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DISPROPORTIONATION OF THE UNSATURATED ESTERS

Ryuichi NAKAMURA*, Seiji FUKUHARA, Shuichi MATSUMOTO,
and Kooei KOMATSU
*Department of Chemical Engineering, Tokyo Institute of Technology,
Ookayama, Meguro-ku, Tokyo 152
Tokyo Research Laboratory of Japan Synthetic Rubber
Ikuta, Kawasaki-shi, Kanagawa 214

The disproportionation reactions of the unsaturated esters such as ethyl 3-butenoate, methyl 10-undecenoate, methyl oleate and 9-octadecenyl acetate were carried out using alkylborane-WCl_6, -$Mo(OEt)_2Cl_3$ and various other catalysts. Both Et_3B-WCl_6 and Et_3B-$Mo(OEt)_2Cl_3$ were found to be the effective catalysts for the above reactions.

Since the early studies by Banks and Bailey,[1)] the disproportionations of the alkenes having no functional group have been investigated by many workers. As a result of their studies a number of catalysts which were effective for this reaction were found out. On the contrary the disproportionation of alkenes having functional groups had not been described until the investigation by Boelhouwer et al.[2)] who studied the metathesis of fatty acid esters using a $(CH_3)_4Sn$-WCl_6 catalyst.

Here, the disproportionation of several unsaturated esters (including new reactions) and the metathesis of the above esters with some alkenes were investigated using alkylborane-WCl_6, -$Mo(OEt)_2Cl_3$, -$MoCl_5$, -$W(OPh)_6$, and various other catalysts.

The reaction was carried out by the use of a conventional three-necked flask with a reflux condenser and a thermometer. Practically pure WCl_6 was obtained by removing the more volatile $WOCl_4$ under a stream of N_2 at 200°C.

In a typical reaction, ethyl 3-butenoate (1 ml) was added to a mixture of chlorobenzene (7 ml), WCl_6 (0.15 mmol) and Et_3B (0.4 mmol) at 293K, and then the mixture was heated under reflux at 405K. After 14 hr diethyl 3-hexenedioate was obtained in a 60% yield (see Table 1).

Methyl 10-undecenoate (1) also disproportionated to several unsaturated diesters and other alkenes. The diesters except for dimethyl 10-eicosenedioate (2) which was the main product of this reaction were produced by the subsequent metathesis reactions of 1 with the unsaturated monoesters which were produced by the isomerization of 1.

In other typical reaction, cis-9-octadecenyl acetate (3) (1 ml) was added to a mixture of decalin (7 ml), WCl_6 (0.15 mmol) and Et_3B (0.40 mmol) at 293K. After heating for 7 hr at 451K 1,18-diacetoxy-9-octadecene (4) and 9-octadecene (5) were obtained. The other olefins were also produced by the combination of the isomerization and the metathesis reactions. Table 1 shows the reaction of several esters including above ones.

Table 1. The disproportionation of the several unsaturated esters using the Et_3B-WCl_6 and Et_3B-$Mo(OEt)_2Cl_3$ catalysts

Substrates (ml)	Catalyst Main- (mmol)	Catalyst Co- (mmol)	Solvent (ml)	Reaction Temp. (K)	Reaction Time (hr)	Yield a)b) (%)	Total Yield a)c) (%)
Ethyl 3-butenoate (1)	WCl_6 (0.15)	Et_3B(0.4)	PhCl (7)	405	14	60	60
Ethyl 4-pentenoate (0.5)	" (")	" (")	" (")	"	5	15	20
Methyl 10-undecenoate (1)	" (0.3)	" (0.8)	" (14)	"	8	40-45	91
9-Octadecenyl acetate (1)	" (0.15)	" (0.4)	Decalin (7)	451	7	10-15	21
"	$Mo(OEt)_2Cl_3$ (0.6)	" (0.8)	PhCl (14)	405	"	3-4	5
Methyl oleate(1) + 1-Decene (2)	WCl_6 (0.3)	" (0.8)	PhCl (14)	"	8	9 d) 3 e)	-

a) Mol % yield based upon the starting ester.

b) Main products produced by the disproportionation of the starting ester itself.

c) Total yield including the products produced by the combination of the isomerization and the subsequent metathesis reactions.

d) 100x (methyl 9-decenoate produced/ methyl oleate used)

e) 100x (dimethyl 9-octadenendioate produced/ methyl oleate used)

The effects of co-catalysts and those of solvents on the disproportionation of methyl oleate are shown in Table 2. Under such conditions as shown in the Table 2 the catalytic activity for this reaction decreases in following order : $Et_3B > Bu_3B > Et_2BCl > Et_3SiH > TiH_4$ which were used as co-catalysts for WCl_6. In all reactions in the Table 2 the isomerization and the subsequent metathesis reactions were also observed.

