Preparation of Unsaturated Hydroperoxides from *N*-Alkenyl-*N'*-*p*-tosylhydrazines

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Unsaturated hydroperoxides ($R^1R^2CHO_2H$), 2-phenylpent-4-enyl hydroperoxide (**1**), 3-phenylhex-5-en-2-yl hydroperoxide (**2**), 5-methylhex-5-en-2-yl hydroperoxide (**3**), cyclo-oct-4-enyl hydroperoxide (**18**), and cyclo-oct-3-enyl hydroperoxide (**24**) have each been prepared from the corresponding carbonyl compound (R^1R^2CO) by the sequence: i, conversion to the *p*-tosylhydrazone ($R^1R^2C{=}N{-}NHTs$); ii, reduction with sodium cyanoborohydride at pH 3.5 to give the *N'*-*p*-tosylhydrazine ($R^1R^2CH{-}NH{-}NHTs$); and iii, oxidation with hydrogen peroxide and sodium peroxide. Isomerisation occurs in the preparation of the cyclo-octenyl hydroperoxides, particularly if the pH falls markedly below 3.5 in the reduction step.

Non-allylic alkenyl hydroperoxides are principal precursors of cyclic peroxides. Studies of the cyclisations, which occur under both radical[1–6] and polar[3,5–8] conditions, contribute to an understanding of important processes such as lipid peroxidation and the oxidative degradation of rubber. The cyclic peroxides themselves serve as useful models for investigating the chemistry of naturally occurring substances such as prostaglandin endoperoxides. They also provide a convenient source of theoretically interesting diradicals, and have potential as intermediates in the stereocontrolled syntheses of polyoxygenated compounds. Certain δ,ε-unsaturated hydroperoxides are also precursors of gem-dialkylperoxonium ions which are a new, and as yet little studied, class of oxygen transfer reagents.[9]

With the single exception of 2-methylhex-5-en-2-yl hydroperoxide, which was prepared by silver(I)-assisted perhydrolysis of the corresponding bromide,[4] all the non-allylic alkenyl hydroperoxides reported in the literature are primary or secondary and have been made by the perhydrolysis of alkenyl methanesulphonates under basic conditions.[1–8,10] We have found several examples where these reactions fail or afford hydroperoxides in only very poor yield. In an attempt to provide an alternative route to such hydroperoxides, we decided to investigate the use of the oxidation of *N*-alkenyl-*N'*-*p*-tosylhydrazines. The method is based on that applied by Caglioti and co-workers[11] to the preparation of a small number of saturated alkyl hydroperoxides (Scheme 1). This approach appears attractive in that high yields are reported for each of the three steps. However, the method has not found general use.

$$R^1R^2C{=}O \xrightarrow{(i)} R^1R^2C{=}N{-}NHTs \xrightarrow{(ii)} R^1R^2CH{-}NH{-}NHTs \xrightarrow{(iii)} R^1R^2CH{-}OOH$$

Scheme 1. *Reagents:* i, H_2NNHTs; ii, B_2H_6; iii, H_2O_2, Na_2O_2.

We reasoned that in the reduction of alkenyl *p*-tosylhydrazones (step ii), the use of diborane would be inappropriate since complications might arise from hydroboration of the alkenyl group. Certain aryl *p*-tosylhydrazones have been reduced to the corresponding *p*-tosylhydrazines by sodium cyanoborohydride at pH 3.5 (Scheme 2; $R^1 = Ar^2CHR^2$).[12] It was therefore decided to modify the sequence in Scheme 1 by incorporating a cyanoborohydride reduction at step ii.

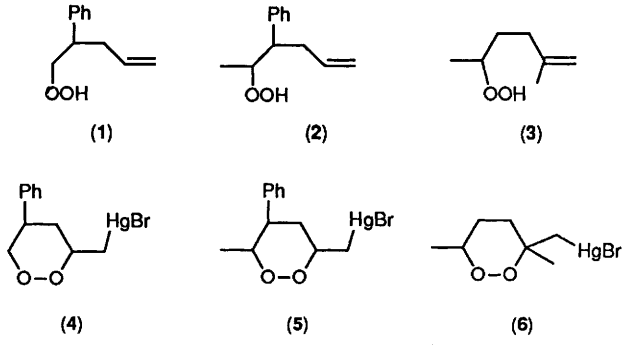
$$Ar^1R^1C{=}N{-}NHTs \xrightarrow[pH\ 3.5]{H^+/NaBH_3CN} Ar^1R^1CH{-}NH{-}NHTs$$

Scheme 2.

We now report the successful application of this modified sequence to the preparation of three acyclic δ,ε-unsaturated hydroperoxides and two isomeric cyclo-octenyl hydroperoxides.

Results and Discussion

Acyclic Alkenyl Hydroperoxides.—Hydroperoxides (**1**)–(**3**) were prepared. The structures were confirmed by ^1H and ^{13}C NMR spectroscopy, positive peroxide test with acidic iron(II) thiocyanate, and conversion by reaction with mercury(II) nitrate and then aqueous potassium bromide into the corresponding 3-bromomercuriomethyl-1,2-dioxanes (**4**)–(**6**) (Scheme 3).



