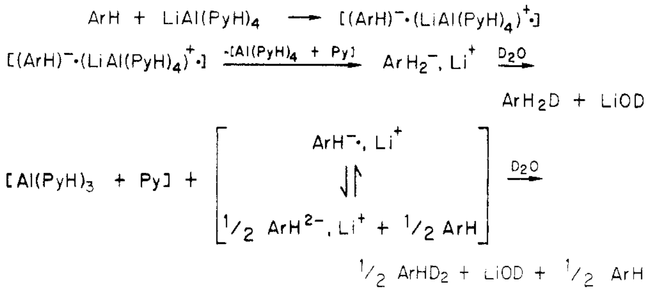
Table I. Reactions of LDPA with Polynuclear Hydrocarbons in THF at 24 °C[a]

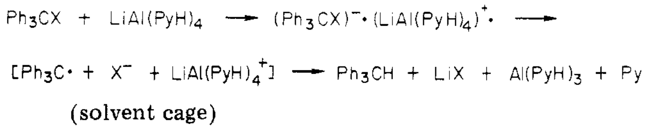
hydrocarbon	10^{-4} M	time, days	color	% radical anion[b]	EPR data	
					g value	no. of lines
anthracene	200	15	light blue	6	2.0029	43
benzo[*a*]pyrene	1	7	violet	38	2.0031	93
chrysene	4	10	blue-green	10	2.0033	111
2,3-benzanthracene	1	5	yellow-green	>55	2.0032	65
phenanthrene	4	10	blue	9	2.0030	73
perylene	1	4	blue	71	2.0029	59

[a] LDPA was used in 20-fold excess. [b] Percentages of radical anion intermediates were calculated from the values of the extinction coefficient as well as by integrating the EPR spectra. Values are within ±5% of the reported values.

Scheme II



Scheme III



is shown in Figure 2. When the mixture obtained from the reaction of LDPA with anthracene was hydrolyzed by D_2O and the products analyzed, both ArH_2D and $ArHD_2$ (ArH = anthracene) were formed. $ArHD_2$ is the expected product when the radical anion is hydrolyzed by D_2O, and the formation of ArH_2D indicates that hydrogen is already transferred from LDPA to the radical anion prior to hydrolysis.

Thus it appears from EPR and visible spectroscopic as well as product formation studies that a single electron is transferred from LDPA to the hydrocarbon, forming initially a radical anion–radical cation pair $[(ArH)^{-}\cdot(LiAl(PyH)_4)^{+}\cdot]$, which not only proceeds to form the product ArH_2Li but also dissociates to generate the radical anion $ArH^{-}\cdot Li^{+}$. The suggested mechanism is shown in Scheme II.

Reactions of LDPA have also been carried out with alkyl halides. When trityl halides (Ph_3CX, where X = Cl or Br) were allowed to react with LDPA in THF, a yellow-orange color developed immediately. The reaction solution was found to be EPR active and showed an EPR spectrum consistent with that of the trityl radical, $Ph_3C\cdot$. This signal was not present in the spectrum of the starting materials. The intensity of the signal increased rapidly and reached a maximum (estimated intensity ~6%) beyond which it decreased slowly. The reduction product of the reaction was triphenylmethane, which continuously formed during the course of the reaction. The suggested mechanism is described in Scheme III. Preliminary results[12] concerning the reaction of 5-hexenyl iodide with LDPA show the formation of cyclized hydrocarbon product, which indicates the involvement of a SET mechanism.[7] We have also found that aryl halides can be reduced by LDPA. Currently we are engaged in exploring the possible involvement of SET in these reactions.

Registry No. Anthracene, 120-12-7; benzo[*a*]pyrene, 50-32-8; chrysene, 218-01-9; 2,3-benzanthracene, 92-24-0; phenanthrene, 85-01-8; perylene, 198-55-0; anthracene radical anion, 34509-92-7; benzo[*a*]pyrene radical anion, 34505-58-3; chrysene radical anion, 34488-57-8; 2,3-benzanthracene radical anion, 34512-30-6; phenanthrene radical anion, 34510-03-7; mesityl phenyl ketone, 78609-86-6; LDPA, 36393-24-5.

E. C. Ashby,* A. B. Goel
School of Chemistry
Georgia Institute of Technology
Atlanta, Georgia 30332

Received June 8, 1981

---

[12] E. C. Ashby, R. N. DePriest, and A. B. Goel, work in progress.

