on the ratio of the oxidation vs. the nucleophilic substitution.

The conclusions of this preliminary study are that the PCC oxidation of tertiary 2-alkylcyclopropylcarbinols results in oxidative homoallylic rearrangement to the transposed β,γ-enones, making the overall process a synthetically useful method for 1,4-carbonyl transposition. Further improvements and applications of the method outlined here are in progress.

Acknowledgment. Financial support by a grant (to T.N.) from the Ministry of Education of the Japanese Government is gratefully acknowledged.

Eiji Wada, Makoto Okawara
Research Laboratory of Resources Utilization
Tokyo Institute of Technology
Midori-ku, Yokohama 227, Japan
Takeshi Nakai*
Department of Chemical Technology
Tokyo Institute of Technology
Meguro-ku, Tokyo 152, Japan

Received January 25, 1979

A Route to Keto Acids (or Esters) or to Dicarboxylic Acids (or Esters) from α-Alkylidenecyclanones

Summary: Baeyer–Villiger oxidation of α-alkylidenecyclanones followed by hydrolysis and esterification gives keto esters; further treatment with H_2O_2 leads to dicarboxylic esters.

Sir: Baeyer–Villiger oxidation of α-alkylidenecyclanones has been shown[1] to provide primarily the lactone derived from insertion of an oxygen atom between the carbonyl and α-olefinic carbon atoms (Scheme I). Surprisingly, hydrolysis of this enol lactone has been neglected[2] as a method of generating keto acids such as **3**.

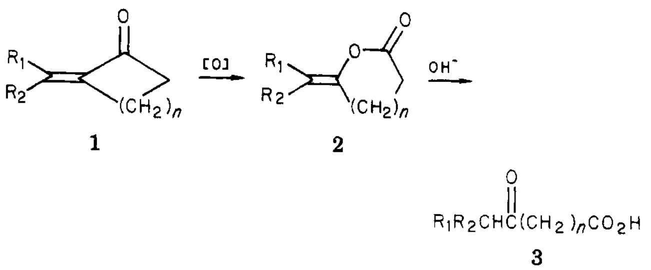
We recently observed that good yields of the keto ester **7**[3] could be obtained by treatment of the α-alkylidenecyclobutanone **4** with 40% peracetic acid,[4] followed by alkaline hydrolysis of the lactone **5**, acidification of **6**, and esterification with CH_2N_2.

When **6** was treated with additional H_2O_2, after separation of epoxide and unreacted starting material, a further oxidation took place to provide a complete conversion, after acidification, to the diacid, which was converted to the diester **8** (Scheme II).

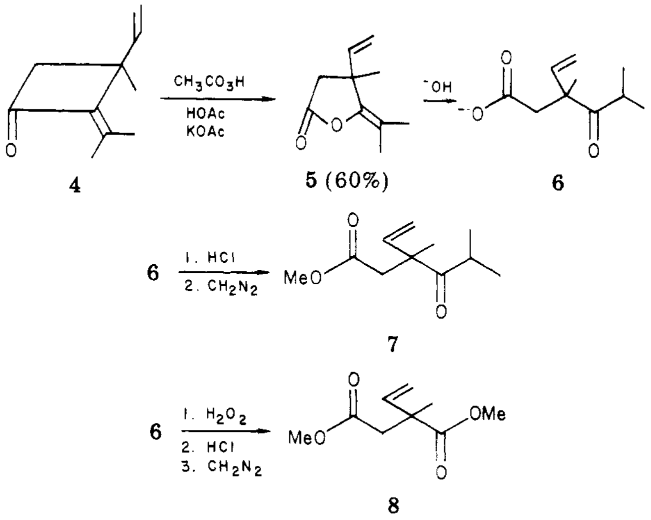
Baeyer–Villiger oxidation of pulegone **9**, followed by alkaline hydrolysis of the lactone **10**, acidification, and esterification resulted in the keto ester **11** (Scheme III). However the yield was lower than that obtained from **4** because of competing formation of the epoxides **12**; epoxidation of **9** was much more evident than epoxidation of **4**.

Presumably, further oxidation of the alkaline solution of the carboxylic acid corresponding to **11** would yield the diacid **13**. A small amount of **13**, isolated as the dimethyl ester **14**, resulted as a byproduct from residual H_2O_2 during alkaline hydrolysis of **10**. Formation of **13** was eliminated by removal of H_2O_2 with sodium thiosulfate before hydrolysis, but this reduced the yield of **11**.

