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STEREOCHEMISTRY AND THE MECHANISM OF THE HYDROGENATION OF SUBSTITUTED CYCLOPENTANONES AND METHYLENECYCLOPENTANES

S. MITSUI, H. SAITO, S. SEKIGUCHI, Y. KUMAGAI and Y. SENDA*
Department of Applied Science, Tohoku University, Sendai, Japan

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Abstract—2-Alkylmethylenecyclopentanes and 2- and 3-alkylcyclopentanones were hydrogenated over several transition metal catalysts. The stereochemistry of the reaction which is discussed in terms of the Horiuti-Polanyi mechanism shows the sharp contrast by the structure of the substrates, catalysts and the reaction conditions. In the platinum catalyst hydrogenation of cyclopentanones and methylenecyclopentanes the shape of the transition state of the hydrogen transfer from the catalyst to the adsorbed species which has olefin-like molecular geometry is considered to be product-like. This would support the previous postulate that the complex aluminium hydride reduction of cyclopentanone has essentially a product-like transition state in which the ring carbon C_1 rehybridizes from sp^2 to $sp.^3$

ALTHOUGH the stereochemistry of the hydrogenation of cyclohexanones is governed by the von Auwers–Skita hydrogenation rule,[1] which was somewhat modified by Barton[2] introducing the concept of conformation, this rule has not been applied always to the hydrogenation of cyclohexanones.[3] Practically, the steric course of the reaction depends on the chemical and the steric structures of the substrates, catalysts and the reaction conditions. In order to investigate the stereochemistry and the mechanism of the hydrogenation of 5-membered ring compounds which have *exo*-cyclic double bond, alkylcyclopentanones and alkylmethylenecyclopentanes which have a structure similar to the corresponding ketones were hydrogenated over Raney nickel, palladium, platinum or rhodium catalyst in ethanol.

The plausible reaction course of the hydrogenation is shown in Scheme 1 on the basis of the Horiuti–Polanyi mechanism.[4] In this scheme, the substrate (**1**) is adsorbed on the catalyst. Two adsorption states, the *cis* and the *trans* adsorbed species (**2a** and **2b**) are expected. Then, the first hydrogen transfers from the catalyst surface to the substrates and the adsorbed species which have olefin-like molecular geometry[5] change to the half-hydrogenated states (**4a**–**4d**) whose molecular geometries are the same as the products through the transition states (**3a**–**3d**). The second hydrogen transfers to the half-hydrogenated states (**4a**–**4d**) and the epimeric products (**5a** and **5b**) will be obtained.

In the hydrogenation of methylenecyclopentane, two types of the half-hydrogenated states in which the carbon-metal bond remains at the ring carbon atom C_1 or the terminal methylene carbon atom are supposed. In the case of cyclopentanones, on the other hand, the oxygen-metal bond may remain more likely than the carbon-metal bond because of the relative stabilities between the carbon-metal bond and the oxygen-metal bond.[6] Therefore, the hydrogenation may proceed mainly *via* the (**4b**) or (**4d**) type half-hydrogenated state.

