The cis- *and* trans-2-*Benzyl*cyclo*hexanols: The Reduction of 2-Benzylidene- and 2-Benzyl*-cyclo*hexanones.*

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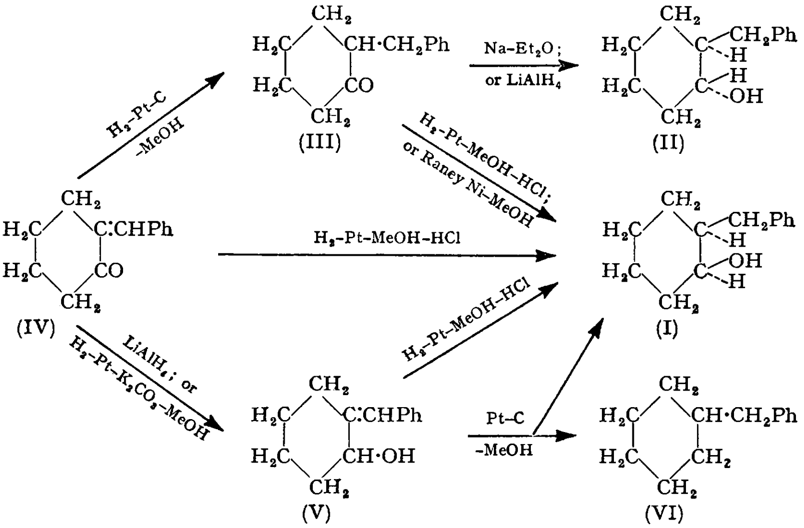
On the basis of evidence already available the known 2-benzyl*cyclo*hexanol of m. p. 77° is assigned the *trans*-configuration following the generalizations of von Auwers and Skita. *cis*-2-Benzyl*cyclo*hexanol has been prepared by catalytic reduction of 2-benzyl*cyclo*hexanone with platinum in acidic methanol. The steric effects of platinum and platinized charcoal catalysts and of lithium aluminium hydride in the reduction of this ketone and of 2-benzylidene*cyclo*hexanone have been investigated.

2-Benzyl*cyclo*hexanol can exist in two racemic forms, *viz.*, *cis* (I) and *trans* (II). However, only one of these (m. p. 77°; 3 : 5-dinitrobenzoate, m. p. 133—135°) has been described. This was prepared by reduction of 2-benzyl*cyclo*hexanone (III) with sodium in moist ether (Cook and Hewett, *J.*, 1936, 62), by the action of benzylmagnesium chloride on *cyclo*hexene oxide (Cook, Hewett, and Lawrence, *ibid.*, p. 75) and of sodium on a mixture of *cyclo*hexanol and benzyl alcohol (Guerbet reaction) (Weitzmann, Bergmann, and Haskelberg, *Chem. and Ind.*, 1937, 587), and by reaction of potassium benzyloxide with *cyclo*hexanone (Mastagli, Charreine, and Lambert, *Compt. rend.*, 1945, **221**, 749). The first of these methods might be expected, by analogy with the similar reduction of 2-methyl*cyclo*hexanone (Skita, *Annalen*, 1923, **431**, 22) or that of other alkyl-substituted hydroaromatic ketones by sodium in ethanol (Vavon, *Bull. Soc. chim.*, 1926, **49**, 668, and later papers), to give the *trans*-isomer. The reaction of *cyclo*hexene oxide with Grignard reagents is usually complicated by rearrangements (Cook, Hewett, and Lawrence, *loc. cit.*;

Winstein and Henderson in Elderfield's " Heterocyclic Compounds," John Wiley and Sons, New York, Vol. I, 1950, p. 55). Benzylmagnesium chloride is remarkable in that it gives the normal product 2-benzyl*cyclo*hexanol (m. p. 77°) in about 50% yield (Cook *et al.*, *loc. cit.*). This is explained by these authors on the grounds that the dibenzylmagnesium, formed in the equilibrium $2PhCh_2MgCl \rightleftharpoons MgCl_2 + Mg(Ch_2Ph)_2$, is unusually reactive towards the oxide and leads to a preponderance of 2-benzyl*cyclo*hexanol in the product; since Bartlett and Berry (*J. Amer. Chem. Soc.*, 1934, **56**, 2683) have shown that the oxide and dialkylmagnesiums, or other nucleophilic reagents (Boeseken and van Giffen, *Rec. Trav. chim.*, 1920, **39**, 184), give almost exclusively *trans*-compounds, the product, isomer of m. p. 77°, should be the *trans*-form (II). Finally Weizmann *et al.* (*loc. cit.*) have shown that, in one case at least (2-butyl*cyclo*hexanol), the Guerbet reaction gives the *trans*-isomer exclusively.

