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Effect of Organic Additives Having Functional Groups in Olefin Metathesis

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The dependence of product yields on the amount of various organic additives containing heteroatom functional groups was investigated for the metathesis of 2-heptene in benzene at room temperature catalyzed by WCl_6–$SnBu_4$ (1:1). Without additives, heptylbenzenes were major products, and 5-decene and 2-butene were minor ones. With increasing amounts of ethers, ketones, sulfides, pyridine, amines, a cyanide, an amide, a sulfoxide, a tertiary phosphine, and alcohols, the yield of 5-decene first increased markedly and that of heptylbenzene decreased; thereafter, the yield of 5-decene was also lowered. When reaction temperatures were elevated to 80 or 120°C, the amount of the additives needed to inhibit metathesis increased. In particular, for ether and ester addition significant metathesis was observed even at an additive/catalyst ratio of 30. This suggests that the metathesis of unsaturated ethers and esters proceeds rather efficiently. A comparison of the relative ability of these additives to inhibit metathesis and alkylation shows that the active species in the former reaction are softer acids than those of the latter. It was shown that additives raise metathesis yields mainly by protecting the active species of metathesis from decay, although the inhibition of the alkylation may also have some effect on the yields. The decay of metathesis species takes place easily in a medium where the alkylation proceeds well.

INTRODUCTION

The mechanism for olefin metathesis in which alkylidene groups are exchanged has been studied extensively. However, there seem to be relatively few papers demonstrating its use in organic synthesis (*1*), even though it could potentially be used to prepare compounds which would be difficult to synthesize by other methods. This may be due to the general tendency for substrate functional groups or impurities to retard the metathesis reaction. Also side reactions such as alkylation, polymerization, and migration of double bonds can predominate. In order to use this reaction effectively as a general synthesis technique, these faults must first be overcome. It has been reported that the addition of triphenylphosphine, pyridine (*2*), and aniline (*3*) inhibits alkylation and dimerization reactions more strongly than olefin metathesis reactions. We found also that side reactions can be reduced while increasing the selectivity of metathesis by addition of certain organic compounds (*4*). The similar effect of acetonitrile was confirmed recently (*1d*). However, causes of the additive effect were not clear enough. One purpose of this study was to define the scope and limitation of metathesis of olefins having functional groups by varying the nature and amount of additive. Another was to learn the reason why metathesis yields are increased by the addition of certain kinds of organic compounds.

EXPERIMENTAL

Materials

Tungsten hexachloride was purified by sublimation of the volatile impurities ($WOCl_4$, WO_2Cl_2). Tetrabutyltin, benzene, and all the additives except for triphenylphosphine and triphenylamine were dried and distilled. The phosphine and the amine were purified by recrystallization from benzene.

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General Method of the Metathesis at Room Temperature

To a thoroughly dried Pyrex glass tube sealed with a neoprene rubber cap, 2-heptene (196 μl, 1.4 mmol), 92 m*M* benzene solution of WCl_6 (750 μl, 0.069 mmol), $SnBu_4$ (22.6 μl, 0.069 mmol), an additive, and benzene were added, in this order, by means of hypodermic syringes. The amount of the benzene is just enough to make the total volume of the reaction mixture 1 ml. The reaction vessel was shaken on a shaker for 2 h and then 0.3 ml of 2-propanol or tetrahydrofuran was added to the reaction mixture to stop the reaction. The mixture was submitted to gc analysis which was performed by use of a 1-m column packed with 10% SE-30 and undecane (internal standard).

The other metathesis reactions at room temperature were carried out in an analogous way.

General Method of the Metathesis at 80 and 120°C

Reaction samples, prepared by the method described above, were heated for 2 h with continuous shaking in a polyethylene glycol bath kept at 80 and 120°C, and then were submitted to gc analyses after quenching by the addition of 2-propanol.

Experiments to Study the Dependence on Time

Curves A and B. Into a dried glass tube sealed with a neoprene rubber cap, 92 m*M* benzene solution of WCl_6 (3.0 ml, 0.276 mmol), $SnBu_4$ (90.4 μl, 0.276 mmol), and benzene (127 μl) were injected by means of hypodermic syringes, in this order, and the mixture was shaken for 11 min at room temperature on a shaker. Then 2-heptene (784 μl, 5.6 mmol) was added to it with a syringe and the shaking was begun again. Samples (0.4 ml) were taken out via syringes after 3, 5, 15, and 30 min and submitted to gc analyses after the addition of 2-propanol (0.1 ml) and undecane (internal standard).

