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OXIDATION OF OLEFINES WITH THALLIUM III SALTS—I

THE OXIDATION OF CYCLOHEXENE

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Abstract—The oxidation of cyclohexene with thallium III acetate has been studied under a variety of conditions and compared with oxidations by lead IV acetate and mercury II acetate under similar conditions. The products obtained vary with conditions but include cyclohexan-1,2-diols, their mono- and diacetates, cyclohex-2-enyl acetate, C-formylcyclopentane and its diacetate. Lead IV acetate produces similar mixtures, but mercury II acetate gives a simpler reaction product.

THE results of a study of the action of thallium III salts upon some olefines has been reported recently.[1] The similarity of the thallium III, lead IV, and mercury II states has been confirmed in respect of their behaviour with olefines. A more detailed account of the work is now given. Kabbe[2] and Grinstead have both recently reported examinations of the action of thallium III salts upon some aromatic and aliphatic olefines and ketones.

The formation of olefin-metal complexes is well known,[3] and in some cases, as for example the complexes formed from mercury II salts, further reaction may occur to give oxidized material, the metal entering its lower valency state. The products of reaction of olefins with lead IV salts are generally more complex than those produced by mercury II salts,[4] and in this case no intermediate lead-olefine complexes are isolated. In both cases solvent plays an important part in determining reaction rates and products. Since thallium lies between mercury and lead in the periodic table and the thallium III state is isoelectronic with the lead IV and mercury II states, similarities in action may be expected.

Without formulating the mechanism, we may formally regard the action of these reagents as proceeding in at least three ways, *viz.* direct attack upon the double bond, attack upon the allylic hydrogens and rearrangement.

Under the conditions used in our experiments, we found products which illustrated all these modes of reaction. Apart from direct effects of relative concentration, changes in solvent and temperature of reaction produced considerable change in the composition of the reaction products.

Initially we examined the oxidation of cyclohexene in glacial acetic acid containing varying molar proportions of thallium III acetate. The reaction was followed titrimetrically at several different temperatures. There is a sharp increase in reaction rate

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[1] J. B. Lee and M. J. Price, *Tetrahedron Letters* No **24**, 1155 (1962).

[2] H. J. Kabbe, *Liebig's Ann.* **656**, 204 (1962).

[3] J. Chatt, *Chem. Rev.* **48**, 7 (1951). R. N. Keller, *Ibid.* **28**, 229 (1941).

[4] J. Chatt, *loc. cit.*, and R. Chiegee, *Neuere Methoden der Praparativen Organischen Chemie* (Edited by W. Foerst) p. 21. Verlag Chemie, G.M.B.H., Weinheim (1949).

with temperature, as may be seen by examination of Fig. 1. The rate was also rather sensitive to changes in solvent and in addition examination of the products from oxidations under similar conditions shows that the relative proportions of the various products alter with temperature (Table 1) as well as with solvent (Table 2).

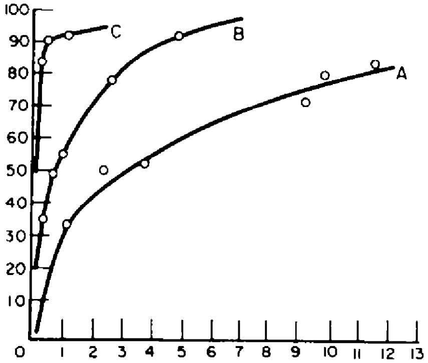

Fig. 1. Reaction of thallium III acetate with cyclohexene in anhydrous acetic acid; percentage reduction of thallium III acetate against time in hr. A—Temp. 18°. B—Temp. 25°. C—Temp. 85°.

Thus, when oxidized in anhydrous acetic acid at room temperature, cyclohexene gave a mixture containing *cis*- and *trans*-cyclohexan-1,2-diol diacetates, (I) and (II), C-formylcyclopentane (III), mainly as its diacetate, (diacetoxymethyl)-cyclopentane (IV), together with some cyclohex-2-enyl acetate, (Va). At higher temperatures the allylic acetate, (Va) increased in relative amount.

Table 1. Approximate percentage composition of the reaction products from the action of thallium III acetate on cyclohexene in anhydrous acetic acid

Compound	Temperature 18°	 25°	 60°	 98°
I	5	5	5	4
II	49	45	46	34
III	6	6	4	12
IV	38	40	38	40
V	2	4	7	10

Table 2. Effect of solvent change upon the (approximate) ratios

(1). Compound I: Compound II
(2). Compound III: Compound IV

Compound	Solvent *a*	Solvent *b*	Solvent *c*
I (*cis*) II (*trans*) cyclohexan-1,2-diol diacetate	$\frac{1}{9}$	$\frac{1}{1}$	$\frac{5}{3}$
III C-formylcyclopentane IV (diacetoxymethyl)-cyclopentane	$\frac{1}{8}$	$\frac{3}{5}$	$\frac{5}{4}$

Solvents:—*a*—anhydrous acetic acid: *b*—95% aqueous acetic acid: *c*—65% aqueous acetic acid.

For comparison, the action of mercury II acetate[5] and lead IV acetate[6] upon cyclohexene in these conditions was examined. From the reaction with mercury II acetate only cyclohex-2-enyl acetate (Va) was obtained, whilst lead IV acetate gave a mixture containing cyclohexane *cis*- and *trans*-diol diacetates (I and II), cyclohex-2-enyl acetate, (Va) and (diacetoxymethyl)-cyclopentane (IV). The allylic acetate (Va) was the major product in this case.