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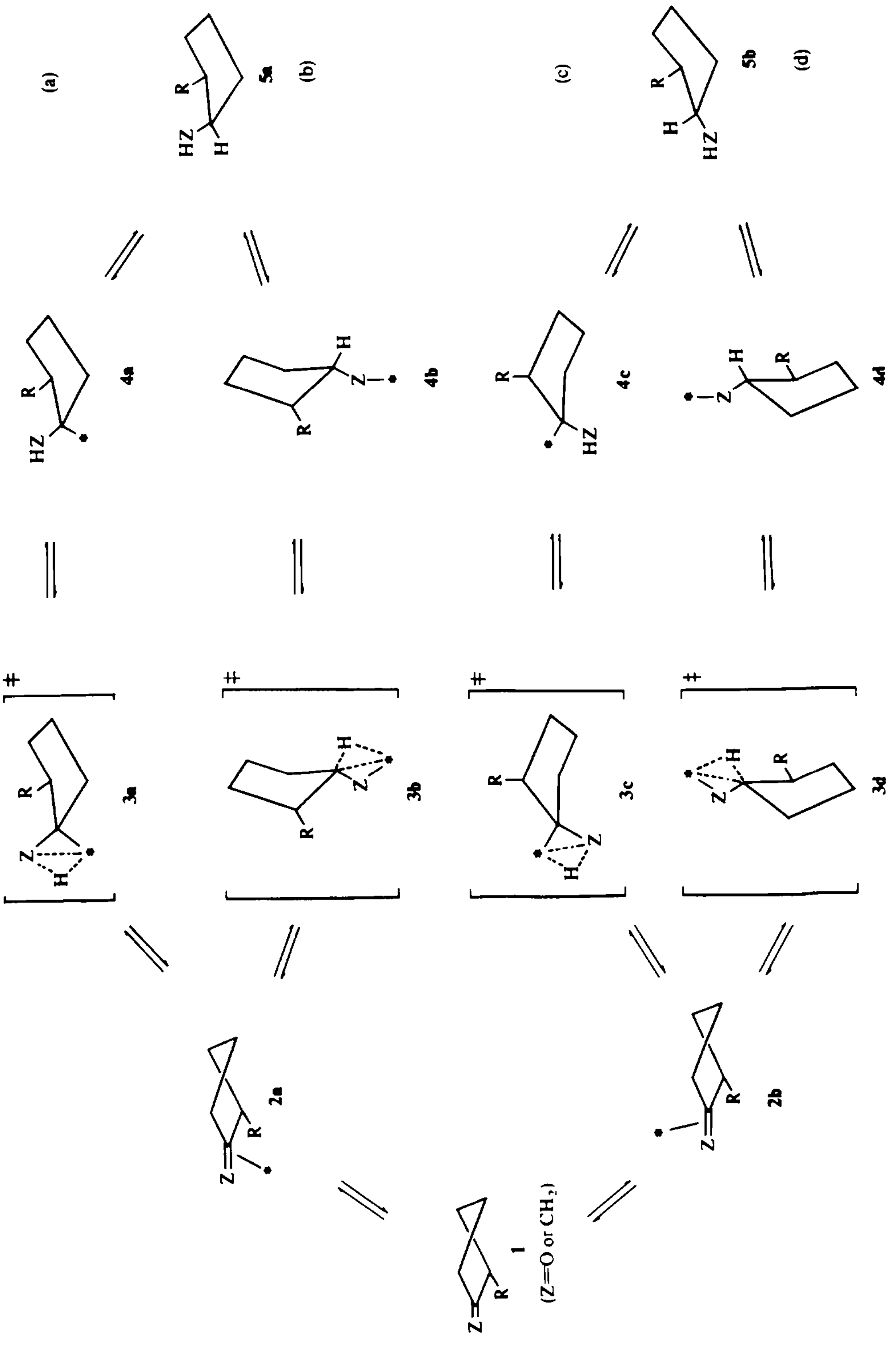
* To whom correspondance should be addressed.



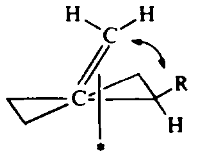
SCHEME 1

2-*Alkylcyclopentanones and methylenecyclopentanes*

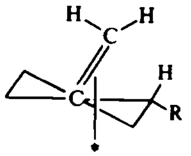
Raney Nickel catalyst. The hydrogenation of cyclopentanones proceeded to give preferably the *cis* saturated products, while that of *exo*-methylene compounds yielded the saturated products, the ratio of which was almost unity when the substituent at the 2 position was the Me group. 2-Cyclopentylmethylenecyclopentane gave preferably the *trans* isomer

Mitsui *et al.* reported that the sterochemical results of the hydrogenation of cyclohexenes, cyclopentenes, cyclohexenols and cyclopentenols over Raney Ni was quite different from those over Pd or Pt catalyst. They proposed that the product determining step of this reaction might be the adsorption of the substrates on the catalyst.[7] The product determining step of the hydrogenation of ketones over Raney Ni is also considered to be the same reaction step as that of olefins.