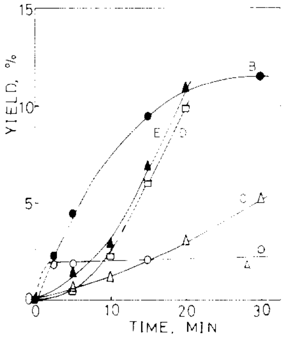

FIG. 1. Dependence of the yields of the products on reaction time. Curves A, C, D, E represent the 5-decene yields in the reaction where WCl_6 (69 m*M*) and $SnBu_4$ (69 m*M*) were mixed first and then 2-heptene (1.4 *M*) was added to the mixture after 11 min at room temperature (○), in the reaction where WCl_6 and $SnBu_4$ were mixed first and then the olefin and propyl acetate were added after 11 min (△), in the reaction where WCl_6, $SnBu_4$, and the additive were mixed first and then the olefin was added after 11 min (□), and in the reaction where WCl_6, $SnBu_4$, the olefin, and the additive were mixed at once (▲), respectively. Curve B represents the heptylbenzene yield in the first reaction (●).

Curve C. Benzene solution of WCl_6 (3.0 ml, 92 m*M*), $SnBu_4$ (90.4 μl), and benzene (100 μl) were put into the glass vessel described above and shaken for 11 min. Propyl acetate (26.5 μl, 0.116 mmol) and 2-heptene (784 μl) were added and then the shaking was begun again. The analyses were performed in the way mentioned above at the time intervals noted in Fig. 1.

Curve D. Benzene solution of WCl_6 (3.0 ml, 92 m*M*), $SnBu_4$ (90.4 μl), propyl acetate (26.5 μl), and benzene (100 μl) were shaken for 11 min and then 2-heptene (784 μl) was added. The mixture was shaken again and analyzed at the time intervals noted in Fig. 1.

Curve E. Benzene solution of WCl_6 (3.0 ml, 92 m*M*), $SnBu_4$ (90.4 μl), propyl acetate (26.5 μl), 2-heptene (784 μl), and benzene (100 μl) were mixed, shaken, and analyzed in the way described above.

RESULTS

Effect of Additives at Room Temperature

For metathesis of olefins containing heteroatoms, WCl_6–SnR_4 (R = an alkyl group) systems seem to be used most widely as catalysts because of their high activity and high resistance to poisoning (5). However, they have the disadvantage that they also easily catalyze side reactions involving carbonium ion intermediates such as alkylation, polymerization, and isomerization of olefins (*4a*). As solvents for metathesis, benzene and chlorobenzene are generally used. In this study, benzene was employed because its alkylation products with 2-heptene are easily determined. When a benzene solution of 1.4 *M* 2-heptene, 69 m*M* WCl_6, and 69 m*M* $SnBu_4$ was left for 2 h at room temperature, 0.98 *M* (70% yield) of heptylbenzenes, which mainly consisted of 2- and 3-phenylheptane, was obtained in addition to 28 m*M* (4.0% yield) of 5-decene and 25 m*M* (3.6% yield) of butene. This means that in addition to the metathesis of 2-heptene, alkylation involving the olefin and the solvent also occurred. By adding organic substances having heteroatoms to this reaction system, the distribution of the products was greatly changed; the yields of 5-decene and heptylbenzenes are summarized in Table 1. In the table, the

TABLE 1

The Dependence of the Yield (%) of 5-Decene (DE) and Heptylbenzenes (HB) on the Amount of Additives[a]

