The Role of Vanadium(V) in the Oxidation of Cyclohexanol to Adipic Acid by Nitric Acid

J. R. Lindsay Smith, D. I. Richards, C. B. Thomas,* and M. Whittaker
Department of Chemistry, University of York, Heslington, York YO1 5DD

The oxidation of cyclohexanol to adipic acid by nitric acid takes place by two routes. One of these, in which 2-nitro-2-nitrosocyclohexanone (**5**) and the nitrolic acid (**6**) are intermediates, is not influenced by the presence of vanadium(V). The other, involving cyclohexane-1,2-dione (**8**) and its tautomer, only gives a significant amount of adipic acid if the metal ion is present. The dione and 'predione' (**9**), a dimeric species which can be isolated from the system, appear to be in equilibrium with the monohydrate (**14**). It is this last compound which is selectively oxidised by vanadium(V). The mono-enol (**15**) is formed by slow tautomerisation of the dione and is selectively oxidised in the presence of vanadium(V) to glutaric acid. The mono-oxime (**10**) appears to be the key intermediate linking the two routes.

The major industrial route to adipic acid, a crucial intermediate in the manufacture of Nylon 6,6, is the oxidation by nitric acid of cyclohexanol (**1**) or of a mixture of this alcohol and cyclohexanone (**2**).[1] The optimum conditions for the complex multistep process have been established empirically. Vanadium(V) and copper(II) ions are employed as catalysts[2,3] but the means by which they direct the oxidation toward the formation of adipic acid is unclear. We have, therefore, undertaken a detailed investigation of the reaction with the aim of establishing the mechanism of the oxidation, the intermediates involved, and the function of the metal ions. In this paper we report on the role of vanadium(V) ions.

Many compounds have been isolated from the reactions of cyclohexanol under conditions similar to those used in the industrial oxidation. Some of these can be converted into adipic acid and may well be intermediates in the oxidation; others may arise from side reactions. Scheme 1 represents the consensus view[4] of the oxidation pathways leading to adipic acid though alternative proposals have been made.

Initially oxidation of cyclohexanol gives cyclohexanone (**2**) and nitrous acid.[4,5] In agreement with this a similar product distribution is obtained when the alcohol is replaced by the ketone although the reaction of the ketone is subject to an unpredictable, and potentially dangerous, induction period which is avoided if (**1**) is employed. Sojka *et al.* have questioned this first step on the grounds that oxidation of (**1**) is more rapid than that of (**2**).[6] However, cyclohexanone reacts in the second step by α-nitrosation,[4,7,8] which requires the nitrous acid generated in step one. In the absence of added nitrite ion the ketone will react slowly while the nitrous acid concentration builds up and this could account for the induction period.

The further reaction of 2-nitrosocyclohexanone (**3**)[7] leads to 2-nitro-2-nitrosocyclohexanone (**5**), either by a direct nitration[9] (step 3) or in two steps *via* 2-nitrocyclohexanone (**4**). Evidence for the latter route comes from the conversion of cyclohexanone into 2-nitrocyclohexanone (**4**) by 99% nitric acid.[10] In the presence of water (**5**) is readily hydrolysed (step 6) to give 6-hydroxyimino-6-nitrohexanoic acid (**6**),[9] which has been isolated from the low-temperature oxidation of cyclohexanol by nitric acid.[4,11,12] Finally (**6**) has been shown to be hydrolysed to adipic acid (**7**) under the acidic conditions of the process.[13,14]

Amongst the other compounds isolated from these oxidations have been cyclohexyl nitrate and nitrite,[15] cyclohexane-1,2-dione (**8**), and 5a,10a-dihydroxy-4a,9a-epoxyperhydrodibenzo[1,4]dioxine (**9**) ('predione').[11,16] The first two compounds probably arise from the reversible esterification of cyclohexanol, whilst predione, a dimer of the hydrated dione (**8**), has been suggested to be derived from 2-nitrosocyclohexanone (**3**) by tautomerisation to the mono-oxime (**10**) (step 8) followed by hydrolysis to (**8**)[6,12] (step 9).

