Evidence for a Selective *cis–trans*-Isomerization of Butenes over Alumina with Allylic C–H Bond-breaking

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Summary Sodium exchanged alumina catalyses the *cis–trans*-isomerization of but-2-enes without inducing the formation of but-1-ene, and without any exchange of hydrogen with the catalyst; it involves an allylic C–H bond-breaking step.

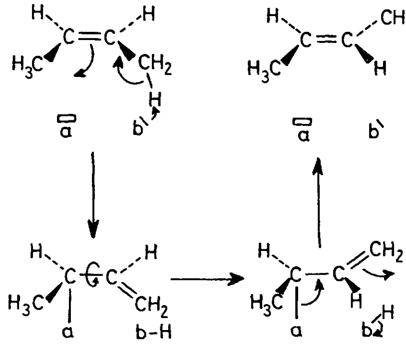
Some catalysts like SnO_2,[1] Ga_2O_3,[2] or aluminium phosphate evacuated at a high temperature[3] catalyse only the *cis–trans*-isomerization of but-2-enes without double bond migration; vinylic intermediates have been proposed for this reaction. On alumina at 250 °C, the use of selectively deuteriated butenes[4] allowed the detection of two parallel reactions: *cis-trans*-isomerization and double bond migration with exchange of hydrogen of the molecule with protonic sites on the catalyst, and an 'intramolecular' *cis–trans*-isomerization without hydrogen exchange. As

TABLE. Isomerization of [2,3-$^2H_2$]-*cis*-but-2-ene and [1,4-$^2H_6$]-*cis*-but-2-ene.

	% Product	Isotope distribution (%)								^{2}H atoms per molecule
		$^2H_0$	$^2H_1$	$^2H_2$	$^2H_3$	$^2H_4$	$^2H_5$	$^2H_6$	$^2H_7$	
[2,3-$^2H_2$]-*cis*-but-2-ene		0·3	0·7	98·8	0·2	—	—	—	—	1·99
trans-but-2-ene	1·43[a]	1·9	3·6	94·1	0·4	—	—	—	—	1·93
	5·57[b]	2·1	3·1	93·8	1·0	—	—	—	—	1·94
[1,4-$^2H_6$]-*cis*-but-2-ene		—	—	—	0·05	0·95	10·7	88·3	—	5·87
trans-but-2-ene	1·36[a]	—	—	—	0·2	3·8	12·3	82·7	1·0	5·80
	2·10[c]	—	—	—	0·1	1·2	11·9	86·4	0·4	5·85

[a] 0·02% but-1-ene. [b] 0·06% but-1-ene. [c] 0·03% but-1-ene.

already stated[5] protonic sites of acid catalysts can be easily exchanged by sodium ions. In an attempt to study the 'intramolecular' *cis–trans*-isomerization alone, alumina similar to that previously used was impregnated with $NaHCO_3$.



SCHEME

The catalyst obtained (0·4 wt. % Na) catalyses only *cis–trans*-isomerization; at 250 °C the ratio of *trans*-but-2-ene to but-1-ene formed from *cis*-but-2-ene is *ca.* 100 : 1. Moreover this reaction occurs without hydrogen exchange between the olefin and the catalyst (see Table); [2,3-$^2H_2$]-*cis*-but-2-ene gives mainly [$^2H_2$]-*trans*-but-2-ene, and [1,4-$^2H_6$]-*cis*-but-2-ene yields [$^2H_6$]-*trans*-but-2-ene. The comparison of isomerization rates for each deuteriated *cis*-but-2-ene with that of [$^2H_0$]-*cis*-but-2-ene shows that the former reaction occurs with no isotope effect ($k_H/k_D = 1·0$) but that the isomerization of [1,4-$^2H_6$]-*cis*-but-2-ene gives rise to an important isotope effect ($k_H/k_D = 2·9$). Therefore *cis-trans*-isomerization involves, not vinylic C–H bond-breaking, but allylic C–H bond-breaking during the rate-determining step.

Such a selective *cis–trans*-isomerization without exchange and with an allylic C-H bond-breaking step has never been mentioned previously in the literature. Only allylic intermediates can account for these observations but such species are generally proposed to explain double bond migration, whether or not this is accompanied by *cis–trans*-isomerization.[6,7] So particular allylic intermediates must be invoked. The mechanism proposed (Scheme), though tentative, may account for our results. Isomerization would occur on a Lewis acid–base pair site, with simultaneous intervention of both parts of the pair: the removal of an allylic proton by the basic part would take place with the concomitant formation of a σ-bond between the molecule and the acidic part. Similarly the reverse reaction (breaking of the σ-bond and returning of the proton to the molecule) would take place only by the same concerted process, which would preclude double bond migration. σ-Bonded carbonium ions[8] or π-allyl species,[7] which would allow double bond migration, are not formed, probably because the acidic and basic parts of the active site are too weak to act separately.

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