The Oxymercuration of Conformationally Biassed Cyclohex-2-enols

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The oxymercuration–reduction of *cis*-5-t-butylcyclohex-2-enol (I) in 50% aqueous tetrahydrofuran proceeds with high stereoselectivity to give *trans*-3-hydroxy-*cis*-5-t-butylcyclohexanol (III). With *trans*-5-t-butylcyclohex-2-enol (II) the reaction is much less stereoselective and the major product is *cis*-3-hydroxy-*trans*-5-t-butylcyclohexanol (IV). Kinetic data for oxymercuration of these and related olefinic substrates have been obtained. The results are considered in terms of the possible directing influence of the hydroxy-group. It is concluded that this influence is predominantly of a polar (inductive) nature, and that a direct stabilising interaction between hydroxy and a *cis*-vicinal mercury atom is small or non-existent.

A considerable amount of interest has been shown recently in the oxymercuration–reduction[1] of cyclohex-2-enol and related derivatives. Although the original claim that stereospecific formation of *trans*-cyclohexane-1,3-diol[2] occurred has not been upheld, since later work[3] has shown that *cis*-diol (*ca.* 20%) and small amounts of 1,2-glycols are also formed, the reaction has some synthetic potential. In the course of other work[4] the *cis*- and *trans*-5-t-butylcyclohex-2-enols[5] were available and we decided to investigate their oxymercuration as examples of conformationally biassed cyclohexenols. After completion of this work a communication by Klein and Levene[6] described the oxymercuration of *cis*-5-t-butycyclohex-2-enol and of *cis*- and *trans*-5-phenylcyclohex-2-enol. Their results will be described later in conjunction with ours.

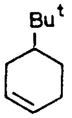
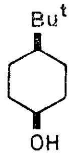
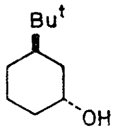
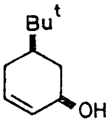
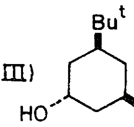
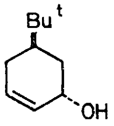
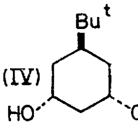
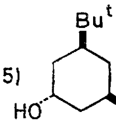
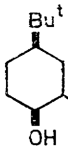
Our results for oxymercuration–reduction in 50% tetrahydrofuran (THF)–water of 4-t-butylcyclohexene and *cis*- (I) and *trans*-5-t-butylcyclohex-2-enol (II) are given in Table 1. Details of the assignment of structure to the products are provided in the Experimental section. Although the structures of the initial oxymercuration adducts can only be indirectly inferred in most cases, the presumption that they are formed *via trans*-diaxial opening of an intermediate mercurinium ion is corroborated in the case of *cis*-5-t-butylcyclohexanol by isolation of the adduct (VI). In the n.m.r. spectrum of (VI) [in $(CD_3)_2SO$] 1-H absorbed at τ 6·0, $W_{\frac{1}{2}}$ 20 Hz, indicative of an axial hydrogen, while absorption due to 3-H, τ 5·65, $W_{\frac{1}{2}}$ 8 Hz, and 2-H, τ 6·98, $W_{\frac{1}{2}}$ 10 Hz was typical of equatorial hydrogens. Reduction of (VI) by alkaline sodium borohydride gave the glycol (III).

Although our results for *cis*-5-t-butylcyclohexenol (I) are in substantial agreement with those of Klein and Levene,[6] our data for *trans*-5-t-butylcyclohexenol (II) do not correlate well with theirs for *trans*-5-phenylcyclohex-2-enol (VII). Thus, they report that (VII) gives *cis*-3-hydroxy-*trans*-5-phenylcyclohexanol (60%) and *trans*-3-hydroxy-*cis*-5-phenylcyclohexanol (5%).