The by-products, carbon dioxide and glutaric and succinic acids, must arise during the course of the reaction and not from further oxidation of adipic acid since these dicarboxylic acids are reported to be inert to degradation by nitric acid.[11,17] It is possible that malonic and oxalic acids are also formed but these would undergo further degradation.[17] The presence of copper(II) and vanadium(V) in the oxidation minimises the formation of by-products which in turn simplifies the purification of the adipic acid. Vanadium(V) has been suggested to improve the conversion of cyclohexanol into adipic acid by diverting the oxidation of predione from succinic and other dicarboxylic acids towards adipic acid.[4]

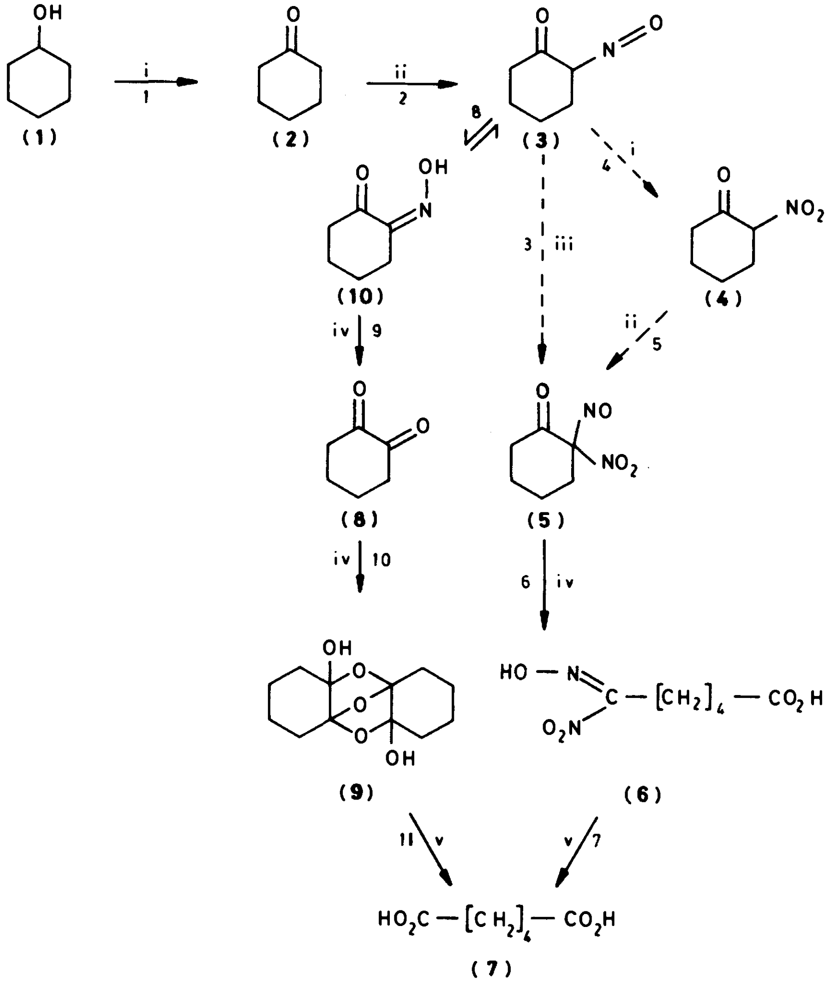
Results and Discussion

A standard set of conditions, close to those employed on an industrial plant, was used for all oxidations. Nitric acid (55% w/w) was used as oxidant at *ca.* 73 °C and at atmospheric pressure. A typical product distribution from reaction of (**1**), with and without added metal ions, is shown in Table 1. We found little difference in the product distribution whether the ketone–alcohol mixture or pure cyclohexanol was employed.

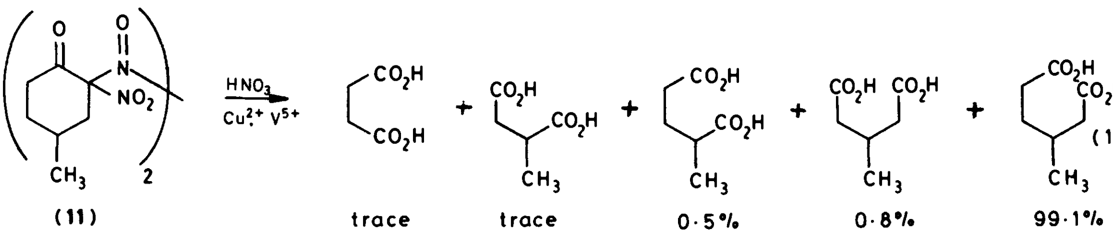
In addition we studied the reactions of many of the suspected intermediates under the same conditions. The nitrolic acid (**6**) was converted in near quantitative yield into adipic acid: the addition of vanadium(V) and copper(II) ions makes little difference to the course of the reaction, as would be expected since it is an acid-catalysed hydrolysis.