From the stereochemical results, the course of the hydrogenation of cyclopentanones seems to be governed by the catalyst hindrance of the substituent. On the other hand, comparing the molecular geometry of the *cis* and the *trans* adsorbed species of methylenecyclopentanes using a Dreiding model, we found that the terminal methylene group which carries the hydrogens is close to the substituent at the 2 position in the *cis* adsorbed species than in the *trans* adsorbed one. As a consequence, the appreciable torsional strain between these two groups may be expected in **2a**, whereas no interaction in **2b**.



cis
2a



trans
2b

The result of the hydrogenation of 2-cyclopentylmethylenecyclopentane favoring the *trans* isomer implies that the steric interaction between the terminal methylene group and the substituent at the 2 position may compensate the catalyst hindrance of the substituent.

Platinum catalyst. Siegel and Smith reported that the product determining step of this reaction is the formation of the half-hydrogenated state in the hydrogenation of cycloalkenes and methylenecycloalkanes.[8] The product determining step of the hydrogenation of ketones is also considered to be the same reaction step of that of olefins. 2-Methylcyclopentanone afforded 74% of the *trans* 2-methylcyclopentanol over Pt black catalyst*. Transfer of the Me group at the 2 position to the cyclopentyl group had no significant influence on the isomer distribution of the products.

Although it has been suggested that the complex metal hydride reduction of cyclohexanones and the hydroboration of methylenecyclohexanes have a reactant-

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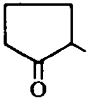
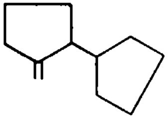
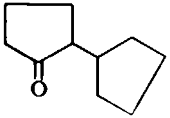
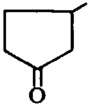
* Pt black is the catalyst which is prepared by the hydrogen reduction of PtO_2 and is washed well with distilled water.

like transition state,[9] from the results of LAH reduction of cyclopentanones and the difference in reactivity between cyclohexanone and cyclopentanone we proposed that the complex aluminium hydride reduction of cyclopentanones has a product-like transition state.[10] If it is possible to extend the above assumption to the hydrogenation of cyclopentanone and methylenecyclopentane, the transition state of the transfer of the first hydrogen to the adsorbed species may be product-like and the relative stabilities of the epimeric half-hydrogenated states (**4b** and **4d**) reflect on those of the transition states (**3b** and **3d**). As a consequence, the *trans* isomer which is obtained from **3d** will be preferred to the *cis* isomer which is obtained from **3b**. Mitsui *et al* found that when PtO_2 was used as the catalyst the ratio of the axial hydroxyl product to the equatorial was always smaller than that when Pt black was used in the hydrogenation of cyclohexanones.[11] They considered that this might be due to the effect of the alkaline substance which was contained in the catalyst. Such trends, however, did not appear in the hydrogenation of cyclopentanones.

In contrast to the ketone, *exo*-methylene compounds gave predominantly the *cis* isomers irrespective of the substituent at the 2 position. Keeping in mind the two assumptions that the *trans* adsorbed species is more stable than the *cis* and that the transition state of the transfer of the first hydrogen resembles the product as in the case of ketone, the *cis* product may be favoured because the *cis* isomeric intermediate (**4a**) is more stable than the *trans* (**4c**) when the carbon-metal bond remains at the C_1 carbon atom in the half-hydrogenated state. On the other hand, when the carbon-metal bond remains at the terminal methylene carbon atom the half-hydrogenated state (**4d**) in which the substituent R is equatorial-like is more stable than **4b** in which the substituent R is axial-like similar to the case of the ketone. Therefore, in contrast to the case in which the carbon-metal bond remains at the C_1 carbon atom, the *trans* product is supposed to be favoured. But the isomer distribution of the products obtained from the hydrogenation infers that the participation of the latter course of the reaction (course b and d) was little. It is said that the stability of the carbon-metal bond is usually in the order; primary > secondary > tertiary,[12] but the IR spectral study shows the hydrogen transfer to the adsorbed propylene on silica-supported Pt had occurred to give the half-hydrogenated intermediate whose carbon-metal bond did not exist at the terminal carbon atoms but at the middle of the carbon chain.[13] The hydrogenolysis of saturated hydrocarbons over Pt catalyst also indicated the carbon-metal bond existed at the more substituted carbon atom in the half-hydrogenated state.[14] This evidence supports the reaction course a and c as being the major ones.

