METATHESIS OF FUNCTIONAL DERIVATIVES OF OLEFINS BY THE ACTION OF THE WCl_6-1,1,3,3-TETRAMETHYL-1,3-DISILACYCLOBUTANE CATALYTIC SYSTEM

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A study was carried out on the metathesis of esters of unsaturated carboxylic acids and nitriles by the action of the WCl_6-1,1,3,3-tetramethyl-1,3-disilacyclobutane catalytic system. The possibility of efficient homometathesis and cometathesis with α-olefins and allyltrimethylsilane was demonstrated for ethyl 4-pentenoate and allyl cyanide.

Since the first reports of the metathesis of functional derivatives of olefins [1], such reactions have attracted attention since they permit the rather facile preparation of mono- and bifunctional derivatives and, in a number of cases, considerably simplify the synthesis of biologically active and natural compounds, pharmaceuticals, and cosmetics.

Of the many reported catalytic systems for metathesis, only two types of catalytic systems are efficient for functional derivatives: heterogeneous Re_2O_7/Al_2O_3–R_4Sn catalysts [2] and homogeneous WCl_6–R_4Sn catalysts [3], as a rule, are active only for substrates, in which the multiple bond and functional group are separated by not less than five to seven methylene units.

We have previously shown that systems based on WCl_6 in four-membered organosilicon and organogermanium heterocycles $Me_2E \overset{\frown}{\underset{\smile}{\cdot}} E'Me_2$ (E, E' = Si, Ge) are efficient catalysts for the metathesis of olefins [4, 5] and the WCl_6–1,1,3,3-tetramethyl-1,3-disilacyclobutane (SCB) catalyst is most available and active for the metathesis of α-olefins when the substrate/catalyst ratio ≥ 10,000. This catalytic system is also efficient for the metathesis of functional derivatives of olefins. Esters of unsaturated aliphatic acids undergo homo- and cometathesis with α-olefins [6] and allylsilanes as demonstrated for the case of the reaction of the ethyl ester of 4-penten-1-oic acid (I):

$$\underset{\text{(I)}}{CH_2{=}CHCH_2CH_2COOC_2H_5} \underset{-C_2H_4}{\overset{Cat}{\rightleftarrows}} \underset{\text{(II)}}{H_5C_2OOCCH_2CH_2CH{=}CHCH_2CH_2COOC_2H_5} \tag{1}$$

$$\text{(I)} + \underset{\text{(III)}}{CH_2{=}CH(CH_2)_4CH_3} \underset{-C_2H_4}{\overset{Cat}{\rightleftarrows}} \underset{\text{(IV)}}{CH_3(CH_2)_4CH{=}CHCH_2CH_2COOC_2H_5} \tag{2}$$

$$\text{(I)} + \underset{\text{(V)}}{(CH_3)_3SiCH_2CH{=}CH_2} \underset{-C_2H_4}{\overset{Cat}{\rightleftarrows}} \underset{\text{(VI)}}{(CH_3)_3SiCH_2CH{=}CHCH_2CH_2COOC_2H_5} \tag{3}$$

The homo- and cometathesis reactions are carried out under mild conditions and permit the one-step preparation of esters of unsaturated mono- and dicarboxylic acids as well as the introduction of an allylsilyl group into ester molecules. These results are shown in Table 1 and imply that in the case of the homometathesis of (I) (reaction (1)), the yield of the desired product is about 50% and the selectivity exceeds 90% when the substrate/catalyst ratio ≥ 100. The selectivity in the cometathesis of α-olefins and allylsilanes is lowered due to the contribution of homometathesis processes of each of the substrates. In the cometathesis of (I) with α-olefins (reaction (2)), 6-dodecene, which is the product of the homometathesis of the olefin, is formed along with a slight amount of (II), which is the product of the homometathesis of (I), in addition to the desired product. In the cometathe-