In another connection, *cis*- and *trans*-2-benzyl*cyclo*hexanol were required. If the evidence for the *trans*-configuration of the product of m. p. 77° is correct then the Skita rule, either in the original form or as modified by Barton (*J.*, 1953, 1029, footnote 23), indicates that catalytic hydrogenation of 2-benzyl*cyclo*hexanone (III) in acidic medium should give the *cis*-alcohol. Catalytic reduction in acidified methanol with a platinum catalyst yielded only 2—3% of the known isomer: the bulk of the product did not crystallize. After several distillations the analysis of this compound and the derived 3 : 5-dinitrobenzoate (m. p. 129°) indicated a formula $C_{13}H_{18}O$. Since oxidation with chromic acid gave the ketone (III) there can be little doubt that this is the epimer, *cis*-2-benzyl*cyclo*hexanol (I).

2-Benzyl*cyclo*hexanone (III) has been prepared previously by Cook and Hewett (*loc. cit.*), Tiffeneau and Porcher (*Bull. Soc. chim.*, 1922, **31**, 331), and von Auwers and Treppmann (*Ber.*, 1915, **48**, 1222). In the present work it was prepared by catalytic reduction of 2-benzylidene*cyclo*hexanone (IV) in methanol with a platinized charcoal catalyst (cf. Baltzly, *J. Amer. Chem. Soc.*, 1952, **74**, 4586). After the absorption of one mol. of hydrogen the reduction ceased and pure 2-benzyl*cyclo*hexanone was isolated in *ca.* 80% yield. In acidic methanol in presence of platinum two mols. of hydrogen were absorbed, the second much the more slowly, to give mainly *cis*-2-benzyl*cyclo*hexanol (I) together with *ca.* 5% of the *trans*-compound.



The reduction of 2-benzyl*cyclo*hexanone (III) with lithium aluminium hydride gave almost pure *trans*-2-benzyl*cyclo*hexanol and is the method of choice for the preparation of this compound. 2-Benzylidene*cyclo*hexanone (IV) with this reagent gave 2-benzylidene*cyclo*hexanol (V) in almost quantitative yield. The 1 : 2-reduction of αβ-unsaturated ketones with the mixed hydride has been remarked previously (Brown, " Organic Reactions," Vol. VI, John Wiley and Sons, New York, 1951, p. 469). The resemblance of the ultra-violet absorption spectrum of (V) ($\lambda_{max.}$ 2430 Å, ε 14,500) to that of styrene ($\lambda_{max.}$ 2440 Å, ε 12,000; see Braude in Rodd's " Chemistry of the Carbon Compounds," Elsevier, London, Vol. 1A, 1951, p. 71), together with the results of the catalytic reduction of the compound (see below), proves the structure.

2-Benzylidene*cyclo*hexanol (V) on catalytic hydrogenation with a platinized charcoal catalyst gave *cis*-2-benzyl*cyclo*hexanol (I) (*ca.* 50%) and a hydrocarbon $C_{13}H_{18}$ (*ca.* 45%); on conversion of the alcohols into the 3 : 5-dinitrobenzoates a very small amount of the *trans*-derivative was isolated. The reduction of (V) may be likened to that of cinnamyl alcohol with a palladized charcoal catalyst, which gives rise to 3-phenylpropanol and propylbenzene (Baltzly and Buck, *J. Amer. Chem. Soc.*, 1943, **65**, 1984). In the present case the hydrocarbon $C_{13}H_{18}$ is almost certainly benzyl*cyclo*hexane (VI) but it was not rigidly identified. Hydrogenation of (V) in acidic medium with a platinum catalyst gave mainly (I) and some (II), but no hydrocarbon was detected.

Hydrogenation of 2-benzylidene*cyclo*hexanone in the presence of a little potassium carbonate with a platinum catalyst was slow. The products were 2-benzylidene*cyclo*hexanol (V) (*ca.* 60%), *cis*-2-benzyl*cyclo*hexanol (I) (*ca.* 30%), and a little *trans*-2-benzyl*cyclo*hexanol (II). Under the same conditions 2-benzyl*cyclo*hexanone (III) was not reduced and the catalyst was found to be partially poisoned when challenged with *cyclo*hexene. Accordingly it is believed that the unsaturated alcohol (V) is the main primary product in the reduction of unsaturated ketone (IV) under these conditions.

