

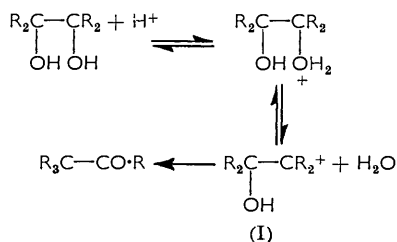
1114. *Tracer Studies on Alcohols. Part V.* The Pinacolic Rearrangement of cis- and trans-1,2-Dimethylcyclohexane-1,2-diol.*

By C. A. BUNTON and M. D. CARR.

The pinacolic rearrangement of both *cis*- and *trans*-1,2-dimethylcyclohexane-1,2-diol in aqueous acid gives 1-acetyl-1-methylcyclopentane and a small amount of 2,2-dimethylcyclohexanone. The variation of rate with acidity, the solvent deuterium isotope effect, and the Arrhenius parameters support an *A-1* mechanism. The pinacolic rearrangement is accompanied by rearrangement of one diol to the other, and exchange of oxygen-18 with the solvent. These observations suggest that a common carbonium-ion intermediate can be captured by water to give both diols, or can rearrange with ring contraction or methyl migration. The epoxide is hydrolysed in acid to the *trans*-diol.

THIS work extends studies on the exchange of oxygen-18 between water and pinacol¹ during the rearrangement of the 1,2-dimethylcyclohexane-1,2-diol. Comparison of the rates of exchange and rearrangement showed that, in dilute acid, an intermediate reverted to the diol several times faster than it went forward to pinacolone. It was supposed that this intermediate was the classical carbonium ion, although oxygen exchange could result from formation and hydrolysis of an epoxide. The latter route of oxygen exchange is not available for an alicyclic *cis*-diol, and therefore we examined both isomers of 1,2-dimethylcyclohexane-1,2-diol. They rearrange to common ketonic products, and to each other, and both exchange their oxygen atoms with water. We conclude that oxygen exchange, at least of the *cis*-diol, is not caused by formation and hydrolysis of the epoxide, because its hydrolysis gives only *trans*-diol.

Collins has reviewed the evidence on the mechanisms of pinacolic rearrangements and concludes that it supports the general scheme:²



The relative rates of return and rearrangement of species (I) depend upon the medium and the diol, and it may be a bridged, non-classical ion, or mixture of ions.

* Part IV, *J.*, 1958, 4747.

¹ Bunton, Hadwick, Llewellyn, and Pocker, *J.*, 1958, 403.

² Collins, *Quart. Rev.*, 1960, **14**, 357.

Kinetics.—Rearrangement was followed by determining the concentration of diols. The *cis*-diol reacts very readily with both periodic acid and lead tetra-acetate, but the *trans*-diol is almost inert to periodic acid, although it reacts with lead tetra-acetate.³ Therefore, by using lead tetra-acetate we measure the overall conversion of diols into ketones, and by using periodic acid we measure the conversion of the *cis*-diol into *trans*-diol and ketones. The rate of rearrangement of the *cis*-diol, measured with periodic acid, was greater than that measured with lead tetra-acetate (Table 1), and therefore the *cis*-diol rearranges to *trans*-diol as well as to ketone. In the next section we show that the *trans*-diol rearranges to *cis*-diol as well as to ketone.

Although the rates of rearrangement depend slightly on the method of analysis and are therefore not strictly comparable, the reactivities of the two diols are very similar to that of pinacol.¹ Plots of the logarithm of the first-order rate constant, k , against

TABLE 1.
Rates of pinacolic rearrangement.
At 59.7° unless specified.

<i>trans</i> -Diol.												
[HClO ₄] (M)	0.61		0.91		1.81	2.78			3.70			
10 ⁶ k (sec. ⁻¹)	6.53 *	13.1 * †	1.41	12.7 *	6.29	20.7	21.2	21.2	62.2			
log (k + H ₀) + 6 ...	—	—	0.99	—	1.10	—	1.19	—	1.23			
<i>cis</i> -Diol.												
[HClO ₄] (M)	0.465		0.91			0.98	1.81	2.78	3.70			
10 ⁶ k (sec. ⁻¹)	3.06 *	6.72 * †	0.85	0.87	7.36 *	154 †	0.88	3.47	10.9 §	11.5	34.1	29.3 §
log (k + H ₀) + 6 ...	—	—	0.77	0.78	—	—	0.76	0.85	—	0.93	0.97	—

* 74.7°. † 97.2°. ‡ D₂O (96%). § Analysis by lead tetra-acetate.

