Ethyl 3-carbethoxythiochromone-2-acetate (5b) was prepared from **1a** (1 mmol) and **2b** (168 mg, 1 mmol) by method C and was purified by recrystallization.

Anal. Calcd for $C_{16}H_{16}O_5S$: C, 59.98; H, 5.03. Found: C, 59.79; H, 4.94.

Ethyl 3-carbethoxychromone-2-acetate (5c) was prepared from **1a** (1 mmol) and **2c** (152 mg, 1 mmol) by method C. Column chromatography gave pure **5c**; exact mass calcd for $C_{16}H_{16}O_6$ 304.0945, found 304.0939.

Ethyl 3-carbethoxy-4-phenylquinoline-2-acetate (5d) was prepared from **1a** (3 mmol) and **2d** (591 mg, 3 mmol) by method A. Column chromatography gave pure **5d**, identical in all respects with an authentic sample.

Ethyl 3-carbethoxy-4-methylquinoline-2-acetate (5e) was prepared from **1a** (3 mmol) and **2e** (405 mg, 3 mmol) by method A. Column chromatography gave pure **5e**; exact mass calcd for $C_{17}G_{19}NO_4$ 301.1314, found 301.1329. The picrate salt was prepared for combustion analysis.

Anal. Calcd for $C_{23}H_{22}N_4O_{11}$: C, 52.08; H, 4.18; N, 10.56. Found: C, 52.19; H, 4.12; N, 10.43.

Ethyl 3-carbethoxyquinoline-2-acetate (5f) was prepared from **1a** (1 mmol) and **2f** (121 mg, 1 mmol) by method A. Recrystallization gave pure **5f**, identical in all respects with an authentic sample.[6]

Ethyl 3-carbethoxy-4-hydroxythiophene-2-acetate (5g) was prepared from **1a** (2 mmol) and **2g** (212 mg, 2 mmol) by method B. Column chromatography gave pure **5g**.

Anal. Calcd for $C_{11}H_{14}SO_5$: C, 51.15; H, 5.46; S, 12.42. Found: C, 51.04; H, 5.52; S, 12.51.

Ethyl 3-carbethoxy-4-hydroxy-5-methylthiophene-2-acetate (5h) was prepared from **1a** (4 mmol) and **2h** (448 mg, 4 mmol) by method B. Column chromatography gave pure **5h**.

Anal. Calcd for $C_{12}H_{16}O_5S$: C, 52.93; H, 5.92; S, 11.77. Found: C, 53.02; H, 6.08; S, 11.99.

Ethyl 4-carbethoxy-1,5-diphenylpyrazole-3-acetate (5i) was prepared from **1a** (1 mmol) and **2i** (212 mg, 1 mmol) by method A. Column chromatography gave pure **5i**, identical in all respects with an authentic sample.[7]

Ethyl 4-carbethoxy-5,6-diphenylpyridazine-2-acetate (5j) was prepared from **1a** (1.5 mmol) and **2j** (336 mg, 1.5 mmol) by method A. Column chromatography gave pure **5j**; exact mass calcd for $C_{23}H_{22}N_2O_4$ 390.1577, found 390.1571.

Registry No. **1a**, 52358-42-6; **2a**, 85-91-6; **2b**, 4892-02-8; **2c**, 119-36-8; **2d**, 2835-77-0; **2e**, 551-93-9; **2f**, 529-23-7; **2g**, 2365-48-2; **2h**, 53907-46-3; **2i**, 579-45-3; **2j**, 5344-88-7; **5a**, 73286-07-4; **5b**, 95421-53-7; **5c**, 95421-54-8; **5d**, 17282-92-7; **5e**, 23301-16-8; **5f**, 95421-55-9; **5g**, 95421-56-0; **5h**, 95421-57-1; **5i**, 41470-68-2; **5j**, 95421-58-2.

Supplementary Material Available: IR and NMR spectra of compounds in Table I (1 page). Ordering information is given on any current masthead page.

Epoxidation of Alkenes with Potassium Hydrogen Persulfate

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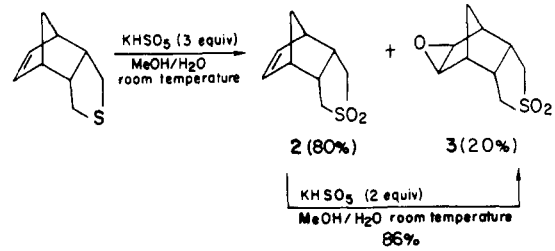
Potassium hydrogen persulfate ($KHSO_5$, potassium caroate), commercially sold as oxone, is a convenient, inexpensive, and powerful oxidant with a wide range of application.[1] It has been recently reported that alkenes[2,3] as well as arenes[4] can be epoxidized by dioxirane intermediates generated in situ by the reaction of potassium hydrogen persulfate with acetone. In the absence of ketones no reaction was observed under the reaction conditions used by the authors. We report now that potassium hydrogen persulfate alone is able to epoxidize water-soluble or insoluble alkenes with good to excellent yields, thus opening a new, efficient, and simple way for epoxide synthesis.

