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STEREOCHEMISTRY AND MECHANISM OF THE HYDROGENATION OF SUBSTITUTED CYCLOPENTENES

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Abstract—1,2- and 2,3-disubstituted cyclopentenes were hydrogenated with several transition metal catalysts. The hydrogenation of 1,2-disubstituted cyclopentenes gave preferably the *cis* products with Raney Ni, whereas 2,3-disubstituted cyclopentenes gave preferably the *trans* isomers. The *trans* products were favoured in the hydrogenation of 1,2- and 2,3-dialkylcyclopentenes with Pt or Pd catalysts. A detailed product analysis of the hydrogenation of 1,2-dialkylcyclopentenes indicates that the double bond migration occurred to form 2,3-dialkylcyclopentenes in advance of the hydrogenation. In contrast, 1-methyl-2-phenylcyclopentene gave predominantly the *cis* product irrespective of the kind of catalyst. These results suggest the formation of a π-benzylic species during the course of the reaction. The mechanism is discussed in terms of the modified Horiuti-Polanyi mechanism.

We have previously pointed out that the stereochemistry of the hydrogenation of substituted methylenecycloalkanes[1,2] and cycloalkanones[1,3] depends on the chemical and steric structure of the substituents, catalysts and reaction conditions. In this paper, the hydrogenation using a variety of transition metal catalysts of 1,2- and 2,3-disubstituted cyclopentenes is reported. Although the hydrogenation of 1,2- and 2,3-dimethylcyclopentene with PtO_2 has been investigated by Siegel *et al*,[4] several disubstituted cyclopentenes were hydrogenated and the mechanism of the reaction is discussed in terms of the modified Horiuti-Polanyi mechanism.[2]

The hydrogenation of disubstituted cyclopentenes was performed at room temperature and at ordinary pressure. The isomer distribution of the products is summarized in Table 1. Scheme 1 shows a possible reaction course on the basis of the modified Horiuti-Polanyi mechanism. In this scheme, the substrate (**1**) is adsorbed on the catalyst to form π-type adsorption species. Two π-type of adsorption states, the *cis* and the *trans* adsorbed species (**2a** and **2b**) are expected. These are converted to σ-type adsorption states (**2'a** and **2'b**). Then, the first hydrogen transfers from the catalyst to the substrates and the σ-type adsorption species whose structure is a 3-membered ring including metal atom change to the half-hydrogenated states (**4a–4d**) whose molecular geometry is the same as the product through the transition states (**3a–3d**). The second hydrogen transfers to the half-hydrogenated states (**4a–4d**) and the epimeric products (**5a** and **5b**) are obtained.

Dialkylcyclopentenes. The hydrogenation of 1,2-dialkylcyclopentenes over freshly prepared Raney Ni gave preferably the *cis* products. In contrast, the *trans* products were favoured in the hydrogenation of 2,3-dialkylcyclopentenes. On Raney Ni aged for 7 days almost the same product distribution was obtained as on the freshly prepared catalyst.

Since the product determining step of the Raney Ni hydrogenation of olefins is the adsorption of the substrate on the catalyst,[2] 1,2-disubstituted cyclopentene is adsorbed on the catalyst surface and the hydrogen transfer from the catalyst occurs subsequently to the adsorbed species to give the *cis* product. The formation of 25–28% of the alternative isomer indicates that some of the parent cyclopentene converted to 2,3-dialkylcyclopentene and/or 2-alkylmethylenecyclopentane by the double bond migration on the catalyst surface. In the case of the hydrogenation of 2,3-disubstituted cyclopentenes we feel that the dominant factor to determine the isomeric product distribution is the effect of torsional angle effects in the transition state for intimate σ-type adsorption species formation from π-type one. In going from one of the π-type adsorption species (**2a**) to the corresponding σ-type one (**2'a**), the Me group at the 2 position is bent toward the same side of the alkyl group at the 3 position and the dihedral angle is decreased. Since the σ-type adsorption species whose structure is assumed to be a 3-membered ring just the same as an epoxide,[2,5] the Me group at the 2 position may not pass by the substituent at the 3 position. Thus, the torsional angle energy contribution to the transition state increases. In contrast, in going from the alternative π-type adsorption species (**2b**) to the corresponding σ-type (**2'b**), the Me group at the 2 position is bent toward the opposite side of the