A Greatly Improved Procedure for Ruthenium Tetraoxide Catalyzed Oxidations of Organic Compounds

Summary: Addition of acetonitrile to the traditional CCl_4/H_2O solvent system for ruthenium tetraoxide catalyzed oxidations leads to a greatly improved system; some applications to olefins, alcohols, aromatic rings, and ethers are described.

Sir: In 1953 ruthenium tetraoxide was introduced by Djerassi and Engle as an organic oxidant.[1] Since that time its utility for a variety of oxidative transformations has been recognized.[2] The expense of ruthenium metal provided incentive for the development of catalytic procedures, the most popular of which involve use of periodate or hypochlorite as the stoichiometric oxidants.[2] The periodate- and hypochlorite-based catalytic methods can be very effective; however, we and others have often encountered problems such as very slow and/or incomplete reactions. These sluggish or failed reactions must be due to inactivation of the ruthenium catalyst (normally present in amounts of 1–5%). We noted that the difficult cases shared a common feature: carboxylic acids were either present or being generated during the course of the oxidation. This led us to speculate[3] that lower valent ruthenium carboxylate complexes[4] might be responsible for the loss of catalyst activity.

---

[1] Djerassi, C.; Engle, R. R. *J. Am. Chem. Soc.* **1953**, *75*, 3838.

[2] Lee, D. G.; van den Engh, M. In "Oxidation in Organic Chemistry"; Trahanovsky, W. S., Ed.; Academic Press: New York, 1973; Part B, Chapter 4.

[3] Dark-colored, ruthenium containing precipitates can usually be observed in inactive systems.

[4] Spencer, A.; Wilkinson, G. *J. Chem. Soc., Dalton Trans.* **1972**, 1570.

Table I. RuO_4 Oxidation of (*E*)-5-Decene[a]

	products[b]		
solvent	recovered olefin, %	*n*-pentanal, %	*n*-pentanoic acid, %
1. CCl_4, H_2O (1:1)	80	17	
2. acetone, H_2O (5:1)	74	20	3
3. CCl_4, CH_3CN, H_2O (2:2:3)[8]			88

[a] Reactions were performed at 25 °C for 2 h, using 0.022 mol equiv of $RuCl_3\cdot(H_2O)_n$ and 4.1 mol equiv of $NaIO_4$. [b] Yields: entries 1 and 2 by GLC; entry 3 is an isolated yield.

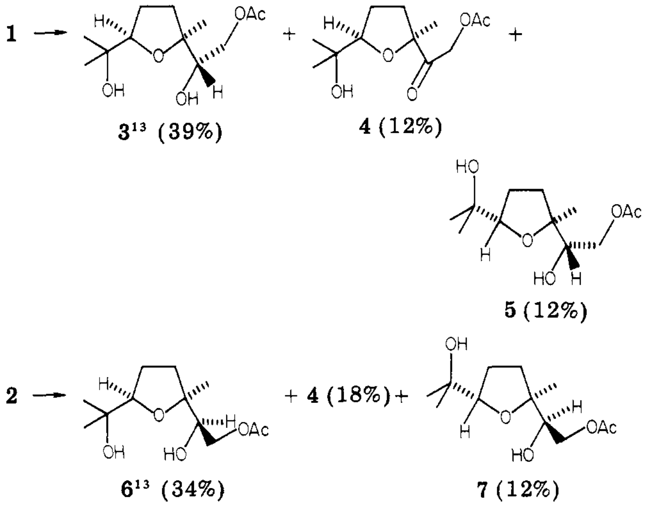
Table II. Cleavage of Olefins by Improved Method[a]

olefin	$NaIO_4$, equiv	time, h	% yield carboxylic acid
1-decene	4.5	2	89[b]
(*E*)-5-decene	4.1	2	88[c]
(*Z*)-5-decene	4.1	1	87[c]
cyclooctene	4.5	1	75[b]
citronellyl acetate	3.1	0.5	83[b]
2,3-dimethyl-2-octene	2.1	6	>95[d]

[a] Performed on 1-mmol scale, using 0.022 mol equiv of $RuCl_3\cdot(H_2O)_n$ catalyst. [b] Isolated as methyl esters (CH_2N_2, Et_2O) and purified by preparative TLC. [c] Isolated as free acids by distillation. [d] Product was 2-heptanone (yield by GLC).