The initial examination of these materials was by gas-liquid chromatography (glc). From the behaviour of the various fractions in comparison with synthetic materials tentative structural assignments were made. The components were separated by a combination of fractional distillation, column chromatography and preparative gas-liquid chromatography, and identified as follows.

The fraction (III), having the lowest retention time upon non-polar columns, contained an aldehydic, but no olefinic or hydroxylic,[9] function. The 2,4-dinitrophenyl hydrazone of this compound melted and analysed correctly for the 2,4-DNP of C-formylcyclopentane.[10] The identity of the diacetyl derivative (IV), shown chemically and spectroscopically to be an ester (no aldehyde, hydroxyl, or olefine, bands) was confirmed by hydrolysis and conversion to the 2,4-DNP of III.

Compounds (I and II), which showed positive ester reactions only, confirmed by their IR bands, had saponification equivalents of approximately 100. *trans*-Cyclohexan-1,2-diol diacetate was synthesized for comparison by ring-opening of cyclohexene oxide followed by acetylation. *cis*-Cyclohexan-1,2-diol diacetate was also synthesized, by treatment of cyclohexene with iodine and silver acetate, followed by acetylation. This method of *cis*-hydroxylation is essentially that used by Woodward and Brutcher in the steroid series.[11] The identity of the products (I and II) was confirmed by comparison of IR spectra.

Compound Va gave tests for an $\alpha\beta$-unsaturated ester[12] (confirmed spectroscopically) and catalytic deacetylation[13] gave cyclohex-2-enol, (Vb), identical with authentic material. The IR spectrum of Va was identical with that of authentic cyclohex-2-enyl acetate.

When cyclohexene was oxidized in aqueous acetic acid at 25° with a large excess of thallium III acetate, the presence of additional materials to those above was noted. These were shown to be *cis*- and *trans*-cyclohexan-1,2-diol monoacetates (VI and VII), together with small traces of cyclohex-2-enone (VIII), as follows.

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[5] G. F. Wright, *J. Amer. Chem. Soc.* **69**, 697 (1947); W. Treibs, G. Lucius, H. Koegler and H. Breslauer, *Liebig's Ann.* **581**, 59 (1953).

[6] R. Criegee, *Liebig's Ann.* **481**, 263 (1930).

[7] F. Feigl, V. Anger and O. Frehden, *Mikrochemie* **15**, 12 (1934); D. Davidson, *J. Chem. Educ.* **17**, 81 (1940).

[8] F. R. Duke and G. F. Duke, *Ind. Eng. Chem.* (*Analyt. Ed.*) **12**, 201 (1940).

[9] F. Buscarons, J. L. Maron and J. Claver, *Analyt. Chim. Acta* **3**, 310, 417 (1949); A. J. Blair and D. A. Pantony, *Ibid.* **13**, 1 (1955); M. Borrel and R. Paris, *Ibid.* **4**, 267 (1950).

[10] G. F. Wright and J. H. Robson, *Canad. J. Chem.* **38**, 17 (1960); **33**, 1002 (1955); H. J. Kabbe *loc. cit.*

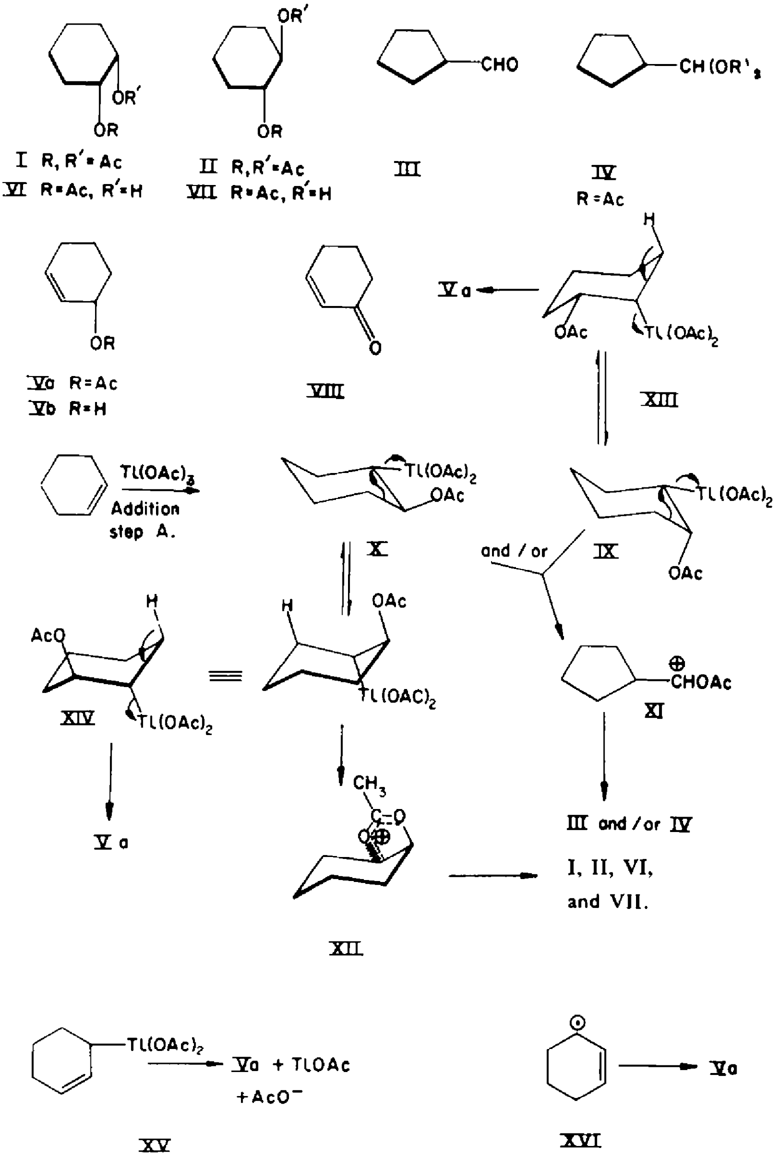
[11] R. B. Woodward and F. V. Brutcher, *J. Amer. Chem. Soc.* **80**, 209 (1958). This method of *cis*-hydroxylation proceeds by way of a neighbouring group replacement reaction cf. S. Winstein M. V. Hess and R. E. Buckles, *Ibid,* **64**, 2787, 2796 (1942).