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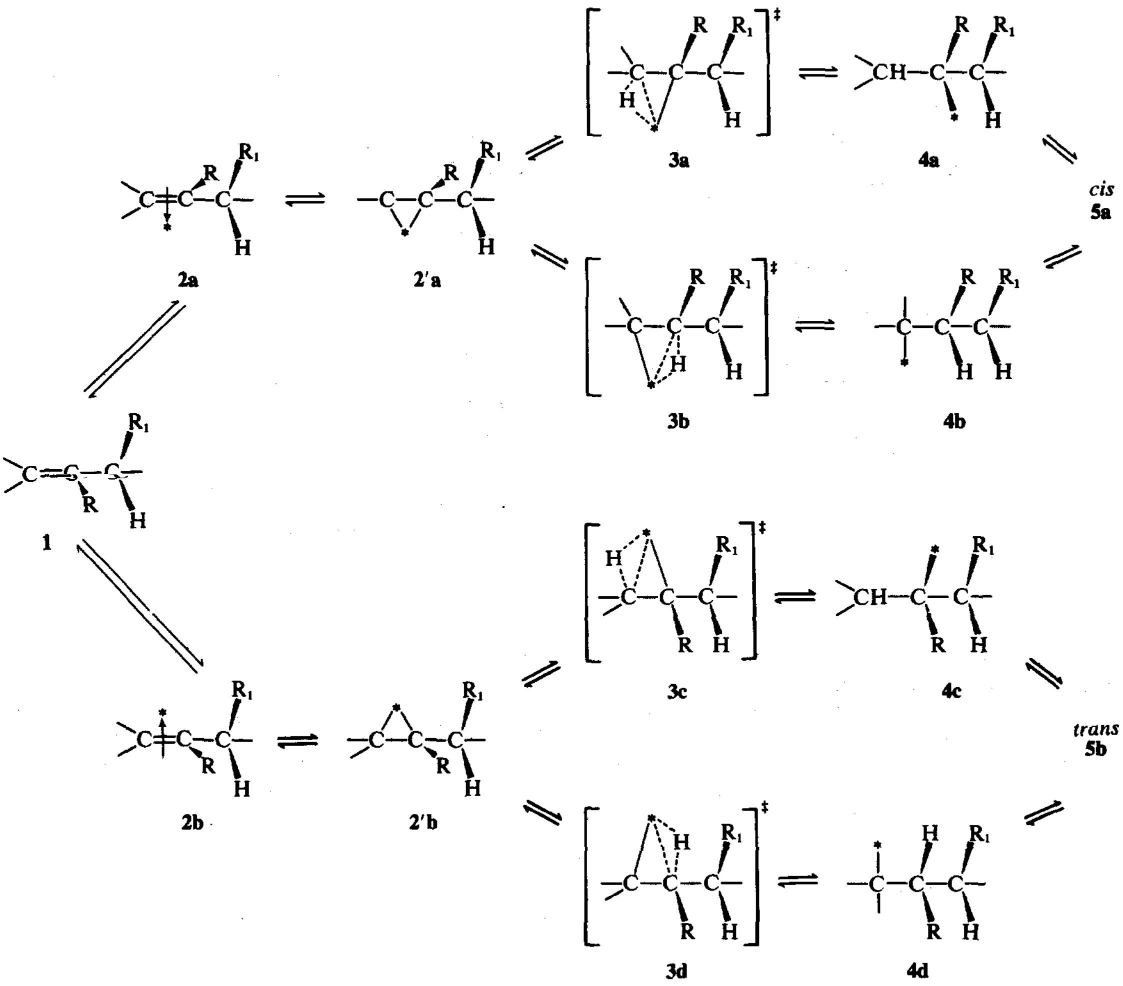
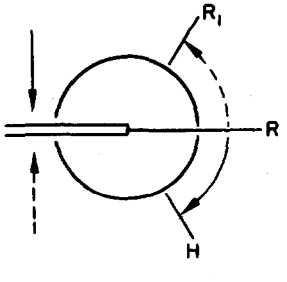


