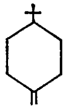
774. *Conformationally Fixed Olefins. Part II.*[1] *The Reaction of 1-Methylene-4-t-butylcyclohexane with Lead Tetra-acetate.*

By B. Cross and G. H. Whitham.

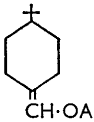
1-Methylene-4-t-butylcyclohexane with lead tetra-acetate in benzene gives a mixture of the enol-acetate (II) of 1-formyl-4-t-butylcyclohexane and the stereoisomeric diacetates (IV) of 1-hydroxymethyl-4-t-butylcyclohexanol.

In a preliminary screening of reagents which might effect allylic substitution, without rearrangement, of the conformationally homogeneous 1-methylene-4-t-butylcyclohexane[1] (I) the reaction with lead tetra-acetate[2] was investigated. This, although failing to produce the desired substitution, gave results of sufficient interest to warrant further study.

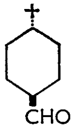
Hydrocarbon (I) reacted smoothly with lead tetra-acetate in benzene and lead diacetate was precipitated. The product, a colourless oil, was obviously a mixture. It had infrared bands at 1748 and 1245 (normal acetate) with an additional band in the carbonyl region at 1775 cm.$^{-1}$. Distillation of the crude product gave material having bands at 1775 and 1203 cm.$^{-1}$ but not at 1748 and 1245 cm.$^{-1}$. The 1775 and 1203 cm.$^{-1}$ bands are characteristic of vinyl acetates and indicated the structure (II) for this substance, which was confirmed by an acetoxyl determination and by acid-hydrolysis to the aldehyde (III), identified through its 2,4-dinitrophenylhydrazone with material prepared by a Grignard reaction from 4-t-butylcyclohexyl bromide[3] and ethyl orthoformate. The aldehyde is assigned the *trans*-configuration shown since it is obtained under conditions leading to the more stable form.



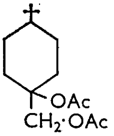
(I)



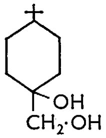
(II)



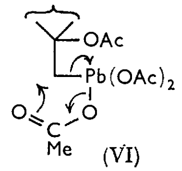
(III)



(IV)



(V)



(VI)

Hydrolysis of the crude lead tetra-acetate product with methanolic potassium hydroxide, followed by chromatography of the neutral fraction on alumina, afforded two crystalline substances, one, which predominated, of m. p. 125°, and the other of m. p. 100°. These were the stereoisomeric glycols (V) since each rapidly consumed one mol. of sodium metaperiodate to give 4-t-butylcyclohexanone. Their configuration is discussed below; they are considered to have been derived from their acetates (IV) present in the original reaction product and responsible for the normal acetate bands in the infrared spectrum.

A new solid material, $C_{22}H_{40}O_2$, was obtained by hydrolysis of the crude lead tetra-acetate product with aqueous hydrochloric acid; on treatment with acidic 2,4-dinitrophenylhydrazine it gave the derivative of the aldehyde (III). It is thus the cyclic acetal

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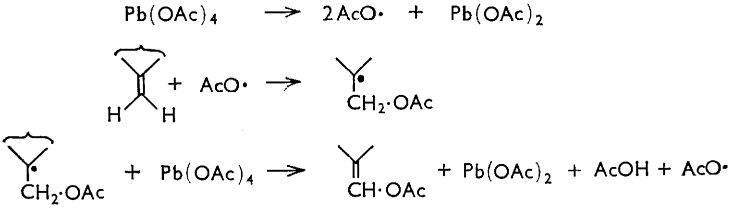
[1] Part I, preceding paper.
[2] Criegee, *Angew. Chem.*, 1958, **70**, 173.
[3] Eliel and Haber, *J. Org. Chem.*, 1959, **24**, 143.

derived from the aldehyde (III) and glycol (V), a structure which was confirmed by formation of the substance on treatment of a mixture of aldehyde (III) and the isomer, m. p. 125°, of glycol (V) with dilute hydrochloric acid. Acetal corresponding to the minor isomer of glycol (V) was not isolated.