To test this hypothesis a μ_3-oxo-triruthenium carboxylate complex $[(Ru_3O(OAc)_6(H_2O)_3{}^{+-}OAc]$ was prepared.[4] This Ru(III)/Ru(II) mixed valence complex was inactive when tested as a catalyst for the oxidative cleavage of 1-octene in the $CCl_4/H_2O/IO_4^-$ system. However, when acetonitrile was added to this inactive system, rapid oxidative cleavage to pentanoic acid ensued.[5] The choice of acetonitrile[6] was dictated by rudimentary considerations of the coordination chemistry of lower valent transition metals. We reasoned that to disrupt the insoluble carboxylate complexes and return the ruthenium to the catalytic cycle, one needed a good ligand for the lower valent (III/II) ruthenium[7] present. The strong oxidizing environment of the present system rules out almost all of the ligands which are known to bind well to lower valent transition metals (e.g., phosphines, sulfides, amines, carbon monoxide, and isonitriles). Nitriles (especially acetonitrile) are unique in their ability to resist oxidation, and yet retain good ligating ability toward lower valent transition metals. We are well aware of the speculative nature of the rationale offered above for the effects of acetonitrile in these oxidations. Nevertheless, it seemed worth presenting since it was this line of reasoning which led us directly to the choice of acetonitrile as a cosolvent. To our disadvantage, we organic chemists too often ignore even the most elementary aspects of the coordination chemistry of the metals we employ as catalysts or reactants.

Scheme I. Abnormal Products from 1,5-Dienes



The results in Table I for oxidative cleavage of (*E*)-5-decene allow comparison of the two commonly used catalytic systems (entries 1 and 2) with our new system (entry 3). The enhanced reactivity of this new system is readily apparent.

This new method is rapid and mild.[9] Further examples of its application to olefins are shown in Table II.

A representative experiment is as follows. A flask is charged with a magnetic stirrer, 2 mL of carbon tetrachloride, 2 mL of acetonitrile, 3 mL of water,[8] 189 μL (140 mg, 1 mmol) of (*E*)-5-decene, and 877 mg (4.1 equiv) of sodium metaperiodate.[10] To this biphasic solution 5 mg (2.2 mol %) of ruthenium trichloride hydrate[11] was added, and the entire mixture was stirred vigorously for 2 h at room temperature. Then 10 mL of CH_2Cl_2 was added, and the phases were separated. The upper aqueous phase was extracted 3 times with CH_2Cl_2. The combined organic extracts were dried ($MgSO_4$) and concentrated. The resulting residue was diluted with 20 mL of ether, filtered through a Celite pad, and concentrated.[12] The crude product was purified by bulb-to-bulb distillation and afforded 180 mg (88%) of pentanoic acid. Although the above procedure is for a 1-mmol scale oxidation, we have encountered no difficulties in larger scale (e.g., 20 mmol) reactions.

Application of our standard procedure (and using 3.1 equiv of IO_4^-, 0 °C, 15 min) to geranyl acetate (**1**) and to neryl acetate (**2**) did not give the expected cleavage products. As revealed in Scheme I these 1,5-dienes afforded only products containing the tetrahydrofuran moiety. These unusual products are analogous to those first reported in 1965 by Klein and Rojahn[14] from permanganate oxidations of geranyl acetate (**1**) and neryl acetate (**2**). The "abnormal" permanganate oxidation of

---

(5) In a related type of experiment, addition of acetonitrile to reaction mixtures in which catalysis had ceased (due to precipitation of the ruthenium catalyst in the course of an oxidation) resulted in dissolution of the precipitate and restoration of full catalytic activity.

(6) Acetonitrile was the first cosolvent tried, but in the end it remained the most effective of many solvents which were examined. It should be noted that acetonitrile and water alone are not effective; the third solvent component, CCl_4, plays an important role.

(7) Dehand, J.; Rosé, J. *J. Chem. Res.* **1979**, 155.

(8) This is the optimum solvent ratio, and deviations from it led, for some substrates, to slower reactions and poorer yields.

(9) For an example of a sensitive case where it succeeded when other oxidative cleavage methods failed, see Rossiter, B. E.; Katsuki, T.; Sharpless, K. B. *J. Am. Chem. Soc.* **1981**, *103*, 464.

(10) Potassium metaperiodate is also satisfactory. Sodium hypochlorite is unfortunately much less effective. "Oxone" (Du Pont) works but is slower and is required in large excess.

