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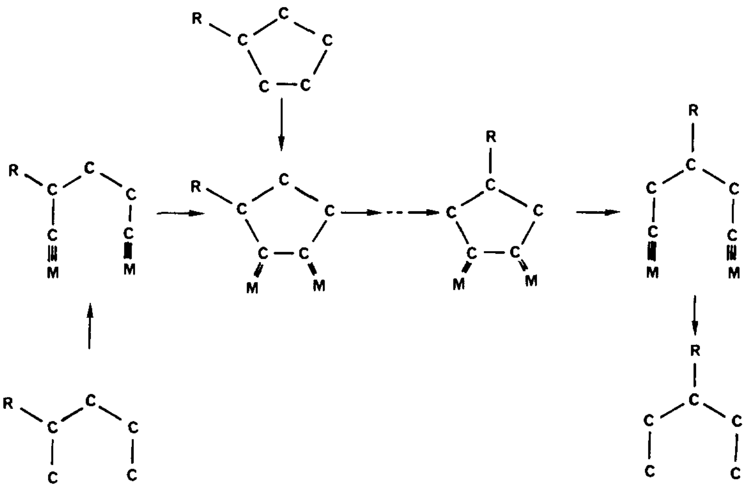
NOTES

1–3 Bond-Shift Isomerization of Methylpentanes on Iridium Catalysts

There is relatively little known about the mechanisms of hydrocarbon reactions on iridium. The pioneer work was done by Weisang and Gault (*1*), who showed that the major isomerization on iridium is a selective carbocyclic mechanism which involves the participation of metallocarbenes and metallocarbynes as reaction intermediates.



SCHEME 1. Selective cyclic mechanism: R = Me or Et.

On the other hand Somorjai and coworkers (*2*) found out that a stepped iridium surface Ir(755) is not more active for the dehydrocyclization of *n*-heptane and dehydrogenation of cyclohexane than is the iridium(111) surface.

We therefore decided to investigate in detail the isomerization of methylpentanes on various Ir/Al_2O_3 catalysts with mean particle size changing from 40 to 10 Å. Three iridium catalysts with a metal loading of 10, 0.5, and 0.25% by weight, supported on γ-alumina (obtained from Woelm A.G.: specific area 164 m^2/g; mean pore diameter 34 Å; no metal detected by X-ray fluorescence; sulfur content 30 ppm, used in previous studies (*10*)) were prepared by the usual impregnation method (*3*) and were reduced at 300°C for 12 hr. The catalytic experiments were monitored in a flow system free of grease as already described (*4*). The labeled hydrocarbons used in these experiments were 2-methyl[4-^{13}C]pentane and 3-methyl[3-^{13}C]pentane. All the isomerization reactions were performed at 220°C under 1 atm of hydrogen and 5 Torr of hydrocarbon. The hydrogenolysis of the methylcyclopentane was studied at 160°C only and yielded almost exclusively 2-methylpentane and 3-methylpentane on iridium catalysts (*1*); as seen in Table 1, the ratio r_{hydr} = 3MP/*n*-H is always ≥19 on the three catalysts studied.

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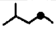
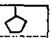
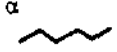
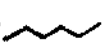
TABLE 1

Reactant											
products / catalyst	α^a 				^{c} % C.M.	α^a 				^{c} % C.M.	$r_{hydr}^b = \frac{3MP}{n-H}$
10% Ir (40 Å)	0.36 (8 %)	0	100	0	0	0.31 (4 %)	0	66	34	66	52
0.5% Ir (20 Å)	0.14 (6 %)	0	95	5	10	0.27 (4 %)	0	43	57	43	19
0.25% Ir (10 Å)	0.18 (21 %)	0	100	0	0	0.91 (14 %)	0	50	50	50	19
Cyclic Mechanism		-	50	50			-	100	0		
Bond Shift		-	100	0			-	0	100		

a = α  is the amount of n-hexane obtained in isomerization reactions for 100 moles of reactant; in brackets are the percentages of n-hexane in the isomer products

b = r_{hydr} is obtained from the hydrogenolysis of methylcyclopentane

c = % C.M. is the percentage of cyclic mechanism, one of the two reaction mechanisms commonly believed to be involved in skeletal rearrangements on metals (5), the other being the bond-shift mechanism