[12] A. V. Baeyer and V. Villiger, *Ber. Dtsch. Chem. Ges.* **33**, 2496 (1909).

[13] G. Zemplen and A. Kunz, *Ber. Dtsch. Chem. Ges.* **56**, 1705 (1923); **59**, 1254 (1926); **62**, 1613 (1929); **69**, 1827 (1936).

Compound VIII was shown chemically and spectroscopically to be an $\alpha\beta$-unsaturated ketone, and its 2,4-DNP was identical with that of authentic material (m.p. and mixed m.p.). Compounds VI and VII were shown to be hydroxy esters, which on hydrolysis gave material which reduced periodate, indicating a *vic*-glycol. The periodate-oxidized product was aldehydic in nature and the UV spectrum of its 2,4-DNP showed that it was not an $\alpha\beta$- or an $\alpha\gamma$-dicarbonyl compound or an $\alpha\beta$-unsaturated carbonyl compound.

cis- and *trans*-Cyclohexan-1,2-diol monoacetates, synthesized as described above, were identical with VI and VII.



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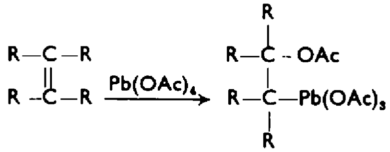
[14] R. P. Linstead and B. C. L. Weedon, *Qualitative Organic Analysis*, Butterworths, London (1954).

In a dilute aqueous acetic acid solution of thallium III acetate, cyclohexene gave larger amounts of C-formylcyclopentane and cyclohexan-1,2-diols. Under the same conditions, treatment of cyclohexene with mercury II acetate gave only cyclohex-2-enol (Vb) and C-formylcyclopentane (III), the latter predominating.

These results, together with others recently reported in the literature,[2,15] show the basic similarity in action of lead IV and thallium III acetates and, to a lesser extent, of mercury II and thallium III acetates, in their action upon olefines; differences in detail are naturally to be expected.

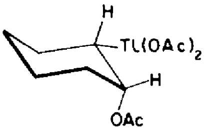
Unlike mercury II acetate, no intermediate complex has been isolated from the action of lead IV salts on olefins. Nevertheless such a complex is generally assumed to be formed as an initial stage (XVIII → XIX):[16,17]



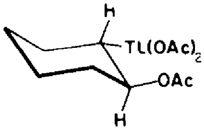
XVIII XIX

We have not so far been able to isolate a thallium complex from any reaction with olefins or terpenes. However, since both styrene and *o*-allyl phenol have been shown to give oxythallation adducts,[18] it is likely that this is a primary process in thallium-olefine oxidations generally.

Both heterolytic and homolytic bond fission have been suggested for breakdown of the intermediate lead esters.[19] A heterolytic sequence, such as that shown below,



IX



X

will account for the main products isolated as described above. A corresponding scheme involving homolytic breakdown could be also formulated.

The initial stage (A) of oxythallation may be formulated as either *cis* (IX) or *trans* (X) addition (or both). With cyclohexene, ring contraction via XI to give the III and IV can occur readily from either formulated adduct. (Some sterically more restricted

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[15] R. G. Grinstead, *J. Org. Chem.* **26**, 239 (1961); R. Criegee, *Angew. Chem.* **70**, 173 (1958), cf. Refs. 5 and 6.

[16] O. Dimroth and O. Friedemann, *Ber. Dtsch. Chem. Ges.* **53**, 481 (1920); **54**, 3050 (1921); **55**, 1223 (1922); **56**, 1371 (1923); R. Criegee and H. Pilz, *Liebig's Ann.* **481**, 263 (1920); *Angew. Chem.* **53**, 321 (1940); H. O. L. Fischer and L. Ahlstrohm, *Ber. Dtsch. Chem. Ges.* **63**, 1732 (1930); **65**, 345 (1932).

[17] R. Criegee and H. Beuker, *Angew. Chem.* **53**, 321 (1940); **70**, 173 (1958); *Neuere Methoden der Praparativen Organischen Chemie* (Edited by W. Foerst) p. 21 *Verlag Chemie, G.M.B.H., Weinheim* (1949); L. F. Fieser, *Experiments in Organic Chemistry* p. 436, J. Wiley, New York, N.Y. (1941).

[18] J. H. Kabbe, *loc. cit.*; R. Criegee, *Angew. Chem.* **70**, 173 (1958).