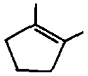
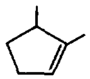
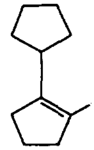
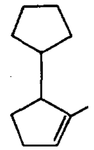
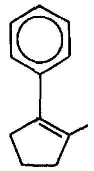
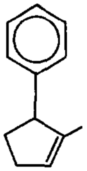
SCHEME 1



alkyl group at the 3 position and the dihedral angle is increased. Thus, the torsional angle energy contribution to the transition state decreases. Torsional angle effects, therefore, favour the *trans* product formation over the *cis* product. We must also take the catalyst hindrance into consideration, but the isomer distribution of the products indicates that the torsional angle effects may be dominant over the catalyst hindrance of the substituent at the 3 position. More *trans* saturated product from 2-methyl-3-cyclopentylcyclopentene than 2,3-dimethylcyclopentene also infers that the dominant controlling factor to determine the product distribution is not the catalyst hindrance but the torsional angle strain. When 2,3-dialkylcyclopentenes were hydrogenated, the formation of a small amount of 1,2-disubstituted cyclopentenes was found during the reaction. Such a double bond migration supports our previous postulate that the double bond migration occurs *via* π-allylic adsorbed species as a by-pass route[2] (Table 2) (Scheme 2).

The *trans* saturated products were favoured over PtO_2 in ethanol. In acetic acid less stereoselectivity was observed. Similar isomeric product distribution was obtained over Pt-black. The isomeric product distributions from 1,2-disubstituted cyclopentenes were very close to those of 2,3-disubstituted ones. Detailed product analysis is shown in Table 3. These results suggest that the double bond migration of 1,2-disubstituted cyclopentenes occurred to

Table 1. Hydrogenation of substituted cyclopentenes[a, b]

Substrate						
Catalyst	Product Composition (cis %)					
Raney Ni-A[c]	72	30	73	17	100	46
Raney Ni-B[d]	73	35	75	17	—	—
PtO_2	31	22	17	21	92	41
PtO_2(AcOH)	44[e]	—[f]	42	—	93	42
Pt-black	26	30	23	18	93	47
Pt-black(AcOH)	—	—	—	—	94	—
Pd-C	20	21	13	13	99	90
Pd-C(AcOH)	—	—	14	—	98	73
Rh-C	82	42	80	42	98	66

[a] In ethanol unless otherwise indicated.

[b] Substrate, 1/2000 mol: Catalyst; Raney Ni, 100 mg; PtO_2, 10 mg; Pt, 10 mg; Pd-C, 20 mg; Rh-C, 10 mg; Solvent, 2·0 ml.

[c] Freshly prepared catalyst.

[d] Aged for 7 days.

[e] Siegel and Dmuchovsky report that 1,2-dimethylcyclopentene gives 43% of *cis*. (Ref 4).

[f] Siegel and Dmuchovsky report that 2,3-dimethylcyclopentene gives 42% of *cis*. (Ref 4).

