filled with $CO_2$-free $N_2$ and 100 mL of pyruvate solution (previously degassed by bubbling through it $CO_2$-free $N_2$ for at least 30 min) was injected through the sidearm. The solution was stirred and thermostatted at 30 °C for 30 minutes. Next 0.5 mL of thiamin (or $CHDT^+Cl^-$ sans pyruvate) was injected through a rubber septum to initiate the reaction. The reaction was quenched (syringe cap) with 5 mL of concentrated $H_2SO_4$ after ca. 200 $\mu$mol of $CO_2$ had evolved (as calculated from the $f$ values determined above).

The reaction vessel was then attached to the vacuum line at a different point and frozen with liquid $N_2$ and the nitrogen in the vessel was removed by the vacuum pump until no further significant pressure decrease in vacuum gauge reading could be observed. The flask was then warmed slightly and refrozen in a dry ice–acetone bath and the $CO_2$ was distilled into a U tube which was cooled in liquid $N_2$. The liquid nitrogen was replaced by dry ice and the $CO_2$ was passed to the Toepler pump bulb. The dry ice–acetone was removed from the U tube and the condensed gases were pumped until the vacuum gauge read below 50 $\mu$m. Then the gas was transferred to a sample tube for mass spectrometric measurement. In the reaction catalyzed by thiamin, $CO_2$ was purified by passage through $H_2SO_4$.

**Mass Spectrometric Analysis.** The isotope ratio ($^{13}CO_2/^{12}CO_2$) was determined on a Consolidated-Nier Model 21-201 isotope ratio mass spectrometer.[13] The atom fraction of $C^{13}$, $N_x$, corrected for $C^{12}O^{16}O^{17}$, was calculated from the expression

$$10^6 N_x = \frac{\bar{r}_{\text{sample}} 11134}{\frac{1}{2}(\bar{r}_{\text{tank before}} + \bar{r}_{\text{tank after}})} - 800$$

where $\bar{r}_{\text{sample}}$ is the average ratio of six readings of $CO_2$ sample and $\bar{r}_{\text{tank before}}$ and $\bar{r}_{\text{tank after}}$ are the average ratios of six readings of tank $CO_2$ (Matheson Research Purity) measured before and after the sample measurement, respectively. The number 800 was provided by the manufacturer to compensate for the $O^{17}$ isotope ratio ($C^{12}O^{16}O^{17}$)·(11134 ± 5) × $10^{-6}$ is the average value of the 1362 readings of the 45/44 mass ratio of tank $CO_2$ during the entire course of the present experiments.

$N_{x0}$ for the thiamin-catalyzed reaction was the average value of the $N_{x0}{}^2$ determined for $CHDT^+Cl^-$ and of the $N_{x0}$ determined for the holoenzyme-catalyzed reaction[2] as these two are in close accord. This had to be done since the thiamin-catalyzed reaction leads to acetolactate (and thence acetoin) so that the $CO_2$ is liberated from two sources. However, at low conversion (even with a 100% error in the estimate of $f$ in the range of $f \simeq 0.01$) the source of $CO_2$ is exclusively pyruvate (rather than acetolactate) since the subsequent steps are much slower.

**Registry No.**—$CHDT^+Cl^-$, 29510-46-1; sodium pyruvate, 113-24-6; thiamin hydrochloride, 67-03-8.

## References and Notes

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# Oxidation of Olefins with Peroxouranium Oxide ($UO_4 \cdot 4H_2O$)[1]

George A. Olah* and John Welch

*Institute of Hydrocarbon Chemistry, Department of Chemistry,*
*University of Southern California, Los Angeles, California 90007*

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Peroxouranium oxide was found to be an effective oxidizing agent for alkenes. The oxidations are suggested to proceed through an oxyuranylation path with resulting carbocationic rearrangement of the intermediates. The used reagent may be recovered and regenerated effectively.

Although many dioxygen–metal compounds are known,[2] little is known about their reactions. The preparation of peroxouranium oxide from uranyl nitrate and hydrogen peroxide has been known for nearly a century.[3] The structure has been established by Gordon and others[4] as being a true peroxo complex, $UO_2(O_2)\cdot 4H_2O$.[2a] The aqueous chemistry of peroxouranium(VI) has been found to be complicated. Peroxouranium oxide tetrahydrate forms peruranates of varying composition with aqueous hydrogen peroxide, culminating in the formation of the most stable $UO_8{}^{2-}$ species.[2b] So far the oxidizing ability of $UO_4$ in organic systems was not explored.