The major primary products of the reaction of hydrocarbon (I) with lead tetra-acetate in benzene are thus the enol-acetate (II) and the two stereoisomeric diacetates (IV). The formation of diacetate by addition of two acetate residues across a double bond has ample precedent in lead tetra-acetate reactions and is readily rationalised by Criegee's mechanism [2] of decomposition of an intermediate (VI) formed by Markownikow addition of lead tetra-acetate to the double bond. That addition in this sense might be expected is shown by recent results on the addition of mercuric acetate to methylenecyclohexane.[4]

Formation of the enol-acetate (II) is, however, difficult to rationalise in terms of intermediate (VI); addition of the equivalent of acetoxyl cation or acetoxyl radical to the exocyclic carbon atom could be followed by proton (or hydrogen) abstraction to give the enol-acetate. The following observations favour a radical mechanism. (*a*) Reaction of hydrocarbon (I) with lead tetra-acetate in glacial acetic acid, which would be expected to favour a polar mechanism, led solely to a diacetate mixture (IV) giving on hydrolysis the same proportion of glycol isomers (V) as before. (*b*) When the reaction of hydrocarbon (I) with lead tetra-acetate in benzene was carried out in the presence of iodine, as radical scavenger,[5] the formation of enol-acetate (II) was completely inhibited.* A radical chain mechanism of the type shown is thus compatible with these observations.



Although acetoxyl radicals are usually considered to decompose spontaneously into carbon dioxide and methyl radicals,[6] examples of reactions which probably involve acetoxyl radicals as such have been recently described.[7]

Previous instances of the formation of enol acetates from olefins and lead tetra-acetate have involved rearrangement of the carbon skeleton of the olefin, *e.g.*, production of the enol-acetate of homocamphenilone from camphene.[8] Here the products are explicable in terms of intermediates of type (VI).[2]

Initial attempts to establish the stereochemistry of the two glycols (V) involved selective acetylation of the primary hydroxyl group followed by competitive dehydrations of the tertiary alcohols by phosphorus oxychloride in pyridine. In this way the monoacetate derived from the glycol of m. p. 125° was dehydrated more rapidly than that from the glycol of m. p. 100° [each gives the product with an endocyclic double bond, as shown by the absence of bands attributable to the enol-acetate (II) in the infrared spectrum of the product]. The tentative assignment of configuration was thus (IX) (axial tertiary OH) for the glycol of m. p. 125° and (VIII) for the other. This assignment was, however, suspect on two counts: first, the rates of dehydration of the two corresponding tertiary alcohols (X) and (XI) do not differ very greatly [1] and could readily be swayed by a different

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* The enol-acetate was shown to be stable to these conditions.

[4] Robson and Wright, *Canad. J. Chem.*, 1960, **38**, 21.

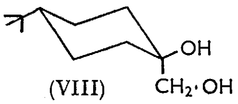
[5] Hammond and Sofer, *J. Amer. Chem. Soc.*, 1950, **72**, 4711.

[6] Walling, "Free Radicals in Solution," John Wiley and Sons Inc., New York, 1957, p. 493; Rembaum and Szwarc, *J. Amer. Chem. Soc.*, 1955, **77**, 3486.

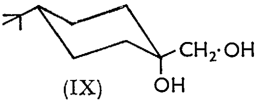
[7] Shine and Slagle, *J. Amer. Chem. Soc.*, 1959, **81**, 6309; Smith and Gilde, *ibid.*, 1959, **81**, 5325.

[8] Hückel, *Chem. Ber.*, 1947, **80**, 41.

degree of acetate participation in the primary acetates. Secondly, the infrared spectrum (in carbon disulphide) of the monoacetate of the glycol of m. p. 125° resembled that of the alcohol (X) in the region 1100—800 cm.$^{-1}$. Unambiguous correlation between one of the glycols (V) and the corresponding tertiary alcohol (X or XI) of known stereochemistry was thus sought. The glycol of m. p. 125° gave with toluene-*p*-sulphonyl chloride in pyridine the corresponding monoprimary toluene-*p*-sulphonate which on reduction with lithium aluminium hydride gave the tertiary alcohol (X). The glycol of m. p. 125° is therefore *cis*-1-hydroxymethyl-4-t-butylcyclohexanol (*cis*-Bu^t/CH$_2$·OH) (VIII), and the glycol of m. p. 100° is the *trans*-glycol (IX).