[19] W. A. Waters, *Nature, Lond.* **158**, 380 (1946); *Organic Chemistry* (Edited by H. Gilman) p. 1185, J. Wiley, New York, N.Y. (1953); R. Criegee and H. Beuker, *Liebig's Ann.* **507**, 159 (1933); **522**, 75 (1936); **599**, 81 (1956); J. P. Cordner and K. H. Pausaker, *J. Chem. Soc.* 102 (1953); V. Prelog, K. Schenker and W. Kung, *Helv. Chim. Acta* **36**, 471 (1953).

systems are being examined to gain further evidence upon this point). On simple conformational grounds, assuming the absence of hydrogen-bonding and/or dipole effects, the diequatorial product (X), which could arise by diaxial or diequatorial addition, would be most favoured,[20] and would presumably be the major product if step (A) was rapidly reversible (and therefore subject to thermodynamic control) and permitted both *cis* and *trans* addition.

An intermediate acetoxonium ion (XII), would seem likely in the decomposition of the adduct to give I, II, VI and VII. A *trans* arrangement of acetate and diacetoxythallium groups in the adduct would favour formation of this acetoxonium ion (XII), but the *cis* or *trans* nature of the products from the acetoxonium ions would depend upon the reaction conditions.[21] In aqueous acetic acid competition for the acetoxonium ion between the acetic acid and water molecules will lead to formation of a mixture of diol mono- and di-acetates. The free cyclohexane diols presumably arise in dilute aqueous acetic acid by hydrolysis of the monoacetates.

Although products showing apparent allylic attack are often isolated in reactions of this type,[22] it seems unnecessary, in this case, to postulate a separate mechanism for their production. Formation of cyclohex-2-enyl acetate can be formulated as proton elimination simultaneously with, or subsequent to, loss of the diacetoxythallium ion (XIII and XIV → Va).

This will proceed with greatest facility when the diacetoxy thallium group is held axially.[20] This axial arrangement will arise most favourably conformationally when the acetate group is equatorial, i.e. for a *cis* adduct, and in addition, in the case of a *trans* adduct the alternative formation of an acetoxonium ion would be favoured.[21] Alternative routes to the allylic acetate would be solvolysis of an intermediate allylic derivative, or allylic attack by acetate radicals (XV → XVI → Va).[23]

Decomposition of lead IV acetate to give acetate radicals[24] is known to be favoured by increased temperature and the increased yield of allylic acetate at elevated temperature could be held to support a similar mechanism. In agreement with this is the very high yield of allylic acetate obtained with the lead salt, which could be related to the readier formation of acetate radicals in this case, since we find lead IV acetate to decompose more readily in these conditions than does the thallium salt.

It must be also noted, however, that the 1-acetoxy-2-acetomercuricyclohexanes decompose under these conditions *exclusively* to the allylic acetate and presumably not by the radical type mechanism suggested above.

The preferred conformation of the adduct, whether *cis* or *trans*, would have the large diacetoxythallium group in the equatorial position, and this arrangement is unfavourable to elimination other than by ring contraction. The relative yields of the different products are in line with this difference in the thallium case. However, on

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[20] R. C. Cookson and D. H. P. Barton, *Quart. Rev.* **10**, 44 (1956).

[21] S. Winstein and R. M. Roberts, *J. Amer. Chem. Soc.* **75**, 2297 (1953); **64**, 2787 (1942) and other papers in the series.

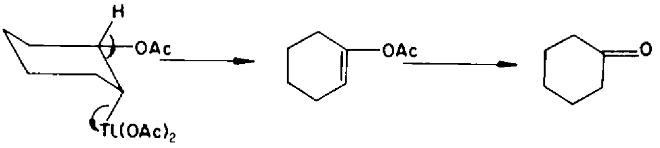
[22] R. Criegee, *loc. cit.*; and Refs. 16 and 17.

[23] W. A. Waters, *loc. cit.*; J. P. Cordner and K. H. Pausaker, *loc. cit.*

[24] For a discussion of these points see C. Walling, *Free Radicals in Solution* p. 536. J. Wiley, New York, N.Y. (1957); and Refs. cited; W. A. Waters, *Chemistry of Free Radicals* p. 227 et seq. Oxford University Press (1948).

purely conformational grounds the behaviour of lead, thallium and mercury would, if proceeding *via* similar oxymetalation intermediates, be expected to be closely parallel, which is obviously not the case and further evidence on the mechanism is being sought.

There remains a further possible elimination route for the intermediate (XIII);



XIII XX XXI

namely, to form the enol acetate (XX). No evidence was obtained for this in glacial acetic acid, nor was its hydrolysis product cyclohexanone (XXI) isolated.

Finally it should be noted that formation of a mercuri-acetate complex occurred rapidly in each case with mercury II acetate and cyclohexene, but whereas in glacial acetic acid the only product formed on further reaction was the allylic acetate (V), in aqueous solution the main product was the rearranged aldehyde (III) together with some of the allylic alcohol (Vb). This further emphasizes the large effects of changes in solvent upon reaction route.

So far we feel that not enough evidence is available to distinguish between the heterolytic and homolytic routes and more evidence is needed before the mechanism can be unequivocally defined.

