Olefin Dimerization over Cobalt-Oxide-on-Carbon Catalysts

II. Butene and Hexene Dimerization

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Butene and hexene dimerizations over cobalt-oxide-on-carbon catalysts have been studied and the structures of the products determined. Dimerization of internal olefins has been demonstrated using catalysts containing both dimerization and isomerization functions. A mechanism for the reaction is proposed.

The dimerization of ethylene to mixed n-butenes over cobalt-oxide-on-carbon catalysts has been known for many years (2). The specificity of this reaction for dimerization and the previously reported large decrease in dimerization activity when propylene was used in the system (2 c,f,k) would seem to preclude dimerization of higher olefins. However, our studies on propylene dimerization with highly active catalysts (1) indicated that higher olefin dimerization might be possible. In addition to catalysts of high activity, it seemed probable that catalysts could be found which would be capable of effecting the previously unreported dimerization of internal olefins [for example, butene-2] by first promoting isomerization of the internal olefin to an equilibrium mixture of isomers, followed by selective dimerization of the α-olefin component. On the basis of the mechanism proposed for propylene dimerization (1) is was postulated that dimerization of higher olefins should also afford substantial amounts of linear and monomethyl-branched dimers.

EXPERIMENTAL

The techniques of catalyst preparation, activation, and storage and of olefin di-

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merization used in the present work have previously been reported in our studies on propylene (1). All olefin feeds used were Phillips Petroleum Co. Pure Grade treated with silica gel prior to use. Isomer distribution analyses were made using capillary column gas chromatography (dimethylsulfolane and squalane liquid phases). Because of the complexity of the olefinic reaction products, the crude reaction mixtures were hydrogenated over Adams' catalyst and the saturated products were examined. Identification of specific isomers was by comparison with authentic samples either commercially available or prepared by the Wurtz reaction on appropriate bromoalkanes.

RESULTS AND DISCUSSION

For simplicity in the discussion of results, the information has arbitrarily been divided into sections on the butenes, on hexene-1, and on hexene-2.

The catalyst chosen for initial study was a doubly ammoniated cobalt oxide on carbon which had been activated at 450–500°C. Activation at this temperature had previously been shown to impart a high level of isomerization activity to the catalyst (1). When catalysts which had been activated at lower temperatures (for example, 275°C) were used, it was found that α-olefins could

be dimerized rather easily, but that internal olefins were totally unreactive. On the other hand, the catalyst which had been activated at 450°C was able to dimerize both α-olefins and internal olefins. The products obtained from these isomerization–dimerization reactions of internal olefins could be characterized as arising from olefin isomerization followed by selective dimerization of α-olefins or their precursors. Since the catalysts used possessed high isomerization power, little information could be gained by characterization of the large number of olefin isomers present. Instead, the total olefin product was hydrogenated and the pattern of formation of the carbon skeletons was determined.

Butene Dimerization

Results are shown in Table 1 for the dimerization of specific n-butene isomers. Under these reaction conditions isobutene was totally unreactive. Extensive isomerization of the unreacted butenes was found in all cases. It may be seen that 1-butene gave high levels of n-octenes, as was expected, and

higher olefins should occur through reaction of a cobalt hydride (I) to give preferred cobalt alkyls (II and III) [Eq. (1)] which would react only with α-olefins to afford the linear (IV) or singly branched (V) cobalt alkyl with very much smaller amounts of the alkyls VI and VII [Eq. (2)]. The decomposition of these alkyls would afford the olefin precursors of the observed hydrogenated products [Eq. (3), next page]. The observed differences in product distribution between dimer products of α-olefins and internal olefins is readily explained by assuming that during the isomerization of internal olefins by the cobalt-oxide-on-carbon catalyst a cobalt alkyl intermediate (III) is formed which is capable of inserting another olefin molecule as well as reverting to a cobalt hydride and an isomerized olefin [Eq. (4)].

Hexene-1 Dimerization

A comparison of hexene-1 dimerization activity of doubly ammoniated cobalt-oxide-on-carbon catalysts activated at 275°C

TABLE 1

DIMERIZATION OF THE n-BUTENES OVER COBALT OXIDE ON CARBON[a]

Olefin feed	Conversion (% of butene feed)	Composition of hydrogenated dimer [%]			Composition of recovered unreacted butenes [%]		
		n-Octane	3-Methyl-heptane	3,4-Dimethyl-hexane	Butene-1	cis-Butene-2	trans-Butene-2
1-Butene	13.6	65.3	34.4	0.3	10.6	31.1	58.2
cis-2-Butene	11.0	25.4	73.4	1.2	7.9	33.2	58.9
trans-2-Butene	2.5	26.9	68.1	5.1	—	—	—

[a] Doubly ammoniated 13% cobalt oxide on carbon activated at 500°C in nitrogen. Reaction temperature, 150°C; time, 6 hr. Initial butene pressure 450 psig (at 150°C).

that the 2-butenes also gave a surprisingly large amount of linear product. Little difference in product distribution was noted between cis- and trans-butene-2 but as might well be expected, because of the decreased stability of the π-olefin complex, the overall yield of product from trans-butene-2 is lower. Dimerization specificity in all cases was better than 90%.