There is only one reported synthesis of the nitro nitroso ketone (**5**),[9] which exists, like most nitrosoalkanes, as a dimer. Our attempts to make it by this route gave only a small amount of impure material. However, we were able to obtain a pure sample of the dimer of the 4-methyl analogue (**11**) from 4-methylcyclohexanone. We argued that the methyl group should not have a major influence on the course of the reaction although its presence doubles the number of succinic and glutaric acid by-products. When (**11**) was treated with nitric acid in the presence of copper(II) and vanadium(V) ions, 3-methyladipic acid was obtained in very high yield with small amounts of the glutaric acids and traces ($<0.2\%$) of the succinic acids [reaction (1)].

This result was expected since the conversion of nitronitroso-



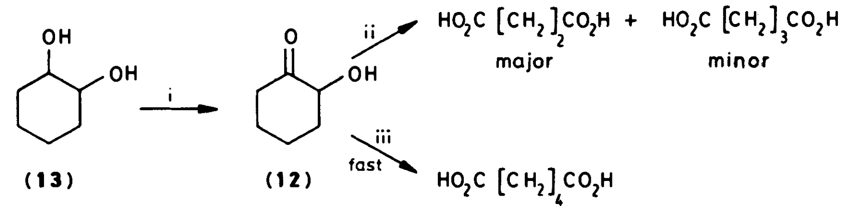
Scheme 1. *Reagents:* i, HNO_3, $-HNO_2$; ii, HNO_2; iii, HNO_3; iv, H^+, H_2O; v, V^V



cyclohexanone into adipic acid is a hydrolytic and not an oxidative process; it should not be influenced by metal ions. Although it is possible that reaction of (**11**), a dimer, does not reflect the behaviour of the monomer, the product distribution is fully consistent with the selectivity observed in the reaction of cyclohexanol, and thus with (**5**) being an intermediate in this reaction.

Two reported syntheses[10,18] of 2-nitrocyclohexanone were unsuccessful in our hands and the compound was eventually obtained by reaction of cyclohex-1-enyl acetate with acetyl nitrate.[19] The nitro ketone is a low melting solid which is difficult to crystallise, partly because it can exist in any of three tautomeric forms.[20] A ^{13}C n.m.r. study showed that the proportion of the keto form (**4**) is solvent-dependent and increases considerably as the polarity of the organic solvent is increased. In the oxidation system, with nitric acid as solvent, we might, therefore, expect the compound to exist almost exclusively as (**4**). Oxidation of the compound gave predominantly adipic acid with a minor amount of glutaric acid. Furthermore the presence of vanadium(v) ion has no effect on the product distribution, although copper(II) ion improves greatly the total recovery of dicarboxylic acids and the yield of adipic acid.

Dimeric 2-nitrosocyclohexanone was also oxidised. The product distributions, however, are significantly different from those obtained from oxidising cyclohexanol. Whilst overall accountability is high the yield of adipic acid is always less than that obtained from cyclohexanol. This result cannot be taken to preclude the monomer (**3**) from being an intermediate in the cyclohexanol oxidation since we have no knowledge of the rates of interconversion of monomer and dimer *vis-à-vis* their rates of oxidation under the conditions of the reaction.



Scheme 2. *Reagents:* i, HNO_3 or V^V; ii, HNO_3; iii, V^V

Table 1. Products from the reaction of nitric acid with cyclohexanol and some of the proposed intermediates in its oxidation[a]

Substrate	Metal ions		Yield of $HO_2C[CH_2]_nCO_2H$ (%)			
	Cu^{2+}	V^{5+}	$n = 2$	$n = 3$	$n = 4$	Total
(1)	−	−	6.5	13.1	78.5	98.1
	+	+	1.7	3.7	94.6	100.0
	+	−	4.4	3.6	90.9	98.9
	−	+	4.2	10.5	83.4	98.1
(6)	−	−		0.8	99.4	100.2
	+	+			99.9	99.9
(4)	−	−		8.8	80.8	89.6
	+	+		4.9	94.7	99.6
	+	−		3.6	96.4	100.0
	−	+		9.6	78.3	87.9
dimer of (3)	−	−	13.7	23.8	57.3	94.8
	+	+	7.6	20.3	71.5	99.4
	+	−	12.9	19.3	64.2	96.4
	−	+	10.8	31.3	55.9	98.0

[a] Conditions: substrate (0.01 mol) added slowly to 55% nitric acid (20 cm^3) at 73 ± 1 °C; copper(II) ions (0.27% w/w) and vanadium(V) (0.05% w/w) added to the nitric acid as appropriate.

