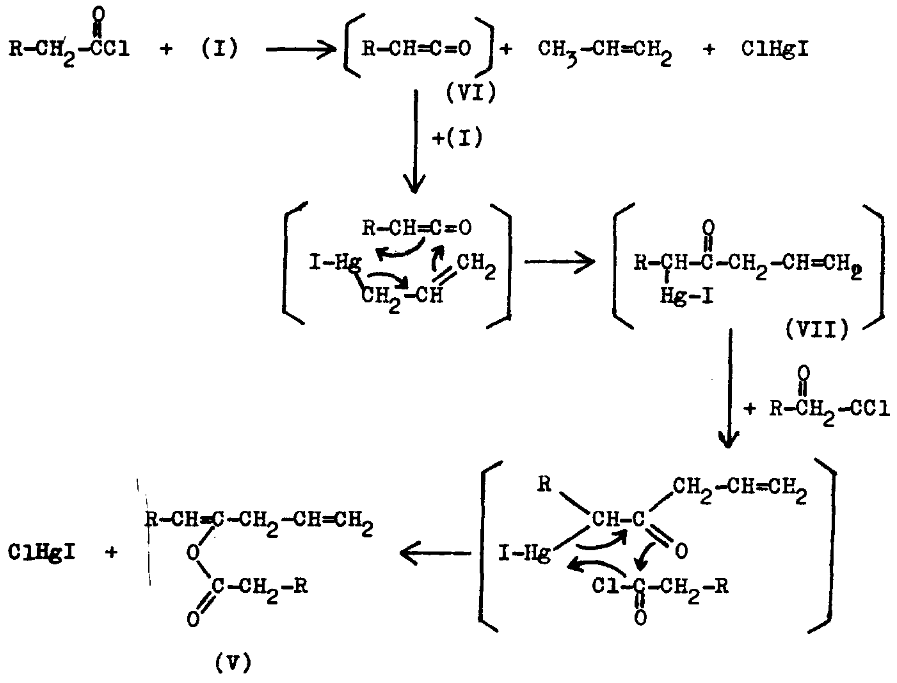
(V)

	R	Yield(%)		B.p. °C/mmHg	Analysis			
		Propylene	Ester(V)		found		calcd.	
					C	H	C	H
Va	C_6H_5	36	46	128/0.08	81.17	6.81	81.01	6.65
Vb	$C_6H_5CH_2$	68	52	161-2/0.12	82.00	7.00	82.32	7.24
Vc	$CH_3-(CH_2)_7$	63	47	150/0.07	79.12	12.24	78.80	12.08
Vd	$CH_3-(CH_2)_{15}$	51	40	M.p. 20-21°c	81.05	12.73	81.46	12.97

* In each case, mercuric chloride iodide was obtained quantitatively.

The structures of the products were confirmed to be 2-acyloxy-1,4-pentadiene derivatives by infrared, ultraviolet and nmr spectra and elemental analyses. For example, in the case of (Vd), the infrared spectrum has the peaks of ester carbonyl at 1755 cm^{-1}, carbon-carbon double bond at 1635 cm^{-1} and vinyl group at 990 and 915 cm^{-1}. Further, ultraviolet spectrum shows no peak from 210 mμ to 340 mμ region attributable to conjugated double bond. The nmr spectrum of (Va) shows absorptions at τ 6.95(multiplet. 2 protons), 6.47(singlet. 2 protons), 4.83-5.30(multiplet. 2 vinyl protons), 3.70-4.60(multiplet. 2 olefinic protons) and 2.70-3.15(10 aromatic protons).

The formation of unfavorable non-conjugated vinyl ester may be explained by assuming the following mechanism; initially, allylmercuric iodide(I) acts as dehydrohalogenation reagent to yield the corresponding ketene(VI) from acyl halide. The ketene(VI) thus formed, reacts with another molecule of allylmercuric iodide(I) to give the addition product, α-iodomercurated alkyl allyl ketone(VII). The ketone(VII) further reacts with acyl halide to produce the vinyl ester(V) similar to the reaction of acyl halide with chloromercuriacetaldehyde reported by Nesmeyanov et al.1)



This mechanism is supported by the following two separate experiments. In the case of the reaction with isobutyryl chloride, dimethylketene dimer, derived from dehydrochlorinated product, can be detected by IR spectrum of the crude mixture, which shows a strong peak at 1815 cm^{-1}.3) Further, when an equimolar amount of diphenylketene was treated with allylmercuric iodide, the addition product, 1,1-diphenyl-2-diphenylacetoxy-1,4-pentadiene was obtained. These results show that the ketene is a key intermediate, which add to allylmercuric iodide as shown in the above equation.

REFERENCES

1) A. N. Nesmeyanov, I. F. Lutesenko, and Z. M. Tumanova, Izvest. Akad. Nauk S. S. S. R., Otdel Khim. Nauk 1949, 587; Chem. Abstr., 44, 7225d (1950).
2) P. D. Sleezer, S. Winstein, and W. G. Young, J. Am. Chem. Soc., 85, 1890 (1963).
3) R. H. Hasek, R. D. Clark, E. U. Elam, and J. C. Martin, J. Org. Chem., 27, 60 (1962).