Table 2. Hydrogenation of substituted cyclopentene over Raney Ni[a]

Cyclopentene	Catalyst	Composition of Resulting Mixture (%) Cyclopentane	Cyclopentene Original	Cyclopentene Isomerised
1,2-Dimethyl-(I)	A[b]	46	54	t[e] (II)
	B[c]	68	32	t (II)
2,3-Dimethyl-(II)	B	78	25	7 (I)
1-Cyclopentyl-2-methyl-(III)	A	34	66	t (IV)
	B	28	72	t (IV)
2-Methyl-3-cyclopentyl-(IV)	C[d]	62	34	4 (III)
2-Methyl-3-phenyl-(VI)	A	54	56	t (V)

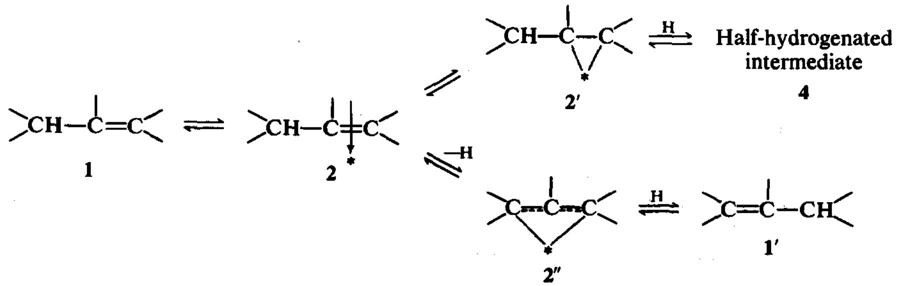
[a] In ethanol.

[b] Freshly prepared.

[c] Aged for 7 days.

[d] Aged for 15 days.

[e] Trace.



Scheme 2
Double bond migration *via* π-allylic species

Table 3. Hydrogenation of substituted cyclopentene over Pt catalyst[a]

Cyclopentene	Catalyst	Composition of Resulting Mixture (%) Cyclopentane	Cyclopentene Original	Isomerised
1,2-Dimethyl-(I)	PtO_2	92	0	8 (II)
	Pt-black	46	52	2 (II)
2,3-Dimethyl-(II)	Pt-black	76	0	24 (I)
1-Cyclopentyl-2-methyl-(III)	PtO_2	43	55	2 (IV)[b]
	Pt-black	66	33	1 (IV)
1-Methyl-2-phenyl-(V)	PtO_2	44	17	39 (VII)[c]
	Pt-black	64	26	10 (VII)
2-Methyl-3-phenyl-(VI)	PtO_2	44	52	4 (V)
	Pt-black	35	61	4 (V)

[a]In ethanol.
[b]2-Methyl-3-cyclopentylcyclopentene.
[c]2-Phenyl-3-methylcyclopentene.

form 2,3-disubstituted cyclopentenes in advance of the hydrogenation. Consequently, the apparent product ratio obtained in the hydrogenation may be that from the corresponding 2,3-disubstituted cyclopentenes. Since the hydrogen transfer from the catalyst surface to the σ-type adsorption species is product determining over Pt,[6] the predominance of the *trans* isomer in the hydrogenation of 2,3-dialkylcyclopentene is ascribed to torsional angle effects. In the presumed transition states (**3a–3d**) the carbon–metal bond of the σ-type adsorption species is hydrogenolysed; the *cis* product forms from **3a** or **3b** and the *trans* from **3c** or **3d**. In **3a** and **3b** the Me group is bent further toward the same side of the alkyl group at the 3 position and is almost exactly eclipsed or may pass by the alkyl group at the 3 position. By contrast, in the case of the transition state, **3c** or **3d**, only the torsional angle strain between the Me group at the 2 position and the hydrogen at the 3 position is expected. The *trans* product, therefore, will be predominant.

The hydrogenation of 1,2- or 2,3-dialkylcyclopentenes over Pd gave predominantly the *trans* products. The product determining step of the hydrogenation of olefin on Pd is the hydrogen transfer from the catalyst surface to the half-hydrogenated intermediate.[7] In the hydrogenation over Pd, the double bond migration occurred *via* π-allylic adsorbed species[2] as well as the half-hydrogenated intermediate to form the mixture of 1,2- and 2,3-dialkylcyclopentene during the hydrogenation (Table 4). Since the relative rate of the hydrogenation of trisubstituted olefin is much faster than that of tetrasubstituted olefin, the hydrogenation of 1,2-disubstituted cyclopentenes proceeded essentially *via* 2,3-disubstituted ones. As a consequence, the *trans* product may be predominant.