According to the reaction pathway postulated for propylene (1),* dimerization of

* The formalism used to describe the active site on the cobalt-on-carbon catalysts is that which we have previously described (1).

and 450°C was made (Table 2). The relative amount of linear product found in dimerization of hexene-1 with a nonisomerizing catalyst (82.8%) is considerably greater than that found under similar conditions using propylene (~55%).

In addition, a curious distribution of isomers was found in the recovered unreacted hexenes from dimerization of hexene-1 with a "nonisomerizing" catalyst (275°C activation, Table 2). Coupling this observation with the increased specificity for linear dimer product one is led to propose that a
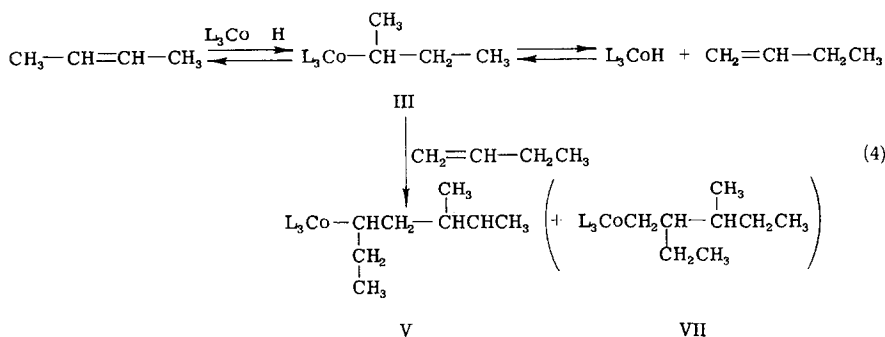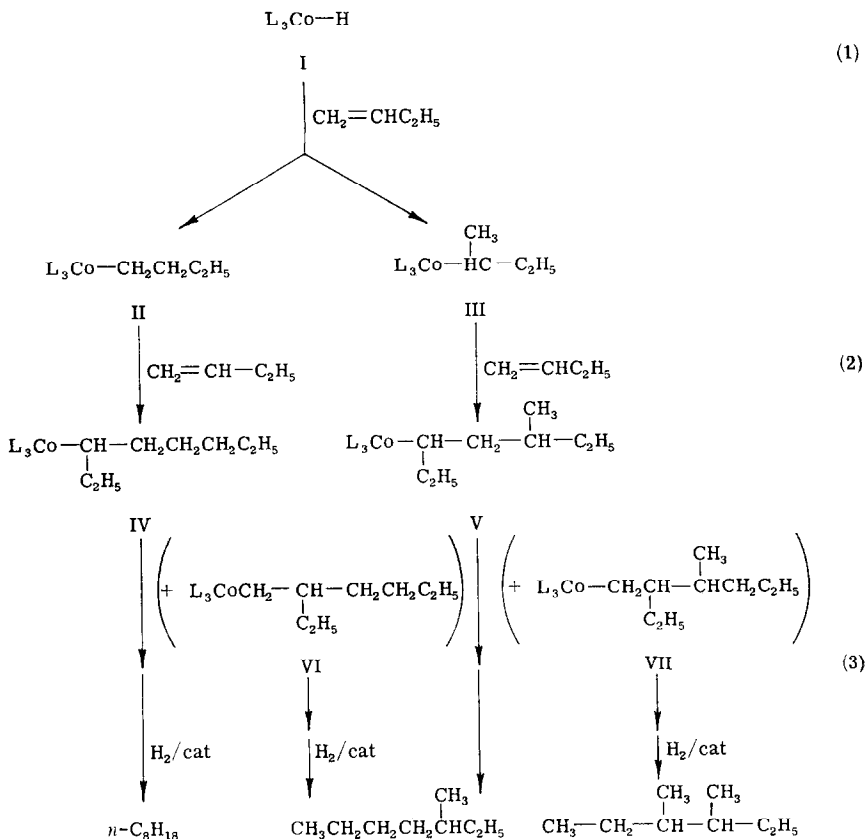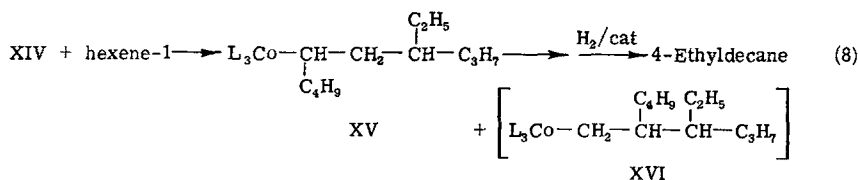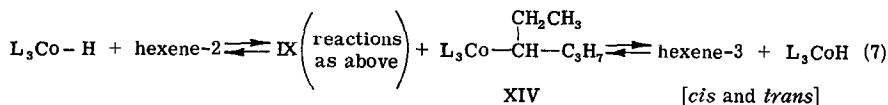
$$L_3Co-H$$

