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METATHESIS OF OLEYL CHLORIDE

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The metathesis of oleyl chloride (1-chloro-cis-9-octadecene) with an alkene such as 1-hexene, 5-decence, 2-butene, etc., and the disproportionation of oleyl chloride were found to be effectively catalyzed by a modified or unmodified Re_2O_7-Al_2O_3 catalyst at ambient temperature. The activity of the modified catalyst with Me_xO_y such as V_2O_5, MoO_3, WO_3, GeO_2, Re_2O_7-Me_xO_y-Al_2O_3, was very high even at low Re contents. This reaction should be important in a synthesis of telechelic compounds or bioactive substances for insects such as sex attractant pheromones.

Numerous studies on the metathesis of alkenes have been reported over various heterogeneous[1,2] and homogeneous[3,4] catalysts. However, only a few catalysts for the metathesis of the acyclic olefins having functional groups have been known. Boelhouwre et.al.[5] first reported that a $WCl_6/(CH_3)_4Sn$ system catalyzes the metathesis of the unsaturated fatty acid esters such as methyl oleate (methyl cis-9-octadenoate) at > 70°C. We have already reported that a WCl_6/R_3B[6] system is effective for the metathesis of the unsaturated carboxylic acid esters at > 70°C, and moreover $WCl_6/(CH_3)_3Al_2Cl_3$ or $Mo(OC_2H_5)_2Cl_3/(CH_3)_3Al_2Cl_3$ is active for that of the olefins having various functional groups such as ethyl 3-butenoate, methyl oleate, oleyl acetate, 9-octadecene nitrile, ethyl 9-octadecenyl ether, etc. at mild conditions.[7]

A few patents[8] suggest, but they do not afford the details, that the metathesis of the halogen atom substituted acyclic olefins such as 5-chloro-1-pentene proceeds by some homogeneous catalysts such as $Py_2Mo(NO)_2Cl_2/(CH_3)_3Al_2Cl_3$, $WCl_6/C_2H_5AlCl_2$, etc.. On the contrary, the metathesis of the olefin having functional groups over supported metal oxide catalysts has not been reported. We now report the metathesis of oleyl chloride (**1**) with some alkenes such as 1-hexene (**2**), trans-5-decene (**3**), and cis-2-butene (**4**), and the disproportionation of (**1**) by the use of the Me_xO_y-modified or unmodified Re_2O_7-Al_2O_3 catalyst in the liquid phase.

The binary support, Me_xO_y-Al_2O_3, was prepared by mixing alumina sol (from Nissan Chemical Co. Ltd.) with a slurry of finely powdered Me_xO_y, drying at 120°C. The resulting solid was ground, sieved, and calcined in air at 550°C for 5 hr. Al_2O_3 was prepared in the same manner without the use of Me_xO_y.

Re_2O_7-Al_2O_3 and Re_2O_7-Me_xO_y-Al_2O_3 were prepared by the impregnation of Al_2O_3 and Me_xO_y-Al_2O_3 respectively with an aqueous solution of rhenium heptoxide (> 99.99%

Table 1.

Metathesis of oleyl chloride over various heterogeneous metal oxide catalysts

Catalyst (1.0g) (Re/Al),[Me/Al]	Substrates and conditions	Conversion of (1) (%)	Yield (%)					
			(5)	(6)	(9)	(10)	(7)	(8)
Re_2O_7-Al_2O_3(5/95),[–]	(A)	65	60	60	–	–	trace	trace
" (3/97),[–]		10	8	8	–	–	"	"
" (1/199),[–]		1	trace	trace	–	–	"	"
Re_2O_7-V_2O_5-Al_2O_3 (5/95),[5/95]		75	72	70	–	–	"	"
" (1/199),[5/95]		12	10	11	–	–	"	"
Re_2O_7-WO_3-Al_2O_3 (5/95),["]		85	80	76	–	–	"	"
Re_2O_7-MoO_3-Al_2O_3 (1/199),["]		15	10	12	–	–	"	"
Re_2O_7-GeO_2-Al_2O_3 ("),[1/9]		5	4	5	–	–	"	"
MoO_3-Al_2O_3 (–),[5/95]		1	0	0	–	–	"	"
WO_3-Al_2O_3 (–),["]		2	"	"	–	–	"	"
V_2O_5-Al_2O_3 (–),["]		0	"	"	–	–	"	"
WO_3-SiO_2 W/Si=5/95		2	"	"	–	–	"	"
Re_2O_7-Al_2O_3 (5/95),[–]	(B)	70	28	30	32	35	"	"
Re_2O_7-V_2O_5-Al_2O_3 (5/95),[1/9]		89	35	40	40	42	"	"
" (1/199),[5/95]		15	6	7	7	7	"	"
Re_2O_7-Al_2O_3 (5/95),[–]	(C)	72	67	70	–	–	"	"
Re_2O_7-Al_2O_3 (5/95),[–]	(D)	12	–	–	–	–	5	5
Re_2O_7-V_2O_5-Al_2O_3 (5/95),[5/95]		15	–	–	–	–	7	6

(A) (1) oleyl chloride ($CH_3(CH_2)_7CH=CH(CH_2)_8Cl$, cis) : 1 ml, trans-5-decence: 4 ml, 25°C, 3 hr.

