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METATHESIS OF ALKENES HAVING FUNCTIONAL GROUPS

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$WCl_6/(CH_3)_3Al_2Cl_3$ and $Mo(OC_2H_5)_2Cl_3/(CH_3)_3Al_2Cl_3$ were found to be the effective catalysts for the metathesis of alkenes having various functional groups such as -COOR, -OCOR, -OR, -CN, -COR, and $-CONR_2$. These reactions should be quite important in a synthesis of telechelic compounds or bioactive substances such as sex attractant pheromones.

Numerous studies[1-11] on the metathesis of the alkenes having no functional groups have been reported and the various catalysts such as $WCl_6/C_2H_5OH/C_2H_5AlCl_2$,[2,6] WCl_6/C_4H_9Li,[3] $ReCl_5/(C_4H_9)_4Sn$,[4] WCl_6/Oxygen/$(C_2H_5)_3Al$,[7] $(Py)_2Mo(NO)_2Cl_2/(CH_3)_3Al_2Cl_3$,[8] $WCl_6/RMgX$,[9,10] and $WCl_6/LiAlH_4$[11] are known as typical catalysts for the metathesis of the alkenes. The metathesis of the acyclic alkenes having functional groups, however, had not been described until the investigation with respect to the methathesis of unsaturated fatty acid esters using a $WCl_6/(CH_3)_4Sn$ catalyst reported by Boelhouwer.[12,13] We have aheadly reported in concerning with the methathesis of various unsaturated fatty acid esters using new catalyst systems such as a WCl_6/R_3B etc.[14] We now report the methathesis of the alkenes having various functional groups, that is to say, unsaturated esters, nitriles, ketones, ethers, and amides to give the telechelic compounds and the metathesis of oleyl acetate with hexene or 5-decene to give mainly 9-tetradecenyl acetate using $WCl_6/(CH_3)_3Al_2Cl_3$, $Mo(OC_2H_5)_2Cl_3/(CH_3)_3Al_2Cl_3$, $MoCl_5/(CH_3)_3Al_2Cl_3$, and $W(CO)_6/(CH_3)_3Al_2Cl_3$ catalyst systems.

The reactions were carried out by the use of a conventional glass reactor in a nitrogen atomosphere at 20 - 70°C. The products were analysed by gas chromatographs and identified by NMR and IR spectra and the retention times of the products on the gas chromatograms. Practically pure WCl_6 was obtained by removing more volatile $WOCl_4$ under a stream of N_2 at 200°C.

One of the typical reactions is illustrated below and the others are shown in Table 1, 2, and 3.

Into a thoroughly dried glass vessel, which had been flushed with nitrogen to replace the air, were introduced 5ml of chlorobenzene, 0.5ml of 9-octadecenenitrile (1), and 2ml of a chlorobenzene solution of WCl_6 (0.05mole/l). After about one

Table 1. Metathesis of 9-octadecenenitrile (1)$^{a,b)}$

Catalyst	(mM)		(mM)	Solvent	(ml)	Conversion of (1) (%)	Yield (%)		
							(2)	(3)	Total$^{c)}$
WCl_6	(0.1)	$(CH_3)_{1.5}AlCl_{1.5}$	(0.3)	PhCl	(7)	30	8	7	25
$W(CO)_6$	(0.2)	"	(0.6)	"	(9)	10	2	0.5-1	4-5
$W(OPh)_6$	(0.2)	"	(")	"	(")	5	1	0.5	3
$ReCl_5$	(0.2)	"	(")	"	(")	5	1	0.5	3
$Mo(OC_2H_5)_2Cl_3$	(0.2)	"	(")	"	(")	20	5	3	15
WCl_6	(0.1)	$(C_2H_5)_3Al$	(0.3)	"	(7)	<5	tr	tr	tr
"	(")	$(C_2H_5)_2AlCl$	(")	"	(")	<5	0.5	tr	1
"	(")	$(C_2H_5)_{1.5}AlCl_{1.5}$	(")	"	(")	<5	tr	tr	tr
"	(")	$C_2H_5AlCl_2$	(")	"	(")	<5	tr	tr	tr
"	(")	"	(")	"	(")	<5	tr	tr	tr
"	(")	$(CH_3)_{1.5}AlCl_{1.5}$	(")	$AcOC_2H_5$	(5)	35	10	9	30
$RuCl_3 \cdot H_2O$	(0.2)	"	(0.6)	PhCl	(7)	<5	0	0	0
"	(")			"	(")	<5	0	0	0
Re_2O_7-Al_2O_3	(Re/Al=5/95 atomic ratio, 1g)			"	(")	<5	0	0	0

a) Reaction temperature, 60°C; reaction time, 17 hr;
$CH_3(CH_2)_7CH{=}CH(CH_2)_7CN$ (1), 0.5ml.