## Results and Discussion

Peroxouranium oxide tetrahydrate was found to be an effective oxidizing reagent for hydrocarbons, particularly olefins. Data are summarized in Table I. Ring-contracted, ring-expanded, and epoxidized products were obtained. The reaction is viewed as proceeding via the complexation of the olefin by the coordinatively unsaturated uranium. The increasing electron density at the metal results in a lengthening of the metal–dioxygen bond until a metal–carbon bond is formed, while the developing charge-deficient carbon forms a bond to the displaced oxygen. The cyclic intermediate de-

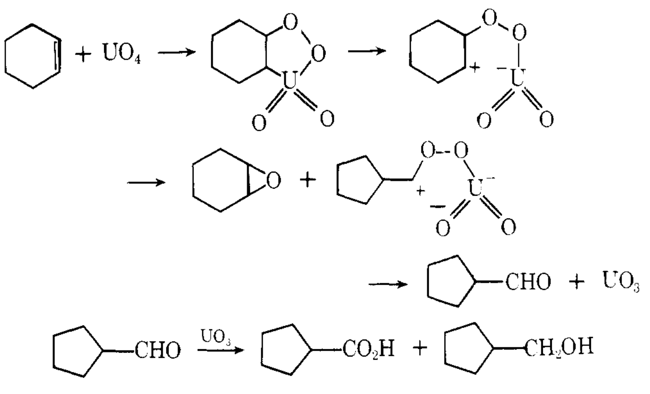

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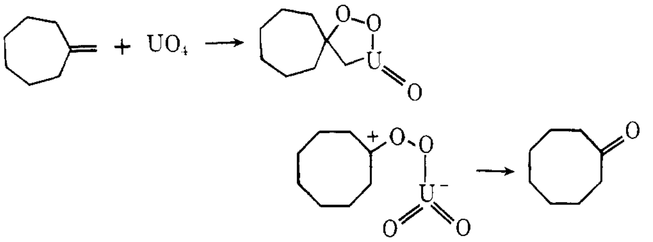
**Table I. Oxidation of Olefins with Peroxouranium Oxide**

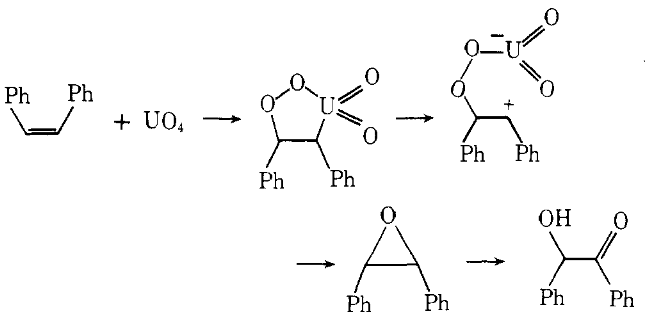
| Olefin | Registry no. | % yield of oxygenated products[a] | Product distribution[b] | Registry no. |
|---|---|---|---|---|
| Cyclohexene | 110-83-8 | 34 | Cyclopentanecarboxylic acid (46%) | 3400-45-1 |
| | | | Cyclopentanecarbinol (54%( | 3637-61-4 |
| 1-Methylcyclohexene | 591-49-1 | 58 | Methyl cyclopentyl ketone | 6004-60-0 |
| Cyclooctene | 931-88-4 | 44 | Cyclooctene oxide (83%) | 286-62-4 |
| | | | Cyclohexanecarboxylic acid (17%) | 1460-16-8 |
| Cyclododecene | 1501-82-2 | 43 | Cyclododecene oxide (69%) | 286-99-7 |
| | | | Cycloundecanecarboxylic acid (31%) | 831-67-4 |
| Methylenecycloheptane | 2505-03-5 | 30 | Cyclooctanone | 502-49-8 |
| Methyleneadamantane | 875-72-9 | 48 | Adamantanone | 700-58-3 |
| 2-Methylenenorbornane | 497-35-8 | 31 | 2-Bicyclo[3.2.1]octanone | 5019-82-9 |
| | | | 3-Bicyclo[3.2.1]octanone | 14252-05-2 |
| 1,1-Diphenylethylene | 530-48-3 | 53 | Benzophenone (83%) | 119-61-9 |
| | | | α-Methylbenzhydrol (17%) | 599-67-7 |
| 4-Phenyl-1-butene | 768-56-9 | 64 | 3-Phenylpropionic acid (50%) | 501-52-0 |
| | | | 4-Phenyl-2-butanone (50%) | 2550-26-7 |
| Chalcone | 94-41-7 | 50 | Benzaldehyde (11%) | 100-52-7 |
| | | | Benzoic acid (89%) | 65-85-0 |
| *trans*-Stilbene | 103-30-0 | 36 | Stilbene oxide (12%) | 17619-97-5 |
| | | | Benzoin (88%) | 119-53-9 |

