Unusual, CO Assisted Cyclo-oligomerization Reactions of Ethylene: Formation of Cyclopentane and Cyclohexane Derivatives by Ytterbium Ziegler–Natta Catalysts

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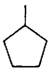
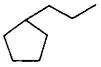
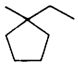
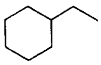
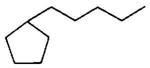
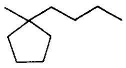
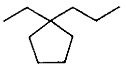
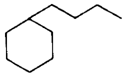
A new oligomerization of ethene to alkylcyclopentanes and/or alkylcyclohexanes using $YbCl_3/AlEtCl_2$ or $ZrCl_4/AlEtCl_2$ Ziegler–Natta type catalysts is described in which addition of carbon monoxide is essential.

Polyethylenes and α-alkenes are products of immense practical importance. There have been only scattered reports about unusual oligomerization reactions of ethene which are not in agreement with normal growth reactions. Co-workers of the Union Carbide Corporation have described the trimerization of ethene to hex-1-ene,[1] and Gragin has reported the synthesis of aromatics from ethene.[2] Also noteworthy in this connection is the work by Grubbs, who reported the formation of cyclobutane starting from nickelacyclopentane.[3] To our knowledge there are no reports of the conversion of ethene to cyclic alkanes in the literature.

Table 1. Oligomerization of ethene ($AlEtCl_2 : YbCl_3 = 40:1$)

Oligomers		Structure		
	%			%
C_4	0.1	Butenes		100
C_6	3.2		(1)	94
C_8	10.8		(2)	38
			(3)	43
			(4)	15
C_{10}	10.0		(5)	38
			(6)	22
			(7)	20
			(8)	13
C_{12}	75.8	So far unidentified		

The reaction of mixtures of ethene and carbon monoxide ($CO : C_2H_4 = 1:8$—10) with the Ziegler–Natta catalyst $YbCl_3/AlEtCl_2$ in n-heptane at 120 °C yielded a wide range of C_4 to C_{30+} oligomers. The turnover numbers reached about 900 mol C_2H_4/mol Yb. Table 1 lists the C_4—C_{10} oligomers identified so far. Compounds (**2**), (**3**), (**5**), (**6**), and (**7**) were separated by preparative GC and characterized by mass, IR, and NMR spectroscopy. The ^1H and ^{13}C NMR spectra of (**1**), (**4**), and (**8**) are identical with commercial samples. As is obvious from the percentage numbers in Table 1, there are many unidentified products left, and the unknown C_{12+} fraction amounts to 75.8%. However, from the position of the GC peaks and from the mass spectral data it can be concluded that the reaction pattern observed for the C_8/C_{10} oligomers is continued for every fraction of oligomers possessing the same carbon number, and the data are in agreement with n-alkylcyclopentanes, n-alkylcyclohexanes, and disubstituted cyclopentanes.

The amounts of n-alkylcyclopentanes and n-alkylcyclohexanes depend strongly on the Al/Yb ratio applied (Table 2). When $AlEtCl_2 : YbCl_3 = 10$, only n-alkylcyclopentanes are found. With ratios greater than 60, mainly n-alkylcyclohexanes are observed. It should be emphasized that the catalyst $YbCl_3/AlEtCl_2$ under the conditions used for the oligomerization does not convert propylcyclopentane (**2**) to the corresponding cyclohexane.

If the system $YbCl_3/AlEtCl_2$ is applied in the absence of carbon monoxide only linear alkenes in the C_4—C_{30+} range are formed. This underlines the remarkable impact of carbon monoxide. Normally carbon monoxide is used in Ziegler–Natta catalysis to deactivate the system. In preliminary experiments $ZrCl_4/AlEtCl_2$ also produced cyclic oligomers.

Interestingly, the reaction of ethene with $YbCl_3/Et_2AlCl$ instead of $YbCl_3/EtAlCl_2$ yielded only highly linear α-alkenes. The addition of CO reduced the activity drastically.[4]

It would be too speculative to propose a reaction mechanism discussing the function of carbon monoxide. It can be assumed that CO plays a role as ligand *via* labilization.[5] In addition, the products obtained formally can be derived much more easily from a metallacycle than from the Cossee-Arlman

Table 2. Impact of changes in the Al/Yb ratio.

	$AlEtCl_2/YbCl_3$		10	20	40	50	60	$AlEtCl_2$
C_6	Methylcyclopentane %	(**1**)	71	92	94	100	100	No products observed
C_8	Methylethylcyclopentane	(**3**)	21	8	43	22	23	
	Propylcyclopentane	(**2**)	58	71	38	40	0	
	Ethylcyclohexane	(**4**)	0	12	15	38	77	
C_{10}	Methylbutylcyclopentane	(**6**)	19	19	22	25	33	
	Ethylpropylcyclopentane	(**7**)	19	17	20	20	22	
	Pentylcyclopentane	(**5**)	45	47	38	24	0	
	Butylcyclohexane	(**8**)	0	6	13	31	45	

mechanism,[6] which may support a metallacyclopentane pathway.

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