EXPERIMENTAL

M.ps are uncorrected. Cyclohexene was dried over $MgSO_4$. Acetic acid was dried and stored over P_2O_5. Mercury II and thallium III acetates were dried by heating *in vacuo* with acetic anhydride at 50–60° until no more solvent distilled. Lead IV acetate was kept before use in a vacuum desiccator over KOH pellets.

trans-*Cyclohexan-1,2-diol monoacetate*

Cyclohexene (160 g) in alcohol-free ether (700 ml) was added to a vigorously stirred mixture of freshly prepared Hg II oxide (220 g) and water (32 ml). The mixture was cooled and I_2 (496 g) was added to the slurry in small portions, so that the colour almost disappeared before each addition and finally when the colour had discharged, the mixture was filtered and the residues washed several times with ether. The combined ethereal washings and the filtrate were then shaken with KI aq. and $NaHSO_3$ aq. After treatment with decolourizing charcoal the ethereal layer was dried (Na_2SO_4) and the ether removed *in vacuo*. The oily residue dissolved in anhydrous methanol (2 l.) containing sodium methoxide (115 g) was kept several days at room temp. The solution was then heated under reflux for a short period, cooled and several portions of solid CO_2 added. Methanol was distilled off from the filtered solution and the remaining higher boiling material fractionated.

The cyclohexene oxide obtained was dissolved in excess glacial acetic acid and the mixture refluxed gently for several hr and then set aside at room temp for a further 4 days. Glacial acetic acid and some unchanged cyclohexene oxide were removed by distillation and the residual liquid fractionated by chromatography upon alumina eluted successively with pet. ether, benzene, chloroform and alcohol. Preliminary examination of the fractions by IR spectroscopy was followed by vacuum distillation of the requisite fractions to give *trans*-cyclohexan-1,2-diol monoacetate,[25] b.p. 128–135 8 mm, peaks in the IR at 3200–3450 cm^{-1} (broad), 1739 cm^{-1}, 1246 cm^{-1}.

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[25] J. Findlay, *J. Amer. Chem. Soc.* **67**, 412 (1945); H. Boeseken, *J. Prakt. Chem.* (2) **131**, 285 (1931); G. Frankel-Conrat and H. Olcott., *J. Amer. Chem. Soc.* **66**, 1420 (1944); P. Hoering, *Ber. Dtsch. Chem. Ges.* **38**, 2296 (1905).

trans-*Cyclohexan*-1,2-*diol diacetate*

trans-Cyclohexan-1,2-diol monoacetate (2 ml) was dissolved in anhydrous pyridine (5 ml) containing acetic anhydride (3 ml) and the mixture kept at 30–35° for 72 hr. Water (25 m) was added and the emulsion extracted with chloroform (2 × 20 ml). The combined chloroform extracts were washed with 5N H_2SO_4 (15 ml) and water (10 ml). The dried chloroform layer was fractionated to give *trans*-cyclohexan-1,2-diol diacetate,[26] b.p. 100–105°/5 mm, n_D^{21} 1·4455, bands in the IR at 1742 cm^{-1} and 1240 cm^{-1}.

cis-*Cyclohexan*-1,2-*diol monoacetate*

Silver acetate (25 g) was added to glacial acetic acid (400 ml) in a 3-necked flask equipped with stirrer, thermometer and water-condenser. The solution was vigorously stirred and cyclohexene (60 ml redistilled) was added, followed by I_2 (20 g, AnalaR grade) added in small portions over 2 hr. Water (1·2 ml) was added and the mixture was kept with vigorous stirring, for 12 hr at room temp, then the temp was raised slowly to 80–90° and kept in this range for several hr. The cooled mixture was shaken with decolourizing charcoal and filtered through Celite and the residue washed with several portions of chloroform and benzene. The combined filtrate and washings were evaporated *in vacuo* to give a dark syrup which was dissolved in hot methylated spirit, treated with a further portion of animal charcoal and again filtered through Celite. The filtrate was passed quickly down an ion-exchange column (Deacidite FF, $OH^{\ominus}$ form) and the solvent removed at the pump. The residue was fractionated to give *cis*-cyclohexan-1,2-diol monoacetate,[27] b.p. 137–143°/14 mm, IR bands at 3400 cm^{-1}, 1738 cm^{-1} and 1250 cm^{-1}.

cis-*Cyclohexan*-1,2-*diol*

Cyclohexan-1,2-diol monoacetate (1·5 g) was dissolved in anhydrous benzene (40 ml) and the solvent removed at the pump. Methanol (30 ml Grignard dried and in which ca. 50 mg Na had been dissolved) was added and the mixture set aside at room temp for several days. The solution was neutralized with a portion of solid CO_2 and evaporated to dryness *in vacuo*. The residue was recrystallized from hot ether followed by carbon tetrachloride and *cis*-cyclohexane-1,2-diol[28] obtained, m.p. 95–98 .

trans-*Cyclohexane*-1,2-*diol*

Cyclohexan-1,2-diol monoacetate (3 g) was dissolved in hot sodium-dried toluene (50 ml) and the volume reduced at the pump to about 10 ml. Methanol (50 ml Grignard-dry and containing a trace of Na) was added and the mixture kept at room temp for several days. The solution was neutralized with solid CO_2 and the solvent removed *in vacuo*. The residue was recrystallized from carbon tetrachloride to give *trans*-1,2-cyclohexandiol,[29] m.p. 100–102°.

Cyclohex-2-enyl acetate

Acetic anhydride (150 ml) and selenium dioxide (11 g) were heated in a flask fitted with dropping funnel and condenser to about 70°. A mixture of acetic anhydride (20 ml) and cyclohexene (17 ml) was added dropwise but fairly rapidly. A red precipitate formed immediately. Heating was continued for several min after completing the addition. The mixture was cooled and stirred with ice water (1 l.) and chloroform (250 ml) for 1 hr. The chloroform layer was separated, dried and fractionally distilled (red press.) to give cyclohex-2-enyl acetate,[30] b.p. 66–70°/12 mm, n_D^{16} 1·4604.