2-Benzyl*cyclo*hexanone was hydrogenated with difficulty in the presence of Raney nickel, the product being mainly the *cis*-alcohol (I).

The annexed reaction scheme shows only the main products.

EXPERIMENTAL

*2-Benzyl*cyclo*hexanone* (III) —2-Benzylidene*cyclo*hexanone (18·6 g.) (Wallach, *Ber.*, 1907, **40**, 71) in methanol (50 ml.) was shaken in hydrogen at *ca.* 30 lb. pressure with platinized charcoal (from 1 g. of charcoal and 0·1 g. of platinum, see Baltzly, *loc. cit.*). Uptake of hydrogen was rapid and reduction stopped after absorption of 1 mol. The catalyst was removed, the solvent evaporated off, the residue dissolved in ether, the ethereal solution stirred with a saturated solution of sodium hydrogen sulphite over-night, and the solid bisulphite compound collected and washed with ether. The bisulphite compound was dissolved in hot water (*ca.* 500 ml.), and the solution made acid with concentrated sulphuric acid. After cooling, the oily material was extracted with ether and washed with sodium hydrogen carbonate solution and with water. After being dried, the ether was removed and the ketone distilled (15 g.; b. p. 160°/12 mm.) (Cook and Hewett, *loc. cit.*, give b. p. 155/10 mm.). With semicarbazide hydrochloride in sodium acetate solution the semicarbazone, m. p. 168°, was formed [von Auwers and Treppmann, and Cook and Hewett (*locc. cit.*), give 166—167°].

The original solution after removal of any traces of ketone as the semicarbazone gave an oil which partly solidified on cooling (3 g.).

cis-*2-Benzyl*cyclo*hexanol* (I).—2-Benzyl*cyclo*hexanone (9 g.), in methanol (50 ml.) acidified with concentrated hydrochloric acid (0·5 ml.) was shaken with Adams's catalyst until uptake of hydrogen ceased. The catalyst and most of the methanol were removed, the solution was diluted with water, and the oil extracted with ether. The ethereal solution was washed with dilute sodium hydrogen carbonate solution and then with water. After being dried, the ether was removed and the residue was kept at 0° for 12 hr. after being seeded with the *trans*-alcohol. The very small amount of crystalline material (*ca.* 0·2 g.) was filtered off and the oily cis-*isomer* distilled (b. p. 90—95°/0·15 mm.; 7·5 g.) (Found: C, 82·5; H, 9·8. $C_{13}H_{18}O$ requires C, 82·2; H, 9·5%).

Treatment with 3 : 5-dinitrobenzoyl chloride in benzene–pyridine gave the 3 : *5-dinitrobenzoate*, needles (from ether–hexane, methanol, or ethanol), m. p. 129° (Found: C, 62·6; H, 5·4. $C_{20}H_{20}O_6N_2$ requires C, 62·5; H, 5·2%).

trans-*2-Benzyl*cyclo*hexanol* (II).—2-Benzyl*cyclo*hexanone (9 g.) in ether (30 ml.) was added to a suspension of lithium aluminium hydride (2 g.) in ether (25 ml.) during 2 hr., with stirring. The mixture was then refluxed for 4 hr. and, after cooling, the reagent was decomposed by the addition of water. The ethereal layer, after being washed with water and dried, gave on evaporation an oil which solidified (8·0 g.). Recrystallization from pentane gave needles, m. p. 77°. The 3 : 5-dinitrobenzoate formed prisms, m. p. 134°, from ethanol. These were contaminated with very small quantities of the *cis*-ester from which they were separated by virtue of their lower solubility. Both the alcohol, m. p. 77°, and the 3 : 5-dinitrobenzoate, m. p. 134°, were identical with samples prepared by the reduction of 2-benzyl*cyclo*hexanone with sodium in moist ether (Cook and Hewett, *loc. cit.*).