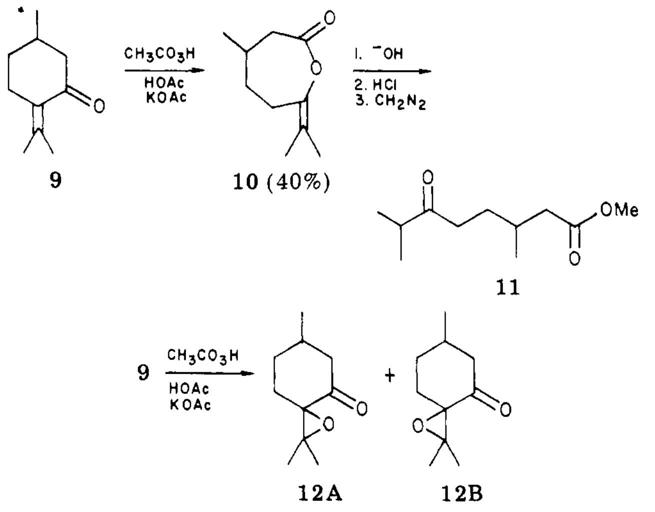
Scheme I

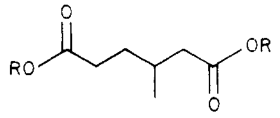


Scheme II



Scheme III





13, R = H
14, R = Me

A typical procedure is given for the case of **4**. To a solution of 500 mg (3.3 mmol) of **4** in 2.0 mL of acetic acid saturated with potassium acetate (pH 4.3–4.5)[1] was added, at 25 °C and all at once, 473 μL (3.6 mmol, 1.1 equiv) of 40% CH_3CO_3H.[4] The mixture, after stirring overnight, was

---

(1) H. M. Walton, *J. Org. Chem.*, **22**, 1161 (1957).

(2) Walton,[1] while investigating the reaction of 40% CH_3CO_3H with aralkylidenecyclanones, characterized the resultant enol lactones by hydrolysis to the keto acid and formation of the semicarbazone. He did not pursue the formation of the keto acids further.

(3) Identified previously as an anomalous product from an attempted Wharton rearrangement: J. R. Handley, A. A. Swigar, T. Ueda, and R. M. Silverstein, *J. Org. Chem.*, submitted for publication.

(4) F. P. Greenspan, *Ind. Eng. Chem.*, **39**, 847 (1947).

(5) NMR, IR, and mass spectra, and combustion analyses are in accord with the designated structures.

0022-3263/79/1944-2954$01.00/0

poured into 40 mL of H_2O and basified with 20% NaOH (to pH 12). This solution was stirred 4 h and then extracted with ether to remove any epoxide and unreacted starting material. Acidification of the aqueous layer, followed by extraction with ether, drying and removal of solvent, and esterification with diazomethane provided a 79% yield (based on unreacted starting material) of keto ester 7.

Alternatively, the basic aqueous layer was treated with 2 equiv of 30% H_2O_2, stirred for 4 h, and worked up to provide a near quantitative conversion to the dimethyl ester 8.

The procedures described appear to represent a general route to keto acids (or esters) or to dicarboxylic acids (or esters) from α-alkylidenecyclanones, which are generally available. Optimization of reaction conditions to reduce competing epoxidation, and extension to three- and five-membered rings are projected.

Acknowledgment. This work was supported by a grant from the National Science Foundation.

Supplementary Material Available: NMR, IR, and mass spectral and elemental analyses of compounds **5**, **7**, **8**, **10**, **11**, **12**, and **14** (4 pages). Ordering information is given on any current masthead page.

John R. Handley, Andrew A. Swigar
Robert M. Silverstein*
SUNY College of Environmental Science & Forestry
Syracuse, New York 13210

Received March 30, 1979

Nickel(II) Bromide Catalyzed Oxidations of Primary and Secondary Alcohols to Carbonyl Compounds by Benzoyl Peroxide

Summary: Primary and secondary alcohols are oxidized to their respective carbonyl compounds in high yield by benzoyl peroxide through the action of nickel(II) bromide, which serves as an effective mediative catalyst and as an alcohol template in these transformations.

Sir: Numerous processes for the conversion of alcohols to carbonyl compounds through oxidation by active halogen[1-6] or peracid[7] reagents have been recently reported. Although each of these methods is generally suitable for the production of ketones from secondary alcohols, their application to primary alcohols usually results in overoxidation. Only the chlorine–dimethyl sulfoxide oxidative procedure[6] appears to offer the required selectivity and efficiency for this sensitive transformation. However, we have found that direct oxidation of alcohols by benzoyl peroxide in the presence of nickel(II) bromide (eq 1) is a conveniently

$$R_2CHOH + (C_6H_5COO)_2 \xrightarrow{NiBr_2} R_2C{=}O + 2C_6H_5COOH \quad (1)$$

employed alternative to this process. As we now report, the combination of inexpensive benzoyl peroxide with catalytic amounts of nickel(II) bromide serves not only as an effective reagent for the conversion of secondary alcohols to ketones but, through employment of nickel(II) as an alcohol template, also provides convenient access to aldehydes.

