

Effect of Ring Size on Hydrogenation of 2-Benzylidenecycloalkanols

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Reduction of 2-benzylidenecycloalkanones with lithium aluminium hydride gave the corresponding allylic cycloalkanols. After catalytic hydrogenation of these cyclic allylic alcohols, over a number of catalysts, five components were obtained by chromatography. In each case these were the hydrogenolysis product, the *cis*- and *trans*-2-(cyclohexylmethyl)cycloalkanols, and the *cis*- and *trans*-2-benzylcycloalkanols. The stereochemistry of the resulting, separated, epimeric cycloalkanols was determined by an n.m.r. method. The proportions of the products are interpreted in terms of stereochemical arguments.

SINCE the work of Linstead on the reduction of phenanthrenes,¹ many aspects of the stereochemistry of catalytic hydrogenation have been made comprehensible in terms of the approach, fit, and binding of the reducible molecule to the catalyst surface.^{2,3} These ideas have been successfully applied to molecules whose geometry or substituents present severe steric hindrance to this approach or fit.⁴ More recently, instances⁵⁻⁷ have been reported in which the presence of polar substituents, notably OH, has produced hydrogenation stereochemistry opposite that predicted on the basis of purely steric considerations. It is logical to interpret this effect in terms of an attractive interaction binding the hydroxy-group to the catalyst surface during reduction so as to enforce addition of hydrogen from the same side.

Hydrogenolysis of benzylic alcohols occurs with retention of configuration over nickel and with inversion over palladium, suggesting that the difference in affinities of nickel and palladium for the oxygen atom not only controls the stereochemistry of the hydrogenolysis, but will also control that of the hydrogenation of the double bond of allylic alcohols.^{6d} In order to ascertain the combined effects of hydroxy-group and ring size on the stereochemistry of hydrogenation of allylic alcohols, five-, six-, and seven-membered 2-benzylidenecycloalkanols have been studied.

RESULTS AND DISCUSSION

2-Benzylidenecyclopentanol (1).—Calculations on cyclopentane derivatives containing sp^2 -hybridised atoms, such as methylenecyclopentane and cyclopentanone, suggest that such molecules exist in the half-chair form, with the maximum puckering at carbon atoms 3 and 4,

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¹ R. P. Linstead, W. E. Doering, S. B. Davis, P. Levine, and R. R. Whetstone, *J. Amer. Chem. Soc.*, 1942, **64**, 1985.

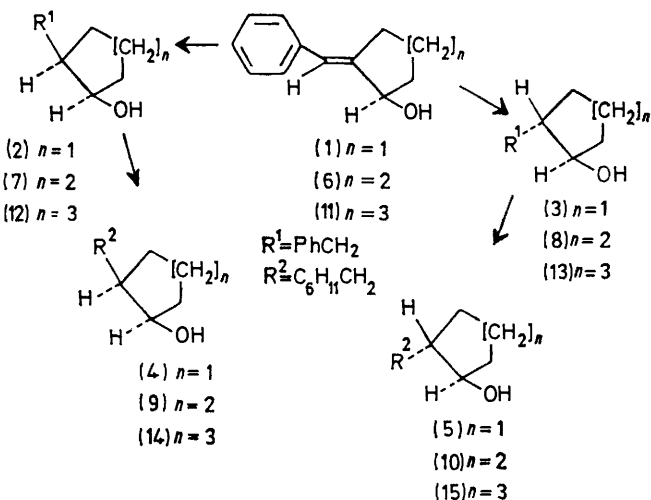
² R. L. Burwell, jun., *Chem. Rev.*, 1957, **57**, 895.

³ (a) S. Siegel and G. V. Smith, *J. Amer. Chem. Soc.*, 1960, **82**, 6082; (b) J. F. Sauvage, R. H. Baker, and A. S. Hussey, *ibid.*, 1960, **82**, 6090; (c) S. Siegel and B. Dmuchovsky, *ibid.*, 1962, **84**, 3132; (d) S. Siegel and B. Dmuchovsky, *ibid.*, 1964, **86**, 2192; (e) S. Siegel, *Adv. Catal. Relat. Subj.*, 1966, **16**, 123.