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TABLE 1. Homo- and Cometathesis of Ethyl 4-Penten-1-oate with 1-Heptene and Allyltrimethylsilane by the Action of the WCl_6–SCB Catalyst at 70°C over 6 h ($[WCl_6]/[SCB]$ = 1:2)

Substrate/WCl_6 mole ratio		Conversion of (I)	Selectivity	Substrate/WCl_6 mole ratio		Conversion of	Selectivity
(I)	(II) or (V)	%		(I)	(II) or (V)	%	
50		48	87		(V)		
100		52	92	25	25	36	58
150		46	94	50	50	30	73
	(II)			50	100	39	86
25	25	41	63	100	100	42	70
50	50	37	70	500	500	2	1
50	100	44	73				

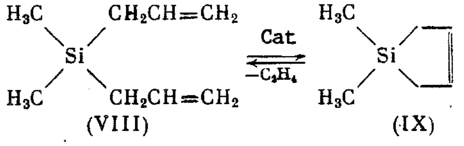
TABLE 2. Metathesis of Allyl Cyanide by the Action of the WCl_6–SCB Catalytic System at 60°C over 10 h ($[WCl_6]/[SCB]$ = 1:2)

(X)/WCl_6 mole ratio	Conversion of (X)	Selectivity
	%	
50	53	82
100	39	85
150	24	86

sis of (I) with allylsilane (reaction (3)), (II) and trace amounts of 1,4-bis(trimethylsilyl)2-butene (VII), which is the product of the homometathesis of (V), are formed in addition to the desired product (VI). When the (I)/(V) ratio is 1:2, the selectivity of the cometathesis approaches 90%. When the substrate/catalyst ratio is increased to 500, the reaction virtually ceases but the yields of (VII) reach 63-73% at lower ratios (100-200).

Allyltrimethylsilane (V) is a rather active substrate for metathesis and reacts by the action of both heterogeneous catalysts [7] and WCl_6 [8]. We have established that a benzene solution of $WOCl_4$ catalyzes the intermolecular metathesis of (V) and the intramolecular reaction of diallyldimethylsilane (VIII):

$$\underset{(V)}{(CH_3)_3SiCH_2CH{=}CH_2} \xrightleftharpoons[-C_2H_4]{Cat} \underset{(VII)}{(CH_3)_3SiCH_2CH{=}CHCH_2Si(CH_3)_3} \qquad (4)$$



(5)

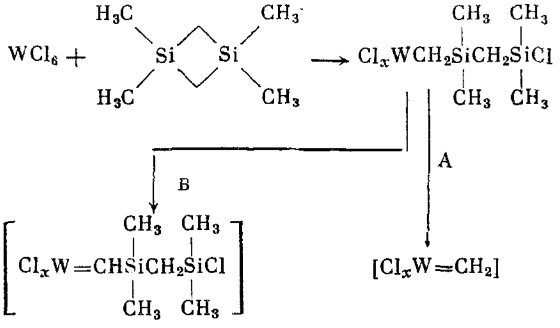
The yield of (VII) in reaction (4) was 10-12% when the $[(V)]/[WOCl_4]$ ratio was 100. The yield of (IX) in reaction (5) reached 27-29% when the $[(VII)]/[WOCl_4]$ ratio was 50. Products of the intermolecular metathesis of (VIII) and the metathetic oligomerization of (IX) are virtually absent. In this case, a heteroorganic cocatalyst is not required. The role of such a cocatalyst is carried out by substrates capable of alkylating tungsten compounds. This is indicated by the finding that the major organosilicon products are $(CH_3)_3 \cdot SiCl$ (for (V)) and $(CH_3)_2Si(CH_2CH{=}CH_2)Cl$ (for (VIII)) when there is an equimolar substrate/$WOCl_4$ ratio.