b) $2\ (1) \longrightarrow CH_3(CH_2)_7CH{=}CH(CH_2)_7CH_3\ (2) + NC(CH_2)_7CH{=}CH(CH_2)_7CN\ (3)$

c) (2) + (3) + the products given by the equation [2] and [3].

Table 2. Metathesis of alkenes having various functional groups using a $WCl_6/(CH_3)_3Al_2Cl_3$ catalyst

Substrate (ml)	Reaction Temp. (°C)	Reaction Time (hr)	products by metathesis (% Yield)
$CH_2{=}CHCH_2OSi(CH_3)_3$ (1)[a]	70	17	$[(CH_3)_3SiOCH_2CH{=}]_2$ (10)
$CH_2{=}CHCH_2 \cdot C_6H_4OCH_3$ (1)	"	"	$[CH_3OC_6H_4CH_2CH{=}]_2$ (10)
$CH_3(CH_2)_7CH{=}CH(CH_2)_7COC_2H_5$ (0.5)	20	"	$[CH_3(CH_2)_7CH{=}]_2$ (3) $[C_2H_5CO(CH_2)_7CH{=}]_2$ (2)
$CH_2{=}CH(CH_2)_2COCH_3$ (1)	60	7	$[CH_3CO(CH_2)_2CH{=}]_2$ (10)
$CH_3(CH_2)_7CH{=}CH(CH_2)_7CON(C_2H_5)_2$ (1)	20	6	$[CH_3(CH_2)_7CH{=}]_2$ (3) $[(C_2H_5)_2NCO(CH_2)_7CH{=}]_2$ (trace)
$CH_3(CH_2)_7CH{=}CH(CH_2)_8NH_2$	70	17	$[CH_3(CH_2)_7CH{=}]_2$ (trace)
$CH_3(CH_2)_7CH{=}CH(CH_2)_7COOH$	"	"	(0)
$CH_3(CH_2)_7CH{=}CH(CH_2)_7OH$ (1)	"	"	(0)
$CH_3(CH_2)_7CH{=}CH(CH_2)_7CONH_2$	"	"	(0)

a) WCl_6, 0.2 mM; Others, 0.1 mM; Al/W = 3.

minute of stirring, 0.6ml of a toluene solution of $(CH_3)_{1.5}AlCl_{1.5}$ (0.5mole/l) was added into the reactor, which was then sealed off at 0°C. The reaction was conducted at 60°C for 17 hr to give 9-octadecene(**2**) in a yield of about 8% and 9-octadecenedinitrile(**3**) in a yield of about 7% (thermodynamical equilibrium yield = each about 25%). The selectivity to **2** or **3** was each about 60%. A considerable number of alkenes having different number of carbon atoms were obtained due to the double bond isomerization and the subsequent metathesis reactions represented by the reaction [2] and [3]. The metathesis yield including these reaction products were about 25%.

$$2R(CH_2)_aCH{=}CH(CH_2)_bX \longrightarrow R(CH_2)_aCH{=}CH(CH_2)_aR + X(CH_2)_bCH{=}CH(CH_2)_bX \qquad [1]$$

$$R(CH_2)_aCH{=}CH(CH_2)_bX \longrightarrow R(CH_2)_{a\pm c}CH{=}CH(CH_2)_{b\mp c}X \qquad [2]$$

$$\begin{aligned} &R(CH_2)_aCH{=}CH(CH_2)_bX + R(CH_2)_{a\pm c}CH{=}CH(CH_2)_{b\mp c}X \\ &\longrightarrow R(CH_2)_{a\pm c}CH{=}CH(CH_2)_aR + X(CH_2)_{b\mp c}CH{=}CH(CH_2)_bX \\ &\quad + \text{other olefins} \qquad [3] \end{aligned}$$

R = Alkyl (or hydrocarbon group) or hydrogen atom.