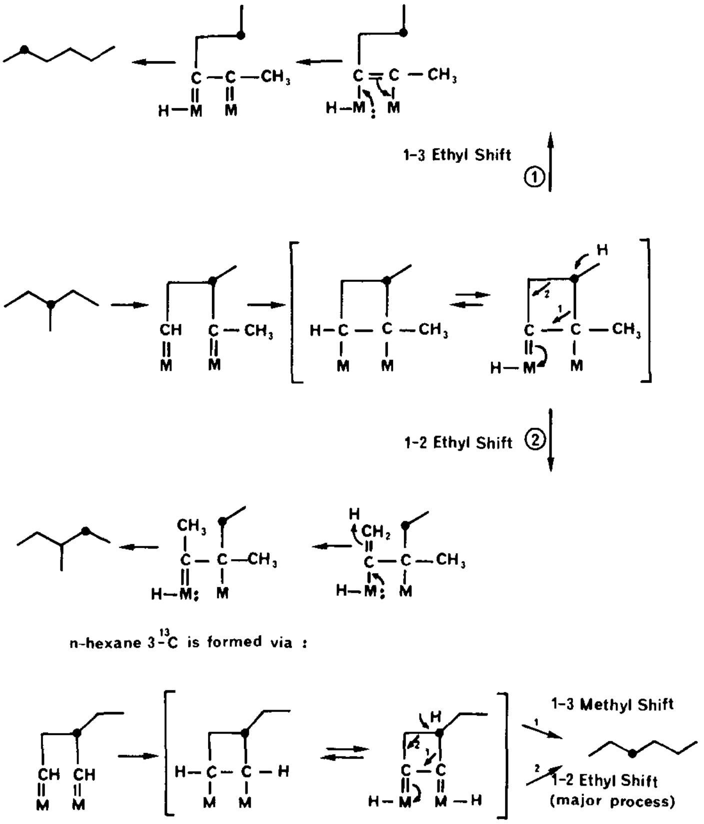
We only focused our attention on the formation of labeled *n*-hexanes from the two labeled hydrocarbons 2-methyl[4-^{13}C]pentane and 3-methyl[3-^{13}C]pentane. This type of isomerization should confirm that the cyclic mechanism is selective. From the results mentioned in Table 1 we can see that the amount of *n*-hexane in the isomer products, although very low, is far from negligible and it increases when the metal particle size decreases. This effect is not observed with the ratio r_{hydr} in the methylcyclopentane hydrogenolysis which always shows a very high selectivity for these catalysts and consequently very little cleavage of the tertiary–secondary C–C bond of the ring.

Furthermore, we can notice a very large discrepancy between the values of the cyclic mechanism if the reactant is 2-methylpentane or 3-methylpentane. With the former molecule we do not observe any cyclic mechanism involving the formation of *n*-hexane. To explain the deviation from the principle of the microscopic reversibility we have to introduce another type of bond-shift isomerization.

In Table 2 we have reported another interesting result, already known in the petroleum industry (*6*), namely, the predominance of the deethylation process in the cracking of 2-methylpentane, a process which is less pronounced for the 3-methylpentane on Ir and Pt–Ir catalyst (*7*).

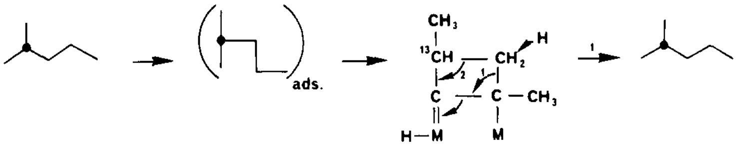
Extensive central bond rupture in *n*-butane hydrogenolysis has been reported by Plunkett and Clarke (*8*) for iridium–gold film catalysts of relatively high gold content; in this respect, these alloy catalysts of very large metallic particle size will resemble pure iridium catalysts of very small metallic particle size. On the other hand, Foger and Anderson (*9*) observed that over catalysts with $\bar{d}_{Ir} \leq 10$ to 15 Å the *n*-butane reaction is strongly selective towards C_{II}–C_{II} (central) bond rupture. Our present results are in good agreement with these two observations. The deethylation (Table 2) strongly predominates on the 0.25% Ir/Al$_2$O$_3$ catalyst with a mean metal particle size, determined by electron microscopy of about 10 Å.

