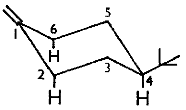
773. *Conformationally Fixed Olefins. Part I. The Epimeric 1-Methyl-4-t-butylcyclohexanols and 1-Methylene-4-t-butylcyclohexane.*

By B. Cross and G. H. Whitham.

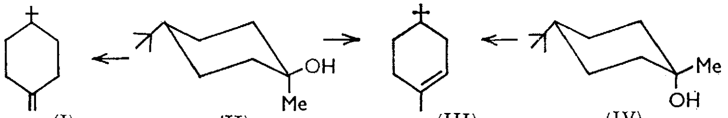
Configurations have been assigned to the two epimeric 1-methyl-4-t-butylcyclohexanols, and their dehydration by phosphorus oxychloride in pyridine has been studied.

1-Methylene-4-t-butylcyclohexane has been prepared by the Wittig reaction.

A simple, conformationally homogeneous system containing an exocyclic methylene group was required for projected experiments on the stereochemistry of olefin reactions. Winstein and Holness,[1] and others,[2] have used the t-butyl group as a means of fixing the conformation of simple cyclohexane derivatives, the free-energy difference between the two possible chair conformations of t-butylcyclohexane being 5·4—5·8 kcal./mole in favour of the form with the t-butyl group equatorial. Thus 1-methylene-4-t-butylcyclohexane (I) appeared to be a suitable compound since it should exist almost exclusively in conformation (Ia). In the cyclohexylidene system[3] the distance between the axial 4-hydrogen atom and the axial 2- and 6-hydrogen atoms is 2·37 Å, *i.e.*, an appreciable decrease with respect to the diaxial 1,3-hydrogen distance in cyclohexane (2·53 Å). Thus there should be an even greater destabilisation of that conformation of hydrocarbon (I) with the t-butyl group axial than in the t-butylcyclohexane case.*



(Ia)



(I) (II) (III) (IV)

Dehydration of *cis*-1-methyl-4-t-butylcyclohexanol (II) (t-butyl *cis* to methyl) was first investigated as a means of preparing the methylene hydrocarbon (I). Such dehydrations of six-membered ring tertiary alcohols, by phosphorus oxychloride in pyridine, have been fairly extensively studied for fused polycyclic systems.[5] Tertiary alcohols with an equatorial hydroxyl group give mainly the exocyclic olefin, whereas those with an axial hydroxyl group give the endocyclic olefin: the preferred *trans*-diaxial transition state for elimination cannot be achieved in formation of endocyclic olefin from the compound with an equatorial hydroxyl group.

The two epimeric tertiary alcohols obtained by reaction of methylmagnesium iodide on 4-t-butylcyclohexanone were separated by chromatography into one isomer, more readily eluted, m. p. 66—67°, and the other, m. p. 89—90°. Configurations (IV; axial OH) and (II; equatorial OH) respectively, were assigned initially, on the basis of the chromatographic behaviour[6] and the reactions with phosphorus oxychloride in pyridine described below. However, since these alcohols were required as reference compounds (see following

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* The contribution of boat forms is considered to be negligible in the absence of any special effect destabilising the more stable chair conformation.[4]

[1] Winstein and Holness, *J. Amer. Chem. Soc.*, 1955, **77**, 5562.

[2] Eliel and Ro, *Chem. and Ind.*, 1956, 251; *J. Amer. Chem. Soc.*, 1957, **79**, 5992, 5995; Eliel and Lukach, *ibid.*, 1957, **79**, 5986; Lau and Hart, *ibid.*, 1959, **81**, 4897; Curtin, Stolow, and Maya, *ibid.*, 1959, **81**, 3330; Stolow, *ibid.*, 1959, **81**, 5806.

[3] Corey and Sneen, *J. Amer. Chem. Soc.*, 1955, **77**, 2505.

[4] Barton, Lewis, and McGhie, *J.*, 1957, 2907; Djerassi, Finch, and Mauli, *J. Amer. Chem. Soc.*, 1959, **81**, 4997.

[5] (*a*) Barton, Campos-Neves, and Cookson, *J.*, 1956, 3500; (*b*) Heusser, Wahba, and Winternitz, *Helv. Chim. Acta*, 1954, **37**, 1052; Corey and Sauers, *J. Amer. Chem. Soc.*, 1959, **81**, 1739.

[6] Barton, *J.*, 1953, 1027.

paper) additional confirmation of the configurations was obtained as follows. (*a*) The C–O stretching regions of the infrared spectra in carbon disulphide (see Table) show close agreement with the spectra of the corresponding β-terpineols and *p*-menthanols,[7] the configurations of which are unequivocally based.[8] (*b*) The O–H stretching frequencies in the infrared spectra of dilute solutions (carbon tetrachloride) were at 3617 for alcohol (IV) and 3612 cm.$^{-1}$ for alcohol (II). Cole *et al.*[9] have recorded the spectra of a limited number of cyclic tertiary alcohols and quote 3617—3619 for axial hydroxyl and 3613 cm.$^{-1}$ for equatorial hydroxyl. (*c*) Interaction of 1-methyl-4-t-butylcyclohexene (see below) with mercuric acetate in water followed by reduction with hydrazine gave the alcohol (IV); this parallels the corresponding reaction with carvomenthene[7] which gives the known *trans-p*-menthanol.