⁴ H. I. Hadler, *Experientia*, 1955, **11**, 175.

i.e. away from the sp^2 -hybridised atom.⁸ In the hydrogenation of compound (1) over Raney nickel, a catalyst of low isomerising ability,⁹ 49% of the *cis*-benzyl derivative (2) is obtained.

A model of structure (1) shows that there are two possible adsorption conformations of the unsaturated



alcohol: in one the OH is directed towards the catalyst surface (A), and in the other it is directed away (B). It

⁵ (a) L. S. Minckler, A. S. Hussey, and R. H. Baker, *J. Amer. Chem. Soc.*, 1956, **78**, 1009; (b) W. G. Dauben, J. W. McFarland, and J. B. Rogan, *J. Org. Chem.*, 1961, **26**, 297; (c) M. C. Dart and H. B. Henbest, *J. Chem. Soc.*, 1960, 3563; (d) T. G. Halsall, W. J. Rodewald, and D. Willis, *ibid.*, 1959, 2798; (e) N. B. Haynes and C. J. Timmons, *Proc. Chem. Soc.*, 1958, 345.

⁶ (a) T. J. Howard, *Chem. and Ind.*, 1963, 1899; (b) T. J. Howard, *Rec. Trav. chim.*, 1964, **83**, 992; (c) S. Nishimura and K. Mori, *Bull. Chem. Soc. Japan*, 1963, **36**, 318; (d) S. Mitsui, Y. Senda, and H. Saito, *ibid.*, 1966, **39**, 696; (e) T. J. Howard and B. Morley, *Chem. and Ind.*, 1967, 73; (f) R. K. Sehgal, R. U. Koenigsberger, and T. J. Howard, *J. Org. Chem.*, 1975, **40**, 3073.

⁷ (a) J. E. McMurry, *Tetrahedron Letters*, 1970, 3731; (b) H. W. Thompson, *J. Org. Chem.*, 1971, **36**, 2577; (c) G. Brieger, D. L. Hachey, and D. Ciarimitaro, *ibid.*, 1969, **34**, 220; (d) H. W. Thompson and R. E. Naipawer, *J. Amer. Chem. Soc.*, 1973, **95**, 6379.

⁸ K. S. Pitzer and W. E. Donath, *J. Amer. Chem. Soc.*, 1959, **81**, 3213.

⁹ R. L. Augustine, 'Catalytic Hydrogenation,' Arnold, London, 1965, p. 68.

seems that the phenyl group suppresses the effect of the OH group to a large extent. As the molecule approaches the catalyst surface, it is adsorbed through the π -electrons of the double bond and the phenyl group with its face lying parallel to the surface from which hydrogen is abstracted, with the OH either directed away from or towards the catalyst. Both conformations seem equally favourable, the phenyl group controlling the mode of

C_γ -equatorial OH and C_α -H only, whereas in conformer (Ib) the strain is that due to the interaction of OH with two axial hydrogen atoms. To a first approximation, it is more likely that in this case (I) exists predominantly as conformer (Ia) with the ring substituent equatorial.^{5c} In the hydrogenation of compound (6) over Raney nickel, 56% of the *cis*-benzyl derivative (7) is obtained.

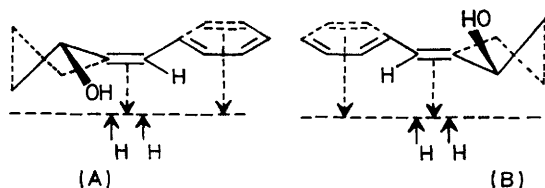
Molecular models of structure (6) show that the only

TABLE I
Products of hydrogenation of 2-benzylidenecyclopentanol^a (% total chromatographic area)^b