Table I. Isolated Yields of Ketones from Oxidations of Representative Secondary Alcohols by Benzoyl Peroxide in the Presence of Nickel(II) Bromide[a]

alcohol	ketone	yield, %[b]
2-adamantanol	2-adamantanone	85
benzhydrol	benzophenone	85
cyclobutanol	cyclobutanone	93[c]
cyclopropylphenylmethanol	cyclopropyl phenyl ketone	81
cyclooctanol	cyclooctanone	90
2-decalol	2-decalone	98
2,4-dimethyl-3-pentanol	2,4-dimethyl-3-pentanone	84
1,2-diphenylethanol	2-phenylacetophenone	94
1-phenylethanol	acetophenone	90

[a] Reactions usually performed with dibromo(1,2-dimethoxyethane)nickel(II). [b] Isolated weight yield of ketone; no other oxidized product could be detected by NMR or GLC analysis. [c] Isolated as the 2,4-dinitrophenylhydrazone derivative.[10]

In a typical oxidation procedure, a homogeneous solution of 1,2-diphenylethanol (1.98 g, 10.0 mmol), benzoyl peroxide (3.07 g, 12.7 mmol), and either anhydrous nickel(II) bromide or dibromo(1,2-dimethoxyethane)nickel(II)[8] (2.6 mmol) in 20 mL of anhydrous acetonitrile is heated at 60 °C for 24 h. The reaction solution is then cooled and aqueous potassium iodide is added to decompose excess peroxide. Following extraction with ether, subsequent acid and base washings of the ether solution, and solvent removal, 2-phenylacetophenone is obtained as the sole reaction product (1.84 g, 9.40 mmol, 94% yield). Isolated yields of carbonyl compounds formed in similar reactions with representative secondary alcohols are given in Table I. In all cases quantitative conversion of the secondary alcohol to the corresponding ketone is observed by analyses performed prior to product isolation. Benzoic acid is the sole product from peroxide reduction, and nickel(II) bromide may be quantitatively recovered from the reaction solutions.

Although acyl peroxides are potentially capable of serving as two-electron donors in alcohol oxidations, prior studies of thermal, electrophilic, and selected metal ion catalyzed decompositions of acyl peroxides have indicated that these reactions occur with the formation of acyloxy radicals as reaction intermediates.[11] Benzoyl peroxide[12] and related acyl peroxides[13] or peresters[14] undergo induced radical chain decomposition and, in the limited number of cases that have been examined, oxidize secondary alcohols to ketones in relatively high yield, but only when

---

(1) Pinnick, H. W.; Lajis, N. H. *J. Org. Chem.* **1978**, *43*, 371.

(2) Ueno, Y.; Okawara, M. *Tetrahedron Lett.* **1976**, 4597.

(3) Al Neirabeyeh, M.; Ziegler, J.-C.; Gross, B. *Synthesis* **1976**, 811.

(4) Lee, G. A.; Freedman, H. H. *Tetrahedron Lett.* **1976**, 1641.

(5) (a) Saigo, K.; Morikawa, A.; Mukaiyama, T. *Chem. Lett.* **1975**, 145. (b) Ogawa, T.; Matsui, M. *J. Am. Chem. Soc.* **1976**, *98*, 1629.

(6) Corey, E. J.; Kim, C. U. *Tetrahedron Lett.* **1973**, 919.

(7) (a) Cella, J. A.; McGrath, J. P.; Regen, S. L. *Tetrahedron Lett.* **1975**, 4115. (b) Cella, J. A.; Kelley, J. A.; Kenehan, E. F. *J. Org. Chem.* **1975**, *40*, 1860.

(8) Anhydrous nickel(II) bromide is effective as the oxidation catalyst even when used in amounts as low as 5 mol % relative to the reactant alcohol. However, because of the limited solubility of anhydrous $NiBr_2$ in acetonitrile, the soluble dimethoxyethane complex (available from Alfa or conveniently synthesized[9]) may be preferred.

(9) (a) Ward, L. G. L. *Inorg. Synth.* **1971**, *13*, 160. (b) Nylander, L. R.; Pavkovic, S. F. *Inorg. Chem.* **1970**, *9*, 1959.

(10) Meyer, K.; Roček, J. *J. Am. Chem. Soc.* **1972**, *94*, 1209.

(11) Hiatt, R. in "Organic Peroxides", Vol. 2, Swern, D., Ed.; Wiley-Interscience: New York, 1971; Chapter VIII.

(12) (a) Cass, W. E. *J. Am. Chem. Soc.* **1947**, *69*, 500. (b) Bartlett, P. D.; Nozaki, K. *Ibid.* **1947**, *69*, 2299. (c) Hasegawa, S.; Nishimura, N.; Mitsumoto, S.; Yokoyama, K. *Bull. Chem. Soc. Jpn.* **1963**, *36*, 522 and prior articles in this series. (d) Gelissen, H.; Hermans, P. H. *Chem. Ber.* **1925**, *58*, 765.

(13) Kharasch, M. S.; Rowe, J. L.; Urry, W. H. *J. Org. Chem.* **1951**, *16*, 905.

(14) (a) Walling, C.; Azar, J. C. *J. Org. Chem.* **1968**, *33*, 3888. (b) Sosnovsky, G.; Yang, N. C. *Ibid*, **1960**, *25* 899.

0022-3263/79/1944-2955$01.00/0