Table 2. Products from the reaction of cyclohexane-1,2-dione and some of its derivatives with nitric acid[a]

Substrate	Metal ions		Yield of $HO_2C[CH_2]_nCO_2H$ (%)			
	Cu^{2+}	V^{5+}	$n = 2$	$n = 3$	$n = 4$	Total
(9)	−	−	15.3	12.6	4.5	32.4
	+	+	0.9	16.6	84.5	101.7
	+	1%		7.0	91.7	98.7
	+	−	30.4	11.6	3.4	45.4
	−	+		14.2	86.4	100.6
(12)	−	−	33.8	4.1		37.9
	+	+	1.0	10.8	83.7	95.5
	+	1%	1.0	2.8	95.6	99.4
	+	−	41.4	5.0	2.5	48.9
	−	+	1.8	15.1	82.4	99.3
	−	1%	0.5	2.2	98.2	100.9
(13)	+	+	1.5	14.0	79.7	95.2
	+	1%	0.6	2.1	97.7	100.4
	+	−	37.7	4.5		42.2
	−	+	2.0	15.7	82.1	99.8
	−	1%	0.6	1.9	96.7	99.2
(15)	−	−	0.7	5.7	6.1	12.5
	+	+	5.7	90.7	3.9	100.3
	+	1%	4.6	94.7	1.7	100.9
	+	−	22.7	9.2	2.3	34.2
	−	+	7.7	89.0	1.7	98.4
(10)	−	−	5.8	1.8	86.0	93.6
	+	+	1.1	5.0	93.1	99.2
	+	−	4.9	3.5	84.6	93.0
	−	+	0.6	3.1	92.7	96.4
(16)[b]	−	−	44.0	8.1	0.2	52.3
	+	+	3.9	31.6	52.1	87.6
	+	−	45.9	7.8	0.3	54.0
	−	+	3.4	26.4	53.8	83.6

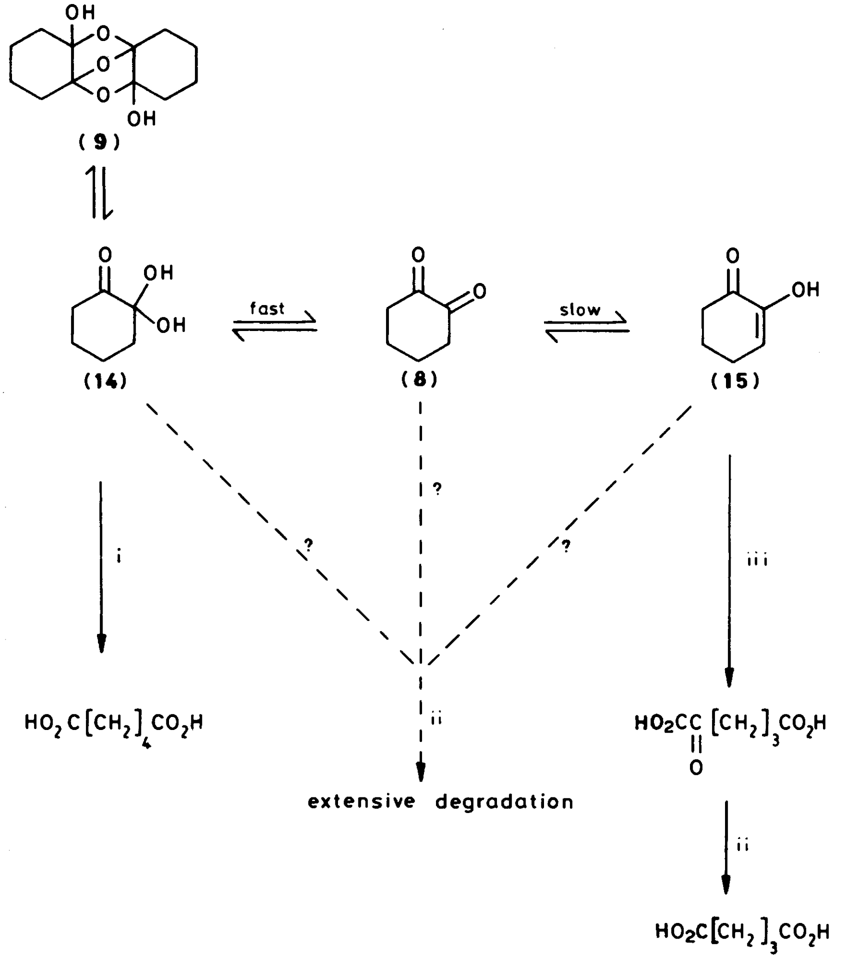
[a] Conditions as in Table 1 unless otherwise stated. [b] Aqueous solution of the mono hydrogen sulphite complex employed for this oxidation.