(VIII)



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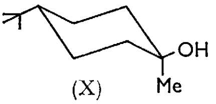

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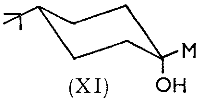
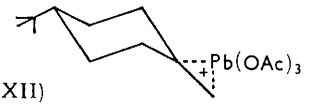
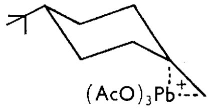


(XI)

If one allows that the glycol acetates are produced from an intermediate of type (VI), the stereochemistry is already determined at this stage. If it is assumed that the intermediates (VI) are produced *via* a bridged ion of the type postulated in the acetoxymercuration of olefins [9] the above stereochemical results can be rationalised by invoking the initial formation of the bridged ions (XII) and (XIII) followed by *trans*-Markownikow addition of acetoxyl anion. In this way, the ion (XIII) would lead to glycol (VIII), and the ion (XII) to glycol (IX). The relative proportion (4 : 1) of the glycol (VIII) to glycol (IX) should reflect the ratio of ion (XIII) to ion (XII), the forward reaction from the bridged ion being assumed to be faster than any reversal from it. On this basis, therefore, a preference for attack on the methylene hydrocarbon (I) from the side *cis* to the t-butyl group is postulated in the case of reagents which add *via* a three-membered bridged intermediate. A similar preference for attack from this side has also been found in the epoxidation of 1-methylene-4-t-butylcyclohexane.[10]

(XII)





(XIII)

EXPERIMENTAL

Infrared spectra refer to CCl$_4$ solutions unless otherwise stated. Other details as in Part I.[1]

Reaction of 1-*Methylene*-4-*t-butylcyclohexane with Lead Tetra-acetate in Benzene*.—Lead tetra-acetate (8·8 g.) was added to 1-methylene-4-t-butylcyclohexane (2·0 g.) in dry benzene (200 c.c.), and the solution was heated under reflux during 3 hr. After filtration of the precipitated lead diacetate the solution was washed with water, dried, and evaporated, giving the crude product as a colourless oil (3·1 g.).

Distillation of crude product (2·5 g.) gave the following fractions: (i) (0·5 g.) b. p. 22—25°/0·1 mm., unchanged methyl hydrocarbon; (ii) (0·2 g.) b. p. 52—54°/0·1 mm., $\nu_{\text{max.}}$ 1740 cm.$^{-1}$ (? unsaturated acetate), not further investigated; (iii) (0·4 g.), b. p. 154—157°/0·1 mm., $\nu_{\text{max.}}$ 1775 and 1740 cm.$^{-1}$; (iv) (0·5 g.) b. p. 159°/0·1 mm., $\nu_{\text{max.}}$ 1775 and 1200 cm.$^{-1}$. Redistillation of fraction (iv) gave the enol-acetate of 1-formyl-4-t-butylcyclohexane (Found: Ac, 22·3. $C_{13}H_{22}O_2$ requires Ac, 20·4%).

The enol-acetate (100 mg.) was heated under reflux with aqueous-methanolic 2N-hydrochloric acid (20 c.c.) during 2 hr. After steam-distillation the distillate was extracted with ether and evaporation of the dried extract gave a colourless oil (28 mg.), $\nu_{\text{max.}}$ 2720 and 1740 cm.$^{-1}$ (CHO). The 2,4-dinitrophenylhydrazone, formed in the usual way, had m. p. 170—171°, undepressed on admixture with authentic 2,4-dinitrophenylhydrazone of 1-formyl-4-t-butylcyclohexane.

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[9] Lucas, Hepner, and Winstein, *J. Amer. Chem. Soc.*, 1939, **61**, 3102; Henbest and Nicholls, *J.*, 1959, 227.

[10] Cross and Whitham, unpublished results.