Scheme 3.

The aldehyde precursor (**8**) of hydroperoxide (**1**) was prepared as shown in Scheme 4. The overall yield of isolated hydroperoxide (**1**) from aldehyde (**8**) was 16%. This seemingly poor yield must be judged by comparison with the methane-

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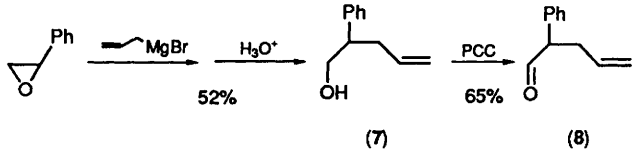
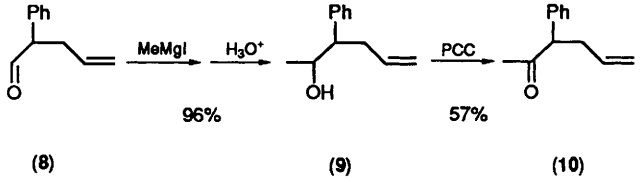


Scheme 4.

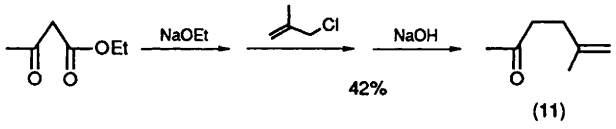


Scheme 5.

sulphonate route from alcohol (**7**) which failed to give any hydroperoxide.

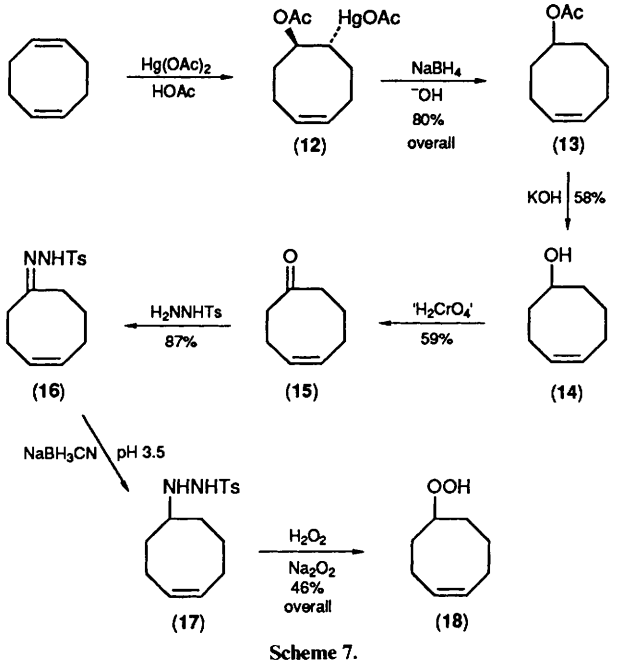
The ketone precursor (**10**) of hydroperoxide (**2**) was prepared as shown in Scheme 5. Although the *p*-tosylhydrazone from (**10**) was obtained in a yield of 55%, the remainder of the sequence afforded only 8% of hydroperoxide (**2**). The small scale of the preparation probably contributed to this low yield which, as the result below for hydroperoxide (**3**) shows, is not general for secondary alkenyl hydroperoxides.

The acetoacetic ester synthesis was employed to prepare the ketone precursor (**11**) of the hydroperoxide (**3**) (Scheme 6). The yield of isolated hydroperoxide (**3**) based on the ketone (**11**) was 38%.



Scheme 6.

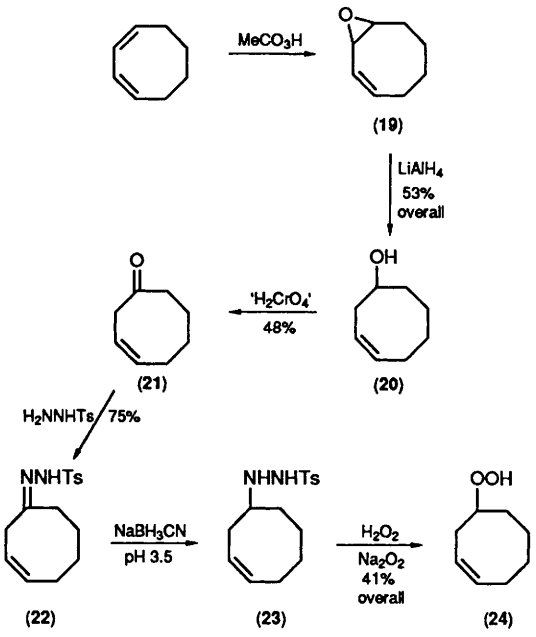
Cyclo-octenyl Hydroperoxides.—The methanesulphonate route failed to yield any cyclo-oct-4-enyl hydroperoxide (**18**), but the *p*-tosylhydrazine route gave an overall yield of 40% based on cyclo-oct-4-enone (**15**). The complete synthetic pathway from commercially available cyclo-octa-1,5-diene is shown in Scheme 7, and the overall yield for the seven steps was 11%.



Scheme 7.

