

STEREOSELECTIVE REDUCTION WITH RANEY NICKEL CATALYSTS

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The selective reduction of the exocyclic methylene group to produce one stereoisomer is frequently required in the synthesis of terpenoid natural products¹ or in industrial processes².

Homogeneous and heterogeneous hydrogenations of 4-t-butylmethylenecyclohexane³, β -pinene⁴, and 2-methylmethylenecyclohexane⁵ have been carried out with noble metal catalysts and a comprehensive examination made of the reduction of the isomeric methylmethylenecyclohexanes (I) which will be described elsewhere⁵.

Nickel catalysts have not been used in such reductions and a novel effect has now been found in which the ratio of stereoisomeric dimethylcyclohexanes produced depends upon the age of the catalyst. High proportions of the cis or trans isomer are produced with Raney nickel catalysts as shown typically in Table 1 (fresh catalyst compared with 16 hrs. aged catalyst).



TABLE 1

PROPORTIONS OF DIMETHYLCYCLOHEXANES OBTAINED FROM EXOCYCLIC (I) AND ENDOCYCLIC OLEFINS (II) WITH RANEY NICKEL CATALYSTS

Raney Catalyst	(I) 2-methyl		(I) 3-methyl		(I) 4-methyl		(II) 4-methyl	
	cis	trans	cis	trans	cis	trans	cis	trans
New	59	41	70	30	32	68	45	55
Old	72	28	27	73	72	28	67	33

Following these general results obtained with no special precautions a more detailed examination of the preparative aspects was made in an attempt to obtain higher yields of the cis and trans isomers.

These are described in Table 2 where all the experiments relate to new (unaged) catalyst.

TABLE 2
VARIATION OF PREPARATIVE CONDITIONS USED FOR RANEY NICKEL CATALYSTS

Expt. No.	Conditions of Catalyst Preparation	Compound Hydrogenated	Composition of Product (dimethylcyclohexane)	
			cis	trans
1	control runs with fresh catalyst without special precautions in the catalyst preparation.	3-methylmethylene cyclohexane	70	30
2		4-methylmethylene cyclohexane	22	78
3	with N ₂ . No outgassing of catalyst. Adsorbed H ₂ used.	3-methylmethylene cyclohexane	X.S.	
4	Catalyst prepared in hydrogenation apparatus containing N ₂ . Adsorbed H ₂ used.	3-methylmethylene cyclohexane	81	19
5	Catalyst prepared in hydrogenation apparatus containing N ₂ . Added H ₂ used.	4-methylmethylene cyclohexane	15	85
6	Catalyst prepared and left in alkaline solution overnight (with H ₂ present), washed.	3-methylmethylene cyclohexane	81	19
7	H ₂ O only used in catalyst preparation. No methanol wash. H ₂ atmosphere. H ₂ O used in hydrogenation. Slowed rate of reaction.	3-methylmethylene cyclohexane	86	14
8	H ₂ atmosphere maintained in preparation of catalyst. Washed with H ₂ saturated H ₂ O, MeOH.	3-methylmethylene cyclohexane	83	17
9	minimum vol. of H ₂ O used and methanol only for hydrogenation. N ₂ atmosphere.	4-methylmethylene cyclohexane	17	83
10	Fresh catalyst. N ₂ atmosphere.	1,4-dimethyl cyclohexene-1	-	more than 90%

Since it seemed likely that some deterioration of fresh catalyst would result from oxygen present in the water and methanol used, experiments nos. 5,7,8 carried out established that the selectivity of the fresh catalyst was enhanced by the exclusion of air. Ageing of the catalyst, normally evident after a few hours, did not occur and its high activity was maintained if the prepared catalyst was left in alkaline suspension overnight (expt. 6). It is evident that the results are not due to a directional effect, one isomer arising from adsorbed hydrogen⁶ and the other from the addition of gaseous hydrogen, since the same results were obtained with and without a nitrogen atmosphere (expts 3,4,9). Furthermore the same isomer distribution would have been likely for all the methylmethylenecyclohexanes.

Experiments as yet incomplete are in hand with D_2H_2 to elucidate the mechanism.

It seems most likely that a fresh Raney catalyst causes some isomerisation of the exocyclic to an endocyclic olefin (there is some GLC evidence for this) both of which would lead to different proportions of dimethylcyclohexanes. The adsorbed hydrogen in the fresh catalyst which allows hydrogenation to proceed in a nitrogen atmosphere may also encourage facile isomerisation.

Fresh and aged Sabatier-type catalyst prepared by the decomposition of nickel formate did not behave in a similar selective way. The behaviour of Raney nickel in the present instance is apparently associated with the surface-absorbed hydrogen and its diffusion, both consequent upon the nature of the alloy used in the catalyst preparation. In view of its cheapness the above observations have, it is believed, some practical significance since it is evident that Raney nickel dependent upon its age can fulfil the role of both palladium and platinum catalysts¹.

1. J.H.P. Tyman and B.J. Willis, Tetrahedron Letters, 1970, 51, 4507.
2. B.D. Sully, Chem. and Ind., 1964, 263.
3. T.R.B. Mitchell, J.Chem.Soc., (C), 1970, 823. S. Siegel and B. Dmichovsky, J.Amer.Chem.Soc., 1962, 84, 3132.
4. G.C. Bond, G.H.D. Royston and D.E. Webster, Abstracts, 4.18, Joint Annual Meeting. R.I.C./Chem.Soc., Nottingham, April 1969.
5. S. Siegel and G.V. Smith, J.Amer.Chem.Soc., 1960, 82, 6082.
6. J.H.P. Tyman and P.N. Fiveash, J.H.P. Tyman and R.C. Owen (unpublished work). Contribution to Joint Annual Meeting R.I.C./Chem.Soc., Nottingham, April 1969.
7. R.J. Kokes and P.H. Emmett, J.Amer.Chem.Soc., 1959, 81, 5032.