We have also obtained kinetic data for oxymercuration of the above substrates in 50% aqueous THF at 25°. The formation of adduct, which shows strong end absorption in the u.v. region, could be monitored at 220—225 nm. (*cf.* ref. 7). Rates were first order in mercury(II) acetate and substrate, and the following second-order rate constants (l. M^{-1} sec.$^{-1}$) were obtained: cyclohexene, 1·92 ± 0·05; 4-t-butylcyclohexene, 1·92 ± 0·05; cyclohex-2-enol, 0·80 ± 0·04; *cis*-5-t-butylcyclohexenol (I), 0·41 ± 0·02; and *trans*-5-t-butylcyclohexenol (II), 0·069 ± 0·003. Although these rates are several orders of magnitude slower than those reported by Halpern and Tinker[7] for oxymercuration with

Table 1

Products from oxymercuration–reduction [THF–water, (1 : 1), at 20°]

Substrate	Products[a]		
	 (47)	 (53)	
(I) 	(III)  (96)	Other glycols (4)	
(II) 	(IV)  (75)	 (17)	(V)  (8)

[a] Figures quoted in parentheses are percentage of total hydroxylic product determined by g.l.c. of acetates in the case of the alcohols, and of trimethylsilyl ethers in the case of the glycols. Structures were assigned by isolation of products and spectroscopic and analytical data and/or by comparison with authentic samples of known compounds. [b] Klein and Levene quote *cis,cis*-5-t-butylcyclohexane-1,3-diol (4%); we did not accurately estimate the minor products since the starting material contained about 3% of the *trans*-isomer which we were unable to remove.

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[1] H. C. Brown and P. Geoghegan, *J. Amer. Chem. Soc.*, 1967, **89**, 1522.

[2] S. Moon and B. H. Waxman, *Chem. Comm.*, 1967, 1283.

[3] B. Rickborn and M. R. Johnson, *Chem. Comm.*, 1968, 1073; (*b*) S. Moon, C. Ganz and B. H. Waxman, *ibid.*, 1969, 866; (*c*) M. R. Johnson and B. Rickborn, *J. Org. Chem.*, 1969, **34**, 2781.

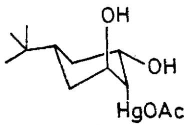
[4] P. Chamberlain, M. L. Roberts, and G. H. Whitham, *J. Chem. Soc.* (*B*), preceding paper.

[5] R. J. Ferrier and N. Prasad, *J. Chem. Soc.* (*C*), 1967, 1417.

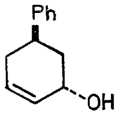
[6] J. Klein and R. Levene, *Tetrahedron Letters*, 1969, 4833.

[7] J. Halpern and H. B. Tinker, *J. Amer. Chem. Soc.*, 1967, **89**, 6427.

mercury(II) acetate in aqueous perchloric acid, *e.g.* they report $k = 5 \times 10^3$ and $4{\cdot}3 \times 10^2$ l. M^{-1} sec.$^{-1}$ for cyclohexene and cyclohex-2-enol, respectively, the trend is in the expected direction for the different reaction conditions. In aqueous perchloric acid and reactive mercury species is probably hydrated Hg^{2+} or $HgClO_4^+$ while in aqueous THF it is probably $Hg(OAc)_2$. The change in solvent ionising power from water to 50% aqueous THF also should have a rate-retarding effect.

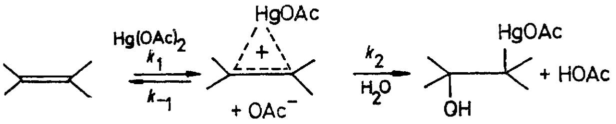


(VI)



(VII)

We accept the premise that oxymercuration of olefins involves rapid pre-equilibrium formation of a mercurinium ion as unstable intermediate, followed by rate- and product-determining attack of solvent[8] *i.e.* reaction (1),



(1)

where $k_{-1} > k_1 \gg k_2$. Within this context, the stereochemistry of oxymercuration of cyclohex-2-enols can be discussed in terms of three factors:[3,6] (*a*) preferential diaxial opening of the mercurinium ion through a chair-like transition state, (*b*) predominant attack of solvent at C-3 rather than at C-2 owing to the inductive influence of the hydroxy-group,* and (*c*) assistance by the hydroxy-group of *cis*-attack by mercury(II) species due to complex formation.