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[26] K. Awers and V. Dersch, *J. Prakt. Chem.* **124**, 235 (1930); report b.p. 113°/11·5 mm, n_D^{20} 1·4464.

[27] S. Winstein and R. M. Roberts, *J. Amer. Chem. Soc.* **75**, 2297 (1953) and other papers in this series; R. B. Woodward and F. V. Brutcher, *loc. cit.*

[28] R. Criegee and H. Stanger, *Ber. Dtsch. Chem. Ges.* **69B**, 2753 (1936) report m.p. 96–98° for this compound; M. F. Clark and L. N. Owen, *J. Chem. Soc.* 315 (1949); H. Adkins, *J. Amer. Chem. Soc.* **70**, 4041 (1948); S. Winstein and R. E. Buckles, *ibid.* **64**, 2780 (1942).

[29] Lit. m.p. 104–105°; M. F. Clark and L. N. Owen, *loc. cit.*; H. Adkins, *loc. cit.*; S. Winstein and R. E. Buckles, *loc. cit.*

[30] J. A. Arbusov and N. I. Shuiken, *Bull. Acad. Sci. U.S.S.R.* 163 (1945); report b.p. 58–59°/9 mm, n_D^{15} 1·461 for this compound.

Oxidation of cyclohexene by anhydrous mercury II *acetate in acetic acid*

Glacial acetic acid (220 ml) and acetic anhydride (80 ml) were heated, in a 3-necked flask fitted with stirrer, condenser and drying tubes, at 45° overnight. Anhydrous mercury II acetate, (55·3 g) was added, and the mixture kept with stirring a further 20 hr at room temp. Anhydrous cyclohexene (17·3 ml) was added and the stirred mixture was kept at room temp for 17 hr at the end of which time only very little mercury II acetate remained undissolved. After heating the mixture several min on the steam bath, a dense precipitate of white needle-like crystals formed. Heating was continued for a further 2 hr, the solution gradually darkening as metallic Hg was deposited. The solution was allowed to stand at room temp for 96 hr and then added in portions to a vigorously stirred slurry of ice and $CaCO_3$. Chloroform (100 ml) was then added and the mixture stirred until no more ice remained. The mixture was filtered, the chloroform layer separated and the aqueous layer extracted thrice more with chloroform (3 × 30 ml). The combined chloroform extracts were washed with $NaHCO_3$ aq., 50 ml and water, 50 ml. Examination of the solution by glc showed that only one component was present. Examination by glc upon several different columns (apiezon, silicone oil, polyglycol and dinonyl phthalate) all on Celite support, showed identity of behaviour with authentic cyclohex-2-enyl acetate. The solvent was removed at the pump and the residue distilled to give cyclohex-2-enyl acetate,[30] b.p. 58–61°/8 mm, $n_{\mathrm{D}}^{17^\circ}$ 1·4601.

Oxidation of cyclohexene in aqueous mercury II *acetate*

A solution of mercury II acetate (28 g) in water (150 ml) and acetic acid (80 ml) in a flask fitted with a reflux condenser was stirred vigorously and cyclohexene (9·5 ml) added in one portion. The mixture was warmed gently and after some time a white crystalline solid separated. The mixture was kept with stirring for 12 hr at room temp and was then heated under reflux for 3 hr. The mixture was allowed to cool and set aside with stirring for a further 96 hr at room temp. Chloroform (100 ml) was then added, the mixture well shaken and rapidly filtered through kieselgur. The chloroform and water layers in the filtrate were separated; Na_2SO_4 (80 g) added to the aqueous layer which was shaken until no more salt seemed to dissolve and the layer then re-extracted with chloroform. The residue was washed with several portions of chloroform.

The chloroform layers were all combined, dried (Na_2SO_4) and examined by glc. The presence of small amounts of unreacted cyclohexene (approx. 4%) was noted, together with two other materials showing longer retention times. An examination of the IR absorption spectrum of the mixture showed bands at 3400 cm^{-1} (OH) 3035 cm^{-1} (C=C) 2750 cm^{-1} (aldehyde), 1647 cm^{-1} (C=C) 1729 cm^{-1} 1405 cm^{-1} (aldehyde). Fractionation gave materials:

(a) C-Formylcyclopentane,[31] b.p. 47–55°/17 mm, giving positive Schiff, Brady and Fehling tests, slowly reduced acidified dichromate, yellow 2,4-DNP m.p. 155–156°. Examination of the IR spectrum showed absence of hydroxyl, olefine, ester and other functional groups except for aldehyde (1733 cm^{-1}). Comparison with authentic C-formylcyclopentane confirmed its identity in both glc and IR spectroscopic characteristics.

(b) Cyclohex-2-enol,[32] b.p. 160–166°, n_{D}^{142} 1·4, giving negative Brady, Schiff, hydroxamic acid and iodoform tests, but strongly reducing acidified sodium dichromate aq., neutral aqueous manganate and aqueous bromine solutions; giving strong Baeyer, vanadium oxine and cerium nitrate tests. Bands characteristic of carbonyl (ester, ketone, aldehyde) groups were absent in the IR but alcohol (3400 cm^{-1}, 1059 cm^{-1}) and olefine (3035 cm^{-1}, 1645 cm^{-1}) groups were confirmed.