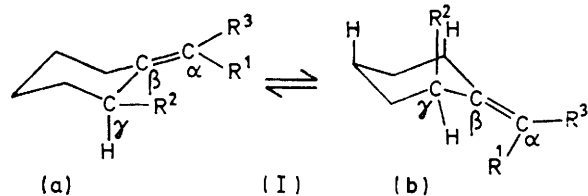
Catalyst	Conditions	2-Benzyl cyclopentane	Mixture of epimeric 2-(cyclohexylmethyl) cyclopentanols	<i>cis</i> -2-Benzylcyclopentanol	<i>trans</i> -2-Benzylcyclopentanol
B.D.H. Raney nickel	98–65 atm, 6 h 13–28 °C			49	51
Pd-C	10 atm, 2 h	4		55.5	40.5
Pd black	10 atm, 2 h	5		60	35
Ni ₂ B P-1	70 atm, 6 h			64	36
Pd-C	98–100 atm, 6 h	3	7	51.5	38.5
Ru-C	82.5 atm, 6 h	6	14	44	36
Pt-C	10 atm, 2 h	27	4	46	23
Rh-C	10 atm, 2 h	1	93	4	2

^a Over various catalysts at room temperature. The product consisted of five components. However, there appeared to be four components under the conditions of quantitative analyses. Product compositions were determined by g.l.c. on a bentone 34-silicone oil column. ^b The technique of g.l.c. with an argon ionization detector for quantitative analysis of high molecular-weight components was applied by C. C. Sweeley and Ta-C. L. Chang (*Analyt. Chem.*, 1961, **33**, 1861) to elucidate the relation of structure to molar response. The presence of most functional groups slightly lowered the response in comparison with hydrocarbons. Since the components obtained on hydrogenation are similar in nature, no significant variation in molar response is expected.

adsorption. The results of hydrogenation of compound (1) over a number of catalysts are presented in Table I.



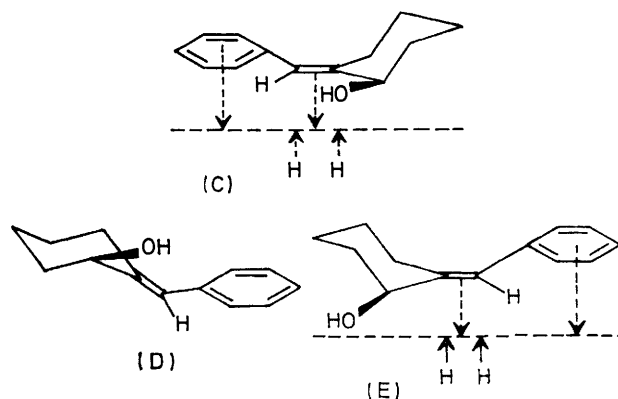
2-Benzylidenecyclohexanol (6).—Aspects of steric hindrance associated with substituted allylic groups in conformers (a) and (b) of structure (I) have been considered.¹⁰ Models of structure (Ia) show that even when



R^2 and R^1 are only moderately large they will interfere with each other drastically; in fact more so than if they were 1,3-diaxially related in a cyclohexane ring. Barring rearrangement of the double bond, relief of this strain can be attained most easily by conformational inversion to (Ib). If R^1 and R^2 are small, the equilibrium should lie to the left; if they are of medium size or large it should lie to the right.¹¹ Thus if $R^1 = H$ and $R^2 = OH$, in the conformer (Ia) the strain is that due to the interaction of

¹⁰ F. Johnson and S. K. Malhotra, *J. Amer. Chem. Soc.*, 1965, **87**, 5492.

adsorption conformation with OH equatorial in which the double bond can be presented in a planar manner to the surface is that shown in (C). Addition of hydrogen *cis* from the catalyst surface will then give (7).



To explain the formation of 44% of the *trans*-benzyl derivative (8), it is suggested that as the molecule approaches the catalyst surface from the alternative side for adsorption (D), owing to the directing effect of the phenyl group, a conformational inversion takes place: one chair form flips into the other chair form (E). The adsorption conformation (E), with OH axial and which will give the *trans*-benzyl derivative (8) by addition of hydrogen *cis* from the catalyst surface, can be presented in a planar manner to the surface. Thus, as in the case of (1), the phenyl group, by controlling the mode of

¹¹ S. K. Malhotra and F. Johnson, *J. Amer. Chem. Soc.*, 1965, **87**, 5493.

adsorption, has a powerful directing effect. The results of hydrogenation of (6) over a number of catalysts are presented in Table 2.