1-*Formyl*-4-*t-butylcyclohexane*.—The Grignard reagent prepared from 1-bromo-4-t-butylcyclohexane [3] (22 g.) and magnesium (2·5 g.) in ether (75 c.c.) was treated with ethyl orthoformate (16 c.c.) in dry ether (100 c.c.) and heated under reflux during 7 hr. After decomposition of the Grignard complex with dilute acid the product was isolated with ether and was heated under reflux with aqueous-methanolic 7N-hydrochloric acid during 2 hr. The product, isolated with ether, was distilled, giving fractions (i) (5·2 g.), b. p. 25—30°/0·1 mm., n_D^{20} 1·4507, presumaly t-butylcyclohexenes, and (ii) (4·8 g.) the *aldehyde* (III), b. p. 58—60°/0·1 mm., n_D^{20} 1·4613 (Found: C, 78·75; H, 12·15. $C_{11}H_{20}O$ requires C, 78·5; H, 12·0%) [2,4-*dinitrophenylhydrazone*, m. p. 169—170° (from ethanol) (Found: C, 58·95; H, 6·9; N, 15·8. $C_{17}H_{24}N_4O_4$ requires C, 58·6; H, 6·95; N, 16·1%)].

cis- *and* trans-1-*Hydroxymethyl*-4-*t-butylcyclohexanol* (VIII) *and* (IX).—Crude product (3·1 g.) from the reaction of hydrocarbon (I) with lead tetra-acetate was hydrolysed with aqueous-methanolic potassium hydroxide at 20° during 24 hr. After distillation of methanol the product was isolated by ether-extraction as a solid (1·8 g.) which was chromatographed in light petroleum on alumina. Elution with light petroleum gave unchanged hydrocarbon (I) (0·18 g.); elution with benzene–ether (85 : 15) gave trans-1-*hydroxymethyl*-4-*t-butylcyclohexanol* (0·25 g.), plates (from carbon tetrachloride), m. p. 100·5° (Found: C, 70·95; H, 11·95. $C_{11}H_{22}O_2$ requires C, 70·9; H, 11·9%). Further elution with benzene–ether (4 : 1) gave cis-1-*hydroxymethyl*-4-*t-butylcyclohexanol* (0·75 g.), feathery crystals (from carbon tetrachloride), m. p. 125° (Found: C, 71·0; H, 11·9%). Elution with ether–methanol (1 : 1) gave a solid (12 mg.), having m. p. 360° after crystallisation from light petroleum: this was not further investigated. Each of the glycols consumed one mol. of sodium metaperiodate and gave 4-t-butylcyclohexanone (identified by m. p. and mixed m. p.).

8-*t-Butyl*-2-(4-*t-butylcyclohexyl*)-1,3-*dioxaspiro*[4,5]*decane*.—(*a*) Crude product (1·26 g.) from the reaction of hydrocarbon (I) and lead tetra-acetate was heated under reflux with 2N-methanolic hydrochloric acid during 4 hr. The product (0·72 g.) was isolated with ether and chromatographed on alumina. Elution with light petroleum gave the acetal (0·45 g.), m. p. 160—164° (from ethanol) raised on recrystallisation to 166—167° undepressed on admixture with a sample prepared as under (*b*). With 2,4-dinitrophenylhydrazine sulphate in methanol the acetal gave the 2,4-dinitrophenylhydrazone, m. p. 170—171°, of 1-formyl-4-t-butylcyclohexane. Further elution of the column with light petroleum–benzene gave 1-formyl-4-t-butylcyclohexane (64 mg.), identified as its 2,4-dinitrophenylhydrazone.

(*b*) *cis*-1-Hydroxymethyl-4-t-butylcyclohexanol (69 mg.) and 1-formyl-4-t-butylcyclohexane (70 mg.) were heated under reflux with 3N-methanolic hydrochloric acid during 3 hr. The product, isolated with ether, was chromatographed on alumina. Elution with light petroleum followed by crystallisation from ethanol gave the *acetal*, m. p. 165—166° (Found: C, 78·45; H, 11·8. $C_{22}H_{40}O_2$ requires C, 78·5; H, 12·0%).