A portion was acetylated at room temp (acetic anhydride-pyridine-72 hr) giving cyclohex-2-enyl acetate, b.p. 60–65°/11 mm, n_{D}^{16} 1·4609, identical in IR spectrum with authentic material.[30]

Oxidation of anhydrous cyclohexene with lead IV *acetate*

(a) Anhydrous acetic acid (15 ml) containing lead IV acetate (83 g) was stirred at 29° and cyclohexene (18 ml) added in one portion. When the solution no longer gave a positive test for Pb IV, it was treated as described subsequently for thallium III acetate oxidations. The crude product was a mixture of I, II, IV and Va separated and identified as described subsequently. The major component was the allylic acetate V; no free C-formylcyclopentane was found.

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[31] J. H. Robson and G. F. Wright, *loc. cit.*; D. A. Shearer and G. F. Wright, *Canad. J. Chem.* **33,** 1002 (1955).

[32] A. Kotz and K. Richter, *J. Prakt. Chem.* **III** (ii), 383 (1925), report b.p. 163°; K. Hock and K. Ganiche, *Ber. Dtsch. Chem. Ges.* **71,** 1430 (1938).

(b) Cyclohexene in acetic acid containing one mole per mole of water was heated on the steam bath under reflux and lead IV acetate in acetic acid was added in small portions. Isolation of the materials described subsequently gave in addition to compounds previously isolated, some of the free aldehyde (III). The allylic acetate (Va) was again the major product.

Oxidation of anhydrous cyclohexene with thallium III *acetate*

A preliminary investigation showed that when a mixture of thallium III acetate in cyclohexene (1 mole:2 mole) was kept at 80° for several hr no Th III remained in the solution.

An initial examination of reaction rate was made. In view of the complexity of the products isolated a detailed kinetic study was not attempted.

Solutions of anhydrous cyclohexene in anhydrous acetic acid and thallium III acetate in anhydrous acetic acid were brought separately to the bath temp of the thermostat. They were then rapidly mixed and aliquots were removed at suitable time intervals and quenched by treatment with KI, the I_2 released being titrated with thiosulphate.[33] Graph 1 illustrates the effect of a temp. change, using one mole oxidant per two moles cyclohexene.

The following general method was used, with slight variations, in all oxidations in glacial acetic acid. (The molar proportions and reaction temp and time were varied).

Anhydrous thallium III acetate in acetic acid was stirred during the dropwise addition of cyclohexene in a flask held at the required temp in a suitable water bath or thermostat. The mixture was kept at this temp for a predetermined period and in some cases periodical sampling was carried out to determine the state of reaction.

The solution was then poured slowly in a thin stream into a vigorously stirred conc. $NaHCO_3$ aq., the aqueous layer being extracted with several lots of chloroform. Occasionally the aqueous layer was treated with anhydrous Na_2SO_4 and continuously extracted with ether.

The organic layers were combined and examined by glc. Separation of the various components was effected as follows.

Solvent was removed to give a conc. solution containing the following approximate proportions of compounds I to V (as determined by glc) I, 4-5%; II, 35-50%; III, 4-12%; IV, 38-40%; V, 2-10%.

Fractionation under high vacuum produced a considerable amount of intractable residue. A low boiling fraction b.p. 40-50°/10 mm showed mainly one peak on glc and a second fraction b.p. 55-65°/10 mm, also consisted mainly of one compound, corresponding to the impurity in the lower boiling fraction. A high boiling fraction b.p. 110-125°/10 mm was shown to contain 3 components. Consequently the mixture of products was subjected to chromatography upon alumina (Woelm, Basic Grade 1) eluted successively with pet. ether (60-80°), increasing amounts of benzene, through pure benzene, thence to chloroform, to alcohol.

Solvent was removed from each sample and those fractions of similar IR spectrum were combined. Finally, they were fractionated on a small scale by glc. The lower boiling fractions were likewise purified. The following products were obtained.

Compound I. This was identified as *cis*-cyclohexan-1,2-diol diacetate[27] as follows: No characteristic bands in the UV. Bands in the IR at 1740-1750, 1235-1260 (several strong bands), 1220, 1057, 1025, 990, 958 and 850 cm^{-1}. No action upon neutral permanganate, bromine in carbon tetrachloride, Brady reagent, Schiff, Fehling, Tollens, cerium nitrate or vanadium-oxine reagents, slowly reduced hot acidified dichromate, approximate equiv. wt. (saponification with alkali) 100, (gave positive hydroxamic acid test); comparison of IR spectrum with spectra of cyclohexyl acetate and cyclohexenyl acetate showed non-identity, but comparison with synthetic *cis*-cyclohexan-1,2-diol diacetate showed identity; b.p. 116-119°/12 mm, n_D^{17} 1·4439.

Compound II. IR spectrum very similar to I, reactions parallel. Identified as *trans*-isomer of I by comparison with spectrum of synthetic material;[34] b.p. 110-115°/11 mm, n_D^{19} 1·4458.

Compound III. IR spectrum showed a strong band at 1733 cm^{-1}. Pale yellow precipitate with Brady reagent, m.p. 154-157°, (Found: C, 51·3; H, 4·8; N, 20·3. $C_{12}H_{14}O_4N_4$ requires: C, 51·8; H, 5·04; N, 20·2%) gave a positive Schiff test, reduced Fehling solution and acidified dichromate (slowly), was without action upon cold neutral permanganate, bromine water, cerium nitrate or vanadium-oxine reagents and gave negative iodoform and hydroxamic acid tests. This was C-formylcyclopentane, b.p. 45-48°/14 mm, n_D 1·4388.