TABLE 2.
Composition of ketonic products.

Mole % of 1-acetyl-1-methylcyclopentane. Temp. 59.7° unless specified in parentheses.
[HClO₄] = 3.12M.

trans-Diol 98% (25°); 97%; 92% (100°).
cis-Diol 93%; 91% (100°).

Hammett's acidity function, $-H_0$, are linear with slopes *ca.* 1.1 (Table 1). Plots of log ($k + H_0$) against log a_{H_2O} (a_{H_2O} is the activity of water) are not linear. Their slopes vary from -2.6 to -1.5 for the *cis*-diol, and from -5.8 to -1.5 for the *trans*-diol. This variation of slope is understandable for a multi-step reaction where increase of acidity, and decrease of a_{H_2O} , favours rearrangement of the carbonium ion to ketones rather than its return to diol. The original form of the Zucker-Hammett hypothesis,⁴ or Bunnett's recent modification of it,⁵ supports an *A-1* mechanism. Further evidence is that, as for the rearrangement of pinacol, the deuterium solvent isotope effect, $k_{D_2O}/k_{H_2O} \approx 2$ (Table 1), and the entropies of activation are positive.^{6,7}

The entropies and energies of activation are: ΔS , *trans*-diol + 18, *cis*-diol + 19, pinacol + 12 e.u.; and E , *cis*- and *trans*-diol 34, pinacol 32 kcal. mole⁻¹ (the values given in ref. 1 are incorrect).

Products.—The major product is 1-acetyl-1-methylcyclopentane (cf. ref. 8). Small

³ (a) Criegee, *Angew. Chem.*, 1958, **70**, 173; (b) Bunton and Carr, *J.*, 1963, 770.

⁴ Long and Paul, *Chem. Rev.*, 1957, **57**, 935, and refs. cited therein.

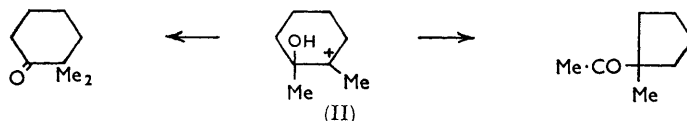
⁵ Bunnett, *J. Amer. Chem. Soc.*, 1961, **83**, 4956.

⁶ Duncan and Lynn, *Austral. J. Chem.*, 1957, **10**, 1.

⁷ (a) Long, Pritchard, and Stafford, *J. Amer. Chem. Soc.*, 1957, **79**, 2362; Pritchard and Long, *ibid.*, 1956, **78**, 6008; 1958, **80**, 4162; (b) Bunton and Shiner, *ibid.*, 1961, **83**, 3207.

⁸ (a) Nametkin and Delektorsky, *Ber.*, 1924, **57**, 583; Meerwein, *Annalen*, 1939, **542**, 123; (b) Bartlett and Pöckel, *J. Amer. Chem. Soc.*, 1937, **59**, 820; Bartlett in "Organic Chemistry," ed. Gilman, Wiley, New York, 1953, Vol. III, p. 60.

amounts of 2,2-dimethylcyclohexanone (2—9%) were isolated by gas-liquid chromatography; there was no epoxide. The ratio of products was approximately the same for each diol and did not change during reaction, but the amount of 2,2-dimethylcyclohexanone increased slightly with increasing temperature (Table 2). A common intermediate (II) could rearrange to either ketone.



The amount of rearrangement of one diol to the other was estimated by stopping the reaction and analysing the mixture of unchanged diols (Table 3). The small amount of *cis*-diol formed by rearrangement of the *trans*-diol can be estimated directly with periodic acid. It is more difficult to estimate the amount of *trans*-formed by rearrangement of the *cis*-diol, because we compare the small difference between two large titres, one of (*cis* + *trans*)-diol obtained from oxidation by lead tetra-acetate, and the other of *cis*-diol obtained from oxidation by periodic acid.

