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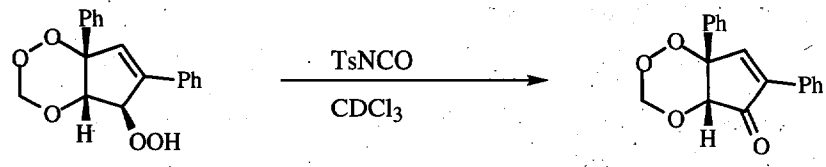
EXPERIMENTAL

General Procedures and Methods. ^{1}H NMR spectra were recorded on a Bruker AM400 spectrometer. ^{13}C NMR spectra were recorded at 100 MHz. Chemical shifts were reported in parts per million (ppm). The residual solvent peak was used as an internal reference. Fast atom bombardment (FAB) mass spectra were obtained with 3-nitrobenzyl alcohol or glycerol as the matrix. Sodium iodide was added when indicated. Chemical ionization (CI) mass spectra were obtained with ammonia as the reagent gas. Fourier transform infrared spectra were obtained as films on sodium chloride plates.

Analytical thin layer chromatography (TLC) was performed with E. Merck pre-coated TLC plates, silica gel 60F-254, layer thickness 0.25 mm. Flash chromatography separations were performed on E. Merck kieselgel 60 (230-400) mesh silica gel.

All reactions were conducted under an argon or nitrogen atmosphere. Reaction vessels were flame-dried or oven-dried and allowed to cool under an inert atmosphere.



4 **5**

To a solution of hydroperoxide **4** (5.0 mg, 16 μmol) in $CDCl_3$ (0.4 mL) was added TsNCO until TLC indicated complete consumption of starting material. No products of rearrangement were detected by crude ^{1}H NMR. The mixture was concentrated and purified by size-exclusion chromatography to give enone **5** (3.3 mg, 70%).

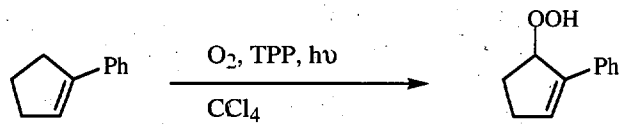
Data for enone **5**:

^{1}H NMR ($CDCl_3$): 7.82 ppm (2H, m), 7.65 (2H, m), 7.50 (2H, t, *J*=7.5 Hz), 7.49 (1H, s), 7.45 (4H, m), 5.39 (1H, d, *J*=8.0 Hz), 5.33 (1H, d, *J*=8.0 Hz), 4.80 (1H, s).

^{13}C NMR ($CDCl_3$): 215.25 ppm, 200.57, 147.96, 145.76, 130.37, 129.05, 128.96, 128.85, 127.55, 126.42, 92.59, 84.05, 77.05.

IR (film): 3062 cm^{-1}, 2926, 2872, 1733, 1495, 1449, 1164, 1074, 965, 761.

HRMS (CI, NH_3) *m/z* 312.1241 ($M + NH_4^+$) (calcd. for $C_{18}H_{14}O_4 + NH_4$ 312.1236).



6

To a 50 mL pear-shaped flask equipped with a reflux condenser and side-arm was added phenylcyclopentene (225 mg, 1.56 mmol), CCl_4 (15 mL) and TPP (2-3 mg). Oxygen was bubbled via a needle through the flask side-arm, while irradiating the solution at very close distance with a 150W sodium lamp. After 30 min, irradiation was discontinued and the mixture

was concentrated. Silica gel chromatography (8:1 hexanes/ethyl acetate) afforded 2-phenyl-cyclopentenyl hydroperoxide **6** (160 mg, 58%).

Data for 2-phenylcyclopentenyl hydroperoxide **6**:

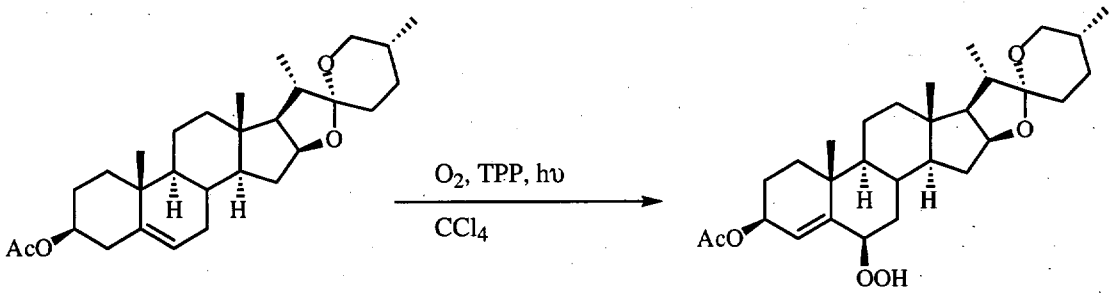
^{1}H NMR ($CDCl_3$): 7.56 ppm (2H, br d, *J*=7.1 Hz), 7.35 (2H, t, *J*=7.7 Hz), 7.26 (1H, m), 6.54 (1H, t, *J*=2.6 Hz), 5.53 (1H, dt, *J*=2.2, 7.1 Hz), 2.69 (1H, m), 2.46 (1H, qt, *J*=2.9, 8.8 Hz), 2.36 (1H, qt, *J*=2.4, 8.0 Hz), 2.27 (1H, m).