[33] J. Kolthoff and R. Belcher, *Volumetric Analysis* part III; p. 370. Interscience, New York (1957).

Compound IV. IR bands[34] at 1767, 1280, 1245, 1210, 1055 and 1050 (doublet), 980, 945, 870 and 755 cm^{-1}. No characteristic absorption in the UV; reduced Fehling and acidified dichromate solutions rather slowly and gave positive hydroxamic acid and saponification tests. Compound IV was without action upon Brady reagent, Schiff reagent, aqueous permanganate solution, bromine in carbon tetrachloride, vanadium oxinate, iodine in aqueous alkali or cold Tollens reagent. A portion of IV was steam distilled from aqueous acid into Brady reagent, giving a pale yellow 2,4-DNP, m.p. 151–153° (from 96% ethanol) slightly raised by authentic C-formylcyclopentane-2,4-dinitrophenylhydrazone, depressed by the corresponding derivatives of cyclohexanone[35] and cyclohex-2-enone.[36] Compound IV was (diacetoxymethyl)-cyclopentane, b.p. 109–113°/9 mm.

Compound V. This showed bands in the IR at 3012, 1730, 1648, 1227 (a number of strong bands from 1218–1253), 1032, 960, 950, 908, 860, 800 and 730 cm^{-1}. It rapidly reacted with aqueous permanganate and bromine solutions, with Baeyer reagent, slowly reduced hot acidified sodium chromate solution and gave a positive hydroxamic acid reaction. It was without action upon Brady, Tollens (weakly positive), Fehling (very slow action), Schiff and alkaline-iodine solutions. A portion was taken up in hot toluene and the solvent removed; the residue was dissolved in Grignard-dry methanol (containing a trace of Na). After 24 hr at room temp, the solution was neutralized and cyclohex-2-enol, identical upon IR spectroscopy and glc with authentic material, was isolated (b.p. 160–170°). The IR spectrum of cyclohex-2-enyl acetate was identical with that of V: b.p. 63–65°/14 mm, n_D^{21} 1·4583.

Oxidation of cyclohexene in aqueous acetic acid

(a) Glacial acetic acid (50 ml) and water (2 ml) containing cyclohexene (10 ml) were heated at 50–60° during the portionwise addition of glacial acetic acid containing thallium III acetate (0·3 mole). Heating was continued several hr. The products, isolated as above, showed small amounts (about 1–3%) of 2 components having very long retention times (comparatively) upon glc. These were identical with materials obtained in larger proportions as detailed subsequently.

(b) Glacial acetic acid (50 ml), water (10 ml) and cyclohexene (10 ml) were stirred vigorously upon the water bath under reflux, whilst thallium III acetate (0·2 mole) in acetic acid (90 ml) was added portionwise. Isolation of materials as above gave in addition to compounds I to V, 2 additional components (VI and VII). These did not distil below 125°/10 mm and therefore were separated by chromatography upon alumina, eluted with chloroform–alcohol mixtures. They were similar in IR spectra, showing bands at 3450 cm^{-1} (s, broad), 1740 cm^{-1}, 1250 cm^{-1} (broad), 1075 cm^{-1}, 1045 cm^{-1} and 990 cm^{-1}. The presence of alcohol and acetate groups was confirmed chemically; negative tests for unsaturation and free carbonyl were obtained. Each compound was hydrolysed by refluxing in 50% KOH aq. Treatment of the neutralized solution, after removal of alcohol, with periodic acid showed rapid uptake of oxidant. A yellow 2,4-DNP was obtained from the solution, which showed UV bands at 358 mμ (alcohol) and 430 mμ (in alcoholic KOH).

(c) In a similar reaction in acetic acid–water (1:1) the presence of cyclohexan-1,2-diols was confirmed by continuous extraction with ether of the aqueous layer saturated with Na_2SO_4 and comparison of the oily products with authentic material.

Apparatus. Glc was carried out using a Perkin Elmer Model 451 Fractometer and a Griffin D6 chromatograph.

Columns employed were apiezon upon Celite, silicone oil upon Celite, dinonylphthalate upon Celite and polyglycol upon Celite.

Spectra were determined upon a Perkin Elmer model. Infracord, a Unicam S.P. 200, 1 Unicam S.P.700 recording, or a Beckman Model D.V.500, spectrophotometer as convenient.

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[34] The rather high carbonyl frequency for this ester compared with the normal acetate carbonyl (1750–1735 cm^{-1}) may be related to the special acetal-ester structure, viz. R′—CO—OC(HR)O—COR′. Similar shifts in the halo-esters of the type R—CO.OCH$_2$CF$_3$ (cf. J. Filler, *J. Amer. Chem. Soc.* **75**, 1376 (1954)) and in 1,1-diacetoxypropane (L. J. Bellamy and R. Williams, *J. Chem. Soc.* 861 (1957) have been attributed to a field effect. We have found that the carbonyl band in a number of sugars containing the R.CO—OC(HR)—CN group to fall in the range 1764–1776 cm^{-1}, presumably as a result of a similar field effect.

[35] J. E. Brenner, *J. Org. Chem.* **26**, 22 (1961).

[36] A. J. Birch, *J. Chem. Soc.* 1270 (1947).