If we assume that in cracking and isomerization the same sites are involved and that a common intermediate is "responsible" for these reactions (*4*) we can explain the difference observed in 2-methylpentane and 3-methylpentane cyclic isomerization by the existence of a new bond-shift mechanism which predominates on iridium catalysts and Pt–Ir catalysts (*7*). As the ethyl group is a good leaving group in cracking we suggest that a 1–3 ethyl migration takes place, instead of the cyclic mechanism, for the formation of *n*-hexane 2-^{13}C.



SCHEME 2. 3-Methylpentane isomerization on Ir catalysts.

In the case of methyl[2-^{13}C]pentane isomerization the intermediate is:



SCHEME 3. Path 1: 1–3 ethyl shift gives the same product: self-isomerization. Path 2: 1–2 propyl shift: minor process.

As we obtain from the 3-methyl[3-^{13}C]pentane 4% of 3-methyl[2-^{13}C]pentane on the 10 and 0.5% Ir/Al_2O_3 catalysts and 10% on the 0.25% Ir/Al_2O_3 catalyst, the mechanism suggested in Scheme 2 can explain at the same time either the chain lengthening or the self-isomerization.

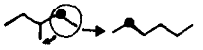
An experiment with 3-methyl[2-^{13}C]pentane was done to confirm these

TABLE 2

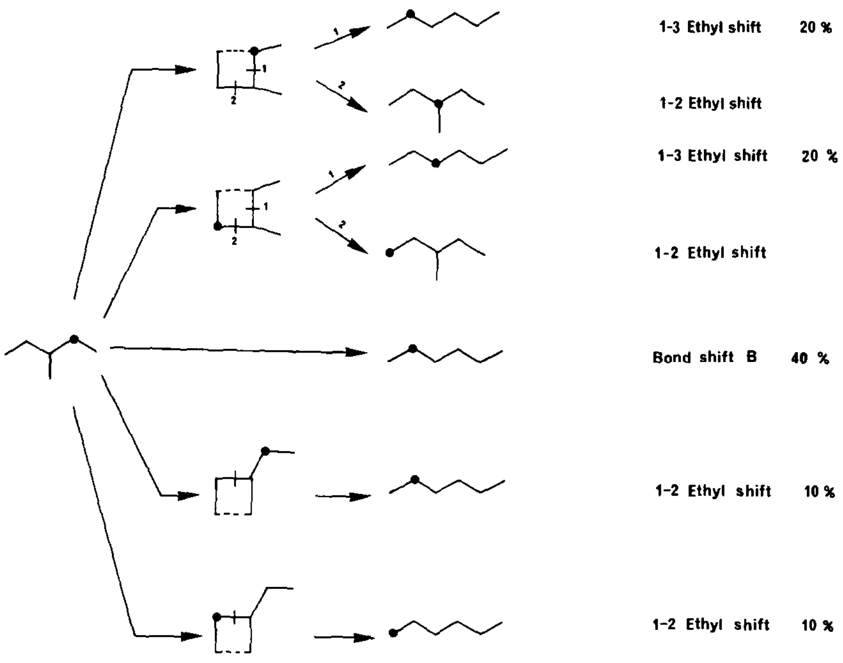
Hydrocracking of Hexanes: Relative Rates Compared to Statistical Rate of Hydrogenolysis