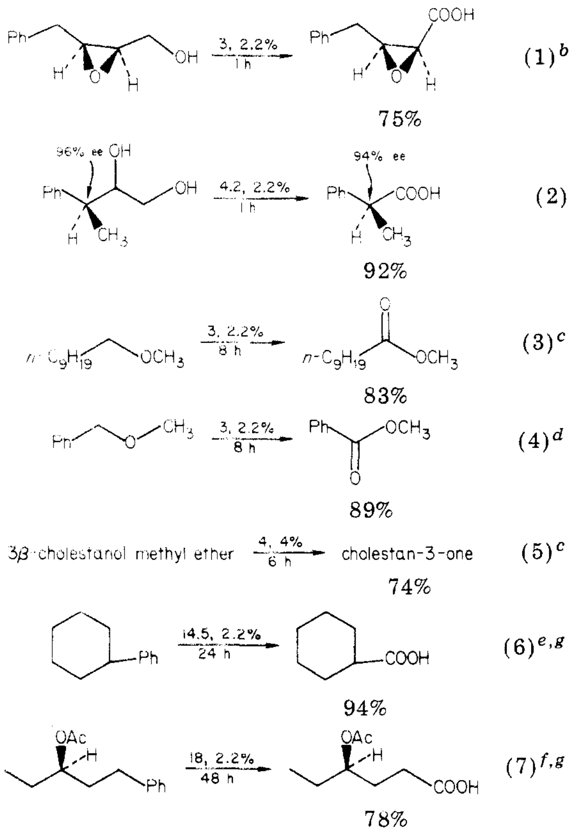
(11) Calculations based on $n = 1$ $[RuCl_3(H_2O)_n]$. Ruthenium dioxide hydrate is equally effective.

(12) This ether treatment precipitates any remaining ruthenium species.

(13) Furans **3** and **6** were identified by comparison with authentic samples.[14] Furans **4**, **5**, and **7** are new compounds; for proof of their structures, see supplementary material (the structures were proved by chemical correlations which, incidentally, involve four uses of the new ruthenium-catalyzed oxidation procedure).

(14) Klein, E.; Rojahn, W. *Tetrahedron* **1965**, *21*, 2353.

Scheme II. Oxidations of Alcohols, Ethers, and Aromatic Rings[a]



[a] Numbers over arrow refer to equivalents of IO_4^- and mol % of $RuCl_3$·hydrate catalyst: the reaction time is given below the arrow. All reactions were run at room temperature. The reactions were performed on a 1-20-mmol scale; for other details see experimental procedure given for oxidative cleavage of (*E*)-5-decene. All yields are for isolated pure substances. [b] Muneo Takatani and K. B. Sharpless, unpublished result. [c] A few percent of the corresponding formate was also produced. [d] No formate detectable. [e] The volume of each solvent was twice that normally used. [f] The same modification as for example 6 except the amount of water was more than doubled (i.e., 2.7 the normal amount). [g] In these cases, it was necessary to remove the precipitated sodium iodate before workup.

1,5-dienes has been further studied by Sable,[15] Walba,[16] and Baldwin,[17] and Walba[16b] has recently described an elegant use of the process for stereospecific assembly of part of the monensin skeleton. To the best of our knowledge, however, this is the first example of an "abnormal" 1,5-diene oxidation involving ruthenium tetroxide. The "cis-diol" products **3** and **6** are identical with those obtained in the permanganate oxidations of **1** and **2**, respectively. However, the "trans-diol" products **5** and **7** (which derive formally from the opposite folding of the diene unit) have not been observed in the permanganate oxidations of 1,5-dienes. This interesting difference in outcome between the RuO_4 and MnO_4^- oxidtions of **1** and **2** is probably due to differences in bond lengths and geometries of comparable intermediates.[16a] The longer bonds in the case of the second-row transition metal ruthenium apparently allow incursion of the pathway leading to "trans-diol" products.