The reactions of each of the proposed intermediates (**8**)—(**10**) with nitric acid have been investigated previously.[4,11,21–23] Unfortunately the conditions employed have differed and the results reported are often mutually inconsistent. For these reasons we repeated the oxidations under our standard conditions. In the absence of vanadium(V) ion the overall yield of products from the oxidation of predione (**9**) is not good (predione itself is too involatile to be analysed by g.l.c. even if it survives the reaction) and the major product is succinic acid with lesser amounts of glutaric acid and very little adipic acid (Table 2). The presence of vanadium(V) ion dramatically changes the product distribution, with adipic acid now being the major product: copper(II) ion has little effect on the yields. A ten-fold increase in the vanadium(V) ion concentration improves even further the amount of the C_6 diacid. These results are in broad agreement with those of van Asselt.[4]

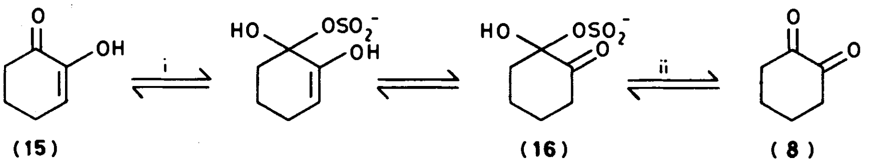
The oxidations of 2-hydroxycyclohexanone (**12**) and cyclohexane-1,2-diol (**13**) are very similar to those of the predione (**9**). A low yield of dibasic acids containing predominantly succinic acid is converted by the presence of vanadium(V) ion into an excellent yield of a product with adipic acid as major component. The very efficient oxidative cleavage of α-hydroxy ketones by vanadium(V) ions[24] accounts for the effect of this metal on the oxidation of (**12**). However, since vanadium ions have much less effect on the analogous oxidation of 1,2-diols[25] the diol (**13**) is probably first oxidised to (**12**) by nitric acid and this is subsequently cleaved by the metal ion. Once again larger amounts of the catalyst lead to further increases in the yield of adipic acid. We conclude that the vanadium(V) ion diverts the course of the reactions of (**12**) and (**13**) with nitric acid by virtue of its ability to cleave oxidatively 2-hydroxycyclohexanone before nitric acid brings about an alternative mode of oxidation (Scheme 2).

Although the results from the predione oxidations resemble those from (**12**) and (**13**) in all important details, the predione is in a higher oxidation state than (**12**) or (**13**) and will not, therefore, be converted into either under the reaction conditions. One explanation for the behaviour of the compound involves the intermediacy of the monohydrate (**14**) of cyclohexane-1,2-dione (**8**). The dione is rapidly hydrated in aqueous solution[26] and in the reaction mixture the dione and its hydrate should be in equilibrium with the predione (**9**). The hydrate, which is an α-hydroxy ketone, should be oxidised rapidly by vanadium(V) ions (Scheme 3). This would provide an effective route from (**8**), (**9**), and (**14**) to adipic acid.

The oxidation of commercial cyclohexane-1,2-dione in the presence of vanadium(V) ion under the standard conditions is in marked contrast to that of predione, for glutaric and not adipic acid is the major product. However, this contrasts with a patent



Scheme 3. *Reagents:* i, V^V; ii, HNO_3; iii, HNO_3, V^V

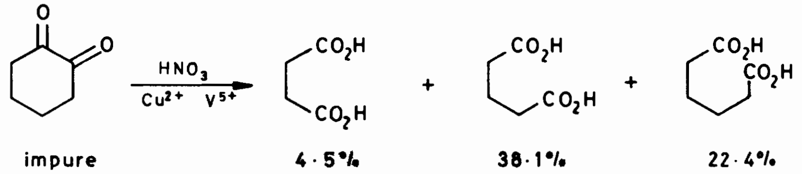


Scheme 4. *Reagents:* i, HSO_3^-; ii, H^+, $-H_2SO_3$

that claims that oxidation of the dione with vanadium(v) ion gives a high yield of adipic acid (>80%).[27] An explanation for the discrepancy between these results probably lies in the tautomeric equilibria of the dione. Commercial cyclohexane-1,2-dione is predominantly the mono-enol (**15**), and ketonisation of the enol is slow even in a strongly acidic medium.[26,28] On the other hand hydration of (**8**) is rapid. Compound (**15**) would be expected to react in nitric acid by attack at C-3, by analogy with the behaviour of cyclohexanone which reacts at the 2-position of the enol.[29] Hence (**15**) should undergo ring cleavage to give 2-oxoadipic acid and, ultimately, glutaric acid (Scheme 3).