The operation of the first factor is clearly shown in the oxymercuration of 4-t-butylcyclohexene to give solely the axial 3- and 4-t-butylcyclohexanols. It is not easy to differentiate between the relative importance of factors (*b*) and (*c*). Our rationalisation for the formation of products from *cis*- and *trans*-5-t-butylcyclohex-2-enols is depicted in the Scheme. At first sight it might appear that the appreciable amount of products (III) and (V) obtained in defiance of factors (*a*) and (*b*), respectively, from the *trans*-alcohol (II) is indicative of the operation of the third factor (*c*). However, the free energy difference between the relevant transition states (XII) and (XI) leading to (IV) and (III) is only 0·4 kcal./mole (Curtin–Hammett principle), while that between (IX) and (VIII) can similarly be estimated as 0·8 kcal./mole (accepting Klein and Levene's[6] percentages). Since, in the absence of a stabilising interaction between OH and vicinal HgOAc, the free energies of the twist boat transition states (VIII) and (XI) would be expected to be equal (the hydroxy-groups are isoclinal in both cases), a rough estimate of 0·4 kcal./mole for the free energy difference between (IX) and (XII) can be made. This is of the order of magnitude of the conformational preference for a hydroxy-group in a cyclohexane ring.[10] The difference between the two substrates (I) and (II) can therefore be ascribed primarily to the axial hydroxy-group present in transition state (XII).

A similar analysis of the oxymercuration–reduction products from cyclohex-2-enol (78% *trans*-1,3-diol and 20% *cis*-1,3-diol in 50% aqueous THF[3]) leads to an estimated free-energy difference of 0·8 kcal./mole between the respective transition states (XIII) and (XIV). Again, within the limits of this treatment, this is of the right order of magnitude for a purely conformational effect determined by the hydroxy-group and requires no special stabilising interaction between OH and HgOAc in (XIII). The solvent effect favouring *trans*-1,3-diol in more aqueous media[3c] is also interpretable in these terms since it is well known that the hydroxy-group is effectively 'larger' in hydrogen-bonding solvents.[11]

We have attempted to glean further information bearing on factor (*c*) from the kinetic data. The rate constants for the allylic alcohols (I) and (II) can be dissected into the contributions for product derived from attack of $Hg(OAc)_2$ *cis* to t-butyl: 0·40 and 0·051 l. M^{-1} sec.$^{-1}$ for (I) and (II), respectively. Thus attack *cis* to t-butyl is eight times faster for (I) than for (II). The free-energy difference between (I) and (II) in aqueous dioxan or aqueous acetone is 0·4 kcal./mole[5] and would be expected to be similar for aqueous THF. Neglecting an earlier estimate, which depended on assumptions about the twist boat transition states (VIII) and (XI) and therefore may be invalid, the free-energy difference between transition states (IX) and (XII) would not be expected to be greater than *ca.* 0·8 kcal./mole (conformational preference for a hydroxy-group) in the absence of a vicinal stabilising interaction between OH and HgOAc in (IX). Hence the estimated $\Delta\Delta G^{\ddagger}$ for attack *cis* to t-butyl in (I) and (II) is 0·4 kcal./mole which corresponds to a twofold rate difference at 25°. The discrepancy between this figure and the value of 8 found amounts to a free-energy difference of 0·8 kcal./mole which could be ascribed to a stabilising interaction between OH and HgOAc. It seems safe to conclude therefore, from this estimate and the earlier stereochemical considerations, that such an interaction in the oxymercuration of cyclohex-2-enols is either very small or non-existent. This conclusion cannot be extrapolated