Additive	Product	Additive/catalyst ratio (ACR)								
		0.2	0.4	0.6	0.8	1.0	1.5	2.0	3.0	5.0
Dibutyl ether	DE	20	40	46	51	48		50	23	6
	HB	22	5	7	2	1		0	0	0
Tetrahydrofuran	DE	8	45	48	50	22	0			
	HB	31	5	2	1	0	0			
Dibutyl sulfide	DE	4	33	26	12	2	0			
	HB	65	2	0	0	0	0			
Tetrahydrothiophene	DE	22	42	50	11	5	0			
	HB	21	4	1	0	0	0			
Pinacolone	DE	8	27	39	50	49	30			
	HB	54	25	10	4	1	0			
Diethyl ketone	DE	5	7	14	34	35	13			
	HB	61	54	7	3	4	0			
Acetone	DE	2	2	27	31	23	4			
	HB	65	48	5	3	2	0			
Propyl acetate	DE	3	14	49	44	6	0			
	HB	71	10	0	0	0	0			
Butyl stearate	DE	8	39	49	39	11	1			
	HB	47	4	2	0	0	0			
Phenyl acetate	DE	3	43	41	34	13	2			
	HB	68	2	0	0	0	0			
Pyridine	DE	34	48	50	45	7				
	HB	13	0	0	0	0				
Cyclohexylamine	DE	1	48	48	12	0				
	HB	42	2	0	0	0				
Dicyclohexylamine	DE	38	50	0						
	HB	5	0	0						

TABLE 1—*Continued*

Additive	Product	Additive/catalyst ratio (ACR)								
		0.2	0.4	0.6	0.8	1.0	1.5	2.0	3.0	5.0
Triethylamine	DE	6	36	3	0					
	HB	19	2	0	0					
Triphenylamine	DE	45	50	13	3					
	HB	2	1	0	0					
Triphenylphosphine	DE	41	5	0						
	HB	4	0	0						
Octyl cyanide	DE	1	7	50	12					
	HB	66	18	0	0					
N,*N*-Dipropylpropionamide	DE	2	48	5	0					
	HB	54	6	0	0					
Dimethyl sulfoxide	DE	8	39	26	0					
	HB	31	3	1	0					
2-Butanol	DE	4	9		11	14	17	15		
	HB	72	66		68	71	44	35		
1-Pentanol	DE	4	5		7	22	10	2		
	HB	68	64		37	17	1	0		

[a] 2-Heptene (1.4 *M*), WCl_6 (69 m*M*), and $SnBu_4$ (69 m*M*) in benzene were left for 2 h at room temperature.

additive/catalyst ratio (ACR) means the mole ratio of an additive to the catalyst. As olefin metathesis is an equilibrium reaction, the yield of 5-decene cannot exceed 50% unless 2-butene escapes from the reaction system.

When ethers, sulfides, ketones, esters, an aromatic heterocyclic compound, amines, a tertiary phosphine, a cyanide, an amide, a sulfoxide, and alcohols were added in suitable amounts, a remarkable elevation of 5-decene yield and a drastic lowering of the yield of heptylbenzenes were observed. However, too much additive lowered the metathesis yield.

In the reactions involving dibutyl ether, tetrahydrofuran, dibutyl sulfide, and tetrahydrothiophene, the yield of heptylbenzene was lowered and that of 5-decene was raised considerably with an ACR of 0.2–0.4. The narrow ACR range suggests that each of the additives hinders alkylation by a similar process. But their ability to inhibit metathesis varied considerably. For example, dibutyl ether did not completely prohibit the reaction even at the ACR of 5.0, while tetrahydrofuran stopped it at the ACR of 1.5. Sulfides retarded metathesis more strongly than ethers. When ketones were added, metathesis proceeded quite well at an ACR of 1.0, and they inhibited the reaction in the order: acetone > diethyl ketone > pinacolone. This order shows that the less sterically hindered ketones cause the reaction to be more strongly retarded. With the addition of esters, metathesis was inhibited fairly well at the ACR of 1.0, and steric hindrance of the additives exerted little influence on either alkylation or metathesis. Pyridine suppressed metathesis moderately. When amines, triphenylphosphine, *N*,*N*-dipropylpropionamide, octyl cyanide, and dimethyl sulfoxide were added, the 5-decene yields were lower than 12% at an ACR higher than 0.8. Unexpectedly, cyclohexylamine repressed metathesis more weakly than dicyclohexylamine, triethylamine, and triphenylamine. 1-Pentanol and 2-butanol did not strongly inhibit alkylation and the 5-decene yields dropped to no more than about 20%. However, in the reaction involving the primary and secondary alcohols, significant metathesis proceeded even at the ACRs of 1.5 and 2.5, respectively. The addition of pentanoic acid, pentanoic anhydride, and 1-nitropropane repressed both metathesis and alkylation, even at an ACR of 0.2. On the basis of arguments described under Discussion, this suggests that metathesis of unsaturated carboxylic acids, carboxylic anhydrides, and nitro compounds is difficult.