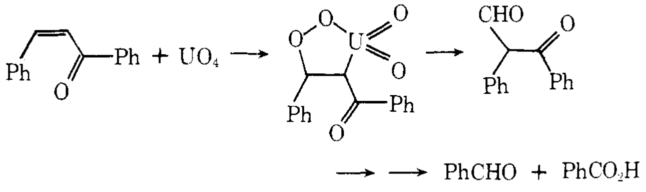
[a] Yields reported are isolated yields of all oxygenated products recovered. [b] Products were identified by isolation, degradation, and derivatization as well as comparison of spectral properties with those of authentic samples.

composes with rearrangement and/or epoxidation. A somewhat similar mechanism was recently also involved by Sharpless et al.[5] in the chromyl chloride oxidation of olefins. Aldehydes formed under the reaction conditions quickly undergo Cannizzaro-type oxidation–reduction reactions which seem to be promoted by $UO_3$, as shown for the reaction of cyclohexene. It can be suggested that exocyclic olefins might react via a similar mechanism to yield ring expanded products, as shown for methylenecycloheptane.



The reaction of exocyclic olefins, however, was accompanied by complete oxidative cleavage of the methylene group to yield the corresponding carbonyl compound in several examples studied. Alicyclic olefins reacted to yield numerous oxygenated products derived from oxidation and rearrangement. The reactions of stilbene and chalcone are typical.





The use of excess hydrogen peroxide in the reaction is not essential as the same products were formed in control experiments when pure peroxouranium oxide ($UO_4{\cdot}4H_2O$) was used alone in dioxane suspension. Peroxouranium oxide thus clearly is an effective oxidizing agent. The use of hydrogen peroxide with $UO_4{\cdot}4H_2O$ is known to form a variety of peroxo species as discussed earlier.[2b] These additional peroxo species seem to enhance the reactivity of the reaction system, i.e., yields are higher for similar reaction times. However, the product distribution is not sensitive to variation of the amount of excess hydrogen peroxide used. Furthermore, pure sodium peruranate, $Na_2UO_8$, prepared by the method of Alcock,[4] is unreactive under the reaction conditions. Presumably the metal is coordinatively saturated and is no longer free to interact with the olefin. The effect of excess hydrogen peroxide must therefore lie in the formation of reactive intermediate peroxo species.

The oxymetalation mechanism[6a,b] formulated for the oxidation reaction of olefins by $UO_4{\cdot}4H_2O$ is well known for oxidation reactions with mercury,[6c] thallium,[7] and lead.[8] A similar oxymetalation reaction has been proposed for the reaction of $MoO_5$ with olefins.[9] Mimoun and co-workers base their conclusions on the proposal that peracids react to form an epoxide via a 1,3-dipolar interaction.[10] Raciczewski has found evidence for metal–carbon interaction in the reactions of pertungstannic acid.[11] Similar interactions were observed with vanadium(V).[12]

The Rh(I) dioxygen complex catalyzed oxidation of hexene[13] and the iridium promoted styrene to acetophenone[14] transformations both yielded products which would be expected by an oxymetalation reaction path. The products found in the reaction of $UO_4{\cdot}4H_2O$ are not simply derived by the Lewis acid promoted rearrangement of the formed epoxide.[15] When cyclooctene oxide was heated with either $UO_3$ or $UO_4{\cdot}4H_2O$ under the usual reaction conditions, the unchanged starting material was recovered. The free-radical mechanism proposed by Collman[16] and Kurkov[17] in the reaction of cyclohexene and cyclopentene with rhodium and iridium compounds would result in the formation of hydroperoxide intermediates. Products derived from such intermediates were not isolated from the reactions of $UO_4{\cdot}4H_2O$. Peroxouranium oxide can be regenerated from the $UO_3$ product by digestion with nitric acid and reprecipitation with hydrogen peroxide.