In the hydrogenations of compounds (1) and (6) over rhodium, the main product is a mixture of cyclohexylmethyl derivatives [(4) and (5) or (9) and (10), respectively], in accord with the observations that rhodium is an outstanding catalyst for hydrogenation of aromatic compounds under atmospheric conditions,¹² and that

2-Benzylidenecycloheptanol (11).—From models, it seems likely that cycloheptanone,^{15,16} a structural analogue of (11), exists as a mixture of conformers. From a study of the cyanohydrin dissociation constants of the methyl-substituted cycloheptanones, it has been concluded that the cycloheptanone ring exists in a flexible chair conformation.¹⁷ There seems to be little difference between the energies of the twist-chair and normal chair conformations, for cycloheptanone.

TABLE 2
Products of hydrogenation of 2-benzylidenecyclohexanol^a (% total chromatographic area)^b

Catalyst	Conditions	2-Benzylcyclohexane	Mixture of epimeric 2-(cyclohexylmethyl)cyclohexanols	<i>cis</i> -2-Benzylcyclohexanol	<i>trans</i> -2-Benzylcyclohexanol
B.D.H. Raney nickel	10 atm, 6 h			56	44
	100—94 atm, 6 h 21—33.5 °C			56	44
Pd-C	10 atm, 6 h	1	1	58	40
Pd black	10 atm, 2 h	2		57	41
Ni ₂ B P-1	10 atm, 2 h			59	41
Pd-C	99—100 atm, 6 h	2	13	50	35
Ru-C	10 atm, 2 h	8	6	45.5	40.5
Pt-C	98—99 atm, 6 h	18	3	46	33
	10 atm, 6 h	15	2	46.5	36.5
Rh-C	10 atm, 2 h	1	62	18	19

^a Over various catalysts at room temperature. The product consisted of five components. However, there appeared to be four components under the conditions of quantitative analyses. Product compositions were determined by g.l.c. on a bentone 34-silicone oil column. ^b See footnote b, Table 1.

TABLE 3
Products of hydrogenation of 2-benzylidenecycloheptanol^a (% total chromatographic area)^b

Catalyst	Conditions	2-Benzylcycloheptane	Mixture of epimeric 2-(cycloheptylmethyl)cycloheptanols	<i>cis</i> -2-Benzylcycloheptanol	<i>trans</i> -2-Benzylcycloheptanol
B.D.H. Raney nickel	10 atm, 6 h			31	69
	82.5—87.5 atm, 6 h, 25.5—28.5 °C	4		33.5	62.5
Pd-C	10 atm, 2 h	2		54	44
Pd black	10 atm, 2 h	3		51.5	45.5
Ni ₂ B P-1	10 atm, 6 h, 16—21 °C	1	1	40	58
Ru-C	99—100 atm, 6 h, 11—21 °C	2	54	17.5	26.5
	10 atm, 9 h, 10—21 °C	9	2	42	47
Pt-C	97.5—99 atm, 6 h, -2 to +10 °C	18	2	35	45
	10 atm, 2 h	1	8	33	58
Rh-C	90—98 atm, 6 h, 0—7 °C	1	97	0.5	1.5

^a Over various catalysts at room temperature. The product consisted of five components. However, there appeared to be four components under the conditions of quantitative analyses. The second component, consisting of a mixture of *cis*- and *trans*-2-(cycloheptylmethyl)cycloheptanols (by n.m.r. in Me₂SO) was not separable by chromatography on all columns tried. Product compositions were determined by g.l.c. on a bentone 34-silicone oil column. ^b See footnote b, Table 1.

this reaction is accompanied by only a small amount of hydrogenolytic cleavage of oxygen and nitrogen substituents.¹³ The results (at 10 atm) indicate that the catalytic activity for hydrogenation of the benzene ring is in the order Rh > Ru > Pt > Pd.¹⁴ Over platinum, the OH is removed to an appreciable extent, in conformity with the extensive hydrogenolysis of methoxy-groups in the presence of platinum.¹³

¹² G. Gilman and G. Cohn, *Adv. Catalysis*, 1957, **9**, 733.

¹³ H. A. Smith and R. G. Thompson, *Adv. Catalysis*, 1957, **9**, 727.

¹⁴ A. Amano and G. Parravano, *Adv. Catalysis*, 1957, **9**, 716.

