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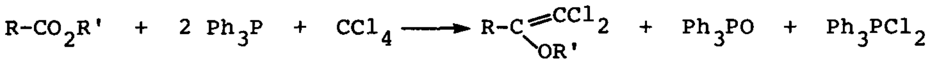
DICHLOROMETHYLENATION OF ESTERS AND LACTONES BY TRIPHENYLPHOSPHINE-CARBON TETRACHLORIDE REAGENT.

Minoru Suda* and Asako Fukushima
Sagami Chemical Research Center
Nishi-Ohnuma 4-4-1, Sagamihara, Kanagawa 229, Japan.

Reaction of triphenylphosphine-carbon tetrachloride reagent with esters and lactones produced 1-substituted 2,2-dichlorovinyl ethers. Hydrolysis of these ethers in acidic conditions afforded the dichloromethyl ketones.

Triphenylphosphine-carbon tetrachloride reagent is known to react with ketones and aldehydes to provide dichloroolefins.[1] However, to the best of our knowledge, reaction of this reagent with esters or lactones has not been reported. We have found that esters as well as lactones do react with triphenylphosphine-carbon tetrachloride reagent in the manner as depicted in the following equation.[2]



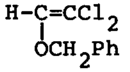
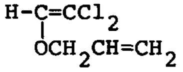
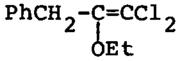
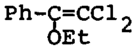
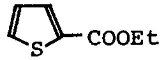
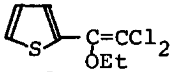
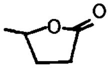
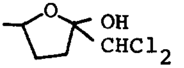
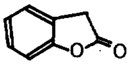
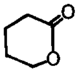
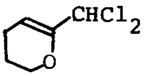
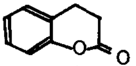
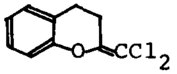
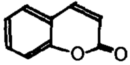
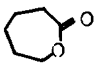
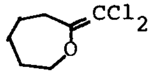
$$R\text{-}CO_2R' + 2\,Ph_3P + CCl_4 \longrightarrow R\text{-}C(=CCl_2)(OR') + Ph_3PO + Ph_3PCl_2$$

Typically, a mixture of dihydrocoumarin 1 (one equivalent) and triphenylphosphine (three equivalents) in excess carbon tetrachloride was heated under reflux for 6 hrs. Crude reaction mixture was absorbed on silica gel, which was then extracted several times with hexane-ether mixture. Solvent was removed under vacuum and purification by column chromatography on silica gel afforded 2-dichloromethylenechroman 2[3,4] in 82% yield.

This dichloromethylenation was found to occur with lactones and esters. Results are summarized in Table 1. As is shown in the table, isolated products from γ-valerolactone 3 and δ-valerolactone 4[5] were hydrolyzed form 5[6] and isomerized ether 6[7] of the expected dichloroolefins, respectively. We assume that these were formed from the dichloroolefins during the work-up procedure (see note 5).

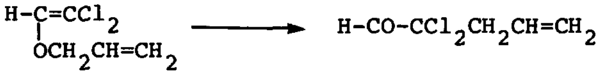
The yields of dichloroolefins (or hydrolysis product) are dependent upon the structure of substrates. Simple esters afford dichloroolefins in fair yields, although a large excess of reagent (more than five equivalents) is required. Exceptionally, benzyl formate reacted almost completely even when 2.2 equivalents of triphenylphosphine was used, and the product was isolated in 77% yield. Among lactones examined, γ-lactones did not produce the expected ethers. Thus, γ-valerolactone gave a dichloromethyllactol 5, and no product was obtained from 2-coumaranone. Six and seven membered lactones seem to react normally, although coumarin was inert completely.

Table 1. Dichloromethylenation of esters and lactones.[a)]

Substrate	Product	Reaction time (hr)	Isolated yield (%)	Recovered ester (%)
$HCOOCH_2Ph$	 $H-\underset{OCH_2Ph}{\underset{\mid}{C}}=CCl_2$	7	77	-
$HCOOCH_2CH=CH_2$	 $H-\underset{OCH_2CH=CH_2}{\underset{\mid}{C}}=CCl_2$	7	23	-
$PhCH_2COOEt$	 $PhCH_2-\underset{OEt}{\underset{\mid}{C}}=CCl_2$	6	27(34)[b)]	33
PhCOOEt	 $Ph-\underset{OEt}{\underset{\mid}{C}}=CCl_2$	16	9	77
		20	(14)	(65)
 3	 5	2.5	58	-
	—	4	-	-
 4	 6	2.5	40	-
 1	 2	6	82	-
	—	4.5	-	-
		3.5	64	-

a) A mixture of ester or lactone (10 mmol) and triphenylphosphine (30 mmol) in carbon tetrachloride (30 ml) was refluxed for appropriate time, and the product was isolated either by silica gel chromatography or by distillation.
b) Yields when five equivalents of triphenylphosphine was used.