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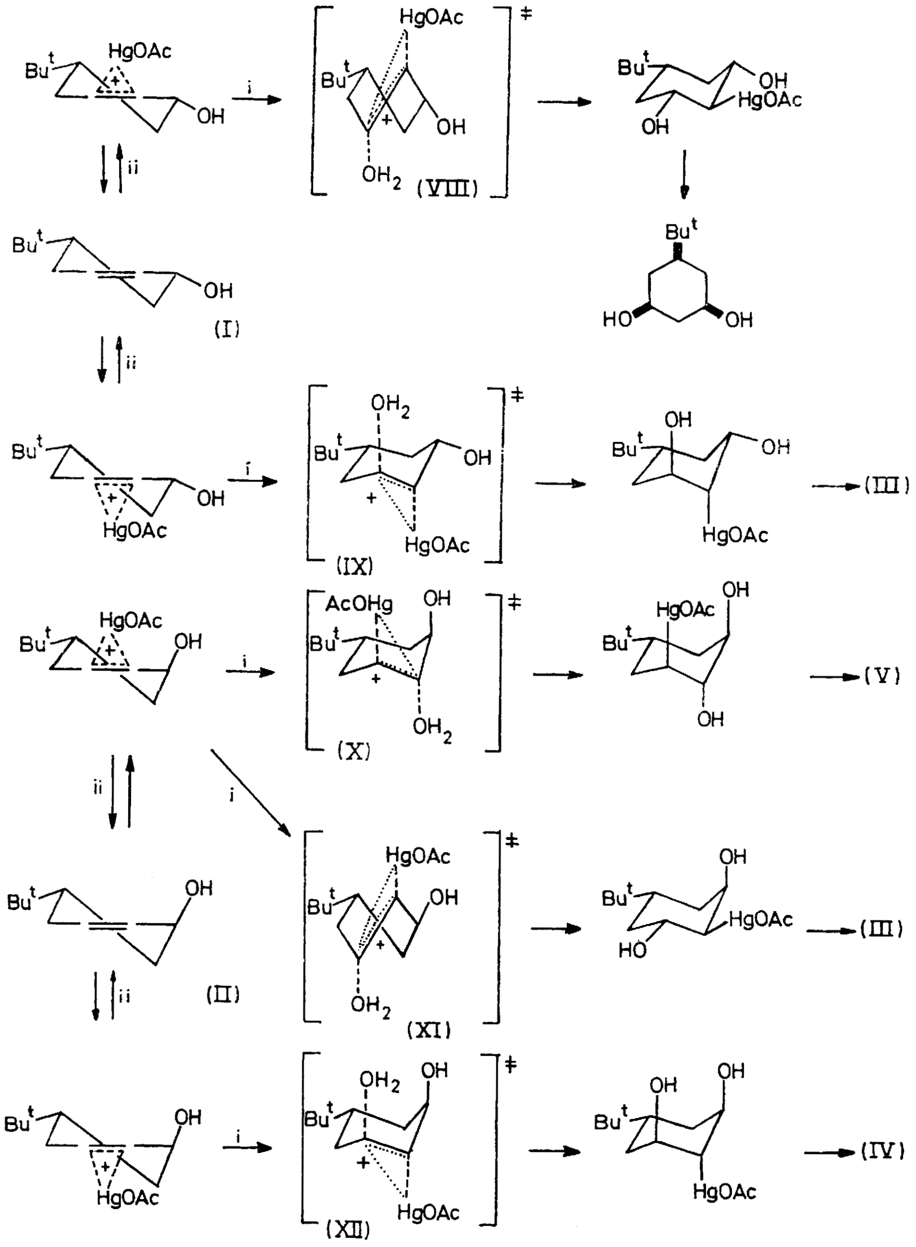
* A similar effect is seen in the cleavage of 2,3-epoxycyclohexanols with hydrogen chloride.[9]

[8] W. Kitching, *Organometallic Chem. Rev.*, 1968, **1**, 61; W. L. Waters and E. F. Kiefer, *J. Amer. Chem. Soc.*, 1967, **89**, 6261; W. L. Waters, W. S. Linn, and M. C. Caserio, *ibid.*, 1968, **90**, 6741.