Reaction of Lead Tetra-acetate with 1-*Methylene*-4-*t-butylcyclohexane in Acetic Acid*.—Hydrocarbon (I) (250 mg.) and lead tetra-acetate (760 mg.) in glacial acetic acid (60 c.c.) were heated under reflux during 2 hr. The product, isolated with chloroform, had an infrared spectrum showing negligible absorption in the 1775 cm.$^{-1}$ region. After hydrolysis with aqueous-methanolic potassium hydroxide at 20° during 12 hr. the neutral fraction was isolated with ether. Evaporation of the ether extract gave a solid residue (140 mg.) which was chromatographed in light petroleum on alumina. Elution with light petroleum gave an oil (14 mg.); elution with benzene–ether (1 : 9) gave *trans*-1-hydroxymethyl-4-t-butylcyclohexanol (20 mg.), m. p. 97—98°, and further elution with ether gave the *cis*-glycol (VIII) (85 mg.), m. p. 123—124°.

Inhibition by Iodine.—Hydrocarbon (I) (107 mg.), lead tetra-acetate (460 mg.), and iodine (300 mg.) were heated under reflux in dry benzene during 5 hr. After being washed with aqueous sodium thiosulphate and water the solution was dried and evaporated, giving the product as an oil. The infrared spectrum showed no band in the 1775 region; a strong band at 1740 cm.$^{-1}$ (normal acetate) was present.

cis- *and* trans-1-*Acetoxymethyl*-4-*t-butylcyclohexanol*.—The *cis*-glycol (VIII) (66 mg.) in acetic anhydride (3 c.c.) containing a trace of pyridine was set aside at 20° for 16 hr. After addition of water the product was filtered off and chromatographed on alumina. Elution with benzene gave the cis-*acetate* (75 mg.), m. p. 79—80° (from light petroleum) (Found: C, 68·7; H, 10·65. $C_{13}H_{24}O_3$ requires C, 68·4; H, 10·5%), $\nu_{max.}$ 3590 (OH), 1748, 1239 (OAc), and 1375 cm.$^{-1}$ (Bu^t).

In a similar way the *trans*-glycol (IX) (61 mg.) gave the *trans*-acetate (71 mg.), m. p. 54—55·5° (from light petroleum).

Dehydration of cis- *and* trans-1-*Acetoxymethyl*-4-*t*-*butylcyclohexanol.*—Phosphorus oxychloride (0·05 c.c.) was added to the cooled solution of the monoacetate in pyridine (1 c.c.). After 30 min. at 20°, water was added, and the product was isolated with ether and introduced on a short column of alumina. Elution with light petroleum–benzene (9 : 1 and 4 : 1) gave the dehydration product, which from its infrared spectrum was probably 1-acetoxymethyl-4-t-butylcyclohexene. Further elution with benzene gave the unchanged monoacetate. Results are tabulated.

	Monoacetate (mg.)	Dehydration product (mg.)	Unchanged monoacetate (mg.)	$\frac{\text{Dehydrated}}{\text{Unchanged}}$
cis	20·4	10·3	5·2	1·98
cis	15·6	8·2	6·0	1·40
trans	16·1	4·2	10·0	0·42
trans	16·0	4·5	11·3	0·40

Conversion of cis-1-*Hydroxymethyl*-4-*t*-*butylcyclohexanol into* cis-1-*Methyl*-4-*t*-*butylcyclohexanol.*—The *cis*-glycol (50 mg.) and toluene-*p*-sulphonyl chloride (53 mg.) in dry pyridine (1 c.c.) were set aside at 20° for 48 hr. Ice was added and after 30 min. at 0° the product was isolated with ether as a solid, $\nu_{\text{max.}}$ 3570 (OH) and 1181 and 1193 cm.$^{-1}$ (toluene-*p*-sulphonate). The crude toluene-*p*-sulphonate was dissolved in dry ether (15 c.c.), and lithium aluminium hydride (100 mg.) was added. After 1 hour's heating under reflux acid was added and the product was isolated with ether as a solid (43 mg.). After chromatography and crystallisation from light petroleum this had m. p. 90° alone or mixed with *cis*-1-methyl-4-t-butylcyclohexanol. The infrared spectra were identical.

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