HYDROGEN TRANSFER FROM 1,3-PROPANEDIAMINE AND 2-ETHYLHEXAHYDROPYRIMIDINE TO CARBON-CARBON DOUBLE BONDS SELECTIVE HYDROGENATION OF DIENES

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(Received in Japan 3 September 1975, received in UK for publication 13 October 1975)

In the course of a survey of the palladium catalyzed amine exchange reaction,¹ we found an efficient method for selective hydrogenation of dienes by hydrogen transfer from diamines, especially 1,3-propanediamine and 2-ethylhexahydropyrimidine catalyzed by palladium black. This is the first example of selective hydrogenation of dienes by transfer hydrogen, although extensive investigations concerning to catalytic transfer hydrogen from organic compounds^{2,3} to olefins have been undertaken. Furthermore, the results may be regarded as a model reaction for biological hydrogen transfer reactions ⁴

A mixture of 1,5-cyclooctadiene (1,5-COD) and three molar equivalents of 1,3-propanediamine (1) was stirred at 140° for 2 hr in the presence of catalytic amount of palladium black (5 wt %) Filtrantion followed by distillation gave cyclooctene (conv 71 %) in 85 % yield along with 2-ethyl-1,4,5,6-tetrahydropyrimidine (2), which is an exclusive product of the amine side. The reaction was accompanied by isomerization of 1,5-COD to 1,4- and 1,3-cyclooctadiene. Cyclooctane could not be detected among the products. This is in contrast to the result that 1,5-COD was not reduced by the reaction with cyclic amines catalyzed by RhCl(PPh₃)₃, although partial isomerization of 1,5-COD to 1,3-COD occurred $\frac{3c}{3c}$



Normal amines such as n-hexylamine are ineffective to hydrogen transfer to 1,5-COD; however, appreciable hydrogen transfer has been observed for diamines of $H_2N(CH_2)_nNH_2$, whose efficiency

depend upon the carbon number between two amino groups as shown in Table 1 Diamine] was the most efficient hydrogen donor among diamines examined Other examples of hydrogenation of dienes by hydrogen transfer from 1 with palladium catalyst are summarized in Table 2

Table 1 Palladium Catalyzed Hydrogen Transfer from Diamines $H_2^{N(CH_2)}_{n}NH_2$ to 1,5-COD ^{a)}						
Dıamıne	Conv of COD(%)	Yield of cyclooctene(%)	Yield of cyclooctane(%)			
H ₂ N(CH ₂) ₂ NH ₂	32	0	l			
H ₂ N(CH ₂) ₃ NH ₂	71	85	0			
H ₂ N(CH ₂) ₄ NH ₂	31	39	2			
н ₂ N(CH ₂)5NH ₂	23	5	-			
H ₂ N(CH ₂)6NH2	33	11	4			

a) A mixture of 1,5-COD (2 mmol), the diamine (6 mmol), and palladium black (0 5 mmol) was reacted at 140° for 2 hr

Diene	0lefin	Fro Conv (%) ^{C)}	$\sum_{\text{Yield}(\%)}^{a}$	Fr Conv (%) ^C	$\operatorname{Yield}(\%)^{d}$
1,5-COD	cyclooctene	71	85	96	65
1,3-COD	cyclooctene	83	70	37	89
norbornadiene	norbornene	41	57	74	51
dicyclopentadiene	tricyclo[5 2 1 0 ^{2,5} dec-3-ene	63	97	90	93
4-vinylcyclohexene	4-ethylcyclohexene	e)	^{e)}	30	85
linalool	3,8-dimethyloct-7-en-3-ol	e)	^{e)}	95	99
nona-1,4-diene	4-nonene	e)	^{e)}	62 ^{f)}	49 ^{g)}
hexa-1,5-dıene	1-hexene	e)	^{e)}	78 ^{f)}	43 ^{h)}

Palladium Catalyzed Hydrogen Transfer from either Diamine 1 or Diamine 3 to Dienes Table 2

a) A mixture of the diene (2 mmol), diamine l((6 mmol), and palladium (0 5 mmol) was reacted at 140° for 2 hr b) A mixture of the diene (2 mmol), diamine \Im (2 mmol), and palladium (0 5 mmol) was reacted at 120° for 2 hr c) Conversion of dienes d) Yields of olefins e) The dienes are insoluble in diamine 1 f) The reaction temperature was 130 $^\circ$ g) Other products were trans-3-nonene(12 %), unknown nonene 1somer(20 %), and n-nonane(6 %) h) Other products were 2-hexene(29 %), 3-hexene(11 %), and n-hexane(4 %)

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Treatment of 1 with palladium in the absence of COD at 200° for 8 hr afforded 2 in 56 % yield. This reaction can be rationalized by assuming that palladium catalyzed reaction of allylamine initially formed, with 1 would give 2-ethylhexahydropyrimidine (3), which is subsequently dehydrogenated to 2. Actually, palladium catalyzed reaction of 1 with allylamine at 25° for 15 hr gave 3 in 82 % yield ¹ Further, amine 3 was converted into 2 quantitatively on treatment with palladium at 200° for 2 hr

In view of the above mechanistic consideration, we examined hydrogen transfer from 3 to 1,5-COD catalyzed by palladium, and found that the selective hydrogen transfer proceeded more smoothly than that from 1. The results summarized in Table 2 indicate that palladium-catalyzed hydrogen transfer from 3 promises to provide an efficient method for selective hydrogenation of dienes, and which may correspond to the selective hydrogenation of dienes with molecular hydrogen by homogeneous catalysts 5

It is noteworthy that dienes are hydrogenated selectively by hydrogen transfer from diamines 1 and 3, since regular hydrogenation of dienes with molecular hydrogen by heterogeneous catalyst proceeds nonselectively. In case of the hydrogen transfer from 1,4-butanediamine to 1,5-COD (Table 1), pyrrolidine may be a real hydrogen donor by analogy with the relationship between 1 and 3. Indeed, hydrogen transfer from pyrrolidine to 1,5-COD occurred efficiently, however, the selectivity was lost. Thus, 1,5-COD was converted into cyclooctene (54 % yield) along with cyclooctane (24 % yield). The key step of the hydrogen transfer reaction would be dehydrogenation of an amine by palladium to give palladium-hydride species by analogy with the amine exchange reaction that we previously reported 1. In contrast to normal amines, cyclic amines such as pyrrolidine and 3, seems to stabilize the palladium-hydride species enough to transfer hydrogen to a carbon-carbon double bond. Further, the chelation of diamines bearing the 1,3-propanediamine structure seems to be essential for selective transfer of hydrogen to a carbon-carbon double bond. Interestingly, such 1,3-propanediamine structures are often involved in key intermediates of biological hydrogen transfer reactions $\frac{4}{2}$

Hydrodeuteration can be readily performed by utilizing deuterated 3. Thus, the reaction of norbornadiene with N,N-dideuterio-3. $(3a)^6$ in the presence of palladium gave exo-5-d₁-norbornene (4a, 63%) along with exo-5,6-d₂-norbornene (4b, 17%) and norbornene (4, 20%) Similarly, treatment of norbornadiene with N,N-diderterio-2-d₁-3. gave 4a (70\%), 4b (14\%), and 4 (16\%) When 2-deuterio-3. (3b) was used, no deuterium cooperation was observed in norbornene formed

These results indicate that dehydrogenation of 3 by palladium proceeds to give 2-ethyl-1,2,5,6tetrahydropyrimidine, which in turn isomerizes to 2 via 1,3-shift



Acknowledgement

The authers wish to thank the Ministry of Education, Japan, for a Grant-in-Aid (No 911511)

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