This new reaction provides a method to prepare allyl vinyl ether derivatives, which can be transformed into unsaturated aldehydes or ketones (Claisen rearrangement). Thus allyl formate was converted to allyl 2,2-dichlorovinyl ether 7[8)] by the procedure disclosed above, and subsequent thermolysis in xylene gave the expected 2,2-dichloro-4-pentenal 8.[9)]

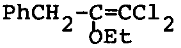
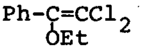
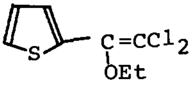
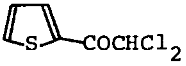
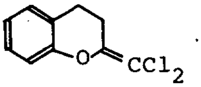
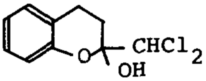


$H{-}C(OCH_2CH{=}CH_2){=}CCl_2 \longrightarrow H{-}CO{-}CCl_2CH_2CH{=}CH_2$

7 8

We then examined the hydrolysis of these dichlorovinyl ethers. Although heating under basic conditions (KOH in methanol) induced no reaction, aqueous trifluoroacetic acid was found to effect clean hydrolysis of vinyl ether group to give dichloromethyl ketones in a fair yield. The results are summarized in Table 2. For all cases, dichloromethyl ketones are isolated. Only a complex mixture was obtained when 2-dichloromethyleneoxepane was treated similarly.

Table 2. Hydrolysis of dichlorovinyl ethers.

Substrate	Reaction time (hr)	Product	Yield(%)
 $PhCH_2{-}C(OEt){=}CCl_2$	3.5	$PhCH_2COCHCl_2$	62
 $Ph{-}C(OEt){=}CCl_2$	7	$PhCOCHCl_2$	76
	4		86
	22.5		46[a)]

a) Starting material was recovered in 22% yield.

Typically, a mixture of 2-(2,2-dichloro-1-ethoxyvinyl)thiophene (300 mg, 1.35 mmol) in trifluoroacetic acid (875 mg) and water (530 mg) was heated to 65°C for 4 hrs. The reaction mixture was diluted with water, and extracted with dichloromethane. The extract was concentrated and chromatography on silica gel afforded 2-dichloroacetylthiophene in 86% yield.

In summary, we have shown that treatment of esters and lactones with triphenylphosphine-carbon tetrachloride reagent produces the corresponding dichlorovinyl ethers, and their hydrolysis under acidic conditions gives dichloromethyl ketones. Thus present method is useful for the introduction of one carbon unit on esters and lactones. Further investigations are underway.

The authors are grateful to Mr. Shinichiro Oshiro of this institute for his technical assistance.

REFERENCES AND NOTES

1) R. Rabinowitz and R. Marcus, J. Am. Chem. Soc., 84, 1312 (1962).
2) Esters have been reported to react with methylenetriphenylphosphorane i to produce isoprenyl group; A. P. Uijttewaal, F. L. Lonkers, and A. van der Gen, J. Org. Chem., 44, 3157 (1979). Also, reaction of β- and γ-lactones with i has been described; H. Kise, Y. Arase, S. Shiraishi, M. Seno, and T. Asahara, Chem. Commun., 1976, 299.
3) All new compounds were characterized spectroscopically and/or by elemental analysis.
4) NMR($CDCl_3$) δ 2.76(4H,s), 6.80-7.33(4H,m); MS m/e 218(10%),216(57),214(85)
5) In this case, standard work-up procedure gave no product. Instead, crude reaction mixture was filtered, and the filtrate was concentrated at r.t. under vacuum. Subsequent distillation (bath temperature 110-120°C/0.2Torr.) afforded 6.
6) NMR($CDCl_3$) δ 1.27(d), 1.35(d) (total 3H), 1.50-2.47(4H,m), 3.18(1H,s), 4.17-4.67(1H,m), 5.70(1H,s); IR 3400 cm^{-1}; MS m/e 186(4%), 184(6), 174(4), 172(26), 170(56).
7) NMR($CDCl_3$) δ 1.70-2.20(4H,m), 4.11(2H,t), 5.10(1H,t), 6.00(1H,s); IR 1615 cm^{-1}; MS m/e 168(2%), 166(3), 132(35), 130(97).
8) NMR($CDCl_3$) δ 4.43(2H,m), 5.17-6.37(3H,m), 6.60(1H,s); MS m/e 154(2%), 152(4).
9) NMR($CDCl_3$) δ 3.11(2H,d), 5.1-6.2(3H,m), 9.37(1H,s).

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