As for other catalyst systems, it has been reported that the addition of aniline in WCl_6–$Et_3Al_2Cl_3$ systems (*3*) and that of triphenylphosphine and pyridine in WCl_6–$EtAlCl_2$ systems (*2*) inhibit side reactions more strongly than metathesis of olefins, whose rates are also greatly reduced. The addition of ethanol is reported to show no effect in WCl_6–$Et_3Al_2Cl_3$ system (*3*).

There has been a report that WCl_6 catalyzes Friedel–Crafts-type reactions by itself at higher temperatures (*6*), but neither WCl_6 nor $SnBu_4$ catalyzed the alkylation of benzene with 2-heptene at room temperature in our experiment. This shows that both WCl_6 and $SnBu_4$ participate in the alkylation at room temperature.

Reactions at Higher Temperatures

Yields of products in metathesis catalyzed by WCl_6–SnR_4 are known to vary with reaction temperature, WCl_6/SnR_4 ratios, olefin/WCl_6 ratios, and so on. Among these variables, temperature seems to alter most effectively the yield of metathesis in the presence of additives (*4a*); we investigated the effect of additives at higher temperatures. In the reaction at 80 and/or 120°C, the dependence of heptylbenzene yield on the ACR was not much different from that in the reaction at room temperature, although in most cases the ACR at which the alkylation was inhibited was a little higher than that in the corresponding reaction at room temperature. The 5-decene yield is summarized in Table 2. For all the additives the upper limits of the ACR at which the metathesis proceeded were higher than those in the corresponding reactions at room temperature. In particular, with dibutyl ether, propyl acetate, and butyl stearate, considerable amounts of 5-decene were formed even at an ACR of 30. In the reactions containing dibutyl sulfide, diethyl ketone, 1-pentanol, and 2-butanol, the 5-decene yields were 3–9% at the ACR of 3.0. The addition of cyclohexylamine, octyl cyanide, *N*,*N*-dipropylpropionamide retarded metathesis more severely.

Dependence on Reaction Time

To clarify the role of the additives in metathesis, the dependence of the yields of products on reaction time and the procedure for addition of the reagents were investigated. The results are shown in Fig. 1. In the reaction where WCl_6 and $SnBu_4$ were mixed in benzene first and then 2-heptene was added to the solution after 11 min, the formation of 5-decene was initially very rapid but stopped abruptly (Curve A), while the yield of heptylbenzenes increased gradually, even after the cessation of metathesis (Curve B). In the case where olefin and propyl acetate were added 11 min after mixing WCl_6 with $SnBu_4$, the yield of 5-decene increased slowly but without stopping (Curve C). In this reaction and the ones described subsequently, no heptylbenzenes were detected. When WCl_6, $SnBu_4$, and the additive were mixed first and then the olefin was added after 11 min (Curve D), and when WCl_6, $SnBu_4$, the olefin, and the additive were mixed simultaneously (Curve E), metathesis proceeded fairly rapidly and without inhibition, although the rates of these reactions were lower than that of the reaction without additives.

DISCUSSION

In general, metathesis of olefins having

TABLE 2

The Dependence of 5-Decene Yield (%) on the Amount of Additives[a]

Additive	Temp. (°C)	Additive/catalyst ratio (ACR)										
		0.2	0.4	0.6	1.0	1.5	2.0	3.0	5.0	10	20	30
Dibutyl ether	80	16	17		18				26	31	34	18
	120	13	17		25				24	22	30	9
Dibutyl sulfide	80	22		45	45		40	0				
Diethyl ketone	80	7	8	10	22	13	13	4				
	120	13	12		13	19	21	9				
Propyl acetate	80	15	32	50	48	49	19		7	6		
	120	14	18		31		18		22	27	18	18
Butyl stearate	80	14	17		41				35	23	11	0
	120	12	13		21	34		37	32		37	15
2-Butanol	80	13	12		17	21	19	8				
1-Pentanol	80		4		4	17	36	3				
	120		6		5	8	8	0				
Cyclohexylamine	80	26	25	36	28	1						
	120	47	14	0								
Triethylamine	80	20	26	7	0							
	120	23	37	40	2	0						
Octyl cyanide	80	13	25	33	3	0						
	120	12		34	19	1						
N,N-Dipropylpropionamide	80	15	25	19	2							

