

A New Selective Dichlorination of C-C Double Bonds

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Abstract: A new dichlorination procedure of C-C double bond was developed with hexachloroethane as chlorinating agent and $\text{RuCl}_2(\text{PPh}_3)_3$ as catalyst. The reaction is highly selective for C-C double bond; other functional groups are unaffected by these conditions.

The addition reaction of polyhalomethane to alkenes is known as the Kharasch reaction.¹⁻⁶ The addition of tetrachloromethane to 3,3-dimethyl-4-pentenoic acid esters (**1**), for example, to give the tetrachlorohexanoic acid derivative (**2**) is well established as an important synthetic process for the pesticidal dichlorovinylcyclopropanecarboxylic acid derivative (**3**).⁷⁻⁹ However, when the addition reaction of hexachloroethane, in analogy with tetrachloromethane, was attempted to **1** under the same reaction conditions, we found that 4,5-dichloro-3,3-dimethylpentanoic acid ester (**4**) was produced, unlike the result with tetrachloromethane. The direct addition of two chlorine atoms to the double bond in **1** occurred in this case without disturbing the active methylene of the ester which is difficult to avoid by conventional chlorinating methods.¹⁰ We were interested in this unusual reaction and thus explored its chemistry with various olefins and reaction conditions. Here, we summarize our results and report a new dichlorination method for a variety of double bonds using hexachloroethane.

First, we examined the reaction conditions as shown in Table 1. A radical initiator, dibenzoyl peroxide (BPO), promoted the reaction giving **4** in a yield corresponding to added BPO, suggesting that the reaction proceeded under a radical mechanism but not by a radical chain process. However, in the case using a catalytic amount of $\text{RuCl}_2(\text{PPh}_3)_3$,^{5,6} the reaction proceeded favourably to give **4** in a high yield.

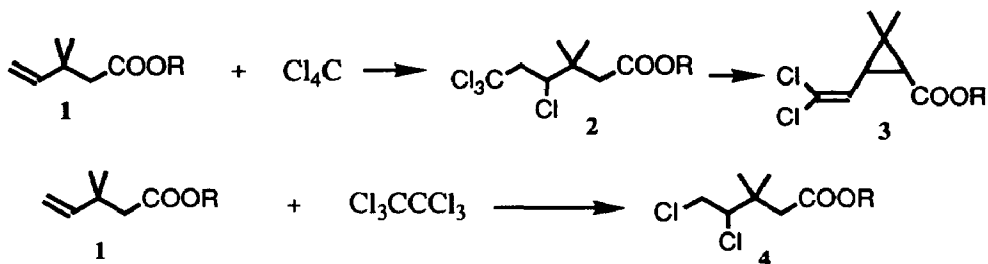


Table 1. Dichlorination of **1** with hexachloroethane to give **4**


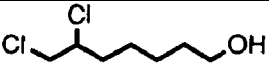

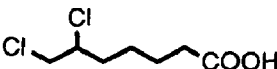

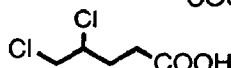


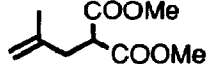
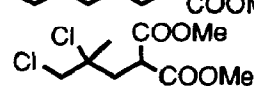
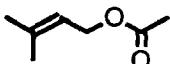
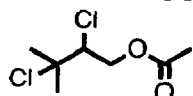
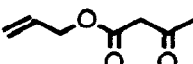
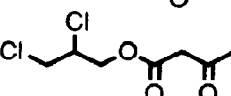

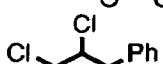
Entry	starting materials C ₂ Cl ₆ / 1 ^{a)}	reaction conditions	product 4 %yield ^{b)}
1	3.5 : 1	BPO (~20%) ^{c)} benzene, reflux 30h	20
2	1.5 : 1	RuCl ₂ (PPh ₃) ₃ ^{d)} benzene, reflux 19h	70
3	1.5 : 1	RuCl ₂ (PPh ₃) ₃ ^{d)} toluene, 120°C ^{e)} 3h	92

a) 1 M solution to **1**. b) Yields were determined by GLC analyses. c) BPO was added sequentially (5% x 4). d) 1 mol% of the catalyst was used. e) Treated in sealed tube.