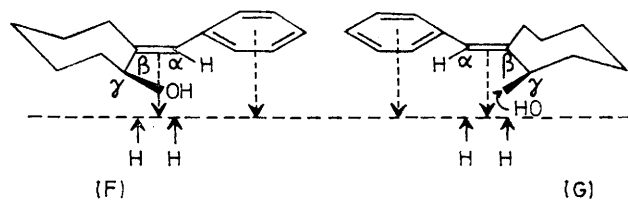
¹⁵ N. L. Allinger, *J. Amer. Chem. Soc.*, 1959, **81**, 5727.

Molecular models of (11) indicate that two adsorption conformations [(F) and (G)] having minimum non-bonded interactions are possible, *i.e.* either side of the double bond can be presented in a planar manner to the catalyst. However, the two adsorption conformations in the normal chair form differ only in that in one the OH is quasi-axial (F) and there is a distance of 1.95 Å between C_α-H and C_γ-OH, whereas in the other the OH is quasi-equatorial (G) and the corresponding distance

¹⁶ C. G. LeFèvre, R. J. W. LeFèvre, and B. P. Ran, *J. Chem. Soc.*, 1959, 2340.

¹⁷ O. H. Wheeler and E. G. de Rodriguez, *J. Org. Chem.*, 1964, **29**, 718.

is 1.45 Å. However, the C_α -H, C_γ -OH interactions could be modified in the twist-chair conformation. Since 69% of the *trans*-benzyl derivative (13) is obtained over Raney nickel, the adsorption conformation (F) appears the more favoured.



The factors responsible for the preference for the conformation (F) are not readily apparent. The possibility that the course of hydrogenation may be controlled primarily by the relative stabilities of the epimeric products cannot be ruled out. The possibility of a [1,3] sigmatropic hydrogen shift also exists.¹⁸ The occurrence of such a shift could lead to more *trans*-product than expected from purely steric considerations. The results of hydrogenation of (11) over a number of catalysts are presented in Table 3.

From hydrogenation over rhodium, the main product is a mixture of cyclohexylmethyl derivatives [(14) and (15)] (at 100 atm). However, at 10 atm only a small amount of this mixture is obtained. Similarly over ruthenium (at 100 atm), a mixture of (14) and (15) is obtained as the major product. As in the case of compounds (1) and (6), the catalytic activity for hydrogenation of the benzene ring is in the order $Rh > Ru > Pt > Pd$, and over platinum the OH is removed to an appreciable extent at 100 atm and to some extent at 10 atm. Dinickel boride has some tendency to cause isomerisation and palladium has the highest isomerising ability.^{6e}

EXPERIMENTAL

Microanalyses were performed in the laboratories of Dr. A. Bernhardt, Mulheim, Germany. I.r. spectra were run for solutions in carbon tetrachloride with a Unicam SP 200 spectrophotometer (only strong absorptions are reported). N.m.r. spectra were taken with a Perkin-Elmer R10 (60 MHz) spectrometer (tetramethylsilane as internal standard). Mass spectra (70 eV) were obtained with an A.E.I. MS-12 instrument. G.l.c. analyses were performed with a Pye-Argon gas chromatograph. Preparative g.l.c. separations were done with an Aerograph Autoprep model 705 gas chromatograph.

Hydrogenation of 2-Benzylidenecyclopentanol (1).¹⁹—Compound (1) was hydrogenated over various catalysts in 95% ethanol under the conditions shown in Table 1. The products were separated by preparative g.l.c. on a bentone 34-silicone oil (B34Si) column. The first component was inferred to be benzylcyclopentane from its i.r. spectrum (ν_{\max} .

† Direct experimental evidence for the configurations and conformations of epimeric 2-benzyl- and 2-(cyclohexylmethyl) cycloalkanols was obtained by an n.m.r. method, in which the magnitude of the splitting of the hydroxy-proton resonance in dimethyl sulphoxide was employed. In all cases the hydroxy-proton of the axial alcohol resonates at significantly higher field than that of the equatorial one, and the method showed promise for detecting conformational differences (see ref. 20).