In a similar way (Scheme 8), cyclo-oct-3-enyl hydroperoxide (**24**) was prepared from cyclo-octa-1,3-diene in an overall yield of 8%, or 31% based on cyclo-oct-3-enone (**21**).

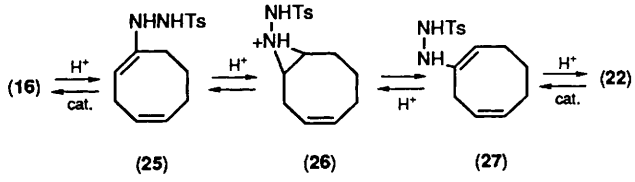
The structures of the cyclo-octenyl hydroperoxides (**18**) and (**24**) were confirmed by ^1H and ^{13}C NMR spectroscopy, positive peroxide test with acidic iron(II) thiocyanate, elemental analysis, and non-identity with the known [13] isomer, cyclo-oct-2-enyl hydroperoxide.



Scheme 8.

Careful control of the pH in the reduction step was particularly important with the cyclo-octenyl compounds, otherwise extensive rearrangement took place. Thus, in two preparations of cyclo-oct-4-enyl hydroperoxide (**18**) in which the pH was allowed to fall considerably below 3.5, the isolated hydroperoxide contained 17 and 42% of cyclo-oct-3-enyl hydroperoxide (**24**). Even with careful control, the *p*-tosylhydrazone (**22**) afforded a sample of hydroperoxide (**24**) which contained about 5% of the isomer (**18**).

It is clear that the isomerisations take place in the reduction step and are favoured by strongly acidic conditions. Double bond migrations in the reduction to alkenes of αβ-unsaturated *p*-tosylhydrazones are well known,[14,15] but the conditions are quite different and the mechanism is inapplicable to our compounds. With the observed formation of hydroperoxide (**24**) from *p*-tosylhydrazone (**16**) and of hydroperoxide (**18**) from *p*-tosylhydrazone (**22**), it is tempting to suggest the participation of a common intermediate. The aziridinium ion (**26**) could fulfil this role and a possible pathway for isomerisation is proposed in Scheme 9. This is consistent with the accepted mechanism of the cyanoborohydride reduction which involves initial protonation at the iminyl nitrogen of the *p*-tosylhydrazone.[16] Fully fledged interconversion of the *p*-tosylhydrazones (**16**) and (**22**) would not be a requirement



Scheme 9.

since hydride attack on the ion (**26**) could provide both *p*-tosylhydrazine precursors of the isomeric hydroperoxides.

However, it is not clear why such a mechanism should be restricted to the cyclo-octenyl compounds. Neither is it obvious why the alternative enamine from *p*-tosylhydrazone (**22**), which would ultimately lead to formation of the undetected cyclo-oct-2-enyl hydroperoxide, should not be formed. An alternative pathway that may account for the apparent selectivity involves acid-catalysed isomerisation to the azohydrazine tautomer,[17] followed by intramolecular abstraction by the NTs group of an allylic proton assisted by protonation at the double bond and deprotonation at C-1. Molecular models indicate that the nitrogen atom can come into close proximity with the allylic hydrogen atoms that facilitate the observed isomerisations, but not with those of the cyclo-oct-3-enyl compound that would lead to the cyclo-oct-2-enyl product.

An investigation of the mechanism of these interesting isomerisations is planned, but for the present preparative purposes it is sufficient to know that careful control of pH in the reduction step minimises the risk of their occurrence.

Experimental

NMR spectra were recorded with a Varian VXR400 or XL200 spectrometer for solutions in $CDCl_3$. Mass spectra were obtained by using a VG7070 F/H mass spectrometer plus Finnigan INCOS data system. IR spectra were measured with a Perkin-Elmer 983 instrument.

Unless otherwise indicated, all reagents were commercial samples which were used as received. Acidified iron(II) thiocyanate was prepared as described previously[18] and the formation of a blood-red colour was taken as a positive test for peroxide. All hydroperoxide products were stored at −30 °C.

Preparation of Carbonyl Compounds.—*2-Phenylpent-4-enal* (**8**). Styrene oxide (120.15 g, 1.0 mol) in dry diethyl ether (200 cm^3) was added with stirring to a freshly prepared solution of allylmagnesium bromide [from allyl bromide (133.08 g, 1.1 mol) and magnesium (29.17 g, 1.20 mol)] in diethyl ether (450 cm^3) cooled in an ice–salt bath. The mixture was set aside overnight. After standard aqueous ammonium chloride work-up, the crude product was distilled under reduced pressure to give 2-phenylpent-4-enol (**7**) (52%), b.p. 87–90 °C at 0.001 mmHg; δ_H 1.75 (1 H, s), 2.43 (2 H, m), 2.84 (1 H, m), 3.68 (1 H, dd, ^3J 7.1 and ^2J 10.7 Hz), 3.73 (1 H, dd, ^3J 6.1 and ^2J 10.7 Hz), 4.97 (2 H, m), 5.68 (1 H, m), and 7.20 (5 H, m); δ_C 36.53, 48.08, 66.48, 116.17, 126.50, 128.01, 128.37, 136.35, and 142.35; ν_{max} 3 372, 3 019, 2 919, 1 638, 1 598, 1 491, 1 448, 1 054, 1 027, 914, 757, and 699 cm^{-1}.