[9] E. J. Langstaff, E. Hamanaka, G. A. Neville, and R. Y. Moir, *Canad. J. Chem.*, 1967, **45**, 1907.

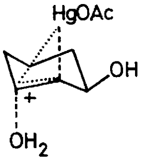
[10] J. A. Hirsch, *Topics Stereochem.*, 1967, **1**, 199.

[11] E. L. Eliel and S. H. Schroeter, *J. Amer. Chem. Soc.*, 1965, **87**, 5030.

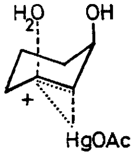


Reagents: i, H_2O; ii, $Hg(OAc)_2$

to all unsaturated alcohols as is shown, for example, by the highly stereospecific formation of *trans*-cyclohexane-1,4-diol from cyclohex-3-en-1-ol.[12]



(XIII)



(XIV)

EXPERIMENTAL

For general points see preceding paper.[4]

Oxymercuration of 4-*t-Butylcyclohexene*.—The method of Brown and Geoghegan [1] was used for all the oxymercurations described. To a stirred solution of mercury(II) acetate (1·6 g., 1 mol.) in water (7 ml.) was added tetrahydrofuran (7 ml., purified by filtration through alumina) followed by 4-t-butylcyclohexene (0·69 g., 1 mol.). The yellow precipitate dissolved in *ca.* 1 min. to give a clear solution. After 1 hr., sodium hydroxide (3M; 5 ml.) was added, followed by sodium borohydride (0·5M) in sodium hydroxide (3M; 5 ml.). The aqueous phase was saturated with potassium carbonate and the precipitated mercury was removed by filtration through Celite. The product was isolated by ether extraction. After drying ($MgSO_4$) and evaporation, a mixture of 3- and 4-t-butylcyclohexanols (0·77 g., 98%) was obtained. G.l.c. (A) showed the presence of less than 1% of equatorial alcohols.

A small sample of product was acetylated under the usual conditions. G.l.c. (C) showed the presence of *trans*-3-t-butylcyclohexyl acetate (53%) and *cis*-4-t-butylcyclohexyl acetate (47%), the identity of the products being confirmed by peak-enhancement with authentic samples.

Oxymercuration of trans-5-*t-Butylcyclohex*-2-*enol*.—*trans*-5-t-Butylcyclohex-2-enol [4,5] (2·5 g., 1 mol.) was oxymercurated with mercury(II) acetate (5·2 g., 1 mol.) in 50% aqueous tetrahydrofuran (30 ml.). Work-up under the usual conditions yielded a mixture of t-butylcyclohexanediols (2·7 g., 96%), $\nu_{max.}$ (liq. film) 3400 (O–H), 2950 (C–H), 1375 (Me_3C), 1115, and 1000 cm.$^{-1}$.

A drop of the crude mixture was treated with pyridine (5 drops), hexamethyldisilazane (2 drops) and trimethylsilyl chloride (1 drop).[13] After 1 hr. the solution of trimethylsilyl ethers was analysed directly by g.l.c. (A) which showed the presence of three products, ratio 8 : 75 : 17%.

The diol mixture was converted into a mixture of diacetates, crude yield 4·0 g. (90%). The product was adsorbed on silica gel (350 g.) from light petroleum. Elution with graded mixtures of light petroleum and ether yielded a mixture of the two minor products (0·66 g.) followed by the major product (3·12 g.).

Recrystallisation of the major product from light petroleum (b.p. 60—80°) yielded cis-3-*acetoxy*-trans-5-*t-butylcyclohexyl acetate* (Found: C, 65·5; H, 9·3. $C_{14}H_{24}O_4$ requires C, 65·6; H, 9·45%), m.p. 59—61°, τ 9·05, (9H, s, Me_3C), 7·7—9·0 (7H, complex m), 8·0 (6H, s, CH_3CO), and 4·9 (2H, m, $W_{\frac{1}{2}h}$ 11 Hz, AcOCH).