Palladium catalyst. Cyclopentanones over Pd catalyst were less reactive than over Pt or Raney Ni. 2-Methylcyclopentanone gave 73% of *trans* 2-methylcyclopentanol at an ordinary hydrogen pressure in the low conversion. Siegel and Smith reported that the hydrogenation of cycloalkenes gave preferably more stable products. From these results they confirmed that the transfer of the second hydrogen to the half-hydrogenated species was the product determining step.[15] The results obtained in the present study show that in the hydrogenation of cyclopentanones over Pd charcoal, which contained a small amount of alkaline substance, the reaction step from the half-hydrogenated intermediates to the products is the product determining step just as in the hydrogenation of alkenes. Thus, the preceding reactants and inter-

TABLE 1. HYDROGENATION OF SUBSTITUTED CYCLOPENTANONES AND METHYLENECYCLOPENTANES[a]

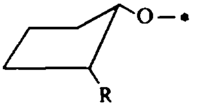
					
Catalyst	Product (*cis* %)				
Raney Ni (aged 1 day)	45	80	26	73	66
Raney Ni (aged 1 day) + NaOH[b]		81	—	—	—
Raney Ni (aged 2–4 weeks)	50	81	24	81	—
Raney Ni (aged 2–4 weeks) + NaOH[b]	—	86	—	—	—
Pt Black	74	27	71	41	75
PtO_2	75	26	71	50	76
5% Rh charcoal	-	54	—	41	50
5% Rh charcoal + NaOH[b]	—	40	—	58	—
5% Pd charcoal	33	27[c]	15	—	72

[a] Hydrogenation was performed in ethanol at ordinary temperature and pressure.

[b] 0·2 mmol.

[c] When the hydrogen pressure was set at 78 atm. 73% of the *cis* 2-methylcyclopentanol was obtained.

mediates tend to become equilibriated with one another. A consideration of the energy states of two epimeric half-hydrogenated intermediates of substituted cyclopentanones supplies a rationale for these results.



4b

4d

The structure **4b** leads to the *cis* isomer, while the *trans* isomer is obtained from **4d**. Of these two isomers **4b** has a much higher energy and is less likely, while **4d** has lower energy and is more favoured. The *trans* saturated product from **4d** may be the major one.

When the hydrogen pressure was set at 78 atm 73% of the *cis* isomer was obtained. This result suggested that at high hydrogen pressure the hydrogen transfer from the catalyst surface to the half-hydrogenated species became easy and the product determining step shifted to the other reaction steps. Comparing this result with that over Pt or Raney Ni, product distribution over Pd was close to that over Raney Ni. This may mean the product determining step of this reaction shifted toward the adsorption of the substrate on the catalyst.

The hydrogenation of methylenecyclopentanes gave preferably the *trans* product. A detailed study of 2-cyclopentylmethylenecyclopentane showed that at the early stage of the hydrogenation the migration of *exo*-cyclic double bond had occurred to afford cyclopentylmethylcylopentenes (Figure 1). Therefore, the product ratio obtained did not indicate the result from the *exo*-methylene compound but that from the