To a rapidly stirred suspension of pyridinium chlorochromate (39.87 g, 185 mmol) in dry dichloromethane (200 cm^3) was added 2-phenylpent-4-enol (**7**) (20.00 g, 123 mmol) in dry dichloromethane (20 cm^3). After 18 h, the supernatant liquid was decanted off and the solid residue extracted with dry diethyl ether (3 × 100 cm^3). The combined dichloromethane and ether solutions were filtered through Celite and silica and the solvent removed under reduced pressure. Distillation of the crude product afforded 2-phenylpent-4-enal (**8**) (65%) b.p. 77–78 °C at 0.3–0.4 mmHg; δ_H 2.50 (1 H, m), 2.82 (1 H, m), 3.62 (1 H, dt, ^3J 1.7 and 7.3 Hz), 5.04 (2 H, m), 5.71 (1 H, m), 7.36 (5 H, m), and 9.70 (1 H, d, ^3J 1.7 Hz); δ_C 33.94, 58.71, 117.15, 127.65, 128.86, 129.04, 134.87, 135.69, and 200.06.

3-Phenylhex-5-en-2-one (**10**). 2-Phenylpent-4-enal (**8**) (10.55 g, 65.9 mmol) in dry diethyl ether (20 cm^3) was added slowly with stirring to a freshly prepared solution of methylmagnesium iodide [from methyl iodide (9.82 g, 69.2 mmol)] in diethyl ether (30 cm^3) cooled in an ice-bath. The mixture was set aside overnight. After standard aqueous ammonium chloride work-up, crude 3-phenylhex-5-en-2-ol (**9**) (96%) was isolated.

Oxidation of (**9**) (11.52 g; 65.3 mmol) with pyridinium chlorochromate (21.14 g, 98 mmol) (see above) and distillation under reduced pressure gave 3-phenylhex-5-en-2-one (**10**) (57%), b.p. 64–66 °C at 0.3 mmHg; δ_H 2.06 (3 H, s), 2.46 (1 H, m), 2.75 (1 H, m), 3.70 (1 H, t, ^3J 7.5 Hz), 4.98 (2 H, m), 5.62 (1 H, m), and 7.31 (5 H, m); δ_C 28.99, 36.14, 59.29, 116.55, 127.31, 128.22, 128.89, 135.72, 138.36, and 207.39.

5-Methylhex-5-en-2-one (**11**).[19] Ethyl acetoacetate (130.14 g, 1.0 mol) was added to a solution of sodium ethoxide [from sodium (23.0 g, 1.0 mol)] in ethanol (600 cm^3) and the mixture brought to reflux. 1-Chloro-2-methylpropene (90.55 g, 1.0 mol) was added during 30 min and the mixture heated at reflux for 4 h. After cooling, the mixture was filtered and most of the ethanol was removed from the filtrate under reduced pressure. The resultant product was hydrolysed by heating with aqueous sodium hydroxide (120 g, 800 cm^3) to give a distillate containing the ketone, water, and ethanol. The mixture was washed with water, dried (K_2CO_3), and distilled under reduced pressure to give 5-methylhex-5-en-2-one (**11**) (42%), b.p. 60 °C at 18 mmHg; δ_H 1.74 (3 H, s), 2.17 (3 H, s), 2.28 (2 H, t), 2.59 (2 H, t), 4.67 (1 H, s), and 4.74 (1 H, s).

Cyclo-oct-4-enone (**15**). 1-Acetoxycyclo-oct-4-ene (**13**) was prepared from cyclo-octa-1,5-diene by acetoxymercuriation and reduction as previously described;[20] δ_C 20.70, 21.85, 24.37, 25.07, 33.18, 33.23, 74.89, 129.07, 129.19, and 169.40. Saponification was carried out by heating the acetate (103 g) at reflux with aqueous potassium hydroxide (100 g, 100 cm^3) for 5 h. After cooling, the mixture was extracted with dichloromethane (3 × 50 cm^3) and the extract washed with water, dried ($MgSO_4$), and the solvent removed under reduced pressure. Distillation under reduced pressure afforded cyclo-oct-4-enol (**14**)[20] (58%), b.p. 45–52 °C at 0.1 mmHg; δ_C 22.73, 24.89, 25.49, 36.21, 37.14, 72.06, 129.06, and 129.85.

Aqueous potassium dichromate (104 g, 900 cm^3) and conc. sulphuric acid (74.5 cm^3) were added very slowly to a stirred solution of cyclo-oct-4-enol (44.7 g) in diethyl ether (650 cm^3) cooled in an ice–acetone bath, the temperature of the mixture being kept below −1 °C. After 30 min, water (750 cm^3) was added and the mixture was extracted with diethyl ether (4 × 500 cm^3). The combined extract was washed with water (2 × 100 cm^3), dried ($MgSO_4$), and the solvent removed under reduced pressure. Distillation under reduced pressure gave cyclo-oct-4-enone (**15**)[21] (59%), b.p. 40–42 °C at 0.2 mmHg; δ_C 21.64, 23.79, 26.15, 40.13, 47.05, 130.11, 130.54, and 214.45.