^{13}C NMR ($CDCl_3$): 139.40 ppm, 134.37, 129.50, 128.53, 127.49, 125.97, 90.74, 31.20, 29.10.

IR (film): 3392 cm^{-1} (broad), 2927, 2854, 1495, 1447, 1330, 1036, 756.

LRMS (EI) *m/z* 143 (M - 33).

(CI, NH_3) *m/z* 176 ($M + NH_4^+ - H_2O$), 194 ($M + NH_4^+$).



7

To a 50 mL pear-shaped flask equipped with a reflux condenser and side-arm was added 3-acetyl diosgenin (167 mg, 0.37 mmol), CCl_4 (11 mL) and TPP (2.2 mg). Oxygen was bubbled via a needle through the flask side-arm, while irradiating the solution at very close distance with a 150W sodium lamp for 2 h. Concentration, followed by silica gel chromatography (5:1 hexanes-EtOAc) afforded a mixture of three hydroperoxides (120 mg). Slow evaporation of this mixture from hexanes-EtOAc yielded **7** (10 mg), as white crystals.

Data for diosgenin hydroperoxide **7**:

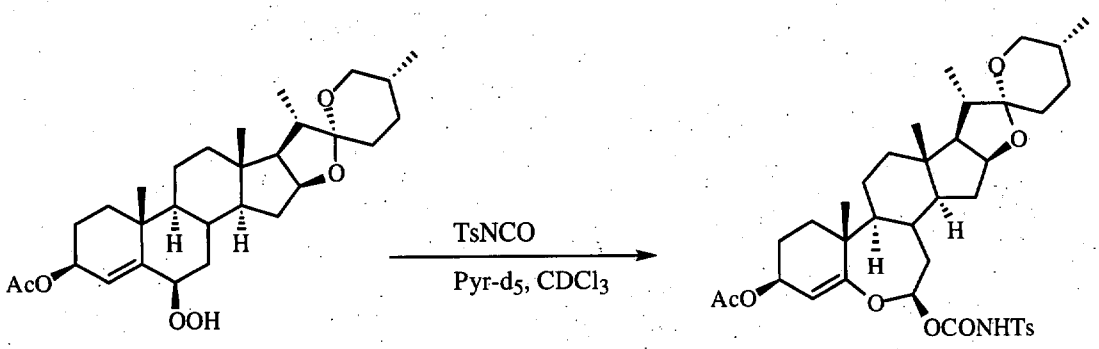
^{1}H NMR ($CDCl_3$): 7.64 ppm (1H, s), 5.60 (1H, br s), 5.23 (1H, br t, *J*=7.5 Hz), 4.39 (1H, q, *J*=7.5 Hz), 4.33 (1H, br s), 3.47 (1H, dd, *J*=3.0, 10.0 Hz), 3.36 (1H, t, *J*=10.9 Hz), 2.06 (3H, s), 2.04-0.98 (22H, m), 0.96 (3H, d, *J*=6.9 Hz), 0.78 (9H, m).

^{13}C NMR ($CDCl_3$): 170.94 ppm, 143.62, 128.78, 109.27, 86.56, 80.61, 70.54, 66.85, 62.00, 55.92, 53.69, 41.60, 40.45, 39.66, 36.68, 36.28, 35.46, 31.60, 31.33, 30.37, 30.27, 28.75, 24.74, 21.37, 20.52, 20.18, 17.11, 16.39, 14.47.

IR (film): 3344 cm^{-1} (br), 2950, 2873, 2861, 1734, 1455, 1374, 1240, 1175, 1156, 1052, 1031, 980, 898, 866, 756.

LRMS (FAB, NaI) *m/z* 511 ($M + Na^+$).

HRMS (FAB, NaI) *m/z* 511.3048 ($M + Na^+$) (calcd. for $C_{29}H_{44}O_6Na$ 511.3036).