Infrared absorption bands in the 900—1200 *cm.*$^{-1}$ *region.*

trans-1-Methyl-4-t-butylcyclohexanol (IV)	909	923	995	1031	1100	1200
trans-p-Menthanol[7]	907	941	988	1000	1084	1167
trans-β-Terpineol[7]	911	930	952	1000	1100	1150
cis-1-Methyl-4-t-butylcyclohexanol (II)	914		979		1103	1142
cis-p-Menthanol[7]	915		981		1120	1150
cis-β-Terpineol[7]	916		982		1110	1145

It is of interest that in the original Grignard reaction a preponderance of the equatorial isomer (II) over the axial isomer (IV) is obtained since it has usually been assumed[10] that formation of the axial alcohol, resulting from equatorial approach of reagent, is the favoured course of Grignard reactions with unhindered cyclohexanones.

Treatment of the axial tertiary alcohol (IV) with phosphorus oxychloride in pyridine gave solely the expected 1-methyl-4-t-butylcyclohexene (III). When the equatorial alcohol (II) was similarly treated the hydrocarbon product, although containing some of the expected olefin (I), was still largely the endocyclic olefin (III). The amount of olefin (I) present in the mixture was estimated on the basis of the ε value of the infrared band at 890 cm.$^{-1}$ derived from the pure compound (see below). A value of *ca.* 8% was obtained. Since olefin (III) would be expected[11] to be thermodynamically more stable than olefin (I) it was necessary to show that the products of dehydration were obtained under conditions of kinetic control. This was done by the recovery of pure olefin (I) after it had been subjected to the reaction conditions with phosphorus oxychloride and pyridine in the presence of pyridine hydrochloride.

In competitive experiments it was shown that the axial alcohol (IV) was dehydrated rather more rapidly than the equatorial isomer (II), though the difference was small.

There is thus a considerable divergence between the present results and those obtaining with fused polycyclic systems.[5] This difference probably reflects the greater flexibility of the simple cyclohexane system which allows greater distortion in attaining the transition state for elimination. However, in comparing the present results with, *e.g.*, the dehydration of 3α-methylcholestan-3β-ol, which gives largely 3-methylenecholestane,[5a] it is noteworthy that in the latter case a transition state involving a partial 3,4-double bond would have considerably higher energy than one involving positions 2,3 because of the steric requirements of the system.[12] Thus on probability grounds alone there is twice the opportunity of obtaining the endocyclic olefin in the present instance.

Consequently an alternative approach was required for preparation of the olefin (I). This was found in the Wittig reaction.[13] Interaction of 4-t-butylcyclohexanone with

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[7] Henbest and McElhinney, *J.*, 1959, 1834.

[8] Barnes, *Austral. J. Chem.*, 1958, **11**, 134; Pascual and Coll, *Anales real Soc. españ. Fís. Quím.*, 1953, **49**, 547, 553.

[9] Cole, Müller, Thornton, and Willix, *J.*, 1959, 1218.

[10] Büchi, Wittenau, and White, *J. Amer. Chem. Soc.*, 1959, **81**, 1968.

[11] Turner and Garner, *J. Amer. Chem. Soc.*, 1958, **80**, 1424.

[12] Turner, Meador, and Winkler, *J. Amer. Chem. Soc.*, 1957, **79**, 4122.

[13] Wittig and Schöllkopf, *Chem. Ber.*, 1954, **87**, 1318.

triphenylphosphinylmethylene gave 1-methylene-4-t-butylcyclohexane in 45% yield. It had the expected infrared spectrum with bands at 3082, 1375, and 890 cm.$^{-1}$ attributable to the methylene group.

EXPERIMENTAL

Unless otherwise stated infrared spectra were taken in carbon disulphide solution and alumina for chromatography had activity III. Light petroleum had b. p. 40—60°.

trans- *and* cis-1-*Methyl*-4-*t-butylcyclohexanol*.—Methylmagnesium iodide (from magnesium, 11 g.) in dry ether was treated during 1 hr. with 4-t-butylcyclohexanone (50 g.) in dry ether (150 c.c.) and the whole was then refluxed for 2 hr. After acidification the product was isolated with ether as a solid (45 g.), and a portion (2·6 g.) was chromatographed on alumina. Elution with light petroleum gave, after a trace of unchanged ketone, trans-1-*methyl*-4-*t-butylcyclohexanol* (IV) (0·62 g., 20%), m. p. 66—67° (from hexane) (Found: C, 77·65; H, 13·0. $C_{11}H_{22}O$ requires C, 77·6; H, 13·0%). Further elution of the column with light petroleum–ether (99 : 1) gave *cis*-1-methyl-4-t-butylcyclohexanol (II) (1·40 g., 44%), m. p. 89—90° (from light petroleum). The latter alcohol was hygroscopic and satisfactory analyses were not obtained; it was therefore characterised as its 3,5-*dinitrobenzoate* (plates from ether–light petroleum), m. p. 156·5—157° (Found: C, 59·15; H, 6·6; N, 7·9. $C_{18}H_{24}N_2O_6$ requires C, 59·35; H, 6·65; N, 7·7%).