The reagent can therefore be recycled without loss of the metal. $UO_4 \cdot 4H_2O$ reactions thus are indeed dependent only on the hydrogen peroxide used, affording an economical route to many oxidations.

## Experimental Section

**Peroxouranium Oxide Tetrahydrate.** Peroxouranium oxide tetrahydrate was prepared by the method of Alcock.[4] To 50.5 g (0.1 mol) of uranyl nitrate hexahydrate (Mallinckrodt) dissolved in 500 mL of 10% nitric acid was added 35 mL of 30% hydrogen peroxide. The pale yellow peroxouranium oxide hydrate precipitated from solution, was separated by suction filtration washed with absolute ethanol, and was dried overnight at 50 °C. The material recovered by filtration from oxidation reactions with peroxouranium oxide was carefully dissolved with stirring in concentrated nitric acid. After stirring for 30 min, the nitric acid solution was diluted to 10% and excess 30% hydrogen peroxide was added. The resultant precipitate was filtered, washed, and dried as described above.

**Oxidation of Cyclooctene with $UO_4 \cdot 4H_2O$. Method A.** To 3.74 g (0.01 mol) of $UO_4 \cdot 4H_2O$ suspended in 100 mL of tetrahydrofuran in a 250-mL round-bottom flask equipped with a reflux condensor was added 1.10 g (0.01 mol) of cyclooctene. The reaction mixture was heated under reflux for 18 h, cooled, filtered, quenched, and extracted as described. Evaporation of the solvent yielded an alcohol, IR (neat) 3440 (s, OH) cm$^{-1}$, whose identity was confirmed by Jones oxidation. Cycloheptanecarboxylic acid (1.2 g; 84% yield), IR (neat) 3300 (w, OH) and 1710 cm$^{-1}$ (s, C=O), was obtained.

**Method B.** To 3.38 g (0.009 mol) of $UO_4 \cdot 4H_2O$ suspended in 100 mL of dioxane and 20 mL of 30% hydrogen peroxide in the previously described apparatus was added 0.96 g (0.009 mol) of cyclooctene. The reaction mixture was heated under relux for 20 h, cooled, filtered, quenched, and extracted as described. Evaporation of the dried solvent yielded 0.51 g (44% yield overall) of product. The product was chromatographed on aluminum oxide (Merck) eluting with 250 mL of petroleum ether (bp 37–56 °C), 250 mL of benzene, and 250 mL of chloroform. From the petroleum ether and benzene solutions was isolated 0.42 g (83% of product) of cyclooctene oxide identified by isomerization with boron trifluoride etherate to cyclooctanone, IR (neat) 1700 cm$^{-1}$ (s, C=O). Evaporation of the chloroform solution yielded 0.09 g (17% yield) of cycloheptanecarbinol, IR (neat) 3440 cm$^{-1}$ (s, OH), identified by Jones oxidation to cycloheptanecarboxylic acid, IR (neat) 3300 (w, OH) and 1710 cm$^{-1}$ (s, C=O).

**Oxidation of 1,1-Diphenylethylene with $UO_4 \cdot 4H_2O$.** 1,1-Diphenylethylene (1.8 g, 0.01 mol) was oxidized according to method B. Crude product (0.960 g; 53% overall yield) was isolated. The material was chromatographed on 30 g of adsorbent alumina eluting with 330 mL of benzene followed by 250 mL of chloroform. Evaporation of the benzene solution yielded 0.72 g (83% yield of product) of benzophenone, IR ($CCl_4$) 1660 cm$^{-1}$ (s, C=O). Evaporation of the chloroform solution yielded 0.14 g (17% of product) of 1,1-diphenyl-1-ethanol, IR (neat) 3460 cm$^{-1}$ (s, OH).