Cyclo-oct-3-enone (**21**). 3,4-Epoxycyclo-octene (**19**) was prepared by epoxidation of cyclo-octa-1,3-diene with peroxyacetic acid as described previously;[22] δ_C 25.30, 25.83, 27.52, 29.13, 53.55, 57.97, 122.92, and 134.14. The epoxide was reduced with lithium aluminium hydride as described previously[22] to give cyclo-oct-3-enol (**20**) (53% from cyclo-octa-1,3-diene), which was purified by distillation under reduced pressure, b.p. 59–61 °C at 0.2 mmHg; δ_C 21.37, 25.68, 28.34, 33.97, 34.84, 71.91, 126.35, and 131.97.

The alcohol was oxidised by chromic acid following the procedure described above for the isomer (**15**). Distillation under reduced pressure afforded cyclo-oct-3-enone (**21**),[21] (48%), b.p. 38–42 °C at 0.3 mmHg; δ_C 24.55, 25.61, 27.03, 42.11, 44.15, 124.11, 131.33, and 213.67.

Preparation of p-*Tosylhydrazones.*[23]—To a stirred suspension of *p*-tosylhydrazine in ethanol at 40–50 °C was added 1 mol equiv. of the carbonyl compound. After 5–15 min, when all the solid had dissolved, the solution was cooled to 0 °C and the *p*-tosylhydrazone crystallised out. The product was recrystallised from ethanol or ethanol–water and dried at 20 then 0.01 mmHg.

2-Phenylpent-4-enal p-*tosylhydrazone* [*from* (**8**)]. Yield

42%; m.p. 109–111 °C; δ_H 2.43 (3 H, s), 2.40–2.68 (2 H, m), 3.52 (1 H, m), 4.89 (2 H, m), 5.53 (1 H, m), 7.00–7.32 (8 H, m), 7.50 (1 H, s), and 7.78 (2 H, d, ^3J 8.3 Hz); δ_C 21.62, 37.03. 48.27, 116.87, 127.07, 127.99, 128.01, 128.66, 129.58, 135.06, 135.22, 139.52, 144.12, and 153.31; *m/z* 329 ($M^+ + 1$, 3.2%), 173 (20.0), 155 (11.3), 133 (29.4), 131 (75.7), 128 (22.2), 115 (20.6), 103 (60.8), 91 (100), 77 (39.2), 51 (27.6), and 41 (57.7) (Found: C, 65.7; H, 6.15; N, 8.7. $C_{18}H_{20}N_2O_2S$ requires C, 65.83; H, 6.14; N, 8.53%).

3-*Phenylhex-5-en-2-on* p-*tosylhydrazone* [*from* (**10**). Yield 55%; m.p. 123–124 °C; δ_H 1.57 (3 H, s), 2.40 (1 H, m), 2.48 (3 H, s), 2.64 (1 H, m), 3.43 (1 H, m), 4.84 (2 H, m), 5.51 (1 H, m), 6.98 (2 H, m), 7.19–7.38 (6 H, m), and 7.89 (2 H, d, ^3J 8.4 Hz); δ_C 15.15, 21.58, 36.62, 53.84, 116.12, 126.89, 127.95, 128.14, 128.43, 129.48, 135.40, 136.23, 140.09, 143.89, and 157.95; *m/z* 343 ($M^+ + 1$, 33.8%), 187 (29.6), 173 (15.2), 155 (6.2), 147 (76.2), 145 (90.5), 131 (34.2), 129 (24.9), 128 (28.5), 115 (74.1), 91 (100), 89 (23.1), 77 (21.2), 65 (19.2), 63 (15.6), 57 (13.4), and 51 (20.6) (Found: C, 66.4; H, 6.5; N, 8.15. $C_{19}H_{22}N_2O_2S$ requires C, 66.64; H, 6.47; N, 8.18%).

5-*Methylhex-5-en-2-on* p-*tosylhydrazone* [*from* (**11**)]. Yield 64%; m.p. 110–111 °C; δ_H 1.61 (3 H, s), 1.76 (3 H, s), 2.14 (2 H, m), 2.35 (2 H, m), 2.43 (3 H, s), 4.60 (2 H, m), 7.31 2 H, d, ^3J 8.5 Hz), 7.85 (2 H, d, ^{3}J 8.5 Hz), and 8.12 (1 H, br s); δ_C 15.68, 21.59, 22.23, 33.84, 36.86, 110.42, 128.05, 129.44, 135.46, 143.85, 144.47, and 157.81; *m/z* 281 ($M^+ + 1$, 1.4%), 155 (13.1), 126 (22.9), 125 (37.7), 111 (19.9), 95 (44.9), 91 (73.8), 89 (25.7), 81 (15.9), 67 (31.1), 55 (47.9), and 41 (100) (Found: C, 60.05; H, 7.25; N, 10.1. $C_{14}H_{20}N_2O_2S$ requires C, 59.97; H, 7.18; N, 9.99%).

