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Oxidation of Cyclopentene by $RuCl_3$–NaOCl Catalyst

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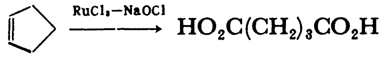
Synopsis. Oxidation of cyclopentene by $RuCl_3$–NaOCl catalyst in an aqueous-organic two phase system was investigated by changing compositions of solvent system and additives to the aqueous solution. Use of acetonitrile as a cosolvent enhanced the reaction rate greatly, and addition of NaOH improved the yield of glutaric acid up to 80%.

Ruthenium tetraoxide is one of the most powerful oxidants of various organic compounds under mild condition.[1] Berkowitz and Rylander[2] reported the oxidation of various organic compounds by using ruthenium tetraoxide as a stoichiometric oxidant. In 1970, Wolfe et al.[3] reported that cyclohexene was oxidized to adipic acid (86—95%) with RuO_4 generated in situ from $RuCl_3$ and sodium hypochlorite. Foglia et al.[4] reexamined the work of Wolfe et al., and found that this procedure gave good yield of cleavage products from *acyclic* alkenes only when the oxidations were carried out with added sodium hydroxide and a *phase transfer catalyst.* Furthermore, the direct oxidation of cyclic olefines to corresponding dicarboxylic acids with RuO_2 (or $RuCl_3$)-hypochlorite oxidant was scarcely investigated.

Sharpless et al.[5] reported an improved procedure for traditional $RuCl_3 \cdot xH_2O$–IO_4^-/CCl_4–H_2O catalytic oxidation system by adding acetonitrile as a cosolvent. The effects of acetonitrile are speculated to disrupt the inactive lower valent ruthenium complexes and return the ruthenium to the catalytic cycle. Although this method is convenient, it also has several drawbacks owing to using periodate as a reoxidant; the relative high cost and high molecular weight of periodate; the precipitation of voluminous quantities of iodate as the reaction proceeds. We describe herein a convenient and effective procedure of the oxidation of cyclopentene to glutaric acid by using readily available sodium hypochlorite in the presence of a catalytic amount of $RuCl_3 \cdot xH_2O$.



Experimental

The reaction was carried out in a three necked flask equipped with a magnetic stirrer, addition funnel, and condenser. The typical experiment is as follows. The flask was charged with 90 ml of CCl_4, 10 ml of H_2O, 3.2 g of cyclopentene (47 mmol), and 0.15 g of $RuCl_3 \cdot xH_2O$ (the molar ratio of $RuCl_3$ to cyclopentene was 0.014 on calculations based on $x=1$). Aqueous sodium hypochlorite (100 g of 21 wt% solution, 282 mmol) with added 4 g of NaOH was added to the stirred CCl_4 solution dropwise for about 2 h while the flask was cooled by means of an ice bath. The vigorous stirring was continued until the color of the reaction solution turned black, at which time the starch iodide test for active chlorine was negative. The reaction mixture was filtered through a Celite pad in order to remove the precipitated RuO_2. After the separation of organic layer, the aqueous phase was washed with CH_2Cl_2, acidified to a pH of one with concd HCl and the solvent was removed under reduced pressure. The residual solid was extracted with ether, and the solvent was removed under reduced pressure to give 4.7 g of white powder. After esterification by BF_3–methanol reagent, gas chromatography showed that 4.4 g of glutaric acid (71 mol% yield based on charged cyclopentene) was produced. The products were also identified by IR.

Results and Discussion

Oxidation of cyclopentene by $RuCl_3$–NaOCl catalyst was investigated under various conditions and the results are shown in Table 1. The reaction time and the yield of glutaric acid were very dependent on the compositions of the organic solvent and the addtion of alkali to the aqueous solution. In the absence of alkali (Runs 1 and 2, the reaction conditions were similar to the work of Wolfe et al.[3]), or when sodium

Table 1. Oxidation of Cyclopentene by $RuCl_3$–NaOCl Catalysts[a]

Run	Solvent ml				Alkali g		Reaction time/h	Products: total amount g	Products: glutaric acid g	Products: yield mol%
1	CCl_4,	90	H_2O,	10	—		8	3.1	2.3	37
2	CH_2Cl_2,	90	H_2O,	10	—		8.5	3.0	2.1	34
3	CCl_4,	90	H_2O,	10	NaOH,	4	8	4.7	4.4	71
4	CCl_4,	90	CH_3CN,	10	NaOH,	4	6.5	5.0	4.9	79
5	CCl_4,	70	CH_3CN,	30	NaOH,	4	2	4.1	4.1	66
6	CCl_4,	50	CH_3CN,	50	NaOH,	4	2	5.2	5.1	82
7	CH_3CN,	90	H_2O,	10	NaOH,	4	2	4.3	4.3	69
8	CCl_4,	90	CH_3CN,	10	$Na_2CO_3 \cdot 10H_2O$,	14	3.5	3.9	2.9	47

a) Cyclopentene 3.2 g, NaOCl aqueous solution 100 g (21 wt%, 282 mmol), $RuCl_3 \cdot xH_2O$ 0.15 g.

carbonate was used instead of NaOH (Run 8), the yield and selectivity of glutaric acid were relatively low. Determination by gas chromatography indicated that a considerable amount of succinic acid (about 10 mol% yield) was produced. This result indicated that the further oxidation of glutaric acid occurred. Furthermore, all of ruthenium catalyst could not be recovered as RuO_2 by means of filtration of the reaction mixture and the aqueous solution remained black even after the filtration.