**Oxidation of 4-Phenyl-1-butene with $UO_4 \cdot 4H_2O$.** 4-Phenyl-1-butene (1.32 g, 0.01 mol) was oxidized by method B. A product yield of (0.95 g; 64% overall) was isolated. Extraction of an ethereal solution of the product with aqueous base yielded after acidification and extraction 0.47 g (50% of product) of 3-phenylpropionic acid, IR (neat) 3400 (s, OH) and 1715 cm$^{-1}$ (s, C=O). Mass spectrum of the product showed an M − 1 peak at *m/e* 150. Evaporation of the ethereal solution remaining after basic extraction after drying yielded 0.48 g (50% of product) of 4-phenyl-2-butanone, IR (neat) 1720 cm$^{-1}$ (s, C=O). Mass spectrum of the product showed a molecular ion peak at *m/e* 148.

**Oxidation of Methylenecycloheptane with $UO_4 \cdot 4H_2O$.** Methylenecycloheptane (0.70 g, 0.006 mol) was oxidized with 2.14 g (0.006 mol) of $UO_4 \cdot 4H_2O$ by method B. Cyclooctanone (0.23 g; 30% yield) was isolated, IR (neat) 1705 cm$^{-1}$ (s, C=O), which was characterized as a 2,4-dinitrophenylhydrazone, mp 132–135 °C.

**Oxidation of Methyleneadamantane with $UO_4 \cdot 4H_2O$.** Methyleneadamantane (0.74 g, 0.005 mol) was oxidized with 1.7 g (0.005 mol) of $UO_4 \cdot 4H_2O$ by method B. 2-Adamantanone (0.36 g; 48% yield) was recovered, IR ($CCl_4$) 1715 cm$^{-1}$ (s, C=O) (lit. 1717 cm$^{-1}$ (s, C=O)).

**Oxidation of Chalcone with $UO_4 \cdot 4H_2O$.** Chalcone (2.08 g, 0.01 mol) was oxidized according to method B. A mixture (1.2 g; 50% yield) of products was isolated. An ethereal solution of the mixture was extracted with aqueous base to yield on reacidification and extraction 0.91 g (89% of product) of benzoic acid: IR ($CCl_4$) 1690 (C=O) and 3440 (OH) cm$^{-1}$: mp 121 °C (lit. mp 122 °C). Evaporation of the dried ethereal solution yielded 0.11 g (11% of product) of benzaldehyde, IR (neat) 1700 cm$^{-1}$ (s, C=O), which was characterized as a 2,4-dinitrophenylhydrazone, mp 230 °C (lit. mp 237 °C).

**Oxidation of *trans*-Stilbene with $UO_4 \cdot 4H_2O$.** *trans*-Stilbene (1.8 g, 0.01 mol) was oxidized according to method B. A mixture (0.69 g; 36% overall yield) of products remained following evaporation of the solvent. The material was chromatographed on adsorbent alumina with 200 mL of petroleum ether (bp 37–55 °C), 250 mL of benzene, and 250 mL of chloroform. Evaporation of the petroleum ether solution yielded 0.085 g (12% of the product) of stilbene oxide: IR 1050 cm$^{-1}$ (s, ROR); mp 58–60 °C (lit. mp 65–67 °C). Evaporation of the benzene and chloroform solutions yielded 0.61 g (88% of the product) of benzoin: IR ($CCl_4$) 3460 (s, OH), 1695 cm$^{-1}$ (s, C=O); mp 132 °C (lit. mp 134–136 °C). The identity of the product was confirmed by gas chromatography using a Perkin-Elmer model F-11 chromatograph equipped with flame ionization detector and a 17 ft × 1/8 in. column packed with 1.75% butanediol succinate on acid washed DMCS treated Chromasorb W at 130 °C and 50 psig.

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**Registry No.**—$UO_4 \cdot 4H_2O$, 15737-34-5; cycloheptanecarbinol, 4448-75-3; cycloheptanecarboxylic acid, 1460-16-8; cyclooctanone 2,4-dinitrophenylhydrazine, 1459-62-7.

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