The general scheme with respect to all reactions described above can be represented by the reactions [1], [2] and [3].

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

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

$$R(CH_2)_aCH{=}CH(CH_2)_bX + R(CH_2)_{a\pm c}CH{=}CH(CH_2)_{b\mp c}X \longrightarrow R(CH_2)_aCH{=}CH(CH_2)_{a\pm c}R + X(CH_2)_bCH{=}CH(CH_2)_{b\mp c}X + R(CH_2)_aCH{=}CH(CH_2)_{b\mp c}X + R(CH_2)_{a\pm c}CH{=}CH(CH_2)_bX \qquad [3]$$

where X is -COOR or -OCOR and $b \pm c \geq 1$.

For example methyl 10-undecenoate can be represented by R=H, a=0, b=8 and X=$-COOCH_3$.

Quite interesting products distribution was found with respect to the products obtained by the subsequent metathesis of methyl 10-undecenoate with methyl n-undecenoate ($3 \le n \le 9$) which was produced by the isomerization of methyl 10-undecenoate. The $X(CH_2)_bCH=CH(CH_2)_{b-c}X$ (b=8; cf. eq. [1], [2]) having b-c > 4 were found in considerable amount and its amount increased in order, namely (b-c=5) < (b-c=6) < (b-c =7) < (b-c=8). However the $X(CH_2)_bCH=CH(CH_2)_{b-c}X$ having smaller (b-c) values than 5 were hardly found. These phenomena may afford useful informations in the reaction mechanism of the metathesis or the isomerization, but in this stage further discussions were omitted because of lack in evidence.

Table 2. The disproportionation of methyl oleate[d] using various catalysts

Catalyst Main- (mmol)		Co- (mmol)		Solvent (ml)		Reaction Temp. (K)	Reaction Time (hr)	Conversion (%)	Yield[a,b] (%)	Total Yield[a,c] (%)
WCl_6	(0.15)	Et_3B	(0.4)	PhCl	(7)	405	8	45	15	33
"	(")	"	(")	Ph_2O	(8)	425	11	40	20	30
"	(0.10)	"	(0.2)	$Br(CH_2)_6Br$	(7)	453	5	40	17	32
"	(0.15)	Bu_3B	(0.4)	PhCl	(7)	405	8	40	10	30
"	(0.30)	Et_2BCl	(0.8)	"	(14)	"	8	12-15	4	10[e]
"	(")	Et_3SiH	(4.0)	"	(7)	"	24	3-4	2	2-3
"	(")	TiH_4	(4.0)	"	(")	"	11	5-10	1	1
WCl_6	(0.30)	Et_3B	(0.4)	PhCl	(7)	405	11	40-50	10	35-40
$W(OPh)_6$	(0.60)	"	(0.8)	"	(14)	"	24	5-10	1	1-2
$W(CO)_6$	(0.30)	"	(")	"	(")	"	11	"	3	4
$MoCl_5$	(0.50)	"	(0.60)	"	(")	"	"	10	3	5
$Mo(OEt)_2Cl_3$	(0.30)	"	(0.4)	"	(")	"	"	40	17	30
$ReCl_5$	(0.30)	"	(0.6)	"	(")	"	"	2	0.3	0.3
$RuCl_3 3H_2O$	(0.60)	"	(0.8)	"	(")	"	"	0	0	0
"	(0.30)	——		BuOH	(")	390	"	15	0	0[f]

a), b), c) See Table 1. d) $CH_3(CH_2)_7CH=CH(CH_2)_7COOCH_3$(cis) 1 ml

e) Methyl oleate 2 ml f) Butyl oleate was obtained in a 15% yield.

Table 2 also shows the disproportionation of methyl oleate using other catalyst systems. It can be seen from this Table both WCl_6-Et_3B and $Mo(OEt)_2Cl_3$-Et_3B are the effective catalysts for this reaction.

REFERENCES

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