Selective Hydrogenation of the Internal Double Bond of Penta-1,3-diene on a ZnO Catalyst

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Summary The hydrogenation of penta-1,3-diene has been studied over various catalysts (MoS_2, ZnO, Cr_2O_3, and Co_3O_4) which normally lead to predominant 1,2- rather than 1,4-addition of hydrogen; ZnO led to hydrogenation of the internal double bond with high (87·3%) selectivity, by 3,4-addition.

Although selective catalytic hydrogenation of the internal double bond of alkadienes yielding mainly α-olefins would be a useful process, only a few homogeneous or heterogeneous catalysts have been reported. Wells and Wilson[1] found that the hydrogenation of penta-1,3-diene on Cu–Al_2O_3 yielded 69% of pent-1-ene in the product, and Pregaglia *et al.*[2] obtained 60% selectivity in pent-1-ene formation with $[RhH(PPh_3)_4]$ as catalyst. More recently, Kawakami *et al.*[3] have reported a novel catalyst composed of $[CoBr(PPh_3)_3]$ and BF_3–Et_2O which is active for the hydrogenation of the internal double bond of conjugated dienes; hydrogenation of penta-1,3-diene yielded 74% of pent-1-ene. We have found a remarkably selective 3,4-addition of hydrogen to penta-1,3-diene (a mixture of 60% *trans* and 40% *cis* isomers) on a ZnO catalyst (Kadox-25 from New Jersey Zinc Co.) pretreated *in vacuo* at 450 °C for several hours.

It is known that the deuteriation of butadiene on such catalysts as MoS_2,[4] ZnO,[5] Cr_2O_3 (from thermal decomposition of ammonium dichromate; 16 m^2 g^{-1}),[6] Co_3O_4 (from thermal decomposition of cobalt nitrate; 2 m^2 g^{-1}),[7] MgO,[8] ThO_2,[9] and ZrO_2[10] gives mainly the $[^2H_2]$-adducts, *i.e.*, the deuterium molecular identity is maintained in the hydrogenated products. The position of deuterium in these $[^2H_2]$-adducts has been determined by microwave or n.m.r. spectroscopy; MoS_2, ZnO, and Cr_2O_3 yield mainly 1,2-adducts while Co_3O_4, MgO, ThO_2, and ZrO_2 have a preference for 1,4-addition.

Effective catalysts for the hydrogenation of the internal double bond of alkadienes might be expected to be those having a preference for 1,2-addition of hydrogen, and we have studied the hydrogenation of penta-1,3-diene over a variety of such catalysts. In this hydrogenation *trans*- and *cis*-pent-2-ene are formed by either 1,2- or 1,4-addition of hydrogen, but pent-1-ene is formed only by 3,4-addition. As shown in Table 1, ZnO shows remarkably high selectivity for the 3,4-addition of hydrogen, yielding pent-1-ene, with conversions as high as 80%, when the reaction was performed in a circulating system (*ca.* 400 ml) with a mixture of hydrogen and pentadiene [*ca.* 50—60 mmHg; $P(H_2)/P(C_5H_8)$ = *ca.* 2—3]. As shown in Table 2, deuteriation of penta-1,3-diene on the ZnO catalyst at room temperature predominantly gives the [$^2H_2$]-adducts (with a negligible amount of the [$^2H_4$]-species). N.m.r. spectroscopic analysis indicates unequivocally the formation of [3,4-$^2H_2$]pent-1-ene and [1,4-$^2H_2$]pent-2-ene. 1,2-Addition of D_2 would yield [1,2-$^2H_2$]-*cis*-pent-2-ene whereas 1,4-addition would yield [1,4-$^2H_2$]-*cis*-pent-2-ene. Thus, the relative importance of 1,2- and 1,4-addition in the formation of *cis*-pent-2-ene can be estimated from the n.m.r. data. Calculations indicate that 1,4-addition accounted for a major proportion (70%) of the formation of *cis*-pent-2-ene. This demonstrates that the ZnO catalyst brings about almost perfect selectivity for the hydrogenation of the internal double bond of penta-1,3-diene because the contribution of 1,2-addition is negligible. As we have inferred previously,[11] 1,4-addition on a ZnO catalyst might occur on sites other than those for 1,2- and/or 3,4-addition.

TABLE 1. Hydrogenation of penta-1,3-diene on various catalysts at room temperature.

		Relative proportions of products			
Catalyst	% Conversion	Pentane	Pent-1-ene	*trans*-Pent-2-ene	*cis*-Pent-2-ene
MoS_2	45·2	10	25·8	48·9	15·2
ZnO	80·0	—	87·3	2·8	9·9
Cr_2O_3	69·0	11·4	4·5	64·4	19·7
Co_3O_4	39·3	—	20·9	42·0	37·0

TABLE 2. N.m.r. analysis of pent-2-ene and pent-1-ene formed by the deuteriation of penta-1,3-diene on ZnO at room temperature.

	Deuterium distribution (%) (0% [$^2H_0$])			Distribution of ^1H in labelled product (values for unlabelled pentenes in parentheses)[a]				
Product (%)	[$^2H_1$]	[$^2H_2$]	[$^2H_3$]	C(1)	C(2)	C(3)	C(4)	C(5)
Pent-1-ene (87·3)	2·4	93·2	4·3	2·0 (2·0)	1·0 (1·0)	1·0 (2·0)	1·1 (2·0)	3·1 (3·0)
trans-Pent-2-ene (2·8)	3·4	91·5	5·1	—	—	—	—	—
cis-Pent-2-ene (9·9)	3·8	91·7	4·5	2·4 (3·0)	2·0 (2·0)		1·1 (2·0)	2·7 (3·0)

[a] Numbers of ^1H atoms on each carbon atom in product, relative to C(1) = 2·0 for pent-1-ene and C(2) + C(3) = 2·0 for *cis*-pent-2-ene. *trans*-Pent-2-ene was not analysed. Numbering scheme:

1 2 3 4 5 and 1 2 3 4 5
C=C–C–C–C C–C=C–C–C.

(*Received*, 16*th September* 1977; *Com.* 965.)

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