The rapid acid hydrolysis of 1,2-dimethylcyclohexane epoxide goes completely to the *trans*-diol, as expected⁹ (see Experimental section).

Oxygen Exchange.—Unchanged diol was isolated from rearrangement in $H_2^{18}O$, and the isotopic abundance of the diol was determined. We always isolated a mixture of two

TABLE 3.

Interconversion of diols at 59.7°.

	<i>trans</i> -Diol; 1.03M-HClO ₄					<i>trans</i> -Diol; 2.06M-HClO ₄				
Reaction (%)	13	24	39	50	84	16	46	61	79	88
[<i>cis</i>] (mole %)	3.1	5.4	7.9	9.5	8.1	5.1	7.0	8.2	7.7	6.5
	<i>trans</i> -Diol; 2.78M-HClO ₄					<i>cis</i> -Diol; 0.982M-HClO ₄				
Reaction (%)	12	22	31	52	67	85	21	39	62	
[<i>cis</i>] (mole %)	1.8	3.4	5.0	6.6	6.3	6.0	2.5	4.5	2.4	

TABLE 4.

Oxygen exchange of the diols at 59.7°.

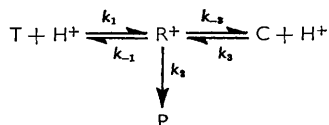
Diol	<i>trans</i> -		<i>cis</i> -	
[HClO ₄] (M)	1.01	2.78	0.89	0.98
10 ⁵ k _e (sec. ⁻¹)	1.23	7.6	0.3*	0.38

* Based on one point at 11% exchange.

diols, and for rearrangement of the *trans*-diol the small amount of accompanying *cis*-diol was destroyed by periodic acid, and the ¹⁸O-abundance of the residual *trans*-diol then determined. This procedure cannot be used for rearrangement of the *cis*-diol; we assumed that the *trans*-diol which is formed will have obtained one atom of ¹⁸O from the solvent, and we corrected the overall isotopic abundance of the mixture of diols accordingly; the correction is small. The rates of oxygen exchange are in Table 4. As for the rearrangement of pinacol,¹ an increase in acidity decreases the amount of exchange relative to rearrangement; it also decreases the amount of interconversion of the diols (Table 3).

Discussion.—We assume a common carbonium-ion intermediate, R⁺, for the rearrangement of both diols, and calculate the relative rates of its decomposition to diols and ketones.

⁹ Parker and Isaacs, *Chem. Rev.*, 1959, **59**, 737.



(C and T are the *cis*- and the *trans*-diol, respectively, and P the ketonic products. The rate constants will depend upon the acidity, and k_1 and k_3 include the equilibrium constants for protonation of the diols.) We assume that formation of the ketones is irreversible (cf. ref. 10). The complicated stationary-state treatments of these reactions can be simplified by considering the rates of both rearrangements and oxygen exchange.

If we start with either diol the other is formed and slowly decays (Table 3). At the maximum concentration of the rearranged diol its net rate of formation is zero, and starting with the *trans*-diol, when $d[\text{C}]/dt \approx 0$, we have:

$$-d[\text{T}]/dt = d[\text{P}]/dt = k_1 k_2 [\text{T}] / (k_2 + k_{-1}). \quad (1)$$

For the rearrangement of the *cis*-diol, when $d[\text{T}]/dt \approx 0$, we have:

$$-d[\text{C}]/dt = d[\text{P}]/dt = k_3 k_2 [\text{C}] / (k_2 + k_{-3}). \quad (2)$$

We evaluate $k_1 k_2 / (k_2 + k_{-1})$ and $k_3 k_2 / (k_2 + k_{-3})$, from the rates estimated graphically from plots of concentration against time (Table 5).

TABLE 5.
Instantaneous rate constants at 59.7°.

Values of $d[\text{P}]/dt$ in parentheses.