Tetrachloroethene was detected in the reaction solution after completion by GLC analysis, indicating that the chlorine atoms in hexachloroethane were transferred to the chlorinated double bond. The procedure was also applicable to 1-pentadecene to give 1,2-dichloropentadecane in 75 % yield. However, for simple aliphatic mono olefins, other more conventional reagents, such as Cl₂ or SO₂Cl₂, are probably more convenient.

Thus, the scope and limitations of this new chlorination reaction to various olefins were examined under the

Table 2. The Dichlorination of Olefins with Hexachloroethane^{a)}

Entry	Olefin	Dichloride Product ^{d)}	Product Yield, % ^{b)}
1			79
2			62
3			(53) ^{c)}
4			89
5			75
6			(34) ^{c)}
7			23
8			(41) ^{c)}

a) Reaction conditions: 1 mol% RuCl₂(PPh₃)₃, olefin 1 mmol, and C₂Cl₆ 1.5 mmol were mixed in toluene 1.5 mL, then heated at 110°C under Ar atm. in a sealed tube until the olefin was consumed. b) Yields were analyzed by GLC.

c) Isolated yield. d) All dichlorides had satisfied the spectral data of ¹H NMR, MS, and IR.

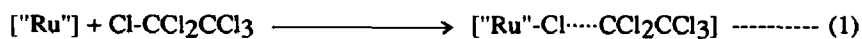
Table 3. The chlorination of conjugate-dienes

Entry	Diene	Products ^{a)}		Ratio ^{b)}	Yield, % ^{d)}
1				67 : 33	35
2				c)	30
3				65 : 35	26

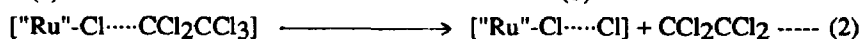
a) Structures were assigned by ¹H NMR. b) Analyzed by GLC or ¹H NMR. c) Not to be separated by GLC or ¹H NMR. d) The isolated combined yields.

catalytic conditions used in the reaction of **1** as shown in Table 1. The results are shown in Table 2. The reaction proceeded for compounds with various kinds of functional groups, such as hydroxy, carboxyl, ester, phenyl, or active methylene structure. However, nitrogen containing functional groups, e.g., amine, amide, imine, and nitrile gave low yields. The conventional catalyst, CuCl,⁸ also, did not effect the reaction. For conjugate dienes, the reaction proceeded through both 1,4- and 1,2-addition mode to give a mixture of dichlorides as shown in Table 3. As the rate difference between 1,4- and 1,2- mode was not so large, selective dichlorination could not be attained. An attempt to dibrominate a double bond with 1,2-dibromotetrachloroethane under the same conditions failed to occur, only giving recovery of the starting materials.

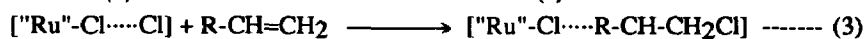
The reaction seems to proceed under a radical mechanism, like the reaction using tetrachloromethane with RuCl₂(PPh₃)₃¹¹ catalyst, which is the subject of a thorough kinetic study as reported by Davis et al.^{12,13} The process, a modification of their mechanism, initiates by a chlorine atom abstraction to the active Ru catalyst ("Ru") (a) to form an adduct (b) (equation 1). The adduct (b) is unstable and releases tetrachloroethene out of the system immediately, then, changes to the next dichloro-adduct (c) (equation 2). The driving force for step 2 may be formation of tetrachloroethene as a very stable compound, thus accounting for a reaction path different from tetrachloromethane. Thus, adduct (c) can serve as chlorine transferring agent as seen in the following steps (equations 3 and 4).



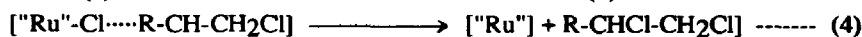
(a) (b)



(b) (c)



(c) (d)



(d) (a)

In conclusion, we developed a novel and convenient dichlorinating method for double bonds of various olefinic compounds using hexachloroethane as the chlorinating agent under catalytic conditions with $\text{RuCl}_2(\text{PPh}_3)_3$. The reaction proceeds under mild conditions, so that the procedure allows for the presence of various active functional groups in the molecules. As shown above, the present process can serve as an efficient synthetic procedure for various kinds of useful compounds. Further applications of this convenient dichlorination procedure to other unsaturated compounds are now in progress.

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