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MECHANISTIC STUDIES ON THE CATALYTIC HYDROGENATION OF α,β UNSATURATED CARBONYL COMPOUNDS WITH PLATINUM OR PALLADIUM, BASED ON INTRAMOLECULAR TRITIUM DISTRIBUTION.

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Recently we have shown (1) that after hydrogenation of crotonic and tetrolic acids with H_2/HT using palladium[a)] or platinum[b)] as catalysts, the resulting butyric and crotonic acids show ratios of tritium fixation at C-3 to that at C-2 between 4.3 : 1 and 5.1 : 1 for butyric acid and 2.4 : 1 for crotonic acid. With [3-T]-crotonic acid we have found that an intramolecular hydrogen shift from C-3 to C-2 is partially responsible for the asymmetry. Smith et al. (2,3) observed asymmetric deuterium distribution even after hydrogenation of α,β unsaturated carbonyl compounds (2,3) and styrenes (3) with D_2 gas. On the basis of these results Smith et al. (2) postulated an intramolecular hydrogen shift during the hydrogenations. In the case of crotonic acid this would mean a transfer of hydrogen at C-3 to the carbonyl group and from there to C-2 of the adsorbed species, forming butyric acid. Both hydrogen atoms at C-3 of butyric acid derive from the gas phase.

Crotonic acid has the trans conformation. Due to the stereochemistry of cis-crotonic acid a hydrogen shift is not possible. Therefore the hydrogenation of cis- and trans-crotonic acids with H_2/HT should result in butyric

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a) 30 % Pd on charcoal; b) according to Adams acids with different intramolecular tritium distributions. We prepared cis-crotonic acid according to Rappe (4) and checked its purity by NMR spectroscopy.

As shown in table 1 the ratio of tritium at C-3 to that at C-2 of cis-crotonic acid is less than unity but hydrogenation of trans-crotonic acid gives a ratio between 4 and 5 to 1 (1) as mentioned above. NMR spectroscopy of partially hydrogenated cis-crotonic acid shows that cis-crotonic acid is converted to the trans form about twice as fast as it is hydrogenated. The NMR spectroscopic determination of such a mixture is possible since the signal of the methyl group of butyric acid appears at 1.0δ, that of trans-crotonic acid at 1.95δ and that of cis-crotonic acid at 2.15δ. The tritium distribution in butyric acid after hydrogenation of cis-crotonic acid should be even more asymmetric when no trans-crotonic acid is formed during hydrogenation. After hydrogenation with platinum more tritium is fixed at C-3 than at C-2 in butyric acid as is the case with trans-crotonic acid. It is possible that platinum isomerises the cis-crotonic acid much faster than hydrogenation occurs. This would explain the higher ratio of tritium at C-3 to that at C-2 after 100 per cent than after 18 per cent hydrogenation.

These results show that the mechanisms for hydrogenation of cis- and trans-crotonic acids are different and that the intramolecular hydrogen shift shown in the case of trans-crotonic acid is not the only reason for the asymmetric tritium distribution. To prove this we hydrogenated 3.3-dimethylacrylic acid using palladium. In this case in two experiments the following tritium distributions were observed: At C-2 7 and 3.4 % T, at C-3 74 and 63 % T and in the two methyl groups 19 and 34 % respectively. Since 3.3-dimethylacrylic acid has no hydrogen at C-3 a similar shift to that in trans-crotonic acid cannot take place.

We found a pronounced difference between palladium and platinum in the hydrogenation of ethylidenemalonic acid diethyl ester. As shown in table 1 the ratio of tritium at C-3 to that at C-2 is about 8 in the case of palladium and nearly unity with platinum. This points to a definite difference in the mechanism of hydrogenation.

The asymmetric tritium distribution depends upon the presence of a carbonyl group in an α-position to the double bond. This can be seen (table 1) from a comparison of the tritium distribution at C-2 and C-3 after hydrogenation, of the acids mentioned and crotonic aldehyde on the one hand, and on the other hand crotyl alcohol. n-Butanol derived from crotyl alcohol shows a symmetrical tritium distribution.

One explanation for the asymmetric tritium distribution would be that, at least partially, a 1.4 addition of the α,ß unsaturated carbonyl compounds takes place. In the course of this reaction one hydrogen atom (or a hydride ion) would be fixed at C-3 and another hydrogen atom (or a proton) at the carbonyl oxygen. One proton migrates to C-2. The orientation in which the unsaturated molecule is fixed at the catalyst surface may influence which proton migrates to C-2, whether it is the one originating from the OH group of the carboxyl group or that from the gas phase. Isotope effects may occur during the splitting of a H-T molecule and also during the afore mentioned migration.

Other authors have also assumed a 1.4 addition of hydrogen (5,6) or a hydride ion and a proton (7) to α,ß unsaturated carbonyl compounds.

The experiments will be continued.

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TABLE 1

Tritium fixation and distribution in butyric acid, ethylmalonic acid diethyl ester, n-butyraldehyde and n-butanol after hydrogenation of cis-crotonic acid, ethylidenemalonic acid diethyl ester, crotonaldehyde and n-butanol with H_2/HT in ethyl acetate using platinum or palladium catalysts.

Hydrogenated compound (Percentage hydrogenation)		Catalyst	$\frac{\text{Mol. T-content in product}}{\text{Mol. T-content in } H_2/HT} \cdot 100$	Intramolecular T-distribution per cent			
				C-1	C-2	C-3	C-4
cis-crotonic acid	(100)	Pd	90	-	21	15	64
"	(100)	Pd	69	-	42	29	27
"	(14[a])	Pd	26	-	35	23	42
"	(100)	Pt	42	-	13	64	23
"	(18)	Pt	6	-	32	47	21
ethylidenemalonic acid diethyl ester	(100)	Pd	110	-	10[b]	77	13
"	(100)	Pd	81	-	11	82	7
"	(100)	Pt	63	-	33	37	30
"	(100)	Pt	37	-	34	32	33
crotonaldehyde	(100)	Pd	90	1	31	67	2
crotyl alcohol	(100)	Pd	68	6	25	27	42
"	(100)	Pt	37	2	45	51	2

a) 17 % based on hydrogen consumption and 11 % based on NMR spectroscopy. Besides butyric acid 59 % cis-crotonic acid and 30 % trans-crotonic acid.

b) The methine group is called C-2, the methylene group C-3 and the methyl group C-4.

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