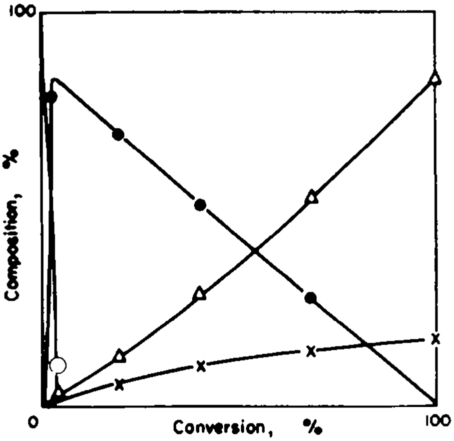


FIG 1. Hydrogenation of 2-cyclopentylmethylenecyclopentane on 5% Palladium-Charcoal
○ 2-Cyclopentylmethylenecyclopentane
△ *trans* 2-Cyclopentylmethylcyclopentane
× *cis* 2-Cyclopentylmethylcyclopentane
● Cyclopentylmethylcyclopentenes
(Substrate 50 mg, 5% Pd-C 10 mg, Ethanol 2·0 ml)

cyclopentene derivatives. When the amount of the catalyst was decreased in the reaction system, the ratio of the epimeric saturated products did not change significantly even at the early stage of the reaction* (Table 2).

TABLE 2. HYDROGENATION OF 2-CYCLOPENTYLMETHYLENECYCLOPENTANE ON 5% PALLADIUM-CHARCOAL

Composition of resulting mixture			*cis* % of
Saturated product (%)	Isomerized product (%)	Starting material (%)	Saturated product
3	34	63	25
6	76	18	27
10	90	0	24

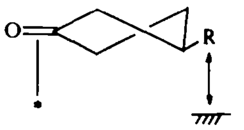
(Substrate 50 mg, 5% Pd-C 2·5 mg, Ethanol 3·0 ml)

Methylcyclopentene is far more stable than methylenecyclopentane.[16] This fact infers that the double bond of methylenecyclopentane easily migrates to the inside of the ring to form methylcyclopentene.

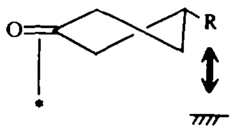
Rhodium catalyst. 2-Methylcyclopentanone gave almost equal amounts of the *cis* and *trans* isomers. By the addition of sodium hydroxide in the reaction system, the amount of *cis* 2-methylcyclopentanol decreased to become 40%. On the other hand, the hydrogenation of 2-cyclopentylcyclopentanone proceeded to give 41% of the *cis* isomer. The presence of alkaline substance increased the amount of the *cis* isomer.

3-*methylcyclopentanone*

The hydrogenation of 3-methylcyclopentanone was also performed. The *cis* isomer was preferably obtained irrespective of the catalysts except in the case of the rhodium catalyzed hydrogenation in which an equal amount of the *cis* and the *trans* isomer was obtained. Since the product determining step of the hydrogenation over Raney Ni is considered to be the absorption of the substrates on the catalyst, the catalyst hindrance may be a major factor in determining the stereochemistry of the reaction. Since two adsorbed species; **A** and **B** are assumed, **A** has less catalyst hindrance than **B** so that the *cis* isomer from **A** will be favoured.



A



B

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* Mitsui *et al.* found that in the hydrogenation of methylenecyclohexane derivatives the ratio of the epimeric saturated products changed significantly depending on the amounts of the Pd charcoal catalyst. Unpublished results.

TABLE 3. EXPERIMENTAL DATA OF CATALYTIC HYDROGENATION[a]