Cyclo-oct-4-enone p-*tosylhydrazone* (**16**). Yield 87%, a 4:1 mixture of two geometrical isomers; m.p. 132–134 °C; δ_H 1.41–1.51 (2 H, m), 1.77–1.84 and 1.94–2.00 (2 H, m), 2.14–2.33 (6 H, m), 2.41 (3 H, s), 5.26 (dt, ^3J 8.13 and 10.45 Hz) and 5.45 (dt, ^3J 7.58 and 10.45 Hz) (major isomer), and 5.38 (dt, ^{3}J 8.15 and 10.42 Hz) and 5.61 (dt, ^{3}J 8.15 and 10.42 Hz) (minor isomer) (2 H), 7.20 and 7.33 (1 H, br s), 7.28 (2 H, d, ^3J 8.28 Hz), and 7.80 and 7.79 (2 H, d, ^3J 8.28 Hz); δ_C major isomer 21.50, 21.56, 23.69, 25.77, 28.48, 39.44, 127.86, 128.05, 129.49, 130.07, 135.73, 143.75, and 161.61, minor isomer 21.06, 22.11, 25.42, 27.30, 31.40, 34.73, 128.34, 128.75, 129.49, 130.07, 130.76, 131.01, and 162.79 (Found: C, 61.9; H, 6.9; N, 9.55. $C_{15}H_{20}N_2O_2S$ requires C, 61.62; H, 6.89; N, 9.58%).

Cyclo-oct-3-enone p-*tosylhydrazone* (**22**). Yield 75%, a 1:1 mixture of two geometrical isomers; m.p. 126–128 °C; δ_H 1.4–2.0 (6 H, m), 2.25 and 2.35 (2 H, m), 2.42 (3 H, s), 2.93 (d, ^3J 5.2 Hz) and 3.00 (d, ^3J 4.5 Hz), 2 H), 5.4–5.6 (2 H, m), 7.30 (2 H, d, ^3J 8.3 Hz), 7.86 (2 H, d, ^3J 8.3 Hz), and 7.8 (1 H, br s); δ_C 21.60 (both isomers), 22.49, 24.15, 24.47 (both isomers), 27.30, 27.98, 28.35, 29.39, 36.60, 37.94, 123.24, 126.53, 127.94 (both isomers), 128.28, 129.50 (both isomers), 129.92, 131.63, 135.53, 135.71, 143.88, 162.89, and 163.21 (Found: C, 61.45; H, 7.15; N, 9.4. $C_{15}H_{20}N_2O_2S$ requires C, 61.62; H, 6.89; N, 9.58%).

Preparation of N-*Alkenyl*-N′-p-*tosylhydrazines*.[12]—*p*-Tosylhydrazone (10 mmol) and Bromocresol Green (*ca.* 5 mg) were dissolved in tetrahydrofuran (50 cm^3) under a gentle stream of nitrogen, the exit gases being passed through a scrubbing line consisting of three Dreschel bottles, the final two of which contained solutions of bleach. To the stirred solution was added, in one portion, sodium cyanoborohydride (2.51 g; 40 mmol) washed in with tetrahydrofuran (50 cm^3). A solution of toluene-*p*-sulphonic acid (3.8 g, 20 mmol) in tetrahydrofuran (40 cm^3) was added in small portions so as to keep the indicator a tan colour (pH 3.5). After 4 h, the reaction mixture was filtered through Celite to remove the white precipitate. The filtrate was concentrated under reduced pressure, water (100 cm^3) was added, and the mixture was extracted with dichloromethane (3 × 50 cm^3). The extract was dried ($MgSO_4$) and the solvent removed under reduced pressure to afford the crude *N*-alkenyl-*N′-p*-tosylhydrazine as a yellow oil.

N-(2-*Phenylpent-4-enyl*)-N′-p-*tosylhydrazine*. δ_C 21.25, 38.09, 43.36, 56.21, 116.17, 127.44, 127.75, 128.33, 129.41, 134.38, 135.60, 144.81, and 143.96.

N-(5-*Methylhex-5-en-2-yl*)-N′-p-*tosylhydrazine*. δ_C 18.23, 21.37, 22.26, 32.17, 33.65, 54.91, 109.64, 128.00, 129.28, 135.18, 143.58, and 145.28.

N-(*Cyclo-oct-4-enyl*)-N′-p-*tosylhydrazine* (**17**). δ_C 21.50, 23.29, 25.86, 26.25, 31.54, 32.96, 60.12, 129.48, 129.58, 129.67, 129.94, 135.98, and 143.61.

N-(*Cyclo-oct-3-enyl*)-N′-p-*tosylhydrazine* (**23**). δ_C 21.51, 22.21, 25.84, 28.73, 28.91, 29.75, 60.59, 126.81, 128.09, 129.40, 131.74, 135.41, and 143.61.

In earlier experiments, the reduction of *p*-tosylhydrazone (**16**) by sodium borohydride under various conditions was examined. This gave inferior yields to the sodium cyanoborohydride method (above), but an analytically pure sample of the *p*-tosylhydrazine (**17**) was isolated as follows.