I
                                                   (1)

$$CH_2=CHC_2H_5$$

$$L_3Co-CH_2CH_2C_2H_5 \qquad\qquad L_3Co-\overset{CH_3}{\underset{}{HC}}-C_2H_5$$

II   III

$$CH_2=CH-C_2H_5 \qquad\qquad CH_2=CHC_2H_5 \qquad (2)$$

$$L_3Co-\underset{\underset{C_2H_5}{|}}{CH}-CH_2CH_2CH_2C_2H_5 \qquad L_3Co-\underset{\underset{C_2H_5}{|}}{CH}-CH_2-\overset{\overset{CH_3}{|}}{CH}-C_2H_5$$

IV   V

$$\left(+\ L_3CoCH_2-\underset{\underset{C_2H_5}{|}}{CH}-CH_2CH_2C_2H_5\right) \qquad \left(+\ L_3Co-CH_2\overset{\overset{CH_3}{|}}{CH}-\underset{\underset{C_2H_5}{|}}{CH}CH_2C_2H_5\right)$$

VI   VII   (3)

$$H_2/cat \qquad\qquad H_2/cat \qquad\qquad\qquad H_2/cat$$

$$n-C_8H_{18} \qquad CH_3CH_2CH_2CH_2\overset{\overset{CH_3}{|}}{CH}C_2H_5 \qquad CH_3-CH_2-\overset{\overset{CH_3}{|}}{CH}-\overset{\overset{CH_3}{|}}{CH}-C_2H_5$$

$$CH_3-CH=CH-CH_3 \underset{\longleftarrow}{\overset{L_3Co\quad H}{\longrightarrow}} L_3Co-\overset{\overset{CH_3}{|}}{CH}-CH_2-CH_3 \underset{\longleftarrow}{\longrightarrow} L_3CoH\ +\ CH_2=CH-CH_2CH_3$$

III

$$CH_2=CH-CH_2CH_3 \qquad\qquad (4)$$

$$L_3Co-\underset{\underset{\underset{CH_3}{|}}{\underset{CH_2}{|}}}{CHCH_2}-\overset{\overset{CH_3}{|}}{CH}CHCH_3 \quad \left(+\ L_3CoCH_2\overset{\overset{CH_3}{|}}{CH}-\underset{\underset{CH_2CH_3}{|}}{CH}CHCH_2CH_3\right)$$

V   VII

TABLE 2
DIMERIZATION OF HEXENE-1 OVER COBALT OXIDE ON CARBON[a]

Catalyst activation temp. (°C)	Conver- sion (%)	Composition of dimer (%) (after hydrogenation)			Composition of recovered unreacted hexenes (%)				
		n-Dodecane	5-Methyl- undecane	4-Ethyldecane	Hexene-1	Hexene-2 cis	Hexene-2 trans	Hexene-3 cis	Hexene-3 trans
275°	18.6	82.8	14.8	2.4	31.3	25.3	36.2	1.9	5.3
450°	8.5	55.5	34.8	9.7	2.1	20.4	51.3	3.4	22.9
—	—	—	—	—	1.5[b]	22.2	45.2	9.0	22.0

[a] Reactions run for 12 hr at 150°C. Olefin:catalyst ratio, 40:1 using doubly ammoniated 13% cobalt oxide on carbon.