<i>trans</i> -Diol, at $d[\text{C}]/dt \approx 0$.		1.03		2.78	
[HClO ₄] (M)				
Time (min.)	600	720	60	80
$-10^3 d[\text{T}]/dt$ (mole l. ⁻¹ sec. ⁻¹)	0.96(0.94)	0.81(0.80)	9.7(10.1)	7.6(7.9)
[T] (mole %)	40.5	34.3	41	31
[P] (" ")	49	55.5	52.5	62.7
$-10^3 [\text{T}]^{-1} d[\text{T}]/dt$ (sec. ⁻¹)	2.4	2.3	24	25
<i>cis</i> -Diol, at $d[\text{T}]/dt \approx 0$; [HClO ₄] = 0.98M.					
Time (min.)	960	1200	1440	
$-10^3 d[\text{C}]/dt$ (mole l. ⁻¹ sec. ⁻¹)	0.51(0.50)	0.44(0.46)	0.42(0.45)	
[C] (mole %)	60.3	53.2	47.1	
[P] (" ")	36.0	42.8	49.4	
$-10^3 [\text{C}]^{-1} d[\text{C}]/dt$ (sec. ⁻¹)	0.85	0.83	0.89	

The first-order rate constant for oxygen exchange of the *trans*-diol is:

$$k_e^{\text{T}} = k_1 k_{-1} / (k_{-1} + k_2 + k_{-3}) \quad (3)$$

(provided that [C] is small).

The first-order rate constant for oxygen exchange of the *cis*-diol is:

$$k_e^{\text{C}} = k_3 k_{-3} / (k_{-1} + k_2 + k_{-3}) \quad (4)$$

(provided that [T] is small).

To calculate the relative rates of partitioning of the carbonium we use the method of successive approximations. Neglecting k_{-3} in the denominator of equation (3) and k_{-1} in equation (4) we calculated, for the *trans*-diol, approximate values of $k_2/k_{-1} = 1.9$ at 59.7° with [HClO₄] = 1M, and 2.6 at HClO₄ = 2.78M [by using equations (1) and (3)].

For the *cis*-diol the approximate value of k_2/k_{-3} is 2.2 at 59.7° with [HClO₄] = 1M [from equations (2) and (4)]. Equations (1) and (3) give:

$$k_2(k_{-1} + k_2 + k_{-3}) / k_{-1}(k_{-1} + k_2) = -d[\text{T}]/dt (k_e^{\text{T}} [\text{T}])^{-1} = 1.9;$$

¹⁰ Rothrock and Fry, *J. Amer. Chem. Soc.*, 1958, **80**, 4349; Barton and Porter, *J.*, 1956, 2483.

and from the approximate values of k_2/k_{-1} and k_2/k_{-3} we calculate:

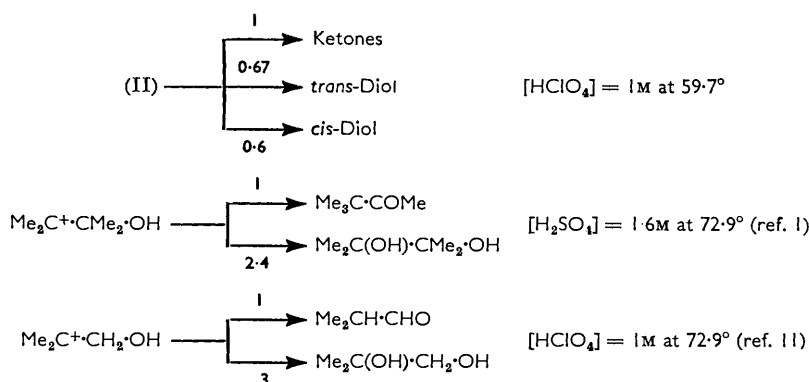
$$(k_{-1} + k_2 + k_{-3})/(k_{-1} + k_2) = 1.3,$$

and therefore, to a second approximation, $k_2/k_{-1} = 1.5$ at 59.7° and $[\text{HClO}_4] = 1\text{M}$. A similar correction can be applied to the reactions of the *cis*-diol, and gives $k_2/k_{-3} = 1.7$. The ratio of the rates of return of the carbonium ion to the *trans*- and *cis*-diol, $k_{-1}/k_{-3} = 1.1$.

These relative rates, and the rates of rearrangement, show that the rate of formation of the carbonium ion (II) from the *trans*-diol is approximately twice that from the *cis*-diol, and because the rates of return of the carbonium ion to the diols are almost the same, they suggest that in water the *cis*- should be thermodynamically more stable than the *trans*-diol. The formation of carbonium ion from both diols is slightly faster than from pinacol.¹

These relative rates of partitioning depend on the assumption that rearrangement of both diols involves a common intermediate, but this seems highly probable because (a) the overall reaction rates are similar to those of pinacol and (b) both diols give almost the same ketonic products.