This work was initiated by the fact that in contrast with Trost's report[5] we observed the partial epoxidation of an isolated double bond by $KHSO_5$ in aqueous methanol: up to 20% of epoxide **3** was formed during the reaction of 4-thiatricyclo[5.2.1.$0^{2,6}$]dec-8-ene (**1**) with oxone at room temperature.[6]



When the sulfone **2** was treated with 2 equiv of oxone in the same conditions, a 86% yield of epoxide **3** was obtained after 24 h. These observations led us to examine the epoxidation of various alkenes with potassium hydrogen persulfate in aqueous methanol. The results are summarized in Table I.

In procedure A the reaction medium is acidic (pH 2–3) and only a few epoxides are stable under these conditions (entries 3 and 9). In the other cases this procedure led to products arising from oxirane ring-opening, and epoxidations were best performed by using method B or C where the pH is adjusted to 6 and kept at this value during the whole reaction by controlled addition of an aqueous solution of potassium hydroxide. This pH value was preferred to the one (pH 7.5) used for epoxidation with the caroate/acetone system[2] since the peroxide autodecomposition is much less at pH 6: for example, the yield of 1,2-epoxycycloheptane (**5**) was only 60% when the oxidation was made at pH 7.5 with 2 equiv of $KHSO_5$.

Cyclododecene (entry 4) failed to react with $KHSO_5$ in aqueous methanol, and this result may be due to the lack of solubility of this alkene in the medium. The solubility criterion might account for the differences between the Trost[5] and Curci[2] reports and this work.

No methanol was necessary for the oxidation of a water-soluble olefin like sorbic acid (entry 8). In this particular case the formation of 4,5-epoxy-2-hexenoic acid (**11**) as the unique reaction product is representative of the high selectivity of the oxidation which is confirmed by the lack of reactivity of *trans*-cinnamic acid.

However, the reaction of 4-vinylcyclohexene (entry 5) is not so clean, and we could not avoid the formation of 20% diepoxide even when only 1 equiv of persulfate was used.

Experimental Section

Equipment and Materials. ^1H NMR spectra were measured on Perkin-Elmer R-12A or Perkin-Elmer R-32 spectrometers. IR spectra were run on a Perkin-Elmer 682 instrument. Mass spectra were obtained on a Hewlett-Packard 5992A GC/MS spectrometer. Controlled pH experiments were performed by using a Metrohm

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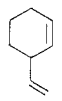
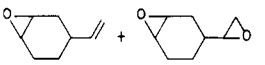
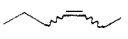
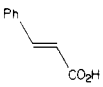
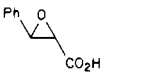
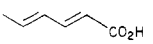
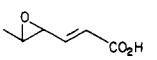
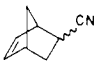
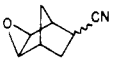
Table I. Reaction of Alkenes with Potassium Hydrogen Persulfate

entry	alkene	method[a]	reactn time, h	$KHSO_5$,[b] equiv	product		yield,[c] %
1	cyclohexene	B	5	2	1,2-epoxycyclohexane (4)		62
2	cycloheptene	B	4	2	1,2-epoxycycloheptane (5)		91
3	cyclooctene	A	4	1.5	1,2-epoxycyclooctane (6)		94
4	cyclodecene $E + Z$	A or B	5	2	no reaction		
5		B	5	1	 7 (46%) 8 (21%)[d]		
		B	5	2	7 (40%) 8 (60%)[d]		
		B	5	5	8		78
6		B	5	2		9	63
7		C or B	5	2		10	10[e]
8		C	1	2		11	84
9		A	3	1.5		12	93

[a] All the reactions were performed at room temperature: method A, oxone in water added to alkene in methanol, uncontrolled pH; method B, same as A, but pH 6; method C, oxone and alkene in water, pH 6. [b] An excess of potassium hydrogen persulfate is necessary, due to competitive peroxide decomposition.[7] [c] Yields are given for isolated epoxides unless noted otherwise. [d] The ratio 7/8 were evaluated by ^1H NMR and GLC coupled with a mass spectrometer; when 1 equiv of $KHSO_5$ was used, 4-vinylcyclohexene was also present in the reaction mixture. [e] Yields evaluated by ^1H NMR.