X = -CN, -COOR, -OCOR etc., a≥0, b≥1, c≥0, b-c≥1 (preferably b>>1, b-c>>1)

Many other results obtained by the experiments in the same manner as in above illustrated one are shown in Table 1, 2, and 3. The reaction of trimethylsiloxy-2-

Table 3. Metathesis of unsaturated fatty acid esters and oleyl acetate[a)]

Substrate (ml)		Catalyst	Reaction Temp. (°C)	Reaction Time (hr)	Conversion (%)	Yield (%)		
Methyl oleate	(1)	I(0.1,0.2)	28	17	50	B(23)	C(21)	Total(50)
"	(1)	II(0.1,0.2)	26	20	30	"(13)	"(12)	" (30)
"	(2)	I(0.1,0.1)	"	"	5	"(1)	"(0.5-1)	" (3)
"	(")	I(0.1,0.2)	"	"	20	"(7-8)	"(4)	" (15)
"	(")	I(0.1,0.3)	"	"	35	"(14)	"(12)	" (30)
"	(")	I(0.1,0.6)	"	"	25	"(8-9)	"(6-7)	" (20)
"	(")	I(0.1,0.1)	"	"	10	"(2)	"(2)	" (5)
Methyl 10-undecenoate	(1)	I(0.1,0.2)	50	4	40	D(>16)	E(16)	" (>35)
Ethyl 4-pentenoate	(0.5)	I(0.1,0.2)	"	17	55	D(>25)	F(25)	" (>50)
Oleyl acetate	(1)	I(0.1,0.2)	27	15	40	B(12)	G(12)	" (35)
"	(1)	I(0.1,0.2)	"	"	40[b)]	B(trace)	G(trace)	
Hexene	(3)					H(15)	I(20)	
Oleyl acetate	(1)	I(0.1,0.2)	"	"	32[b)]	B(trace)	G(trace)	
5-Decene	(3)					H(26)		

Catalysts: I(i,j) ⟶ WCl_6, i mM; $(CH_3)_{1.5}AlCl_{1.5}$, j mM; II (i,j) ⟶ $MoCl_5$, 0.1 mM; $(CH_3)_{1.5}AlCl_{1.5}$, j mM. a) cis-9-Octadecenyl acetate.

b) Conversion of oleyl acetate.

B, Octadecene; C, 9-Octadecene-1,18-dioic acid dimethyl ester; D, Ethylene; E, 10-Eicosene-1,20-dioic acid dimethyl ester; F, 4-Octene-1,8-dioic acid diethyl ester; G, 1,18-Diacetoxy-9-octadecene; H, 9-Tetradecenyl acetate; I, 9-Decenyl acetate.

propene, which was prepared by the reaction of allyl alcohol with $(CH_3)_3SiCl$ in pyridine, to give a symmetrical siloxy-compound is paticuraly suprising in view of the fact that the allylic compound can disproportionate. Allyl chloride, however, did not disproportionate but reacted quickly to give such an alkene represented by the reaction [4] and some polymers.

$$CH_2{=}CH\text{-}CH_2\text{-}Cl \xrightarrow{R_3Al_2Cl_3} CH_2{=}CH\text{-}CH_2\text{-}R \qquad [4]$$

The $WCl_6/C_2H_5OH/C_2H_5AlCl_2$ and the Re_2O_7/Al_2O_3 which are known to be highly active catalysts for the metathesis of the unsaturated hydrocarbons are not effective any more, at least in our conditions, for that of the alkenes having such functional groups illustrated in this paper. It is somewhat strange that the $WCl_6/(C_2H_5)_3Al_2Cl_3$ is almost inactive even for the metathesis of the unsaturated esters and the nitrile —— the latter is shown in Table 1.

The data in the tables show that both $WCl_6/(CH_3)_3Al_2Cl_3$ and $Mo(OC_2H_5)_2Cl_3/(CH_3)_3Al_2Cl_3$ are effective for the functional alkenes, especially for the unsaturated esters, except for the alcohol, amine, and amide. The reactivity in concerning with the functional groups substituted in the alkenes decreased in following order, namely -COOR > -OCOR > -OR > -CN > -COR > $-CONR_2$ > $-NH_2$, -COOH, -OH (= inactive). These reactions should be quitely important in the synthesis of telechelic compounds and various perfumes including precursors there of, bioactive substances of insects, base materials for cosmetics, natural higher carboxylic acids, or alcohols.

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