The mixture of minor products was hydrolysed back to the diols (yield 0·34 g.). The material was adsorbed on silca gel (25 g.) from 10% ether in benzene. Elution with graded mixtures of benzene and ether yielded first a sample of the least abundant product (90 mg.) which was recrystallised from light petroleum–benzene to give a pure specimen, m.p. 139—141°, with a phase-transition prior to melting. It was identical with an authentic sample of *trans*-2-hydroxy-*cis*-4-t-butylcyclohexanol (see later) as judged by m.p., mixed m.p., and i.r. spectrum. Further elution gave the second most abundant glycol (130 mg.), R_F on t.l.c. and i.r. spectrum identical with *trans*-3-hydroxy-5-t-butylcyclohexanol (see later).

cis-3-*Hydroxy*-trans-5-*t-butylcyclohexanol*.—*cis*-3-Acetoxy-*trans*-5-t-butylcyclohexyl acetate (2·5 g.) was hydrolysed with sodium hydroxide in aqueous methanol. Recrystallisation from light petroleum yielded a sample of *cis*-3-hydroxy-*trans*-5-t-butylcyclohexanol, m.p. 53—54°, (1·25 g., 80%), $\nu_{max.}$ (CCl_4) 3621 (O–H free), 3543 (O–H, intramolecular hydrogen bond), 2960 (C–H), 1370 (Me_3C), 1115 (C–O), and 910 cm.$^{-1}$; τ ($CDCl_3$) 9·05 (9H, s, Me_3C), 7·8—9·0 (7H, complex m), 6·2 (2H, s, O–H), and 5·85 (2H, m, $W_{\frac{1}{2}h}$ 8 Hz, *H*–C–OH).

trans-2-*Hydroxy*-cis-4-*t-butylcyclohexanol*.— 1,2-Epoxy-*cis*- and *trans*-4-t-butylcyclohexanes (1·1 g.) acetic acid (5 ml.) and sodium acetate (3 g.) were heated under reflux for 5 hr. The mixture was added to water and the product was isolated by ether extraction. The ethereal layer was washed ($NaHCO_3$), dried ($MgSO_4$), and evaporated to yield a mixture of hydroxyacetates (1·25 g., 91%), $\nu_{max.}$ (liq. film) 3450 (O–H), 2950 (C–H), 1720 (C=O), 1375 (Me_3C), 1250 (C–O), and 1040 cm.$^{-1}$.

The product was heated under reflux with potassium hydroxide (2 g.) in methanol (20 ml.) for 2 hr. The mixture was then added to brine and the product was isolated by ether extraction. Recrystallisation from light petroleum (b.p. 60—80°)-benzene yielded *trans*-2-hydroxy-*cis*-4-t-butylcyclohexanol as plates, m.p. 141—142° (lit.,[14] 141—142°) with a phase-transition prior to melting; $\nu_{max.}$ (Nujol) 3400 (O–H), 1370 (Me_3C), 1160, 1060, 1030, 1020, and 1000 cm.$^{-1}$.

The trimethylsilyl ether (prepared as already described) was pure [g.l.c. (A)].

Oxymercuration of cis-5-*t-Butylcyclohex*-2-*enol*.—*cis*-5-t-Butylcyclohex-2-enol (0·40 g.) was oxymercurated. G.l.c. (A) of the trimethylsilyl ethers showed that the product was 96% pure; the impurities were attributated to the small amount of *trans*-5-t-butylcyclohex-2-enol present in the starting material. The product was acetylated (crude yield 0·59 g., 89%) and adsorbed on silica gel (70 g.) from light petroleum. Elution with graded mixtures of light petroleum and ether yielded some mixed fractions (210 mg.) followed by the major product (330 mg.). Distillation yielded a sample of *trans*-3-acetoxy-5-t-butylcyclohexyl acetate, b.p. 84—88°/0·15 mm., pure by t.l.c., $\nu_{max.}$ (liq. film) 2950 (C–H), 1720 (C=O), 1375 (Me_3C), 1240 (C–O), 1140, and 1120 cm.$^{-1}$, τ 9·05 (9H, s, Me_3C), 7·7—9·0 (7H, complex m), 8·03 (3H, s, CH_3CO), 7·97 (3H, s, CH_3CO), 5·05 (1H, triplet of triplets, J_{aa} 11·5 Hz, J_{ae} 4 Hz, α to equatorial AcO), and 4·9 (1H, t, J 3 Hz, with further fine splitting, α to axial AcO).