[b] Thermodynamic equilibrium mixture at 77°C.

$$L_2CoH + \text{hexene-1} \rightleftarrows L_3Co{-}CH_2CH_2CH_2CH_2CH_2CH_3 \qquad (5a)$$
$$\qquad\qquad\qquad\qquad\quad VIII$$

$$L_2CoH + \text{hexene-1} \rightleftarrows L_3Co{-}\overset{\overset{\displaystyle CH_3}{|}}{CH}{-}CH_2CH_2CH_2CH_3 \rightleftarrows cis \text{ and } trans\text{-hexene-2} + L_3Co{-}H \qquad (5b)$$
$$\qquad\qquad\qquad\qquad\qquad IX$$

$$VIII + \text{hexene-1} \longrightarrow L_3Co{-}\overset{\overset{\displaystyle}{}}{\underset{\underset{\displaystyle C_4H_9}{|}}{CH}}{-}CH_2{-}C_6H_{13} + \left[L_3Co{-}CH_2{-}\underset{\underset{\displaystyle C_4H_9}{|}}{CH}{-}C_6H_{13} \right] \qquad (6a)$$

$$\qquad\qquad\qquad\qquad\qquad X \qquad\qquad\qquad\qquad\qquad\qquad XI$$

$$\qquad\qquad\qquad\qquad\qquad \downarrow H_2/cat \qquad\qquad\qquad\qquad\qquad \downarrow H_2/cat$$

$$\qquad\qquad\qquad\qquad n\text{-dodecane} \qquad\qquad\qquad 5\text{-methylundecane}$$

$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\nearrow H_2/cat$$

$$IX + \text{hexene-1} \longrightarrow L_3Co{-}\underset{\underset{\displaystyle C_4H_9}{|}}{CH}{-}CH_2{-}\overset{\overset{\displaystyle CH_3}{|}}{CH}{-}C_4H_9 + \left[L_3Co{-}CH_2CH{-}\overset{\overset{\displaystyle CH_3}{|}}{CH}{-}C_4H_9 \right] \qquad (6b)$$
$$\qquad\qquad\qquad\qquad\qquad XII \qquad\qquad\qquad\qquad\qquad\qquad XIII$$

$$L_3Co{-}H + \text{hexene-2} \rightleftarrows IX \left(\begin{array}{c}\text{reactions}\\ \text{as above}\end{array}\right) + L_3Co{-}\overset{\overset{\displaystyle CH_2CH_3}{|}}{CH}{-}C_3H_7 \rightleftarrows \text{hexene-3} + L_3CoH \qquad (7)$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad XIV \qquad\qquad [cis \text{ and } trans]$$

$$XIV + \text{hexene-1} \longrightarrow L_3Co{-}\underset{\underset{\displaystyle C_4H_9}{|}}{CH}{-}CH_2{-}\overset{\overset{\displaystyle C_2H_5}{|}}{CH}{-}C_3H_7 \xrightarrow{H_2/cat} 4\text{-Ethyldecane} \qquad (8)$$
$$\qquad\qquad\qquad\qquad\qquad XV \qquad\qquad + \left[L_3Co{-}CH_2{-}\overset{\overset{\displaystyle C_4H_9}{|}}{CH}{-}\overset{\overset{\displaystyle C_2H_5}{|}}{CH}{-}C_3H_7 \right]$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad XVI$$

series of competing reactions occurs [Eq. (5–8)].

In these reactions, the reversible nature of several of the reactions is clearly shown. While the n-hexylcobalt could revert only to hexene-1 [Eq. (5a)] or insert more hexene-1 and go on to products [Eq. (6a)], the sec-hexylcobalt (IX) also being formed from hexene-1 [Eq. (5b)] can revert either to hexene-1 or hexene-2 or insert more hexene-1 and go on to products [Eq. (6b)]. It would appear that reversion to olefin rather than insertion is the preferred path in this case. The hexene-2 can, to a very slight degree, undergo the insertion reactions and form hexene-3 [Eq. (7)] and products [Eq. (8)] thereby accounting for the traces of unpredicted isomers found. It would appear that the insertion of hexene-1 into all the hexyl

cobalts (VIII, IX, and XIV) can occur in only one manner and hexene-2 insertion is not at all favored, since no doubly branched material is found in the hydrogenated products. That is, it is probable that the intermediates (XI), (XIII), and (XVI) below are not formed to an amount that would allow detection of products in the hexene-1 reaction.