AG CH-9100 Herisau combi titrator. Oxone is a stable powder containing 2 mol of $KHSO_5$, 1 mol of K_2SO_4, and 1 mol of $KHSO_4$ and is sold in Europe by Aldrich. Cyclohexene, cycloheptene, cyclooctene, cyclododecene, 4-vinylcyclohexene, *trans*-cinnamic acid, and sorbic acid were commercial products. 2-Cyanobicyclo[2.2.1]hept-5-ene and 4-thiatricyclo[5.2.1.$0^{2,6}$]dec-8-ene were prepared following reported procedures.[6,8]

All the epoxides, but the sulfone **3**, were known compounds and had spectral data that where identical with those given in the literature[2,9–11] or with those of commercial samples.

Epoxy sulfone 3 obtained in 86% yield (method A) after column chromatography; recrystallized (CH_3CO_2Et/*n*-hexane, 4/1): mp 241–242 °C; ^1H NMR ($CDCl_3$) δ 3.27 (br s, 2 H), 2.65–3.65 (m, 8 H), 1.5–1.8 (m, 1 H), 0.8–1.1 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ 48.4, 48.2, 38.2, 37.7, 26.8; IR ($CHCl_3$) 2960, 1315, 1215, 1140, 850 cm^{-1}.

Anal. Calcd for $C_9H_{12}O_3S$: C, 53.98; H, 6.04; S, 16.01. Found: C, 53.73; H, 5.99; S, 16.02.

Typical Procedures. Method A. A solution of oxone (4.62 g, 15 mmol of $KHSO_5$) in water (20 mL) was added in one portion to a solution of cyclooctene (1.1 g, 10 mmol) in methanol (20 mL). The reaction mixture was then magnetically stirred during 4 h at room temperature. After addition of water (50 mL), the solution was extracted with methylene chloride (2 × 20 mL). The extracts were dried ($MgSO_4$) and the solvent removed in vacuo, affording 1.19 g (94%) of 9-oxabicyclo[6.1.0]nonane (**6**) having spectra identical with those of a commercial sample (mp after sublimation 56 °C, lit.[12] mp 56–57 °C).

Method B. A solution of cycloheptene (960 mg, 10 mmol) in methanol (20 mL) was added in 5 min to a solution of oxone (6.15 g, 20 mmol of $KHSO_5$) in water (50 mL). Before the addition was started the pH was adjusted to 6 and it was monitored with a pH electrode and kept at this value during the entire reaction by dropwise addition of KOH (1 M in water). The reaction mixture was stirred for an additional 4 h and extracted with methylene chloride (2 × 20 mL). The organic layer was dried ($MgSO_4$) and the solvent was removed on a rotatory evaporator. The residue was bulb-to-bulb distilled at 85 °C (50 mm) to give 1.02 g (91%) of 8-oxabicyclo[5.1.0]octane (**5**), giving spectra identical with those of a sample prepared by a reported procedure.[13]

Method C. A solution of oxone (6.15 g, 20 mmol of $KHSO_5$) in water (20 mL) was added in one portion to a solution of sorbic acid (1.12 g, 10 mmol) in water (20 mL) while the pH was kept at 6 by addition of aqueous 1 M KOH. After 1 h of stirring, the pH remained constant without KOH addition. The solution was acidified to pH 1 (12 N HCl) and continuously extracted with ether during one night. The ether extract was dried ($MgSO_4$) and the solvent was removed, affording 1.10 g (84%) of 4,5-epoxy-2-hexenoic acid (**11**) pure by ^1H NMR. A sample purified by crystallization (CCl_4/*n*-hexane) had mp 82 °C (lit.[2] mp 81–83 °C).

Registry No. **1**, 2434-67-5; **2**, 83947-07-3; **3**, 95722-43-3; **4**, 286-20-4; **5**, 286-45-3; **6**, 286-62-4; **7**, 106-86-5; **8**, 106-87-6; **9**, 53897-32-8; **10**, 1566-68-3; **11**, 74923-21-0; **12**, 18776-20-0; $KHSO_5$, 10058-23-8; (*Z*)-cyclododecene, 1129-89-1; 4-vinylcyclohexene, 100-40-3; sorbic acid, 110-44-1; cyclohexene, 110-83-8; cycloheptene, 628-92-2; cyclooctene, 931-88-4; (*E*)-cyclododecene, 1486-75-5; 3-heptene, 592-78-9; *trans*-cinnamic acid, 140-10-3; bicyclo[2.2.1]hept-5-ene-2-carbonitrile, 95-11-4.

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Diels–Alder and Retro-Diels–Alder Reactions: From *N'*-(Thioacyl)formamidines to Thio Amide Vinylogues

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As part of our continuing study of the chemistry of sulfur-containing heterocycles, we have developed and generalized the cyclocondensation reactions of *N'*-(thio-

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