We had only limited success in repeating the work cited in the patent[27] primarily because it contains no details of how the di-keto tautomer was obtained. Bakule has reported the preparation of a solution of the diketone (**8**) *via* its hydrogen sulphite complex (Scheme 4) but he found that, if he attempted to isolate this tautomer, decomposition occurred.[30] Interestingly he noted that from a solution of impure (**8**) a crystalline material was obtained and that the same compound precipitated out of a concentrated solution of the mono-enol in acid. Whilst the compound was not identified, the analytical data cited are very similar to those obtained by others for predione (**9**).

When we attempted to prepare (**8**) by the method of Bakule,[30] the isolated oil rapidly turned dark brown, and ^{1}H n.m.r. spectroscopy showed it to contain some of the mono-enol tautomer. On oxidation, this impure material gave a poor overall yield of dicarboxylic acids [reaction (2)], although the proportion of adipic acid, whilst not as high as that reported in the patent, is substantially greater than that obtained from the commercial mono-enol. An aqueous solution of the mono-bisulphite complex (**16**) was also subjected to the reaction conditions on the assumption that hydrolysis of the complex would be faster than its oxidation. This gave an even higher yield of adipic acid (Table 2) and the distribution of products responded to the omission of the metal ions in a similar way to that observed in the oxidation of predione.



(2)

The obvious link between the routes involving oxidation of 2-nitrocyclohexanone and cyclohexane-1,2-dione is the tautomeric equilibrium of the mono-oxime (**10**) and the nitroso compound (**3**). The former is not an easy material to obtain, decomposing at temperatures little above ambient, which may account for the contradictory physical parameters which have been reported.[31,32] Our sample had a sharp m.p. and a ^{13}C n.m.r. spectrum consistent with the structure (**10**). Oxidation of the oxime under the standard conditions gave the same product distribution as that obtained from cyclohexanol. Such a result is consistent with oxidation of the alcohol proceeding *via* the nitroso compound (**3**), which is in rapid tautomeric equilibrium with the mono-oxime (**10**). However, experiments in the absence of either or both metal ions suggest that the situation is more complex. The omission of copper ions makes little difference to the product yields other than to reduce that of the by-product glutaric acid. The absence of vanadium(V) ions both reduces the yield of adipic acid and increases that of succinic acid. In contrast when cyclohexanol is the substrate the proportion of glutaric acid in the product is *increased* by omitting copper.

We conclude that there are two major routes by which cyclohexanol is converted into adipic acid. One proceeds *via* (**5**) and (**6**) and is unaffected by vanadium(V) ion. However, if 2-nitrocyclohexanone (**4**) is an intermediate on this pathway adipic acid formation is favoured by copper(II) ion. The other, involving cyclohexane-1,2-dione, its oxime, tautomers, and hydrate, only gives good yields of adipic acid if vanadium(V) ions are present. In the absence of these ions the latter route results in extensive degradation. The ratios of products obtained from oxidations in the presence of vanadium(V) ion suggest that (**8**), (**9**), (**12**), and (**13**) all react *via* a common intermediate.

Experimental

Chromatography and Spectroscopy.—Gas chromatography was performed with a Pye 104 instrument equipped with a flame-ionisation detector and a pyrolysis inlet system consisting of a stainless steel tube (10 cm × 4 mm i.d.) packed with silica chips and heated to 400 °C. The column employed was either 10% w/w Carbowax 20M on acid-washed Chromosorb W (2 m × 4 mm i.d.) or 0.1% w/w SP-100 on Carbopack C (3.6 m × 4 mm i.d.). Relative peak areas were determined by means of an LDC 308 integrator with pimelic acid as internal standard.

Mass spectra were recorded with an A.E.I. MS3076 spectrometer operating at 70 eV. For combined g.l.c.–mass spectrometry the instrument was coupled *via* a heated jet separator to a Pye 104 instrument. N.m.r. spectra (^1H and ^{13}C) were obtained with a Varian EM 360A and a JEOL FX 90Q instrument respectively. I.r. spectra were recorded for liquid films or Nujol mulls with a Pye-Unicam SP 1025 spectrometer. M.p.s were measured with a Kofler micro-hot stage.