Rhodium catalysed hydrogenation proceeded to give preferably the *cis* product from 1,2-dialkyl- and the *trans* from 2,3-dialkylcyclopentenes. These results indicate that the stereoselectivity of Rh is close to Ni rather than to Pt.

Phenyl substituted cyclopentenes. In the hydrogenation of 1-methyl-2-phenylcyclopentene more *cis* isomer was obtained than in that of 1,2-dialkylcyclopentenes irrespective of the kind of catalyst. On Raney Ni the hydrogenation proceeded only to give *cis* 1-methyl-2-phenylcyclopentane. Although more *trans* isomer was obtained in the hydrogenation of 1,2-dialkylcyclopentenes over Pd-carbon, more than 98% of the *cis* product formed from 1-methyl-2-phenylcyclopentene. Detailed product analysis shows that much double bond migration to form 2-phenyl-3-methylcyclo-

Table 4. Hydrogenation of substituted cyclopentene over Pd-carbon[a]

Cyclopentene	Composition of Resulting Mixture (%) Cyclopentane	Cyclopentene Original	Isomerised
2,3-Dimethyl-(II)	37	4	59 (I)[b]
1-Cyclopentyl-2-methyl-(III)	89	11	0
2-Methyl-3-cyclopentyl-(IV)	36	3	61 (III)
1-Methyl-2-phenyl-(V)	29	28	43 (VII)[c,d]
2-Methyl-3-phenyl-(VI)	13	84	3 (V)

[a]In ethanol.
[b]1,2-Dimethylcyclopentene.
[c]2-Methyl-3-phenylcyclopentene (1%) is included.
[d]2-Phenyl-3-methylcyclopenttene.

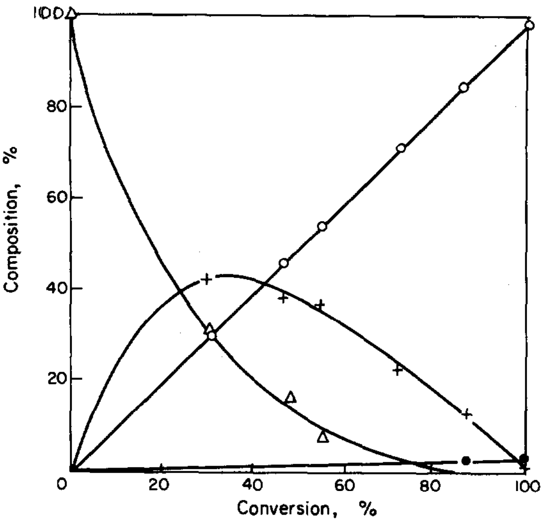
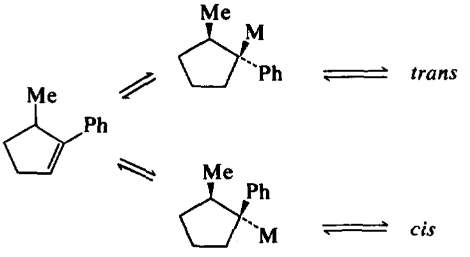


Fig 1. Hydrogenation of 1-methyl-2-phenylcyclopentene over Pd-carbon in ethanol; Δ 1-Methyl-2-phenylcyclopentene; + 2-Phenyl-3-methylcyclopentene; ○ *cis* 1-Methyl-2-phenylcyclopentane; ● *trans* 1-Methyl-2-phenylcyclopentane.

pentene occurred at an early stage of the reaction (Fig 1). This indicates that the apparent product ratio seems to be essentially the result of the hydrogenation of 2-phenyl-3-methylcyclopentene. It is known that in the hydrogenation of C—C double bond with an aryl group at the sp^2 C atom, π-benzylic species forms on Pd because this species may be energetically more favoured than the alternative.[8] Since the hydrogen transfer to the half-hydrogenated intermediate is product determining on this catalyst, the *cis* isomer will be favoured.