The partitioning of other tertiary alkyl carbonium ions can be compared with our values, *e.g.*:



The open-chain carbonium ions are the more readily captured by the solvent, probably because (a) the cyclic carbonium ion is more hindered to solvent attack and (b) both migrating groups in the cyclic carbonium ion are in favourable positions for migration, whereas only some of the open-chain carbonium ions will be formed in the favourable conformation for methyl or hydrogen migration.

Brown and his co-workers have observed a similar interconversion of *cis*- and *trans*-diols during the acid-catalysed pinacolic rearrangements of *cis*- and *trans*-1,2-diphenyl-acenaphthene-1,2-diol in isopropyl or *t*-butyl alcohol, and the evidence suggests that here also a common classical carbonium ion is the intermediate.¹² In a following paper we show that the 1,2-dimethylcyclopentane-1,2-diols behave differently.

We regard the similarity of the rates of heterolysis of pinacol and these cyclohexane-diols as evidence that participation by a migrating group (synartesis or anchimerism) is unimportant. In accord with this view the heterolysis of *t*-butyl alcohol is faster than those of the diols because of the $-I$ effect of the hydroxyl group.¹³ Stiles and Mayer found that the relative rates of rearrangement of the diols $\text{Me}_2\text{C}(\text{OH})\cdot\text{CMeR}\cdot\text{OH}$ were: ¹⁴ R = Me, 1; Et, 7.2; Bu^t > 10³. The very high reactivity of the *t*-butyl compound suggests that its decomposition is assisted sterically, or by participation of a migrating

¹¹ Ley and Vernon, *J.*, 1957, 2987, 3256.

¹² Brown, Nordmann, and Madoff, *J. Amer. Chem. Soc.*, 1952, **74**, 432, and refs. cited therein.

¹³ Dostrovsky and Klein, *J.*, 1955, 791.

¹⁴ Stiles and Mayer, *J. Amer. Chem. Soc.*, 1959, **79**, 1497.

group, but it does not require that participation or steric acceleration assists the rearrangement of the other diols.

Our evidence shows that epoxides are not necessary intermediates in the oxygen exchange of the rearranging 1,2-diol. If epoxides were intermediates in the rearrangement or exchange of these cyclohexanediols the *trans*-diol would exchange its oxygen much more readily than the *cis*-diol does and we should be unable to interpret the results in terms of a common intermediate.

The situation may be different in aryl-substituted diols, because an epoxide has been isolated from the rearrangement of benzpinacol in acetic acid^{15a} and it rearranges to benzpinacolone, although perhaps by reverting to the diol. Also the epoxides of some arylcyclohexenes decompose to the *cis*- rather than the *trans*-diol.^{15b}

Ley and Vernon¹¹ found that hydrolysis of 1,2-epoxy-2-methylpropane gave the diol and a small amount of the rearranged isobutyraldehyde (much less than was obtained from the known carbonium-ion intermediate). The kinetic evidence on the acid hydrolysis of aliphatic epoxides is contradictory,^{7a,9,16} but bond-breaking seems to be more important than bond-making in the transition state, whereas the products of reaction, and their stereochemistry, exclude the existence of a carbonium-ion intermediate in its most stable configuration. A mechanism between the conventional *A-1* and *A-2* models is indicated,⁹ although carbonium ions may well be intermediates in the acid hydrolysis of aryl-substituted epoxides.¹⁵

The carbonium ion intermediate in rearrangement of the cyclohexanediols could be (IIa or b) or a mixture of the two. Ring contraction could occur with either ion, but methyl migration only with (IIa). The increasing proportion of 2,2-dimethylcyclohexanone with increase in temperature may be caused by an increasing proportion of conformation (IIa), which should be the less stable ion because (IIb) can be stabilised by



participation between the hydroxyl group and the carbonium-ion centre. The ion (IIa) is formed by loss of an axial hydroxyl group from the *cis*-diol, or an equatorial group from the *trans*-diol, whereas ion (IIb) is formed by loss of an axial hydroxyl group from the *trans*-diol, or an equatorial from the *cis*-diol.