Oxidation of cis- *and* trans-2-*Benzyl*cyclo*hexanols with Chromic Acid.*—The *cis*- or the *trans*-alcohol with cold chromic acid (cf. Cook, Hewett, and Lawrence, *loc. cit.*) gave 2-benzyl*cyclo*hexanone, the semicarbazone of which melted at 168° alone or mixed with the sample previously described.

trans-2-*Benzyl*cyclo*hexyl Toluene*-p-*sulphonate.*—The alcohol (5 g.) and toluene-*p*-sulphonyl chloride (7 g.) were kept in pyridine (25 ml.) at room temperature for 48 hr. Recovery as usual and several crystallizations from ether–ligroin gave the *ester* as needles, m. p. 94—95° (Found : C, 69·9; H, 7·0. $C_{20}H_{24}O_3S$ requires C, 69·7; H, 7·0%).

*Reduction of 2-Benzylidene*cyclo*hexanone with Platinum in Acid Solution.*—The unsaturated ketone (9·3 g.) in methanol (50 ml.) containing methanolic hydrogen chloride (0·5 ml. of 40%) was shaken with hydrogen and Adams's catalyst. The first mol. of hydrogen was absorbed rapidly but the second at only one-twelfth of the original rate. The product was worked up as in the first example above. In all 9 g. of distilled *cis*-benzyl*cyclo*hexanol were obtained (b. p. 90—93°/0·15 mm.). The 3 : 5-dinitrobenzoate prepared from this alcohol appeared to be pure *cis*-compound, m. p. 129° after recrystallization from ethanol.

2-*Benzylidene*cyclo*hexanol* (V).—2-Benzylidene*cyclo*hexanone (9 g.) in ether (25 ml.) was added to a suspension of powdered lithium aluminium hydride (4 g.) in ether (50 ml.) with stirring during *ca.* 1 hr. Stirring was continued and the mixture refluxed for 2 hr. Decomposition with water, washing with water, drying, and removal of the ether gave an oil which crystallized (8·7 g.). Recrystallization from pentane gave 2-*benzylidene*cyclo*hexanol* as needles, m. p. 63—64° (Found : C, 83·1; H, 8·6. $C_{13}H_{16}O$ requires C, 83·0; H, 8·5%). Ultra-violet max. at 243 mμ (ε 14,500 in EtOH) (Beckman model DU quartz spectrophotometer; cell length 1 cm.).

*Catalytic Reduction of 2-Benzylidene*cyclo*hexanol.*—The unsaturated alcohol (5 g.) in methanol was shaken with platinized charcoal in hydrogen at about 30 lb. pressure, 1 mol. being absorbed in 11 hr. before the reduction stopped. The catalyst was removed, the methanol evaporated off, and the residue dissolved in ether and washed with water. The ethereal solution, after being dried, was evaporated, to give an oil (*ca.* 4·5 g.). On acylation with 3 : 5-dinitrobenzoyl chloride in pyridine the main product was the ester, m. p. 129° (5·0 g.), of *cis*-2-benzyl*cyclo*hexanol, together with 0·1 g. of the *trans*-ester. Some oil which had resisted acylation was also obtained, probably *benzyl*cyclo*hexane* (b. p. 40—45°/0·2 mm.; 1·7 g.) (Found : C, 89·8; H, 10·5. $C_{13}H_{18}$ requires C, 89·7; H, 10·3%).

*Catalytic Reduction of 2-Benzylidene*cyclo*hexanone in Methanol containing Potassium Carbonate.*—The unsaturated ketone (IV) (5 g.) and potassium carbonate (100 mg.) and Adams catalyst were hydrogenated in methanol (50 ml.). One mol. was absorbed at a moderate rate and the second much more slowly, total absorption being about 1·5 mols. The product consisted of about 60—70% of 2-benzylidene*cyclo*hexanol (V) which had its correct m. p. (64°) only after several recrystallizations from pentane; this was identified by m. p., mixed m. p., and ultra-violet spectrum. The residues were converted into the 3 : 5-dinitrobenzoates, the ester, m. p. 129° (2·5 g.), of the *cis*-, and that, m. p. 133—135° (0·2—0·3 g.), of the *trans*-alcohol being isolated by crystallization from methanol.

*Raney Nickel Reduction of 2-Benzyl*cyclo*hexanone.*—The ketone (5 g.), potassium carbonate (100 mg.), and Raney nickel (*ca.* 2 g.) in methanol (50 ml.) were hydrogenated. Uptake was slow and the reaction was stopped after about 0·67 mol. had been absorbed. The catalyst was removed and the methanol solution evaporated to give an oil. After removal of any unreduced ketone by sodium hydrogen sulphite the residual oil was converted into the 3 : 5-dinitrobenzoate, which on crystallization proved to be mainly the *cis*-ester, m. p. 129° (4 g.).

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