trans-3-*Hydroxy*-5-*t-butylcyclohexanol*.— *trans*-3-Acetoxy-5-t-butylcyclohexyl acetate (300 mg.) was hydrolysed with sodium hydroxide in aqueous methanol. Recrystallisation of the crude product from light petroleum (b.p. 60—80°)-benzene yielded trans-3-*hydroxy*-5-*t-butylcyclohexanol* (120

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[12] H. B. Henbest and B. Nicholls, *J. Chem. Soc.*, 1959, 227.

[13] C. C. Sweeley, R. Bentley, M. Makita, and W. W. Wells, *J. Amer. Chem. Soc.*, 1963, **85**, 2497.

[14] N. A. LeBel and R. F. Czaja, *J. Org. Chem.*, 1961, **26**, 4768.

mg., 64%) (Found: C, 69·8; H, 11·7. $C_{10}H_{20}O_2$ requires C, 69·95; H, 11·75%), m.p. 124—127°, $\nu_{max.}$ (Nujol) 3350 (O–H), 2950 (C–H), 1375 (Me_3C), 1040, 1015, and 1000 cm.$^{-1}$. τ ($CDCl_3$) 9·05 (9H, s, Me_3C), 7·7—9·0 (7H, complex m), 6·05 (1H, m, α to equatorial O–H), and 5·7 (1H, m, α to axial OH).

cis-2-,*trans*-6-*Dihydroxy*-cis-4-*t-butylcyclohexylmercury*(II) *Acetate*.—To a stirred solution of mercury(II) acetate (1·47 g., 1 mol.) in water (5 ml.) was added *cis*-5-t-butylcyclohex-2-enol (0·72 g., 1 mol.) in tetrahydrofuran (5 ml.). After 2 hr. the solution was evaporated to yield a viscous crude product. This was dried by azeotroping with benzene. Recrystallisation from benzene–chloroform yielded crystals of *cis*-2-,*trans*-6-dihydroxy-*cis*-4-t-butylcyclohexylmercury(II) acetate (1·1 g., 55%), m.p. 136—138°. $\lambda_{max.}$ (H_2O–THF, 1 : 1) 215 (ε 2980), 222 (1580), and 225 (695) nm. The spectrum was identical with that of a solution of mercury(II) acetate in 50% aqueous tetrahydrofuran to which excess of *cis*-5-t-butylcyclohex-2-enol had been added. τ [$(CD_3)_2SO$] 9·08 (9H, s, Me_3C), 8·0—9·0 (5H, complex m), 8·07 (3H, s, CH_3CO), 6·98 (1H, m, $W_{\frac{1}{2}h}$ 10 Hz, α to –HgOAc), 6·0 (1H, m, $W_{\frac{1}{2}h}$ 20 Hz, α to equatorial O–H), 5·65 (1H, m, $W_{\frac{1}{2}h}$ 8 Hz, α to axial O–H), and 5·5br (2H, O–H).

Reduction of a sample of the organomercurial with alkaline sodium borohydride yielded a product with an i.r. spectrum identical to that of *trans*-3-hydroxy-5-t-butylcyclohexanol.