The ratio of the ketones seems to differ slightly for the two diols (Table 2), suggesting that the carbonium ion in conformation (IIa) is formed slightly more readily from the *cis*- than from the *trans*-diol (cf. ref. 8b).

EXPERIMENTAL

Materials.—The *trans*-diol was prepared by the hydroxylation of 1,2-dimethylcyclohexene with peroxyformic acid;¹⁷ after recrystallisation from hexane it had m. p. 93° (lit.¹⁸ 92.5°). The *cis*-diol was prepared by the hydroxylation of the olefin with osmium tetroxide; after recrystallisation from hexane it had m. p. 48° (lit.^{8a} 50°). Another sample was prepared by oxidation with potassium permanganate.^{8a} 1,2-Epoxy-1,2-dimethylcyclohexane was prepared from the olefin and peroxyoctanoic acid;¹⁹ it was fractionally distilled through a helix-packed

¹⁵ (a) Gebhart and Adams, *J. Amer. Chem. Soc.*, 1954, **76**, 3925; (b) Davies, Dobson, Hayman, Jackman, Lester, Petrow, Stephenson, and Webb, *Tetrahedron*, 1962, **18**, 751.

¹⁶ Koskikallio and Whalley, *Trans. Faraday Soc.*, 1959, **55**, 815; Kwart and Goodman, *J. Amer. Chem. Soc.*, 1960, **82**, 1947.

¹⁷ Roebuck and Adkins, *Org. Synth.*, 1948, **28**, 35.

¹⁸ Huckel and Worffel, *Chem. Ber.*, 1955, **88**, 338.

¹⁹ Parker, Ricciuti, Ogg, and Swern, *J. Amer. Chem. Soc.*, 1955, **77**, 4037; Trevo and Brown, *ibid.*, 1949, **71**, 1675.

column, and the fraction boiling at 152–155° was purified by gas-liquid chromatography on a Tween-Celite column. The preparation of the olefin has been described.^{8b}

Kinetics.—*trans*-1,2-Dimethylcyclohexane-1,2-diol. Portions (2 c.c.) of the kinetic solution ([Diol] = 0.05–0.10M) were added to sufficient sodium acetate in acetic acid (25 c.c.) to neutralise the perchloric acid. *ca.* 0.08M-Lead tetra-acetate in acetic acid (20 c.c.) was then added, and the mixture left in the dark for 20 hr. at room temperature. Aqueous sodium acetate and potassium iodide were then added, and the liberated iodine was titrated with sodium thiosulphate (the sodium acetate prevents precipitation of lead iodide). The amount of diol was estimated by comparison with a control solution of lead tetra-acetate which had been treated as described above. Plots of log[Diol] against time were linear for 80% of reaction, and for the slower reactions their intercept at zero time agreed with that calculated from the initial diol concentration.

cis-1,2-Dimethylcyclohexane-1,2-diol. Portions (2 c.c.) of the kinetic solution ([Diol] = 0.05–0.1M) were added to sufficient sodium hydroxide to neutralise the perchloric acid. Ammonia buffer (NH₃-HClO₄) was then added, followed by sodium periodate, and the solution was left in the dark for 20 hr. at room temperature. An excess of sodium hydrogen carbonate and of potassium iodide were then added and the liberated iodine was titrated with sodium arsenite. (The ammonia buffer catalyses the periodate oxidation very effectively.)

For analysis with lead tetra-acetate the method was that used for the *trans*-diol.

Products.—(a) *Ketones.* The products were formed under kinetically controlled conditions. After complete reaction the crude ketones gave a semicarbazone, m. p. 141°; 1-acetyl-1-methylcyclopentane gives a semicarbazone,^{8a} m. p. 143°. However, gas-liquid chromatography of the pentane extract on a Tween-Celite column at 147° gave two peaks; the larger was that of 1-acetyl-1-methylcyclopentane, and the smaller that of 2,2-dimethylcyclohexanone. The evidence for the identity of this minor product was (a) its retention time was 1.21, relative to cyclohexanone (the relative retention time of 2-methylcyclohexanone is 1.13, and of 1-acetyl-1-methylcyclopentane is 1.07), (b) it gave a semicarbazone, m. p. 198° (lit.,⁸ 200°), and (c) the molecular weight, determined mass-spectrometrically,²⁰ was 126.144 ± 0.001 (Calc. for C₆H₁₄O: *M*, 126.145), and the cracking pattern was very similar to that of 2-methylcyclohexanone, except that it had also the parent peak at mass 126, and the peaks at mass 127 and 128, due to the ¹³C content.