700, 1 455, 2 880, and 2 960 cm^{-1} ; showing a monosubstituted benzenoid system and the absence of a functional group). The second and third components (mixture) were indicated to be the cyclohexylmethyl derivatives (4) and (5) by i.r. (ν_{\max} . 900, 1 025, 1 450, 2 860, 2 950, and 3 680 cm^{-1}) and mass spectra [m/e 182 (M^+) and an intense peak at 164]. The identification was confirmed by preparing authentic samples of (4) and (5) and comparison of retention times on a B34Si column.

cis-2-(Cyclohexylmethyl)cyclopentanol (4). Hydrogenation of the benzyl derivative (2) (100 mg) over rhodium-carbon (5%; 50 mg) in ethanol (25 ml) at a maximum pressure of 43 atm and at room temperature for 6 h gave the product (4) as a single component (g.l.c. on B34Si column); τ [(CD_3)₂SO] † 5.95 (d, J 3.6 Hz, OH) (the peak at τ 5.98 is more intense than that at τ 5.92).

trans-2-(Cyclohexylmethyl)cyclopentanol (5). Hydrogenation of the benzyl derivative (3) (100 mg) over rhodium-carbon (5%; 50 mg) in ethanol (25 ml) at a maximum pressure of 40 atm and at room temperature for 6 h gave the product (5) as a single component (g.l.c. on B34Si column); τ [(CD_3)₂SO] 5.67 (d, J 4.8 Hz, OH).

The fourth component was the *cis*-benzyl derivative (2); m/e 176 (M^+); τ [(CD_3)₂SO] 5.74 (d, J 3.6 Hz OH); the 3,5-dinitrobenzoate had m.p. 91–92° (from ethanol) (lit.,²¹ 90–92°).

The fifth component was the *trans*-benzyl derivative (3); τ [(CD_3)₂SO] 5.54 (d, J 4.8 Hz, OH); the 3,5-dinitrobenzoate had m.p. 66–67° (from ether-hexane) (Found: C, 61.8; H, 5.1; N, 7.85. $\text{C}_{19}\text{H}_{18}\text{N}_2\text{O}_6$ requires C, 61.6; H, 4.9; N, 7.55%).

Catalytic Hydrogenation of 2-Benzylidenecyclohexanol (6).^{5c}—Compound (6) was hydrogenated over various catalysts in 95% ethanol under the conditions shown in Table 2. The products were separated by preparative g.l.c. on a B34Si column. The first component was benzylcyclohexane, ν_{\max} . 700, 1 100, 1 135, 1 450, 2 840, and 2 910 cm^{-1} (monosubstituted benzenoid system; no functional group) (Found: C, 89.45; H, 10.45. Calc. for $\text{C}_{15}\text{H}_{18}$: C, 89.6; H, 10.4%).

The second and third components (mixture) were indicated to be the cyclohexylmethyl derivatives (9) and (10), ν_{\max} . 970, 980, 1 045, 1 445, 2 840, 2 910, and 3 630 cm^{-1} . This identification was confirmed by preparing authentic samples of (9) and (10) and comparison of retention times on a Carbowax column.

cis-2-(Cyclohexylmethyl)cyclohexanol (9). Hydrogenation of the benzyl derivative (7) (250 mg) over rhodium-carbon (5%; 50 mg) in ethanol (25 ml) at a maximum pressure of 45 atm and at room temperature for 6 h gave the product (9), m.p. 47–48° (from ethanol) (lit.,²² 46–48°) [its phenylurethane (from acetone) had m.p. 112° (lit.,²² 114–115°)], τ [(CD_3)₂SO] 5.99 (d, J 3.0 Hz, OH). G.l.c. on a Carbowax column showed a single component.

trans-2-(Cyclohexylmethyl)cyclohexanol (10). Hydrogenation of the benzyl derivative (8) (250 mg) over rhodium-carbon (5%; 50 mg) in ethanol (25 ml) at a maximum

¹⁸ R. Touroude, L. Hilaire, and F. G. Gault, *J. Catalysis*, 1974, **32**, 279.

¹⁹ H. O. House and R. L. Wasson, *J. Amer. Chem. Soc.*, 1956, **78**, 4394.

²⁰ R. K. Sehgal, R. U. Koenigsberger, and T. J. Howard, *Tetrahedron Letters*, 1974, 4173.