Half-hydrogenated intermediate

The *cis* isomer was favoured on Pt similar to the case on Pd-carbon. Mitsui *et al.* reported that in the hydrogenation of phenyl-substituted cyclohexenes, such as 1-methyl-2-phenylcyclohexene and 2-phenyl-3-methylcyclohexene, the *cis* products were preferably obtained irrespective of the kind of catalyst.[8] They suggested that in the σ-type adsorbed state as well as in the adsorbed π-type, the phenyl group is hardly bent toward the opposite side of the catalyst but is retained the initial conformation (The phenyl group is on the same plane as that of the cyclohexene double bond) forming the π-styryl adsorption species (**2d** and **2'd**), and that the hydrogen transfers to the homo-benzylic C atom to form π-benzylic half-hydrogenated intermediate (**4f**). In the case of 1-methyl-2-phenylcyclopentene, π-benzylic and π-styryl species may slso form on Pt or Ni as well as Pd. The torsional angle strain between the phenyl group

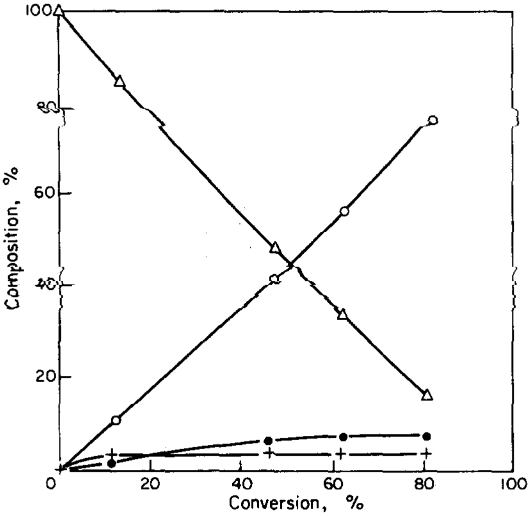
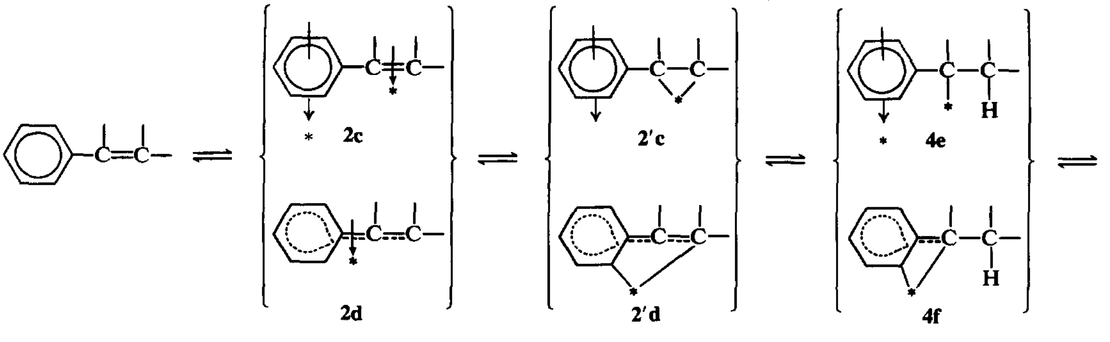


Fig 2. Hydrogenation of 2-methyl-3-phenylcyclopentene over Pd-carbon in ethanol. Δ 2-Methyl-3-phenylcyclopentene; + 1-Methyl-2-phenylcyclopentene; ○ *cis* 1-Methyl-2-phenylcyclopentane; ● *trans* 1-Methyl-2-phenylcyclopentane.