(B) (1) : 1 ml, 1-hexene : 4 ml, 25°C, 3 hr.

(C) (1) : 1 ml, cis-2-butene: 4 ml, 0°C, 1 hr.

(D) (1) : 1 ml, 25°C, 3 hr.

from Mitsuwa Chemicals Co. Ltd.), evaporating and drying at 120°C. The resulting solid was calcined at 510°C for 2 hr. The reaction was carried out by the use of a conventional glass vessel in the liquid phase under a nitrogen atomosphere at 23 ~ 26°C. The products were analyzed by gas chromatography and identified by NMR and IR spectra and the retention times of the products on the gas chromatograms. Typical reactions are illustrated below and the results are shown in Table 1.

In a dried glass vessel (50 ml), two grams of Re_2O_7-WO_3-Al_2O_3 (Re/Al = 5/95, W/Al = 1/9, atomic ratio) was placed and activated in a stream of dry nitrogen at 500°C for 1 hr, and then cooled to the reaction temperature of 25°C. Over this catalyst, 20 ml of (3) and 5 ml of (1) (purity: 90%) were introduced. After stirring for 2 hr at 25°C, 14-chloro-5-tetradecene (5) was formed in a yield of 70 mol% based upon the amount of (1) used. The reaction selectivity was significantly high (> 85%). The product was isolated by a vacuum distillation (140~145°C, 4 mmHg). IR and NMR showed that the product was a mixutre of cis and trans isomers (the ratio of trans/cis = 3~4 : 1). 5-Tetradecene(6) was also formed, and trace amounts of 9-octadecene (7) and 1,18-dichloro-9-octadecene (8) were detected.

When the reaction was conducted in the absence of (3) in the same manner as that described above, (7) and (8) were formed. The conversion of (1) was about 25% and the yields of (7) and (8) were 12 mol% and 10 mol%, respectively. Table 1 shows that the catalytic activity of Re_2O_7-Al_2O_3 (Re/Al = 5/95) is also high, but that of Re_2O_7-Al_2O_3 (Re/Al < 3/97) is not so high. On the contrary, the activity of the modified catalyst, Re_2O_7-Me_xO_y-Al_2O_3 (Me = W, V, Mo, Ge), is high even at lower Re concentrations. The metathesis of (1) with (2) gives four main porducts, (5), (6), 1-decene (9), and 10-chloro-1-decene (10). General reaction scheme is represented by the reaction [1], [2], and [3]. The use of a large excess of a symmetrical alkene (R = R' in the reaction [1] and [3]) simplifies the reaction as described in the first example.

$$(1) + \mathrm{RHC{=}CHR'} \longrightarrow \mathrm{RHC{=}CH(CH_2)_8Cl} + \mathrm{R'HC{=}CH(CH_2)_8Cl} + \mathrm{RHC{=}CH(CH_2)_7CH_3} + \mathrm{R'HC{=}CH(CH_2)_7CH_3} \qquad [1]$$

$$2(1) \longrightarrow (7) + (8) \qquad [2]$$

$$2\ \mathrm{RHC{=}CHR'} \longrightarrow \mathrm{RHC{=}CHR} + \mathrm{R'HC{=}CHR'} \qquad [3]$$

If the symmetrical alkene is difficult to purchase, it can be synthesized through the disproportionation of 1-alkene, which is easy to obtain, by the use of the same catalyst system. For example, trans-5-decene used in this paper was obtained in a 45 mol% yield by the disproportionation of 1-hexene (30 ml) over the Re_2O_7-Al_2O_3 (Re/Al = 5/95) catalyst (2 g) at the ambient temperature.

The metathesis of allyl chloride and vinyl chloride with 1-hexene hardly occurred in these conditions, and moreover the former inhibited the disproportionation of 1-hexene. However, the process described in this paper should be important in the synthesis of telechelic compounds and the precursors of bioactive substances for insects; such as 9- or 12- tetradecenyl acetate.

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