Kinetics of Oxymercuration of the Olefins.—Standard solutions of mercury(II) acetate in water and the appropriate olefin in tetrahydrofuran (purified by filtration through active alumina) were stored in a thermostatted bath, the concentration of the olefin solution being fractionally higher than that of mercury(II) acetate. To each of two flasks containing 20 ml. of a stock solution of 50% aqueous tetrahydrofuran (stored in the thermostatted bath) was added mercury(II) acetate (1 ml.) solution. To one of the flasks was added tetrahydrofuran (1 ml.) and the absorbance of the solution at a fixed wavelength (in the range 220—225 nm.) was recorded. To the other flask was added olefin solution (1 ml.) and the increase in u.v. absorption with time of a sample of the solution was recorded. In the case of the faster reactions the final absorption was recorded directly after at least ten half-lives. For the slow reactions, an alternative procedure was necessary. The olefin and mercury(II) acetate solutions (1 ml.) were mixed directly. After at least 2 hr., stock solution (20 ml.) was added and the absorbance of the solution was recorded.

The concentrations of the various species were calculated directly from the curve. By means of standard integration procedures, a second-order rate plot, first-order in each component, was obtained. The plot was linear over the first 40—70% of the reaction.

The results for cyclohexene are summarised in Table 2.

In a similar way rate constants were obtained for 4-t-butylcyclohexene, cyclohex-2-enol, and *cis*- and *trans*-5-t-butylcyclohexenol. The values obtained are cited in the Discussion section and in each case are the average of three determinations.

In order to confirm the validity of the kinetic method the following competitive experiment was carried out.

Competitive Oxymercuration of Cyclohexene and Cyclohex-2-enol.—Injection of weighed mixtures gave the results in Table 3 under the g.l.c. conditions used (column A, 50—180° temperature programmed at a rate of 8°/min.) (the isomeric diols were not resolvable under the conditions used).

TABLE 2

Oxymercuration of cyclohexene

	1	2	3
Initial concentration of mercury(II) acetate (b)	1·55	1·35	1·29
Initial concentration of olefin (a) (mmole/l.)	2·22	2·22	2·49
Wavelength (nm.)	221	220	221
Initial absorbance	0·248	0·256	0·240
Final absorbance	0·892	0·830	0·788
Gradient of plot $[(a - b)k_2/2{\cdot}303] \times 10^4$	5·90	7·46	9·92
k_2 (l./mole/sec.)	1·89	1·97	1·90

$k_2 = 1{\cdot}92 \pm 0{\cdot}05$ l. M^{-1} sec.$^{-1}$

TABLE 3

Compound	Relative response/mole
Cyclohexene	1·00
Cyclohexanol	1·06
Cyclohex-2-enol	1·18
Cyclohexane-1,3-diols	0·94

To a solution of cyclohexene and cyclohex-2-enol (0·1M in each component) in tetrahydrofuran was added known volumes of water followed by a known volume of mercury(II) acetate solution (0·2M) as shown in Table 4.

TABLE 4

Solution	Mercury(II) acetate (m.)	Water (ml.)	Olefin solution (ml.)	Relative conc. $Hg(OAc)_2$/olefin
1	0·6	1·4	2·0	0·30
2	0·8	1·2	2·0	0·40
3	1·0	1·0	2·0	0·50

After 3 hr. each solution was worked-up with sodium hydroxide–sodium borohydride and the aqueous phase was saturated with potassium carbonate. The tetrahydrofuran layer was decanted and analysed directly by g.l.c. The results (average of two injections) are shown in Table 5.

TABLE 5

Solution	Cyclohexene (%)	Cyclohexanol (%)	Cyclohex-2-enol (%)	Cyclohexane-1,3-diols (%)	Relative rate
1	33	18	40	9	2·42
2	23	25	34	18	2·08
3	16	31	28	25	2·20

The relative rates of oxymercuration were calculated by use of the equation:

$$k_1/k_2 = \log\,[a/(a - x_1)]/\log\,[a/a(a - x_2)]$$

where a is the initial and $a - x$ the final concentration of reactant. The average result, cyclohexene: cyclohexenol $2{\cdot}23 \pm 0{\cdot}19 : 1$ is in excellent agreement with the value $2{\cdot}39 \pm 0{\cdot}15 : 1$ derived from the direct kinetics.

We are grateful to the S.R.C. for the award of a Research Studentship to one of us (P. C.).

[0/141 *Received, January 19th*, 1970]