Selective Isomerization of Methylpentanes on Iridium Catalysts

By FRANÇOIS WEISANG and FRANÇOIS G. GAULT*

(*Laboratoire de Catalyse, Université Louis Pasteur, 4 rue Blaise Pascal, 67008 Strasbourg, France*)

Summary The very fast isomerization of 2-methyl[2-^{13}C]-pentane to 3-methyl[3-^{13}C]pentane and the selective hydrogenolysis of methylcyclopentane to methylpentanes on iridium suggest the participation of metallocarbenes and metallocarbynes as reaction intermediates.

IRIDIUM is a very active catalyst for the hydrogenolysis of alkanes[1] and the isomerization of neopentane to isopentane.[2] However, isomerization of n-butane, n-pentane, and n-hexane was not observed under similar conditions.[3] We therefore decided to investigate in detail the isomerization of hexanes on 10% Ir–Al_2O_3 and on iridium sponge catalysts.

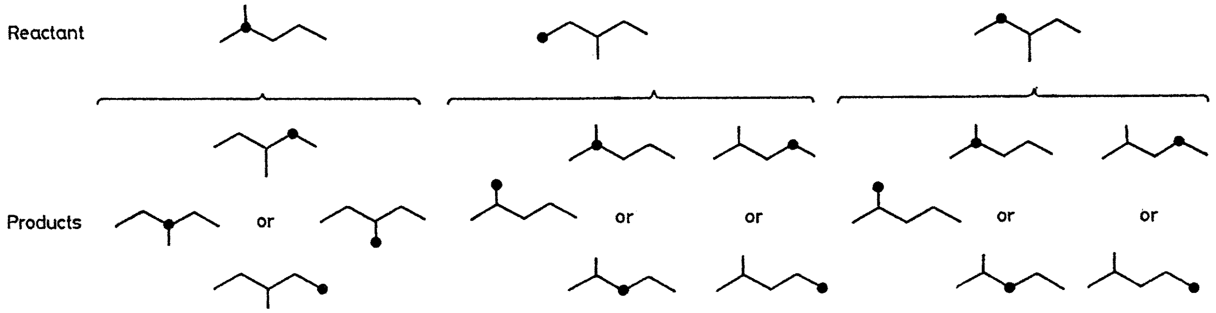
Isomerization of 2-methylpentane to 3-methylpentane and the reverse reaction occur with rates comparable to that of hydrogenolysis, while interconversion between methylpentanes and n-hexane is almost undetectable (Table 1). Isomerizations of 2-methyl[2-^{13}C]pentane, 3-methyl[1-^{13}C] pentane, and 3-methyl[2-^{13}C]pentane were therefore investigated to distinguish between the two reaction mechanisms commonly believed to be involved in skeletal rearrangements on metal:[4] carbocyclic and bond shift. Within the experimental error (±2% for each species[5]), the results (Table 2) are consistent with a carbocyclic mechanism (Scheme 1).

TABLE 1. Initial product distributions.

Reactant	Catalyst[a]	Reaction products (weight %) 2-Methyl pentane	3-Methyl-pentane	n-Hexane	Methylcyclo-pentane	Sh[c]	Reactivity factors:[b] cleavage of C_t–C_p	C_t–C_s	C_s–C_s	C_s–C_p
2-Methylpentane	A	—	28·1	2·0	0·5	67	0·4	0·5	2·5	1·2
„	B	—	43·5	0·0	2·5	48	0·35	0·3	2·25	1·75
3-Methylpentane	A	44·1	—	0·3	1·2	50	0·15	0·6	—	1·8
„	B	49·7	—	0·0	0·1	40	0·1	0·2	—	2·25
n-Hexane	A	0·2	0·2	—	0·0	98·3	—	—	1·1[d]	0·5
„	B	0·4	0·3	—	0·0	89·3	—	—	1·85[e] 0·85[d]	1·0
Methylcyclopentane	A	73·4	26·0	0·3	—	99·7			1·25[e]	
„	B	69·7	28·7	0·4	—	98·2				

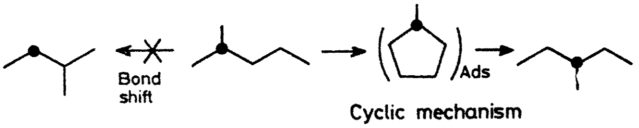
[a] A: Ir–Al_2O_3 at 433 K; B: Ir sponge at 443 K. [b] Observed rate divided by statistical rate of hydrogenolysis (G. Leclercq, L. Leclercq and R. Maurel, *J. Catalysis*, 1977, **50**, 87). [c] Percentage of the products obtained by a one-bond rupture mechanism. [d] C(2)–C(3) and C(4)–C(5) bonds. [e] C(3)–C(4) bond.

TABLE 2. Isomerization: distribution (%) of the isotopic varieties.[a]



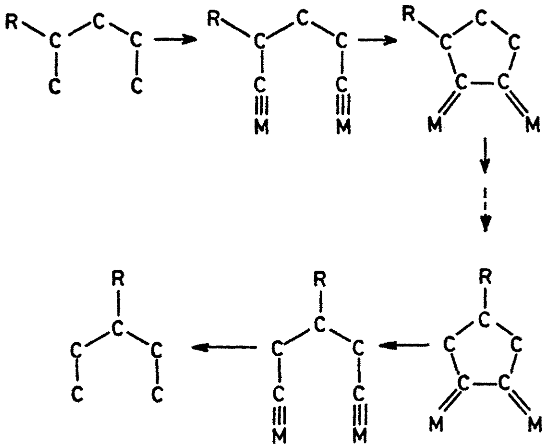
Bond shift	0	100	0	50	0	50	0	50	50
Cyclic mechanisms	100	0	0	0	0	100	50	50	0
Observed	100	0	0	2	0	98	51·5	46·5	2

[a] ● = ^{13}C.



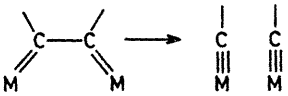
SCHEME 1. ● = ^{13}C.

The hydrogenolysis of methylcyclopentane, which yields 2-methylpentane and 3-methylpentane, but not n-hexane (Table 1), the fast interconversion of 3-methylhexane and ethylpentane, and the failure of 2-methylhexane and n-heptane to isomerize confirm that the major isomerization mechanism on iridium is a selective carbocyclic mechanism in which only secondary–secondary CH_2–CH_2 cyclic bonds are formed and ruptured. Since the dehydrocyclisation step requires the presence in the molecule of two primary carbon atoms in 1 and 5 positions, it is possible that the reaction proceeds *via* a dicarbyne intermediate attached to two metal atoms (Scheme 2).



Scheme 2. R = Me or Et.

Metallocarbenes have been proposed as possible intermediates in exchange of hydrocarbons with deuterium.[6] Also, the importance of metallocarbenes and metallocarbynes in selective and extensive hydrogenolysis of hydrocarbons on cobalt has been emphasized.[7] On iridium, where hydrogenolysis occurs mainly *via* cleavage of one carbon–carbon bond, secondary–secondary (C_s–C_s) and secondary–primary (C_s–C_p) bonds are ruptured much more rapidly than tertiary–primary (C_t–C_p) and tertiary–secondary (C_t–C_s) bonds (Table 1). This suggests that hydrogenolysis of alkanes, like that of alkylcyclopentanes, involves formation of two double bonds between the metal and two contiguous carbon atoms (Scheme 3).



Scheme 3

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