Stereochemistry of 1,4-Addition of Molecular Deuterium to 2-Methylbuta-1,3-diene over ThO_2, MgO, and La_2O_3

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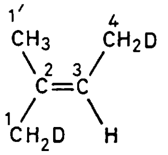
Summary Deuteriation of 2-methylbuta-1,3-diene over ThO_2 gave 90% of (*E*)-[1,4-$^2H_2$]-2-methylbut-2-ene and 10% of (*Z*)-[1,4-$^2H_2$]-2-methylbut-2-ene with retention of the conformation of the reactant, while over MgO and La_2O_3 60% of the (*E*)-form and 40% of the (*Z*)-form were produced.

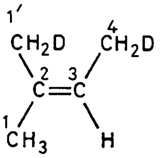
In sharp contrast to the extensive studies of the stereochemical course of 1,2-addition in the hydrogenation of a conjugated diene, little is known of the stereochemistry of hydrogenation by 1,4-addition. The hydrogenation of buta-1,3-diene over MgO selectively yields *cis*-but-2-ene,[1] while *trans*-but-2-ene is mainly formed over ZrO_2,[2] ThO_2,[3] and La_2O_3.[4] We now report the deuteriation of 2-methylbuta-1,3-diene over MgO, ThO_2, and La_2O_3, which enabled us to investigate the deuteriation in more detail.

Magnesium oxide and La_2O_3 were obtained by outgassing the corresponding hydroxides at 1373 and 873 K, respectively. Thorium oxide was prepared by thermal decomposition of thorium oxalate at 773 K in air followed by outgassing at 773 K. A mixture of deuterium (20—27 kN m^{-2}) and 2-methylbuta-1,3-diene (13 kN m^{-2}) was allowed to react over 0·5—0·6 g of catalyst in *ca.* 2·8 × 10^{-3} m^3 of a closed recirculation reactor.

Table 1 shows the product distribution. The three oxides showed similar trends for the deuteriation of 2-methylbuta-1,3-diene to give predominantly [$^2H_2$]-2-methylbut-2-ene. ^1H and ^{13}C N.m.r. analysis of the [$^2H_2$]-2-methylbut-2-ene obtained revealed that (*E*)- (**1**) and (*Z*)-[1,4-$^2H_2$]-2-methylbut-2-ene (**2**) were formed by 1,4-addition of D_2. These isomers have substantially the same thermodynamic stability and can be distinguished by ^{13}C n.m.r. spectroscopy.[5] Their estimated ratios are listed in Table 2. Incorporation of D atoms into the reactant was negligible. This indicates that the reverse process from the half-hydrogenated state is very slow.



(1)



(2)

The stereochemistry of the reaction over ThO_2 was such as to give 90% of the *E*-adduct. This indicates that the reaction course is dominated by the predominant *trans*

TABLE 1. Deuteriation of 2-methylbuta-1,3-diene over three oxide catalysts.

	Composition of products/%			Deuterium distribution of 2-methylbut-2-ene/%			
Catalyst	3-Methylbut-1-ene	2-Methylbut-1-ene	2-Methylbut-2-ene	[$^2H_0$]	[$^2H_1$]	[$^2H_2$]	[$^2H_3$]
MgO[a]	1·6	5·8	92·6	1·8	1·5	95·8	1·0
La_2O_3[b]	0·5	7·8	91·6	2·6	4·5	90·5	2·1
ThO_2[c]	1·0	13·3	85·7	1·0	2·0	95·0	2·0

[a] Conversion 26·4% at 273 K. [b] 22·1% at 273 K. [c] 36·6% at 295 K.

TABLE 2. ^{13}C N.m.r. analysis of 2-methylbut-2-ene.

Catalyst	% CH_2D			% *E* and *Z* isomers of 2-methylbut-2-ene		% *cis* and *trans* isomers of but-2-ene	
	C-1	C-1′	C-4	*E*	*Z*	*trans*[a]	*cis*[a]
MgO	58·9	38·9	100	60	40	17[b]	83[b]
La_2O_3	62·5	33·7	94·1	64	36	82[c]	18[c]
ThO_2	89·1	0·0	100	89	11	92[d]	8

[a] Hydrogenation of buta-1,3-diene. [b] Conversion, 41%. [c] 21%. [d] 9%.

(*syn*) form of the allylic reaction intermediate. Since the reactant is 97·8% in the s-*trans* conformation,[6] the geometrical structure is retained during the reaction. With MgO and La_2O_3, the percentages of the *E* and *Z* isomers formed approached the equilibrium value. This suggests that interconversion between the *trans* and *cis* forms of the allylic species occurs to a considerable extent before the *trans* form is attacked by the second H. Although fast rotation around the C(2)–C(3) bond might occur after 2-methylbut-2-ene had been formed, it is more plausible that the fast rotation occurs in the half hydrogenated state.

It is notable that over La_2O_3 the geometrical structure of the reactant is retained during the hydrogenation of buta-1,3-diene but fast rotation around the C(2)–C(3) bond occurs during the hydrogenation of 2-methylbuta-1,3-diene.

We thank Dr. S. Shimokawa, Hokkaido University, for the ^{13}C n.m.r. analysis.

(*Received*, 15*th August* 1978; *Com.* 895.)

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