Sodium borohydride (1.14 g) was added with stirring to an ice-cold solution of *p*-tosylhydrazone (**16**) (1.00 g) in dichloromethane (40 cm^3) followed by cautious addition of methanol (10 cm^3). After stirring for 2 h, water (50 cm^3) was added and the layers separated. The aqueous layer was extracted with dichloromethane (3 × 10 cm^3). The combined dichloromethane extracts were washed with water (50 cm^3), dried ($MgSO_4$), and the solvent was removed at 10 mmHg and 30 °C. The crude product was recrystallised twice from absolute ethanol to give N-(*cyclo-oct-4-enyl*)-N′-p-*tosylhydrazine* (**17**) as a white crystalline solid, m.p. 87–89 °C (Found: C, 60.9; H, 7.5; N, 9.55. $C_{15}H_{22}N_2O_2S$ requires C, 61.18; H, 7.55; N, 9.52%).

Preparation of Hydroperoxides.[11]—To a stirred solution of crude *N*-alkenyl-*N′-p*-tosylhydrazine (7.5 mmol) in tetrahydrofuran (100 cm^3) cooled in an ice-bath was added 30% aqueous hydrogen peroxide (80 cm^3, *ca.* 750 mmol) and sodium peroxide (0.88 g, 11 mmol). The mixture was stirred for 24 h at room temperature, then water (200 cm^3) was added. The solution was neutralised with 2M hydrochloric acid and extracted with dichloromethane (3 × 75 cm^3). (Ammonium chloride was added if an emulsion was formed.) The combined extracts were dried ($MgSO_4$) and the solvent was removed under reduced pressure to afford the crude hydroperoxide.

The crude hydroperoxide was dissolved in light petroleum (b.p. ≤40 °C; 20 cm^3), cooled to 0 °C, and extracted with ice-cold 4M sodium hydroxide (5 × 10 cm^3). The combined aqueous extracts were washed with light petroleum (b.p. ≤40 °C; 2 × 10 cm^3), mixed with dichloromethane (20 cm^3), and neutralised with ice-cold 2M hydrochloric acid, the temperature being kept below 5 °C. The mixture was extracted with dichloromethane (3 × 20 cm^3). The combined extracts were washed with water (10 cm^3), dried ($MgSO_4$), and the solvent was removed under reduced pressure to give the hydroperoxide. Yields are overall from *p*-tosylhydrazone.

2-*Phenylpent-4-enyl hydroperoxide* (**1**). Yield 39%; δ_H 2.45 2 H, m), 3.13 (1 H, m), 4.15 (1 H, d, ^3J 6.9 Hz), 4.19 (1 H, d ^3J 7.0 Hz), 5.06 (2 H, m), 5.69 (1 H, m), 7.30 (5 H, m), and 8.05 (1 H, s); δ_C 36.92, 43.71, 80.42, 116.48, 126.59, 127.88, 128.40, 136.00, and 141.66.

3-*Phenylhex-5-en-2-yl hydroperoxide* (**2**). The compound was further purified by column chromatography [Merck Kieselgel 60, 70–230 mesh, 0.063–0.20 mm; 30% diethyl ether in light petroleum (b.p. 60–80 °C)]. Yield 8%, a 1:1 mixture of two diastereoisomers; δ_H 1.06 (d, ^3J 6.3 Hz) and 1.18 (d, ^3J 6.4 Hz) (3 H), 2.55 (2 H, m), 2.94 (1 H, m), 4.22 (1 H, m), 5.06 (2 H, m), 5.60 (1 H, m), 7.28 (5 H, m), and 7.74 (1 H, br s); δ_C 15.26, 15.94, 34.41, 36.25, 48.84, 48.92, 84.37, 84.53, 116.17, 116.32, 126.26,

126.54, 128.26, 128.26, 128.51, 128.69, 136.59, 136.66, 140.65, and 140.88.

5-Methylhex-5-en-2-yl hydroperoxide (**3**). Yield 59%; δ_H 1.25 (3 H, d, ^3J 6.1 Hz), 1.5–1.9 (2 H, m), 1.74 (3 H, s), 2.09 (2 H, m), 4.08 (1 H, m), 4.73 (2 H, m), and 8.1 (1 H, br s); δ_C 18.11, 22.45, 31.91, 33.41, 81.19, 110.00, and 145.44.

Cyclo-oct-4-enyl hydroperoxide (**18**). Yield 46%; δ_H 1.5–2.4 (10 H, m), 4.00 (1 H, m), 5.66 (2 H, m), and 81.3 (1 H, br s); δ_C 22.24, 25.30, 25.67, 31.61, 31.77, 86.85, 129.76, and 129.84. An analytically pure sample was obtained by trap-to-trap distillation (Found: C, 67.3; H, 9.8. $C_8H_{14}O_2$ requires C, 67.56; H, 9.94%).