Catalyst	Weight of (mg)	Reaction Time (hr)	The Composition of the Resulting Mixture (%)		Others
			Saturated Product	Starting Material	
(1) 2-Methylmethylenecyclopentane(50 mg) in ethanol(2·0 ml)					
Raney Ni	100	2	79	21	t[c]
Raney Ni*[b]	100	2	80	20	t
PtO_2	10	2	100	0	0
Pt-black	10	2	100	0	0
5% Pd-C	10	2	38	54	8
(2) 2-Cyclopentylmethylenecyclopentane(50 mg) in ethanol(2·0 ml)					
Raney Ni	100	2	81	0	19
Raney Ni*	100	2	89	0	11
PtO_2	10	2	100	0	0
Pt-black	10	2	91	0	9
5% Rh-C	10	2	100	0	0
5% Pd-C	10	2	100	0	0
(3) 2-Methylcyclopentanone(100 mg) in ethanol(5·0 ml)					
Raney Ni	100	20	90	10	t
+ NaOH[d]	100	20	100	0	t
Raney Ni*	200	20	8	92	t
+ NaOH	200	20	81	19	t
PtO_2	5	22	72	20	8
PtO_2	5	22	72	20	8
Pt-black	5	22	65	8	27
5% Rh-C	50	5	37	0	63
+ NaOH	50	16	98	0	2
5% Pd-C	20	32	51	49	t
(4) 2-Cyclopentylcyclopentanone(100 mg) in ethanol(5·0 ml)[e]					
Raney Ni	100	5	99	0	1
Raney Ni*	200	5	100	0	t
PtO_2	20	5	9	91	0
Pt-black	20	5	6	92	2
5% Rh-C	40	5	63	20	17
+ NaOH	40	5	85	10	5
(5) 3-Methylcyclopentanone(100 mg) in ethanol(5·0 ml)					
Raney Ni	100	10	100	0	0
PtO_2	5	10	91	9	0
Pt-black	5	10	8	92	t
5% Rh-C	25	10	85	0	15
5% Pd-C	1000	10	22	75	3
(6) 2-Methylcyclopentanone(100 mg) in ethanol(2·0 ml) at high pressure (initial pressure 78 atm.)					
5% Pd-C	20	5	32	63	5

[a] An ordinary hydrogen pressure unless otherwise indicated.

[b] Raney nickel aged for 2–4 weeks. [c] trace, [d] 0·2 mmol

[e] No hydrogenation occurred on 5% Pd-C.

The *cis* 1,3-disubstituted cyclopentane is thermodynamically more stable than the *trans* isomer.[17] Therefore, in the hydrogenation over a Pt catalyst in which the transfer of the first hydrogen to the substrates is considered to control the product composition, the *cis* isomer may be the major product because the molecular geometry of the transition state of this reaction step is assumed to be product-like. In the case of Pd catalyst, since thermodynamical stabilities of the two half-hydrogenated intermediates are considered to reflect the product distribution as in the hydrogenation of 2-substituted cyclopentanones, the *cis* isomer should be preferred.

EXPERIMENTAL

Materials. 2-Methylcyclopentanone was prepared from 1-methylcyclopentene by the method of Brown *et al.*[18,19] 2-Cyclopentylcyclopentanone was prepared by the method of Hückel *et al.*[20] 3-Methylcyclopentanone was prepared by the aldol-type self-condensation of acetonylacetone in 2% NaOHaq,[21] followed by the hydrogenation over 5% Pd charcoal. 2-Methylmethylenecyclopentane was prepared by the method of Corey *et al.*[22] Sodium hydride, 2·0 g and 20 ml dimethyl sulfoxide (DMSO) was heated for 1 hr at 70° in a N_2 atmosphere and then cooled in an ice bath, and a soln of 20 g methyltriphenylphosphonium bromide in 50 ml DMSO was added. The red soln was stirred for 15 min at room temp; then 5·0 g 2-methylcyclopentanone was added. The mixture was stirred for an additional hr and poured into a large volume of ice water (400 ml) and the soln was extracted 3 times with pentane. After drying on $CaCl_2$, the pentane was removed and 2-methylmethylenecyclopentane was distilled, b.p. 110°, in a yield of 1·5 g (30%). 2-Cyclopentylmethylenecyclopentane was obtained in a yield of 3·8 g (78%), b.p. 90–94° (20 mm). Compounds which had earlier been prepared agreed in physical constants with those reported in the literature. All compounds were also checked by gas chromatography and NMR and IR spectra.

Catalytic hydrogenation. The following general procedure was used. A known amount of substrate and catalyst in EtOH was stirred with hydrogen at an ordinary temp. After the reaction was over the catalyst was filtered off and the mixture was analysed by gas chromatography. At high hydrogen pressure, a known amount of substrate, catalyst and EtOH were placed in a 100 ml autoclave and the initial pressure of hydrogen was set at 78 atm. After stirring for 5 hr the catalyst was filtered off and the mixture was analysed by gas chromatography. The experimental details are summarized in Table 3.