Materials.—Cyclohexanol, cyclohexanone, adipic acid, glutaric acid, pimelic acid, and succinic acid (B.D.H. GP reagents), nitric acid (s.g. 1.42) and ammonium metavanadate (B.D.H. AnalaR reagents), cyclohexanedione mono-enol and 2-and 3-methylglutaric acids (Fluka), and methylsuccinic and 3-methyladipic acids (Aldrich) were commercial samples. Predione was generously donated by Bayer Chemicals and a commercial sample of cyclohexanol–cyclohexanone mixture by I.C.I. Petrochemicals and Plastics p.l.c.

6-Hydroxyimino-6-nitrohexanoic acid was prepared by the method of Godt and Quinn,[11] by reaction of cyclohexanol (25 g) with nitric acid (70%; 100 cm^3) at 20 °C. 6-Hydroxyimino-6-nitrohexanoic acid (3 g, 6%) was obtained as a pale yellow crystalline solid, m.p. 76—82 °C (decomp.) [lit.,[11] 77—78 °C (decomp.)]; δ_C 24.9 (C-4), 25.5 and 25.8 (C-3 and C-5), 34.2 (C-2), 164.0 (C-6), and 177.3 (C-1).

The synthesis of the dimeric 2-nitro-2-nitrosocyclohexanone was attempted by the method of Minisci and Quilico.[9] Cyclohexanone (2 g) was treated with dinitrogen tetraoxide (2 cm^3) in a mixture of acetic anhydride (3 cm^3) and carbon tetrachloride (16 cm^3). 2-Nitro-2-nitrosocyclohexanone dimer (1.5 g, 42%) was obtained as a light blue crystalline solid, m.p. 86—91 °C (decomp.) [lit.,[9] 98 °C (decomp.)]. The compound was only slightly soluble in organic solvents and once in solution it tended to decompose readily. As a result it was not possible to record satisfactory n.m.r. spectra and, whilst the i.r. spectrum was similar to that reported,[9] elemental analysis indicates the compound to be impure.

4-Methylcyclohexanol (57 g) was oxidised by chromic acid, following the method of Vogel[33] for the preparation of cyclohexanone, to give 4-methylcyclohexanone (42 g, 75%) as a colourless liquid, b.p. 56—58 °C at 12 mmHg (lit.,[34] 170 °C); δ_C 21.0 (CH_3), 31.2 (C-4), 34.8 (C-3 and C-5), 40.8 (C-2 and C-6) and 211.8 (C-1). This ketone (6 g) was treated with dinitrogen tetraoxide (5 cm^3) in a mixture of acetic anhydride (8 cm^3) and carbon tetrachloride (32 cm^3) to give *4-methyl-2-nitro-2-nitrosocyclohexanone* (1.69 g, 17%) as a pale green solid, m.p. 90—95 °C (decomp.); $\nu_{max.}$ 1 725, 1 570, 1 315, and 1 290 cm^{-1} (Found: C, 45.3; H, 5.5; N, 15.0%. $C_7H_{10}N_2O_4$ requires C, 45.2; H, 5.4; N, 15.05%).

2-Nitrocyclohexanone was prepared by heating cyclohexanone (50 g), 1-methylvinyl acetate (100 cm^3), and toluene-4-sulphonic acid (0.4 g) at 105 °C with stirring, the propanone produced being removed steadily by distillation. After 48 h the excess of enol acetate was removed under vacuum and the residue distilled to give cyclohex-1-enyl acetate (64.8 g, 90%) as a colourless oil, b.p. 65—67 °C at 12 mmHg (lit.,[34] 180 °C). To this compound (28 g) in acetic anhydride (61 g) cooled in ice, was added with stirring 70% w/v nitric acid (12.6 cm^3) at a rate such as to maintain the temperature of the mixture at 18—20 °C. Acetic acid and unchanged anhydride were removed under vacuum, the residual oil was dissolved in tetrachloromethane (10 cm^3), and the solution was cooled to -30 °C. 2-Nitrocyclohexanone (19 g, 66%) was obtained as a white crystalline solid, m.p. 35—38 °C (lit.,[35] 34—37 °C).

Dimeric 2-nitrosocyclohexanone was prepared by the method of Bischoff and Ohme[32] from cyclohex-1-enyl acetate (28 cm^3), pentyl nitrite (20 cm^3), and concentrated sulphuric acid (6 drops) in acetic anhydride (100 cm^3). 2-Nitrosocyclohexanone dimer (1.67 g, 7%) was obtained as white crystals, m.p. 122—126 °C (decomp.) (lit.,[32] 123—124 °C); δ_H 1.9—2.6 (8 H, complex m, $CH_2CH_2CH_2CH_2$) and 5.85 (1 H, t *J* 9 Hz, CHNO); δ_C 23.5 (C-4), 26.9 and 30.0 (C-3 and C-5), 41.1 (C-6), 73.6 (C-2), and 199.0 (C-1) (Found: C, 56.5; H, 7.2; N, 11.1. Calc. for $C_{12}H_{22}N_2O_4$: C, 56.6; H, 7.2; N, 11.0%).