In Scheme II are shown some other oxidative transformations which were easily achieved with the acetonitrile modified reagent. The oxidations of primary alcohols to the acids proceed via the aldehydes,[18] which are therefore also good substrates for this oxidant system. The gentleness of the oxidation conditions is underscored by the lack of epimerization in example 2 of Scheme II. The ether oxidations in Scheme II are but a few examples from a broader study (~25 ethers).[19] After completion of this work[19] the results of an interesting and selective ether oxidation study by Smith and Scarborough appeared.[20] They used the traditional CCl_4/H_2O solvent combination which required more catalyst, longer reaction times, and gave substantial amounts of the carboxylic acids resulting from hydrolysis of intermediates. For unknown reasons, in our acetonitrile modification hydrolysis is barely detectable and esters are the major, if not exclusive, products (Scheme II). The facility of these selective ether oxidations suggest uses of primary methyl ethers (RCH_2OCH_3) as latent carbomethoxy groups ($RCOOCH_3$), and uses of methyl and benzyl ethers as protecting groups which can be easily removed in cases where the rest of the molecule is robust toward oxidation.

Note also that aromatic rings are smoothly degraded to carboxylic acids (examples 6 and 7, Scheme II). By contrast, when cyclohexylbenzene was subjected to the older conditions (i.e., no acetonitrile but otherwise identical with our conditions) for RuO_4 oxidative cleavage, only a trace of cyclohexanecarboxylic acid was detected.

In summary, we feel that the acetonitrile modification has greatly increased the effectiveness and the *reliability* of catalytic RuO_4 oxidations.

Acknowledgment. We thank the National Science Foundation (CHE77-14628) for financial support.

Registry No. **1**, 105-87-3; **2**, 141-12-8; **3**, 78654-52-1; **4**, 78571-80-9; **5**, 78654-53-2; **6**, 78654-54-3; **7**, 78654-55-4; 1-decene, 872-05-9; (*E*)-5-decene, 7433-56-9; (*Z*)-5-decene, 7433-78-5; cyclooctene, 931-88-4; citronellyl acetate, 150-84-5; 2,3-dimethyl-2-octene, 19781-18-1; pentanal, 110-62-3; pentanoic acid, 109-52-4; methyl formate, 107-31-3; methyl nonanoate, 1731-84-6; methyl octanoate, 111-11-5; 2-heptanone, 111-71-7; *cis*-3-benzyl-2-oxiranemethanol, 78571-81-0; 3-phenyl-1,2-butanediol, 68258-25-3; 1-methoxydecane, 7289-52-3; (methoxymethyl)benzene, 538-86-3; (3*β*)-3-methoxycholestane, 53109-81-2; cyclohexylbenzene, 827-52-1; (*R*)-*α*-ethylbenzenepropanol acetate, 78571-82-1; *cis*-3-benzyl-2-oxiranecarboxylic acid, 78571-83-2; (*S*)-2-phenylpropanoic acid, 7782-24-3; methyl decanoate, 110-42-9; methyl benzoate, 93-58-3; cholestan-3-one, 15600-08-5; cyclohexanecarboxylic acid, 98-89-5; 4-acetoxyhexanoic acid, 78571-84-3; methyl 6-acetoxy-4-methylhexanoate, 64988-49-4; RuO_4, 20427-56-9.

Supplementary Material Available: Physical data and chemical correlations (see ref 13) for **3**, **4**, **5**, **6**, and **7** (2 pages). Ordering information is given on any current masthead page.

Per H. J. Carlsen, Tsutomu Katsuki
Victor S. Martin, K. Barry Sharpless*[21]
Department of Chemistry
Stanford University
Stanford, California 94305

Received June 16, 1981

---

[15] Powell, K. A.; Hughes, A. L.; Katchian, H.; Jerauld, J. F.; Sable, H. Z. *Tetrahedron* **1972**, *28*, 2019.

[16] (a) Walba, D. M.; Wand, M. D.; Wilkes, M. C. *J. Am. Chem. Soc.* **1979**, *101*, 4396. (b) Walba, D. M.; Edwards, P. D. *Tetrahedron Lett.* **1980**, *21*, 3531.

[17] Baldwin, J. E.; Crossley, M. J.; Lehtonen, E-M. M. *J. Chem. Soc., Chem. Commun.* **1979**, 918.

[18] The cleavage of olefins to acids (Tables I and II) also proceeds via the aldehyde. The aldehyde is formed rapidly and then, in a slower step, it is oxidized to the acid. However, the rate differences have so far not been large enough to allow one to stop crisply at the aldehyde stage.

[19] Carlsen, P. H. J.; Sharpless, K. B., unpublished results, Stanford University.

[20] Smith, A. B.; Scarborough, R. M. *Synth. Commun.* **1980**, *10*, 205.

[21] Address correspondence to Department of Chemistry, Massachusetts Institute of Technology, Cambridge, MA 02139.