Another example of the metathesis of olefin functional derivatives holding importance for organic chemistry is found in the reaction of unsaturated nitriles, which permit a one-step preparation of symmetrical dinitriles. In contrast to heterogeneous and homogeneous catalysts [9, 10], our catalytic system permits us to carry out the metathesis of allyl cyanide with rather high yields and selectivity [11]:

$$\underset{(X)}{CH_2CHCH_2CN} \xrightleftharpoons[-C_2H_4]{Cat} \underset{(XI)}{NCCH_2CH{=}CHCH_2CN} \qquad (6)$$

The results are given in Table 2, which implies that the reactions proceed with high yield and selectivity in the substrate/catalyst range from 50 to 100. An increase in this ratio to 150 lowers the yield of the desired product. The product of the isomerization of allyl cyanide, namely, crotonitrile, is formed in slight amounts and does not hinder the metathesis.

Two types of metal carbene active sites, formed upon the decomposition of the organotungsten compound and initiating the metathesis, may apparently exist for the WCl_6–SCB catalytic system:



The highly reactive tungsten methylene complexes may be rapidly deactivated when olefin functional derivatives such as esters and nitriles, which are capable of coordination at the tungsten carbene site at the functional group, are the substrate. This may account for the finding that the efficiency of the catalyst system is significantly lower for the olefin functional derivatives than for olefins not containing functional groups. The B-type tungsten carbene complexes, which contain silicon atoms in the β-position relative to the tungsten atom, are less reactive. Furthermore, in this case, the approach of the functional group to the carbene site is hindered due to the bulky disilamethylene substituent at the tungsten atom and the possible cooperative action of the chlorine atom in this substituent in coordination at the active site. In this case, the catalytic activity may be assumed to result from transformations of the substrate specifically in the coordination sphere of the secondary carbene complex.

EXPERIMENTAL

The products were analyzed by gas–liquid chromatography on a Chrom 5 chromatograph using a 70-m × 3-mm capillary column packed with PÉG 3000 and, in some cases, by chromato-mass spectrometry on an LKB-2091 instrument at 70 eV with a 70-m × 3-mm capillary column packed with SP-2100 through comparison with the spectra of standard compounds. All the operations in the preparation of the substrates and catalyst and the metathesis reactions were carried out in a dry argon atmosphere.

A sample of WCl_6 was distilled in vacuum to remove oxychloride impurities and used as a benzene solution. The α-olefins and benzene were heated at reflux, twice distilled over sodium, and stored in a dry argon atmosphere over sodium wire. The ethyl ester of 4-penten-1-oic acid (I) was obtained according to Ritter [12] and dried with freshly roasted 5-Å molecular sieves. Allyl cyanide was prepared according to a standard procedure [13] and distilled over P_2O_5. Allyltrimethylsilane and diallyldimethylsilane were prepared according to standard procedures [14] and distilled over sodium.

The metathesis reactions were carried either: 1) in an open system, consisting of a thermostatted reactor equipped with a magnetic stirrer, burette for trapping gaseous products, and a special device for taking liquid probes for gas–liquid chromatography; or 2) in sealed ampuls at $1 \cdot 10^{-3}$ torr initial vacuum. The reactor or ampul contained the calculated amount of substrate, benzene solution of WCl_6, and benzene solution of SCB. The reactions were carried out at 60-80°C. The products were separated by distillation and analyzed by gas–liquid chromatography or chromato-mass spectrometry with benzene as the internal standard.

Homometathesis of (I). A sample of 4 ml (28 mmoles) (I), 4 ml (0.28 mmole) WCl_6 solution, and 0.56 ml (0.56 mmole) SCB solution were placed into an ampul. The reaction was carried out at 70°C over 6 h. The conversion of (I) was 52%. The yield of (II) was 92-94%. Mass spectrum of (II), *m/z* (intensity, %): 40 (32), 55 (25), 67 (55), 81 (48), 108 (25), 137 (100), 154 (29), 182 (9), 218 (6, M^+).