Cyclohexane-1,2-dione mono-oxime was obtained from methyl 2-oxocyclohexanecarboxylate[36] (2 g), which was stirred with sodium nitrite (0.88 g) in sodium hydroxide solution (0.5 mol dm^{-3}, 28 cm^3) for 4 h. The mixture was cooled to −5 °C, and dilute sulphuric acid (2 mol dm^{-3}; 7 cm^3) was added with vigorous stirring while the temperature was maintained at −5 °C. The solution was extracted with chloroform and the extracts dried ($MgSO_4$). Removal of the solvent under reduced pressure gave a pale yellow oil which was dissolved in a small amount of methanol and kept overnight at −20 °C. Cyclohexane-1,2-dione mono-oxime was obtained as white crystals containing some solvent of crystallisation. Dissolving the crystals in carbon tetrachloride and then removing the solvent under reduced pressure gave white crystals (0.92 g, 57%) with m.p. 67—70 °C (lit.,[31] 60 °C; lit.,[32] 60—64 and 84—85 °C); δ_H 1.65—2.05 (4 H, m), 2.57 (2 H, t, *J ca.* 7 Hz, CH_2–C=N), and 2.79 (2 H, t *J ca.* 7 Hz, CH_2–C=O); δ_C 21.4, 22.2, 24.9, and 40.6 (*sp*^{3} C), 153.7 (C=NOH), and 197.3 p.p.m. (C=O): *m/z* 127.0638 (65%, $M^{+\bullet}$, calc. for $C_6H_9NO_2$: *M*, 127.0633), 110 (34, *M* − OH), 82 (75, *M* − OH − CO), 55 (100, $C_4H_7^+$), and 41 (33, $C_3H_5^+$). The mono-oxime proved thermally labile in solution and temperatures had to be kept below 25 °C to prevent decomposition.

Cyclohexane-1,2-dione hydrogen sulphite complex was obtained as an aqueous solution by dissolving sodium disulphite (2.5 g) and cyclohexane-1,2-dione (2.5 g) in water (70 cm^3) and stirring overnight. The resultant solution was oxidised without further treatment.

Oxidation Procedure.—Nitric acid (55%) containing copper(II) ion (0.27% w/w) and vanadium(V) ion (0.05% w/w) as appropriate was made up as follows: a solution of nitric acid (s.g. 1.42; 1 000 cm^3) containing copper (5.177 g) was added to an aqueous solution of ammonium metavanadate (2.085 g in 438 cm^3). This oxidising solution (20 cm^3) was placed in a conical flask equipped with a thermometer, a reflux condenser, and a side arm with a gas inlet and a tared 3 cm^3 Lunge-Rey pipette. The solution was heated to 73 °C with stirring while air was bubbled through at *ca.* 1 bubble s^{-1}, and the substrate was added dropwise at such a rate as to maintain the temperature at 73 ± 1 °C. Reactions that were not sufficiently exothermic were heated externally. When addition was complete the pipette was replaced with a stopper and reweighed and the temperature of the solution raised to 90 °C for *ca.* 10 min. After being cooled to 50 °C (lower temperatures could result in precipitation of adipic acid) the reaction mixture was transferred to a tared 100 cm^3 flask using a pre-warmed pipette; the reaction vessel was washed with three portions of warm distilled water (20 cm^3), and the washings were transferred to the flask. The solution was made up to 100 cm^3 with distilled water and the flask reweighed.

The products were analysed as follows. A known weight of the solution was added to a known weight of the standard and the mixture warmed to ensure dissolution. Phenolphthalein was then added as an indicator and the mixture neutralised with 25% w/v tetramethylammonium hydroxide solution. A sample (*ca.* 2 μl) of the neutralised solution was injected into the pyrolysis unit of the gas chromatograph where the ammonium salts of the acids were converted instantaneously into methyl esters, which were eluted and quantified. For substrates which were solids at temperatures greater than 40 °C the pipette was omitted and the sample added by spatula in small portions from a tared sample tube.

Acknowledgements

We thank I.C.I. Petrochemicals and Polymers p.l.c. for financial support, and numerous individuals at their Wilton research laboratories for discussions. Two of us (D. I. R. and M. W.) gratefully acknowledge the award of C.A.S.E. studentships by the S.E.R.C.

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Received 27th February 1985; *Paper* 5/330