The addition of NaOH (the molar ratio of NaOH to cyclopentene is 2) improved the yield of glutaric acid considerably. In these cases, all of the ruthenium catalyst could be recovered by filtration and reused easily. The effects of added NaOH are considered to depress the formation of hypochlorous acid, which often leads to the formation of chlorinated byproducts by addition to the double bond,[6] to prevent glutaric acid from the consecutive oxidation in organic layer by extraction to the aqueous layer as sodium salt, and to promote the precipitation of RuO_2 after all the consumption of charged sodium hypochlorite. Under alkaline conditions, RuO_4 is readily reduced to RuO_4^- and further to RuO_4^{2-}.[7] It was found that the molar ratio of about 2:1 NaOH to cyclopentene gave the good yield of glutaric acid. The further addition of NaOH promoted reduction of RuO_4 to RuO_4^{2-}, which is a good oxidant for alcohols but not for alkenes,[8] and then led to slower reaction and poorer yield.

When acetonitrile was used as a cosolvent of cyclopentene, the reaction rate increased greatly, and the yield of glutaric acid improved up to 82 mol% (Run 6). Although the effect of acetonitrile is not understood well in the present stage, we also speculate that acetonitrile disrupts the inactive lower valent ruthenium carboxylate complexes and makes the regeneration of RuO_4 much easier. In the work of Sharpless et al.,[5] the third solvent component, CCl_4, was necessary for the reaction. However, the solvent system which consisted of acetonitrile and water alone gave the fairly good yield of glutaric acid (Run 7) in the present work.

Although the addtion of propionitrile to the reaction mixture in place of acetonitrile also enhanced the reaction rate, the yield of glutaric acid decreased 80% of that when acetonitrile was used. Adiponitrile was not an effective cosolvent, and rather made the reaction very slow and/or incomplete. This might be due to inactivation of the catalyst owing to its strong bonding to the ruthenium.

The oxidation of other cycloalkenes with $RuCl_3$–NaOCl catalysts was also examined (the reaction conditions were the same as those of run 6 in Table 1). Cyclohexene was oxidized to adipic acid in 56 mol%, and cyclooctene to suberic acid in 36 mol%, pimeric acid in 5 mol%, and adipic acid in 5 mol%. As the ring size of cyclic olefins became bigger, and the reaction took longer time (7 h for cyclohexene and overnight for cyclooctene) and the yield of corresponding dicarboxylic acids decreased. Extention of this catalytic system to cyclododecene oxidation proved impractical, since soap formation seriously complicated reaction procedure. Cyclohexanone was oxidized under similar conditions to adipic acid in 45 mol%, glutaric acid in 1 mol%, and succinic acid in 1 mol%.

Table 2. Ruthenium-Catalyzed Oxidation of Cyclopentene with Various Reoxidants[a)]

Reoxidant	Reaction time	Yield of glutaric acid/%[b)]
NaOCl[c)]	2 h	82
$NaClO_2$[d)]	8.5 h	53
$NaClO_3$[e)]	1 d	—[i)]
$NaBrO_2$[f)]	1 d	32
$NaBrO_3$[g)]	1 d	21
$NaIO_4$[h)]	1 d	68

a) Cyclopentene 3.2 g, $RuCl_3\cdot xH_2O$ 0.15 g, CCl_4 50 ml, CH_3CN 50 ml. b) Determined by GC after esterification. c) 21 wt% NaOCl aqueous solution 100 g, NaOH 4 g. d) $NaClO_2$ 9 g in H_2O 100 ml, NaOH 2 g. e) $NaClO_3$ 7 g in H_2O 100 ml. f) $NaBrO_2\cdot 3H_2O$ 18 g in H_2O 100 ml, NaOH 2 g. g) $NaBrO_3$ 9.5 g in H_2O 100 ml. h) Cyclopentene 1 g, $RuCl_3\cdot xH_2O$ 0.05 g, $NaIO_4$ 15 g in H_2O 100 ml. i) Not reacted.

The ruthenium catalyzed oxidation of cyclopentene with various reoxidants was investigated and the results are tabulated in Table 2. The reaction conditions were slightly different from one to another, but not optimized. Among the reoxidants investigated, NaOCl gave the best yield of glutaric acid. Although $NaIO_4$ gave the fairly good result, reaction took longer time and the precipitation of the voluminous amounts of iodate during the reaction made the reaction system complicated.

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