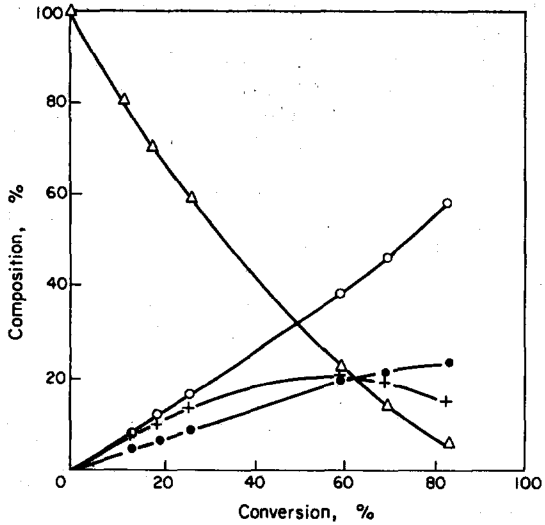


Fig 3. Hydrogenation of 2-methyl-3-phenylcyclopentene over Rh-carbon in ethanol. △ 2-Methyl-3-phenylcyclopentene; + 1-Methyl-2-phenylcyclopentene; ○ *cis* 1-Methyl-2-phenylcyclopentane; ● *trans* 1-Methyl-2-phenylcyclopentane.

and the vicinal alkyl group is not considered as a major factor to determine the isomeric product distribution even in the hydrogenation over Pt.

The hydrogenation of 2-methyl-3-phenylcyclopentene over Pd or Rh-carbon gave preferably the *cis* product; 90% in ethanol and 73% in acetic acid on Pd and 66% in ethanol on Rh. If it is possible to consider that this reaction is similar to the case of 2,3-dialkylcyclopentene, the formation of the *trans* isomer would be favoured. Detailed product analysis shows that a small amount of 1-methyl-2-phenylcyclopentene appeared in the course of the hydrogenation and the *cis* to the *trans* ratio gradually increased as the reaction progressed (Fig 2). Taking account of the rapid migration of the double bond at high catalyst ratio[2] (in the present study, substrate; 79 mg/Pd-carbon; 20 mg), the hydrogenation of 2-methyl-3-phenylcyclopentene which is expected to have some energies of resonance stabilization by conjugation of the double bond with the π-electrons of the phenyl group. Similarly, the *cis* product was favoured on Rh-carbon. The formation of the appreciable amount of 1-methyl-2-phenylcyclopentene and the gradual increase of the stereoselectivity were noticed in the course of the hydrogenation (Fig 3). These results infer the double bond migration over Pt or Ni to some extent resulting in an increase of the amount of the *cis* product compared to the case of 2,3-dialkylcyclopentenes.

EXPERIMENTAL

Materials. 1,2- And 2,3-dimethylcyclopentenes were prepared by the iodine catalysed dehydration of 1,2-dimethylcyclopentanol which was obtained conventionally from 2-methylcyclopentanone and MeMgI. The dried products were distilled, b.p. 100–102°, and the isomers were separated by preparative gas chromatography. 1-Cyclopentyl-2-methylcyclopentene and 2-methyl-3-cyclopentylcyclopentene were prepared similarly from 2-cyclopentylcyclopentanone. Phenyl-substituted cyclopentenes were prepared by the dehydration of 1-methyl-2-phenylcyclopentanol with P_2O_5. These two isomers were separated by fractional distillation; 1-methyl-2-phenylcyclopentene, b.p. 113°/16 mm; 2-methyl-3-phenylcyclopentene, b.p. 120°/34 mm. The assignment of structure is corroborated by the IR and NMR spectra.

Catalytic hydrogenation. The following general procedure was used. A known amount of substrate and catalyst in the solvent was stirred with H_2 at an ordinary temp. After the reaction the catalyst was removed by centrifugal method and the mixture was analysed by gas chromatography.

Gas chromatographic analysis. Hitachi F-6 and K-53 gas chromatograph equipped with flame ionization detector was used with Infotronics digital integrator. The products were analysed on a 45 m × 0·25 mm Goley column of PEG 4000 at 150° (The hydrogenation products from methylphenylcyclopentene), PEG 400 at 60° (The hydrogenation products from dimethylcyclopentene), or Apiezon grease at 140° (The hydrogenation products from cyclopentylmethylcyclopentene).

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