[a] 2-Heptene (1.4 *M*), WCl_6 (69 m*M*), $SnBu_4$ (69 m*M*), and an additive were heated in benzene for 2 h.

functional groups is far more difficult than that of simple olefins. It is reasonable to presume that the amount of an additive needed to inhibit metathesis of a simple olefin is closely related with the easiness of metathesis of an olefin having the same functional group as the additive has, and when more of the additives are needed to inhibit metathesis of the simple olefin, the easier will be that of the functional olefin, for the functional part of the additive and the olefin are considered to poison the catalyst. We chose 2-heptene as a simple olefin. Therefore, it is anticipated that methathesis of a functional olefin will not proceed significantly if that of 2-heptene is suppressed severely by an additive having the same functional group. Further, the yield of heptylbenzenes formed in the Friedel–Crafts-type side reactions between 2-heptene and the solvent (benzene) is presumed to be an index corresponding to the susceptibility of the olefin to all side reactions involving carbonium-type intermediates.

With the addition of dibutyl ether, propyl acetate, and butyl stearate, considerable amounts of 5-decene were formed even at an ACR of 30 in the reactions at 80 and/or 120°C (Table 2). This result agrees with the fact that metathesis of olefinic esters (*1*, *7*) and ethers (*7i*, *8*) mediated by certain catalysts including WCl_6–SnR_4 systems occurs fairly efficiently. In the reactions containing dibutyl sulfide, diethyl ketone, 1-pentanol at the elevated temperatures, the 5-decene yields were 3–9% at an ACR of 3.0. Therefore, effective metathesis of olefinic sulfides, and alcohols mediated by WCl_6–SnR_4 systems appears to be rather difficult.

Metathesis of unsaturated amines, nitriles, and amides with these catalyst systems would be more difficult, because the additives having corresponding functional groups retarded metathesis more severely. As for other catalysts, metathesis of olefinic ketones catalyzed by WCl_6–$Me_3Al_2Cl_3$ (*8a*) and Re_2O_7–Al_2O_3 (*7i*), that of olefinic nitriles by WCl_6–$Me_3Al_2Cl_3$ (*8a*), that of olefinic amines by (mesitylene)$W(CO)_3$–$EtAlCl_2$–O_2 (*9*), that of oleyl chloride by Re_2O_7–co-catalyst systems (*10*), and that of arylolefins by $Mo(NO)Cl_2(PPh_3)_2$–$EtAlCl_2$ and $W(CO)_5PPh$–$EtAlCl_2$–O_2 (*11*), have been reported.

Curves A and B in Fig. 1 show that the catalytic species in the metathesis was more easily deactivated than that in the alkylation, and that there was 2-heptene present when metathesis ceased. In other words, the low metathesis yield is not due to the consumption of the olefin by the side reactions and decay of catalytic intermediates in the metathesis takes place very easily in a medium where side reactions proceed well. A comparison of Curves A and C indicates that, in the presence of the additive, the catalytic species is much less active but loses its activity much more slowly than in the absence of the additive. The presence of olefins is assumed to promote decay of the catalytic species in metathesis, for metathesis occurred slowly when the olefin and the additive were added after 11 min to the admixture of WCl_6 and $SnBu_4$ (Curve C), whereas it stopped within a few minutes when WCl_6, $SnBu_4$, and the olefin were combined at once (Curve A). The similarity of Curves D and E shows that decay of the catalytic species in the metathesis is barely perceptible in the presence of the additive, regardless of the presence or absence of the olefin. The slight decrease of the metathesis yield increment at the initial stage observed in Curve E hints at the existence of an induction period for the formation of the catalytic species of the reaction. On the basis of results described above, it can be said that additives increase metathesis yields mainly by protecting active species in metathesis reactions from decay, although the inhibition of side reactions may also have some effect on the yields.

Dibutyl sulfide inhibited metathesis more strongly than dibutyl ether, tetrahydrothiophene more than tetrahydrofuran, and triphenylphosphine more than triphenylamine while, in their ability to retard alkylation, the sulfur and phosphorus compounds were similar to the corresponding oxygen and nitrogen compounds, respectively. According to HSAB theory (*12*), this phenomenon can be explained by the assumption that the catalytically active species in metathesis are softer acids than those involved in alkylation. This assumption is consistent with the hypothesis that active intermediates in the metathesis catalyzed by WCl_6–co-catalyst systems were W(IV) species (*13*).

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