Reactant	Catalyst			Statistical
	10% Ir	0.5% Ir	0.25% Ir	
2-methylpentane				
Demethylation	1.9	1.4	1.3	3
Deethylation	2.4	3.0	3.4	1
Internal fission	0.7	0.6	0.3	1
3-methylpentane				
Demethylation	3.3	3.3	2.5	3
Deethylation	1.7	1.7	2.5	2

observations. We obtained a similar amount of labeled *n*-hexane (0.8%) with 10% of *n*-hexane 1-^{13}C, 70% of 2-^{13}C and 20% of 3-^{13}C. As we cannot obtain *n*-hexane by methylcyclopentane hydrogenolysis, the amount of *n*-hexane 1-^{13}C corresponds to the 1–2 ethyl shift and the 20% of *n*-hexane 3-^{13}C represents the 1–3 ethyl shift. The latter is twice as important as the former. The amount of *n*-hexane 2-^{13}C formed by 1–3 and 1–2 ethyl shift is equal to 20 and 10%, respectively, as represented in Scheme 4. The remaining 40% of *n*-hexane 2^{13}C measures the importance of the bond-shift B

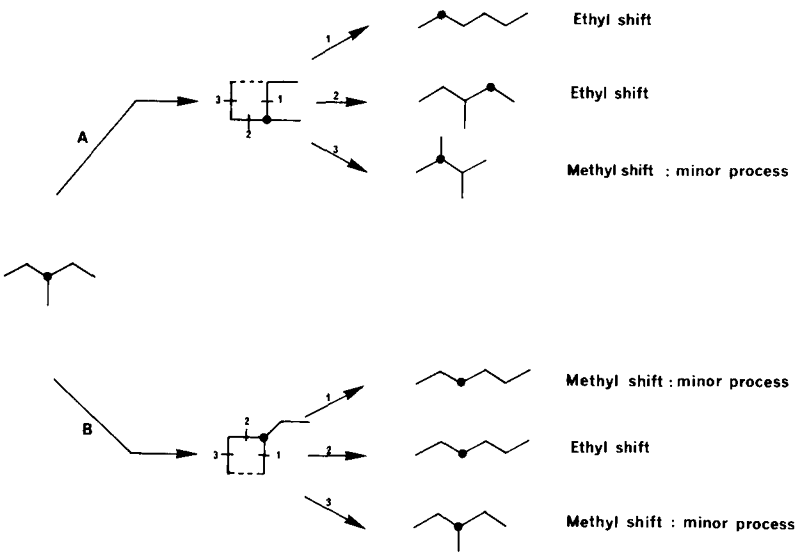

(4)

which corresponds to a 1–2 ethyl shift with retention of configuration for the leaving group.



SCHEME 4. 3-methylpentane[2-^{13}C]isomerization.

On the other hand, in Table 1 we can see that the amounts of *n*-hexane 2-^{13}C and *n*-hexane 3-^{13}C are equal on the 0.25% catalyst. This can be explained by Scheme 5:



SCHEME 5. 3-methylpentane[3-^{13}C]isomerization.

Only the paths A-1 and B-2 are obtained by an ethyl shift, for chain lengthening, which demonstrates the equality of these two products mostly on the 0.25% Ir/Al_2O_3 where the ethyl group is a very good leaving group.

Another explanation of the observed distributions could be via two consecutive 1–2 shifts. In this case, from 2- and 3-methylpentanes, 2,2- and 2,3-dimethylbutanes should be formed. They were never detected. Furthermore, no ^{13}C label has been found on the methyl groups of 2- and 3-methylpentanes labeled initially on the second, fourth, and third carbon atoms, respectively, which excludes either two consecutive 1,2 shifts or a succession of bond-shift and C_5 cyclic mechanisms. Moreover, as mentioned above, the 2,3-dimethylbutane is not formed as would be expected if a true 1,2-dimethylcyclobutane intermediate occurred. For this reason we postulate a concerted mechanism via a quasi-cyclobutane intermediate as represented in Scheme 2. On the other hand, it is known that iridium accepts with great ability electrons from adsorbed hydrocarbon molecules (*11*).

To sum up, a novel bond-shift isomerization mechanism, namely, 1–3 ethyl shift, has been characterized on iridium catalysts by using ^{13}C-labeled molecules especially on the 0.25% Ir/Al_2O_3 (10 Å) catalyst; an effect of the particle size distribution cannot be ruled out. The selective cyclic and 1–3 ethyl shift mechanisms are specific to iridium catalysts. An electronic factor rather than a geometric one may explain the preferential formation of dicarbene species as precursors for these reactions.

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