7 **8**

To a solution of diosgenin hydroperoxide **7** (2.2 mg, 4.5 μmol) in $CDCl_3$ (0.4 mL) was added TsNCO (3 μL, 20 μmol). When TLC indicated complete consumption of starting material (no enone could be detected by crude ^1H NMR), the mixture was concentrated and purified by size-exclusion chromatography to give ring-expanded carbamate enol ether **8** (2.6 mg, 84%).

In a separate run, the presence of pyridine-d5 was shown to have no effect on the outcome of reaction.

Data for diosgenin-derived carbamate **8**:

^1H NMR ($CDCl_3$): 7.93 ppm (2H, d, *J*=8.3 Hz), 7.43 (1H, br s), 7.35 (2H, d, *J*=8.3 Hz), 6.01 (1H, br s), 5.33 (1H, d, *J*=4.5 Hz), 5.19 (1H, m), 4.36 (1H, dt, *J*=7.5, 6.3 Hz), 3.47 (1H, dd, *J*=3.0, 10.0 Hz), 3.36 (1H, t, *J*=10.9 Hz), 2.45 (3H, s), 2.00 (3H, s), 2.00-1.10 (22H, m), 1.01 (3H, s), 0.97 (3H, d, *J*=6.9 Hz), 0.84 (3H, s), 0.80 (3H, d, *J*=6.3 Hz).

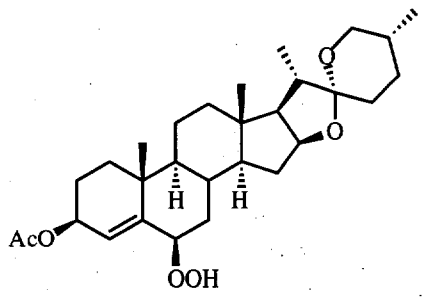
^{13}C NMR ($CDCl_3$): 170.63 ppm, 162.44, 145.20, 135.42, 129.76, 128.29, 112.96, 109.04, 97.05, 79.79, 67.42, 66.89, 62.49, 54.96, 48.25, 41.81, 40.84, 40.71, 39.41, 35.32, 32.56, 31.88, 31.47, 30.61, 30.27, 29.69, 28.80, 23.95, 22.07, 21.69, 21.27, 20.04, 17.14, 16.32, 14.55.

IR (film): 3228 cm^{-1} (br), 2951, 2927, 2878, 2854, 1734, 1455, 1353, 1241, 1167, 1092, 1056, 1018, 977, 898, 762.

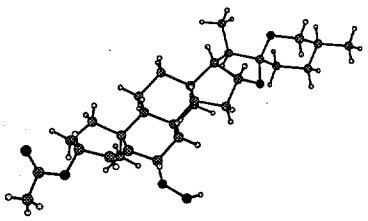
LRMS (FAB, NaI) *m/z* 708 ($M + Na^+$).

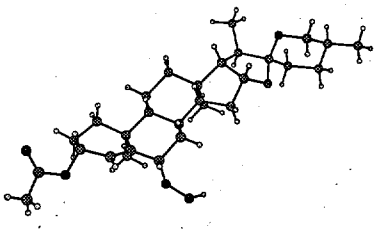
HRMS (FAB, NaI) *m/z* 708.3184 ($M + Na^+$) (calcd. for $C_{37}H_{51}NO_9SNa$ 708.3182).

Crystal Structure Information



7





Crystal data and structure refinement for **7**:

Empirical formula	C29 H44 O6
Formula weight	488.64
Temperature	213(2) K
Wavelength	0.71073 A
Crystal system, space group	Monoclinic, P2(1)
Unit cell dimensions	a = 10.7818(15) A alpha = 90 deg.
	b = 9.4792(13) A beta = 107.805(3) deg.
	c = 13.8552(18) A gamma = 90 deg.
Volume	1348.2(3) A^3
Z, Calculated density	2, 1.204 Mg/m^3
Absorption coefficient	0.082 mm^-1
F(000)	532
Crystal size	0.20 x 0.10 x 0.05 mm
Theta range for data collection	1.54 to 22.50 deg.
Index ranges	-11<=h<=11, -10<=k<=10, -9<=l<=14
Reflections collected / unique	5777 / 3411 [R(int) = 0.0962]
Completeness to 2theta = 22.50	99.8%
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3411 / 1 / 316
Goodness-of-fit on F^2	1.161
Final R indices [I>2sigma(I)]	R1 = 0.0828, wR2 = 0.1413
R indices (all data)	R1 = 0.1678, wR2 = 0.1826
Absolute structure parameter	-1(3)
Largest diff. peak and hole	0.206 and -0.283 e.A^-3