No epoxide could be detected by gas-liquid chromatography, and 1-acetyl-1-methylcyclopentane was stable in aqueous perchloric acid at 100° for times much greater than required for rearrangement of the diols.

(b) *Diols.* The amount of one diol formed during rearrangement of the other was determined by estimating the total (*trans*- + *cis*-)diol by oxidation with lead tetra-acetate, and the *cis*-diol with periodic acid. Because the *trans*-diol reacts, although very slowly, with periodic acid, control mixtures of the *trans*-diol and of (*trans*- + *cis*-)diol were used to check the method.

(c) *Epoxide.* Although the epoxide is almost insoluble in water it is hydrolysed in 0.5M-perchloric acid within 10 min. at room temperature. Extraction of this solution with ether should remove any ketone, but not the diols; the ether solution, tested by gas-liquid chromatography, contained no ketone. (This method would have detected the ketone if it had been formed in *ca.* 1% yield.) Portions of the aqueous solution were treated with lead tetra-acetate and periodic acid. The total diol content was >98% of that calculated from the weight of epoxide, and the amount of the *cis*-diol was less than 1%. Extraction of the aqueous solution with chloroform gave *trans*-diol, m. p. 92°, whose infrared spectrum was identical with that of authentic material.

Oxygen Exchange.—Isotopically normal diols (0.3 g.) were dissolved in H₂¹⁸O (20 c.c.) containing perchloric acid, and rearranged under kinetically controlled conditions. Reaction was stopped by neutralising the acid, and ketonic products were extracted with small amounts of pentane. The diols were then extracted with chloroform, and the solutions were dried (Na₂SO₄). The crude diols crystallised from hexane at -80°, and were dried by azeotropic distillation with "AnalaR" benzene. The dried diols were then sublimed at 10 mm.

Any *cis*-diol in the *trans*-diol was destroyed with periodic acid before extraction (except for two early experiments). For rearrangement of the *cis*-diol we corrected the overall abundance of ¹⁸O for that due to *trans*-diol, on the assumption that the *trans*-diol was 50%

²⁰ Beynon, "Mass Spectrometry," Elsevier, Amsterdam, 1960, Ch. IX.

isotopically enriched. (This assumption is reasonable because only the first 25% of reaction was studied.)

The ^{18}O abundance of the diols was determined by heating them *in vacuo* with phenylenediamine hydrochloride and guanidine hydrochloride, and analysing the evolved carbon dioxide mass-spectrometrically.

The first-order rate constant for isotopic exchange, irrespective of labelling, k_e , was calculated from:

$$tk_e = 2 \ln N_\infty / (N_\infty - N_t)$$

where N_∞ and N_t are the isotopic abundances (in atom % excess) of the diol calculated for complete exchange and at time t . An example is annexed.

trans-1,2-Dimethylcyclohexane-1,2-diol, at 59.7°, $[\text{HClO}_4] = 1.01\text{M}$.

Time (hr.)	Reaction (%)	$N_{\text{H}_2\text{O}}$	N_t	Exchange (%)
1.5	12.5	1.61	0.050, 0.052	3.2
2.5	21	1.61	0.095, 0.097	6
4	32	2.78	0.23, 0.23 *	8
12.4	61	1.80	0.44 †	25

* Calc. from the isotopic abundance of the isolated *cis-trans*-mixture, which contained 10.2% of *cis*-diol. † Calc. as above for the *cis-trans*-mixture which contained 30% of the *cis*-diol. This value is less reliable than the others, because there was considerable rearrangement to *cis*-diol.

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WILLIAM RAMSAY AND RALPH FORSTER LABORATORIES,
UNIVERSITY COLLEGE,
GOWER STREET, LONDON W.C.1.

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