Cometathesis of (I) with (III). A sample of 7 mmoles (I), 7 mmoles (III), 2 ml (0.14 mmole) WCl_6 solution, and 0.28 ml (0.14 mmole) SCB solution were placed into an ampul and cooled with liquid nitrogen. The removal of nitrogen was carried out by evacuation to $1 \cdot 10^{-3}$

torr. The reaction was carried out at 70°C over 6 h. The conversion of (I) was 37%. The products were (IV) in 68% yield, (II) in 5% yield, and 6-dodecene in 23% yield. Mass spectrum of (IV), *m/z* (intensity, %): 40 (79), 55 (80), 69 (80), 88 (100), 96 (41), 110 (80), 152 (37), 198 (10, M^+).

Cometathesis of (I) with (V). A sample of 3.5 mmoles (I), 3.5 mmoles (V), 0.035 mmole WCl_6, and 0.07 mmole SCB were placed into an ampul. The reaction was carried out at 70°C over 6 h. The conversion of (I) was 42%. The products were (VI) in 70% yield, (II) in 26% yield, and (VII) in 3% yield.

The ethyl ester of 6-trimethylsilyl-4-hexen-1-oic acid, $(CH_3)_3SiCH_2CH{=}CHCH_2CH_2CO_2C_2H_5$ (VI), bp 110-111°C (10 mm), n_D^{20} 1.4440. Found: C, 61.45; H, 10.10; Si, 12.97%. Calculated for $C_{11}H_{22}O_2Si$: C, 61.6; H, 9.81; Si, 13.98%. Mass spectrum, *m/z* (intensity, %): 73 (100), 126 (20), 127 (12), 139 (11), 140 (18), 199 (30), 214 (5, M^+). PMR spectrum (δ, ppm): 0 (9H, $Si(CH_3)_3$), 1.25 (3H, $OCH_2\underline{CH_3}$), 1.42 (2H, CH_2), 2.27 (4H, CH_2CH_2), 4.08 (2H, OCH_2), 5.4 (2H, CH=CH).

Metathesis of (V). A sample of 7.47 mmoles (V) and $7.47 \cdot 10^{-2}$ mmole $WOCl_4$ in 5 ml abs. benzene were placed into an ampul and stirred for 60 h at 50°C. The yield of (VII) was 12%. The selectivity was >90%. Mass spectrum of (VII), *m/z* (intensity, %): 73 (100), 97 (18), 112 (14), 200 (M^+, 2).

Metathesis of (VIII). A sample of 4.8 mmoles (VIII) and $9.6 \cdot 10^{-2}$ mmole $WOCl_4$ in 4 ml benzene were placed into an ampul and stirred for 60 h at 50°C. The yield of (IX) was 29%. The selectivity was >90%. Mass spectrum of (IX), *m/z* (intensity, %): 58 (25), 71 (10), 97 (100), 112 (31, M^+).

Reaction of Allylsilanes with $WOCl_4$. A sample of 5.5 mmoles (VIII) and 2.9 mmoles $WOCl_4$ in 8 ml benzene were placed into an ampul and stirred for 60 h at 50°C. The reaction mixture contained 74% Me_2SiCl_2 and 25% $Me_2SiCl(All)$.

A sample of 4 mmoles (V) and 4 mmoles $WOCl_4$ in 24 ml were placed into an ampul and stirred for 60 h at 50°C. After the reaction, the mixture contained 87% Me_3SiCl, 7% $Me_2SiCl(All)$, and 4% Me_2SiCl_2.

Metathesis of (X). A sample of 50 mmoles (X), 1 mmole WCl_6 (3.7 ml solution), and 2 mmoles SCB (1.25 ml solution) were placed into an ampul. The reaction was carried out for 10 h at 60°C. The conversion of (X) was 53%. The selectivity was 83% relative to (XI). (XI) was separated by crystallization, mp 72-73°C (from ethanol) [15]. Mass spectrum, *m/z* (intensity, %): 26 (3), 39 (18), 52 (13), 66 (100), 79 (18), 106 (20, M^+).

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