Cyclo-oct-3-enyl hydroperoxide (**24**). Yield 41%; $\delta_H(CD_2Cl_2)$ 1.3–1.85 (6 H, m), 2.0–2.25 (2 H, m), 2.3–2.5 (2 H, m), 4.00 (1 H, m), 6.55–6.8 (2 H, m), and 8.1 (1 H, br s); δ_C 21.46, 25.81, 28.38, 28.80, 29.13, 85.67, 125.67, and 132.45. An analytically pure sample was isolated by HPLC [5 μm SiO_2, 50 × 4.6 mm + 250 × 10 mm + 250 × 10 mm, 10% diethyl ether in light petroleum (b.p. 60–80 °C)] from a mixture containing 58% of isomer (**18**), which was obtained by oxidation of the *N*-cyclooctenyl-*N'*-*p*-tosylhydrazine formed from *p*-tosylhydrazone (**16**) when *all* the toluene-*p*-sulphonic acid was added and the pH fell considerably below 3.5 during reduction (Found: C, 67.7; H, 10.15. $C_8H_{14}O_2$ requires C, 67.56; H, 9.94%).

Preparation of 3-Bromomercuriomethyl Substituted 1,2-Dioxanes.[7]—A solution of the alkenyl hydroperoxide (2.8 mmol) in dichloromethane (30 cm^3) was added dropwise over 15 min to a stirred suspension of mercury(II) nitrate hemihydrate (0.98 g, 2.95 mmol) in dichloromethane (70 cm^3) under nitrogen. The mixture was stirred for 15 min, then most of the supernatant liquid was decanted off. Water (20 cm^3) then potassium bromide (0.37 g, 3.1 mmol) were added and the mixture was stirred for *ca.* 10 min until the white precipitate had disappeared from the aqueous phase. The dichloromethane layer was isolated and combined with a further dichloromethane extract (20 cm^3) of the aqueous layer. The dichloromethane solution was dried (Na_2SO_4) and the solvent removed under reduced pressure to give the crude 1,2-dioxane which was purified by column chromatography (Merck Kieselgel 60, 70–230 mesh, 0.063–0.20 mm; dichloromethane).

3-Bromomercuriomethyl-5-phenyl-1,2-dioxane (**4**). Yield 75%, a 3:1 mixture of two diastereoisomers; δ_H 1.6–2.3 (4 H, m), 3.23 (1 H, m), 4.21 (d, *J* 8.3 Hz) and 4.46 (m) (2 H), 4.74 (1 H, m), and 7.36 (5 H, m); $\delta_C(CD_2Cl_2)$ major isomer (*cis*) 37.51 [$J(^{199}Hg)$ 1 522 Hz], 40.35, 41.63 [$J(^{199}Hg)$ 29 Hz], 77.15, 80.47 [$J(^{199}Hg)$ 108 Hz], 127.36, 127.62, 128.98, and 140.66; minor isomer (*trans*) 76.22, 77.45, 126.89, 128.16, and 128.80 (Found: C, 28.6; H, 2.65. $C_{11}H_{13}BrHgO_2$ requires C, 28.87; H, 2.86%).

3-Bromomercuriomethyl-6-methyl-5-phenyl-1,2-dioxane (**5**). Yield 70%, a 7:5:5:3 mixture of four diastereoisomers; δ_H 0.96 (d, ^3J 6.3 Hz) and 1.03 (d, ^3J 6.8 Hz) and 1.08 (d, ^3J 6.4 Hz) and 1.14 (d, ^3J 6.6 Hz) (3 H), 1.6–3.0 (5 H, m), 3.5–5.0 (2 H, m), and 7.31 (5 H, m); δ_C 12.58, 16.09, 16.41, 16.93, 32.62, 36.75, 37.13, 37.29, 37.43, 37.59, 40.38, 41.83, 42.93, 43.03, 43.29, 48.83, 75.22, 78.39, 79.53, 79.59, 80.00, 80.18, 81.38, 81.88, 126.57, 126.86, 127.02, 127.40, 127.67, 127.78, 128.37, 128.59, 128.74, 129.39, 140.18, 140.98, and 141.19 (Found: C, 30.1; H, 3.1. $C_{12}H_{15}BrHgO_2$ requires C, 30.55; H, 3.20%).

3-Bromomercuriomethyl-3,6-dimethyl-1,2-dioxane (**6**). Yield 45%, a 1:1 mixture of two diastereoisomers; δ_H 1.15 (d, ^3J 6.4 Hz) and 1.20 (d, ^3J 6.4 Hz) (3 H), 1.31 (s) and 1.46 (s) (3 H), 1.72 (4 H, m), 2.11 (d, ^2J 12.1 Hz) and 2.53 (d) [$^2J(^{199}Hg)$ 206 Hz] and 2.15 and 2.18 (AB, ^2J 11.7 Hz) [$^2J(^{199}Hg)$ 194 Hz] (2 H), and 4.22 (1 H, m); δ_C 18.55, 18.72, 24.59, 28.09, 28.52, 29.67, 34.67, 36.38, 43.1 [$J(^{199}Hg)$ 1 500 Hz], 47.05 [$J(^{199}Hg)$ 1 489 Hz], 76.94, 76.94, 80.34 [$J(^{199}Hg)$ 95 Hz], and 80.50 [$J(^{199}Hg)$ 105 Hz] (Found: C, 20.4; H, 3.2. $C_7H_{13}BrHgO_2$ requires C, 20.52; H, 3.20%).

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