Hexene-2 Dimerization

When cobalt-oxide-on-carbon catalysts without isomerization activity (activated at ~275°C) are used with hexene-2, no dimerization is observed. However, as one increases the catalyst activation temperature, an increasing amount of dimerization and olefin isomerization is found (Table 3). Several other catalyst variables were evalu-
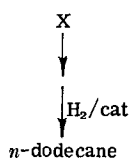
TABLE 3

DIMERIZATION OF HEXENE-2 OVER COBALT OXIDE ON CARBON—EFFECT OF CATALYST
ACTIVATION TEMPERATURE[a]

Catalyst activation temp. (°C)	Conversion		Isomer distribution of recovered hexenes (%)				
				Hexene-2		Hexene-1	
	(%)	g. prod. g. cat. ratio	Hexene-1	cis	trans	cis	trans
275	0	0	4.7	51.8	35.0	2.1	6.4
313	2	0.4	5.6	29.0	48.0	3.4	14.0
357	4.8	1.4	3.8	22.7	48.7	4.4	20.4
427	7.0	1.8	2.0	19.8	51.2	3.9	23.0
477	12.3	3.4	3.8	22.0	47.3	5.6	21.3
530	13.3	3.5	3.9	21.4	48.5	4.6	21.8
563	8.7	2.6	3.7	22.1	46.5	5.5	22.3
			—[b]	86.2	13.8	—	—
			1.5[c]	22.2	45.2	9.0	22.0

[a] Doubly ammoniated cobalt-oxide-on-carbon catalyst; 40:1 olefin:catalyst ratio; run for 12 hr at 150°C.
[b] Starting olefin feed.
[c] Thermodynamic equilibrium mixture at 77°C.

ated in this system as they were for propylene dimerization (1). It was found in this case that the double ammonium hydroxide treatment was neither beneficial

deactivation of the thermally sensitive ammoniated catalyst sites, or to the greater amount of isomerization activity found in the nonammoniated catalysts. The optimum

TABLE 4

EFFECT OF LEVEL OF COBALT OXIDE ON CARBON ON DIMERIZATION OF HEXENE-2[a]

CoO level (%)	1	3	5	10	15	20	25	33	40	50
Conversion (%)	0	15	21	24	24	36	36	27	9	7

[a] Nonammoniated cobalt oxide on carbon activated at 450°C. Reactions run at 150°C for 3 hr.

nor necessary for hexene dimerization as it was for propylene dimerization. This may be due either to the higher optimum reaction temperature (150°C), which could cause

dimerization activity was found to occur at levels of 20–25% cobalt oxide (Table 4). Maximum catalytic activity was reached in zero-time activation by heating to 500°C.

TABLE 5

DIMERIZATION OF HEXENE-2 OVER COBALT OXIDE ON CARBON

Catalyst type[a]	Olefin: catalyst ratio	Reaction time (hr)	Reaction temp. (°C)	Conversion (%)	Hydrogenated product distribution (%)					
					n-Dodecane	5-Methyl-undecane	4-Ethyl-decane	5,6-Dimethyl-decane	4-Ethyl-5-methyl-nonane	4,5-Diethyl-octane
A	40:1	12	150	8.5	27.0	37.3	30.2	5.5	—	—
					(2.3)	(3.1)	(2.5)	(0.6)		
A	2:1	3	150	25.1	12.7	50.3	30.9	2.5	3.2	0.5
					(3.2)	(12.6)	(7.8)	(0.6)	(0.8)	(0.1)
B	2:1	3	150	32.2	8.7	49.4	32.5	3.7	5.2	0.5
					(2.8)	(15.9)	(10.5)	(1.2)	(1.7)	(0.1)

[a] Catalyst type A: Doubly ammoniated 13% cobalt oxide on carbon activated at 450°C; B: untreated 13% cobalt oxide on carbon activated at 450°C.
[b] Values in parentheses represent the percent based on input hexene.

Lower activation temperatures required progressively longer activation times. For example, at 450°C an activation time of 2 hr was necessary for maximum catalytic activity. Prolonging the activation time caused drastically decreased activity. While significant differences in levels of conversion were found in varying the type of support carbon-used, no change in product distribution was found.

Table 5 shows the product distributions found when ammoniated and nonammoniated catalysts were employed. While little difference in distribution was noted between the results from ammoniated and unammoniated catalysts, significant changes were found with increasing depths of conversion. Increasing amounts of product are found and, for the first time, products of insertion of the elements of hexene-2 (to the extent of 0.5% of the product), and of reverse insertion of hexene-1 are found (from intermediates XI, XIII, and XVI above). It may be that these products had been formed in the other dimerizations but, at the lower levels of conversion, were not observed. Even though the amount of linear product appears to decrease when the depth of conversion increases, if one expresses the results in terms of *total* organic materials present,

one is led to conclude that the linear product is formed early in the reaction and that increasing amounts are formed as depth of conversion increases. However, with increasing depth of conversion the amount of singly branched isomers formed increases more rapidly.

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