²¹ A. P. Phillips and J. Mentha, *J. Amer. Chem. Soc.*, 1956, **78**, 140.

²² R. Cornubert, C. Barraud, M. Cormier, M. Descharmes, and H. G. Eggert, *Bull. Soc. chim. France*, 1955, 400.

pressure of 88 atm and at room temperature for 6 h gave the product (10), m.p. 63–64° (from ethanol) (lit.,²² 63–64°) [its phenylurethane had m.p. 105–106° (lit.,²² 106°)], τ [(CD₃)₂SO] 5.74 (d, *J* 4.8 Hz, OH). G.l.c. on a Carbowax column showed a single component.

The fourth component was the *cis*-benzyl derivative (7), m.p. 47–48°; τ [(CD₃)₂SO] 5.81 (d, *J* 3.6 Hz, OH); its 3,5-dinitrobenzoate had m.p. 126–127° (lit.,²³ 129°).

The fifth component was the *trans*-benzyl derivative (8), m.p. 76.5–77° (lit.,²³ 77°); τ [(CD₃)₂SO] 5.50 (d, *J* 6.6 Hz, OH); its 3,5-dinitrobenzoate had m.p. 133.5–134° (from methanol) (lit.,²³ 133–135°).

Catalytic Hydrogenation of 2-Benzylidenecycloheptanol (11).²⁴—Compound (11) was hydrogenated over various catalysts in 95% ethanol under the conditions shown in Table 3. The products were separated by preparative g.l.c. on a B34Si column. The first component was benzylcycloheptane, ν_{\max} 700, 1 455, 2 860, and 2 920 cm⁻¹ (mono-substituted benzenoid system; no functional group). The second and third components (mixture) were indicated to be the cyclohexylmethyl derivatives (14) and (15), by i.r. (ν_{\max} 1 020, 1 045, 1 450, 2 860, 2 940, and 3 680 cm⁻¹) and mass spectra [*m/e* 210 (*M*⁺) and an intense peak at 192]. This identification was confirmed by n.m.r. comparison with authentic samples of (14) and (15).

cis-2-(Cyclohexylmethyl)cycloheptanol (14). Hydrogenation of the benzyl derivative (12) (100 mg) over rhodium-

carbon (5%; 50 mg) in 95% ethanol (25 ml) at a maximum pressure of 88 atm and at room temperature for 6 h gave the product (14) as a single substance (g.l.c. on all columns tried); τ [(CD₃)₂SO] 5.98 (d, *J* 4.8 Hz, OH).

trans-2-(Cyclohexylmethyl)cycloheptanol (15). Hydrogenation of the benzyl derivative (13) (100 mg) over rhodium-carbon (5%; 50 mg) in 95% ethanol (25 ml) at a maximum pressure of 95 atm and at room temperature for 6 h gave the product (15) as a single substance (g.l.c. on all columns tried); τ [(CD₃)₂SO] 5.84 (d, *J* 4.8 Hz, OH).

The fourth component was the *cis*-benzyl derivative (12), ν_{\max} 3 480 cm⁻¹ τ [(CD₃)₂SO] 5.76 (d, *J* 4.8 Hz, OH), *m/e* 204 (*M*⁺); its 3,5-dinitrobenzoate [from ethanol-petroleum (b.p. 60–80°)] had m.p. 134° (Found: C, 63.25; H, 5.8; N, 7.1. C₂₁H₂₂N₂O₆ requires C, 63.3; H, 5.55; N, 7.05%.)

The fifth component was the *trans*-benzyl derivative (13): τ [(CD₃)₂SO] 5.51 (d, *J* 4.8 Hz, OH); its 3,5-dinitrobenzoate (from methanol) had m.p. 102–103° (Found: C, 62.95; H, 5.7; N, 7.1. C₂₁H₂₂N₂O₆ requires C, 63.3; H, 5.55; N, 7.05%).

We thank Professor J. A. Elvidge for his interest, encouragement, and helpful comments.

[5/067 Received, 10th January, 1975]

²³ P. B. Russel, *J. Chem. Soc.*, 1954, 1771.

²⁴ E. A. Braude, W. F. Forbes, and E. A. Evans, *J. Chem. Soc.*, 1953, 2202.