trans-1-*Methyl*-4-*t-butylcyclohexanol from* 1-*Methyl*-4-*t-butylcyclohex*-1-*ene*.—1-Methyl-4-t-butylcyclohexene (5·0 g.) (see below) was treated with mercuric acetate (10·6 g.) in water (200 c.c.), as described by Henbest and McElhinney [7] for (+)-carvomenthene, and after anion-exchange gave the chloromercuric compound (2·8 g.), m. p. 126° [from light petroleum (b. p. 80—100°)]. Reduction with hydrazine hydrate followed by sublimation gave the *trans*-alcohol (IV) (0·4 g.) shown to be identical with that obtained above by m. p. and infrared data.

Infrared Spectra of the Tertiary Alcohols.—Spectra in the O–H stretching region were taken on a grating instrument for dilute carbon tetrachloride solutions (solvent redistilled from phosphorus pentoxide). We are indebted to Dr. J. K. Brown for these determinations.

1-*Methyl*-4-*t-butylcyclohexene*.—A cooled solution of *trans*-1-methyl-4-t-butylcyclohexanol (3·5 g.) in dry pyridine (25 c.c.) was treated with phosphorus oxychloride (5 c.c.) and set aside at 20° for 12 hr. After addition of water the product was isolated with ether. Distillation gave the *olefin* (2·4 g.), b. p. 74—75°/11 mm., n_D^{16} 1·4626, $\nu_{max.}$ 2990 and 805 cm.$^{-1}$ (trisubstituted olefinic linkage) (Found: C, 86·7; H, 13·3. $C_{11}H_{20}$ requires C, 86·75; H, 13·25%).

Dehydration of cis-1-*Methyl*-4-*t-butylcyclohexanol*.—To the *cis*-alcohol (II) (4·3 g.) in dry pyridine (10 c.c.) was added phosphorus oxychloride (5 c.c.) at 0°. After 12 hr. at 20° the product was isolatd as an oil, b. p. 70—71°/7 mm. (3·4 g., 90%). The infrared spectrum was that of 1-methyl-4-t-butylcyclohexene containing *ca.* 8% of 1-methylene-4-t-butylcyclohexane estimated by the intensity of the band at 892 cm.$^{-1}$ ($CH_2{=}C\langle$).

Competitive Dehydrations.—(*a*) The *cis*-alcohol (II) (150 mg.) in dry pyridine (2 c.c.) was treated at 0° with phosphorus oxychloride (6 mol.). After 25 min. at 20° the mixture was decomposed with ice-water, and the product was isolated with ether as an oil (91 mg.). Adsorption on alumina and elution with light petroleum gave a hydrocarbon mixture (34 mg.); further elution with light petroleum–ether (1 : 1) gave unchanged *cis*-alcohol (II) (40 mg.).

(*b*) In a similar experiment the *trans*-alcohol (IV) (148 mg.) gave 1-methyl-4-t-butylcyclohexene (75 mg.) and unchanged *trans*-alcohol (IV) (11 mg.).

1-*Methylene*-4-*t-butylcyclohexane*.—A cooled solution of butyl-lithium (7·4 g.) in dry ether was added to dry finely powdered methyltriphenylphosphonium bromide [13] (41·7 g.) under nitrogen. After 2 hours' shaking the red-brown solution was cooled to 0° and 4-t-butylcyclohexanone (6 g.) in dry ether (50 c.c.) was added. A white precipitate was formed. The mixture was shaken for 1 hr., and then heated under reflux for a further 2 hr. Ether was distilled off and replaced by tetrahydrofuran, and heating under reflux was continued for 7 hr. The cooled solution was diluted with water and the product was isolated with ether. After evaporation of the ether the residue was chromatographed on alumina (activity I). Elution with light petroleum followed by distillation gave the *hydrocarbon* (2·6 g., 44%), b. p. 78—80°/18 mm., n_D^{21} 1·4630 (Found: C, 86·9; H, 13·45. $C_{11}H_{20}$ requires C, 86·75; H, 13·25%). Further elution of the column with light petroleum–benzene (4 : 1) afforded unchanged 4-t-butylcyclohexanone (1·0 g.).

Stability of 1-*Methylene*-4-*t-butylcyclohexane*.—To the hydrocarbon (94 mg.) in dry pyridine

(0·5 c.c.) was added phosphorus oxychloride (0·5 c.c.) and hydrochloric acid (1 drop). After 10 hr. at 20° the product (87 mg.) was isolated as before; its infrared spectrum showed it to be unchanged starting material.

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