Gas chromatographic analyses. Hitachi F-6 and K-53 gas chromatograph equipped with flame ionization detector was used with Infortonics digital integrator. The product hydrocarbons were analysed on a 45 m × 0·25 mm Goley column of PEG 400 at 60° (The hydrogenation products from 2-methylmethylenecyclopentane) or 90° (The hydrogenation products from 2-cyclopentylmethylenecyclopentane). Cyclopentanols obtained were analysed on a 45 m × 0·25 mm Goley column of PEG 4000 at 120° (The hydrogenation products from 2-methylcyclopentanone) or 150° (The hydrogenation products from 2-Cyclopentylcyclopentanone). The products of 3-methylcyclopentanone were analysed as acetates on a 45 m × 0·25 mm Goley column of PEG 400 at 80°.

REFERENCES

[1] K. von Auwers, *Liebigs Ann.* **420**, 91 (1920); A. Skita, *Ibid.* **431**, 1 (1923); A. Skita and W. Faust, *Ber. Dtsch. Chem. Ges* **64**, 2878 (1931)

[2] D. H. R. Barton, *J. Chem. Soc.* 1027 (1953)

[3] W. G. Dauben, *J. Am. Chem. Soc.* **78**, 3752 (1956); E. G. Pepplatt and R. J. Wicker, *J. Chem. Soc.* 3125 (1955); D. N. Jones and G. H. R. Summers, *Ibid.* 2594 (1959)

[4] J. Horiuti and M. Polanyi, *Trans. Faraday Soc.* **30**, 1164 (1934)

[5] I. Jardine and F. J. McQuillin, *J. Chem. Soc.* 5535 (1964)

[6] K. Hanaya, *Bull. Chem. Soc. Japan* **43**, 442 (1970)

[7] Y. Sugi, A. Nanbu and S. Mitsui, *Shokubai* (*Catalyst*) **12**, 67p (1970)

[8] S. Siegel and G. V. Smith, *J. Am. Chem. Soc.* **82**, 6082 (1960)

[9] J. Klein and D. Lichtenberg, *J. Org. Chem.* **35**, 2654 (1970); and the refes cited

[10] Y. Senda, S. Mitsui, R. Ono and S. Hosokawa, *Bull. Chem. Soc. Japan* **44**, 2737 (1971)

[11] S. Mitsui et al., unpublished result

[12] S. Mitsui and A. Kasahara, *The Chemistry of Alkenes* (Edited by J. Zabicky) Vol. 2, p. 188, Wiley, London (1970)

[13] N. Sheppard, *Pure and Appl. Chem.* **4**, 71 (1962)

[14] H. Matsumoto, Y. Saito and Y. Yoneda, *J. Catal.* **19**, 101 (1970)

[15] S. Siegel and G. V. Smith, *J. Am. Chem. Soc.* **82**, 6087 (1960)

[16] S. Forsen and M. Milsson, *The Chemistry of Carbonyl'Group* (Edited by J. Zabicky) Vol. 2, p. 167. Interscience, London (1970)

[17] I. Lillien and K. Khaleeluddin, *Chem. & Ind.* 1028 (1964)

[18] H. C. Brown and C. P. Garg, *J. Am. Chem. Soc.* **83**, 2951 (1961)

[19] H. C. Brown, K. J. Murrary, L. J. Murray, J. A. Sonver and G. Zweifel, *Ibid.* **82**, 4233 (1960)

[20] W. Hückel, M. Maier, E. Jordan and W. Seeger, *Liebigs Ann.* **616** 46 (1958)

[21] H. Hunsdiecker, *U.S.* 2,387–587, Oct. 23, 1945, *Chem. Abstr.* **40**, 3131 (1946)

[22] R. Greenwald, M. Chaycovsky and E. J. Corey, *J. Org. Chem.* **28**, 1128 (1963)