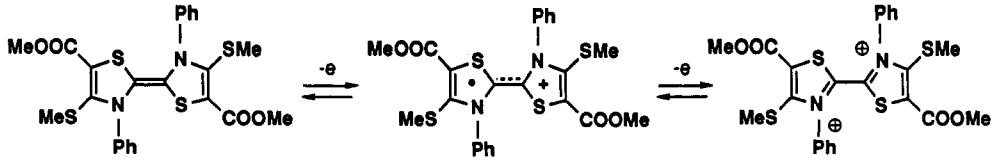
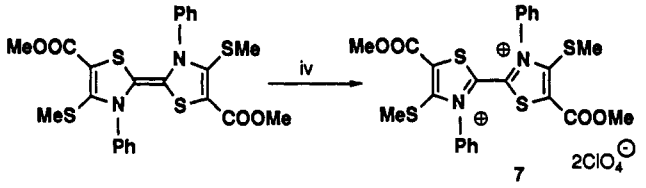
Scheme II



Scheme III[a]



[a] (iv) $PhI(OOCMe)_2$, $HClO_4$, dioxane, 61%.

methyl groups disappears for the dication salt 7 in $CDCl_3$ solution. The existence of 4 as an E/Z mixture is not unique among tetrathiafulvalene analogues. Thus, *sym*-diselenadithiafulvalene exists in solution as an almost equal mixture of E and Z isomers.[8]

The observed properties of compound 4 strongly suggest that bis(thiazolinylidenes) bearing appropriate electron-withdrawing groups may function as a new class of donors in the synthesis of conducting charge-transfer salts. This possibility is under investigation in our laboratories.[9]

Experimental Section

General. Cyclic voltammograms were measured in dichloroethane solution (with 0.1 M TBAHFP supporting electrolyte) with a BAS CV-27 cyclic voltammograph, platinum disk (working), platinum wire (auxiliary), and SCE (reference) electrodes. Scan rate was 0.070 V/s.

5-Carbomethoxy-4-(methylthio)-3-phenylthiazoline-2-selone (6). To a solution of 4-(methylthio)-3-phenyl-2-thioxo-1,3-thiazoline-5-carboxylic acid methyl ester (1.00 g, 3 mmol) in 15 mL of $CHCl_3$ were added $HC(OEt)_3$ (2 mL) and Et_2OBF_3 (2 mL). The reaction mixture was heated to boling and left overnight. The resulting 2-(ethylthio)-1,3-thiazolium fluoroborate was precipitated with ether, filtered off, dried, and dissolved in 15 mL of dry acetonitrile. This solution was added dropwise to a solution of sodium hydroselenide made from powdered selenium (0.53 g, 6 mmol) and sodium borohydride (0.25 g, 6.6 mmol) in 30 mL of absolute ethanol under nitrogen. After stirring for 20 min, the reaction mixture was diluted with water (100 mL). The precipitate was filtered off and washed with water. The resulting yellow solid was dissolved in benzene, and the solution was dried over $CaCl_2$ overnight then filtered through silica gel, eluting with benzene (6 × 40 mL). After removal of the solvent yellow crystals of selone 6 (1.05 g, 91%), mp 172 °C, were obtained: UV, λ_{max} ($\log_{10}\epsilon$), EtOH 327 (3.88), 380 (4.08) nm. Anal. Calcd for $C_{12}H_{11}O_2NS_2Se$: N, 4.07; S, 18.62. Found: N, 4.05; S, 18.75.

Bis(5-carbomethoxy-4-(methylthio)-3-phenyl-2-thiazolinylidene) (4). Selone 6 (1.5 g, 4.36 mmol) was suspended in triethyl phosphite (2.25 mL, 13.08 mmol), and the mixture was heated for 10 min at 100 °C. After the mixture was cooled to rt 10 mL of methanol was added, and the precipitate was filtered off, washed with methanol, and dried to give deep violet crystals of 4 (1.15 g, 100%): mp 254 °C; ^1H NMR ($CDCl_3$) δ 7.51–7.28 (m, 10 H, Ph), 3.83 and 3.79 (s, 6 H, OMe), 2.19 and 2.12 (s, 6 H, SMe); MS m/e 530 (M^+, 84), 453 (100), 291 (28), 265 (7), 150 (9), 135 (22). Anal. Calcd for $C_{24}H_{22}N_2O_4S_4$: C, 54.32; H, 4.18; N, 5.28; S, 24.16. Found: C, 53.88; H, 4.09; N, 5.27; S, 24.08.

Acknowledgment. We thank the National Science Foundation for partial support of this work through Grant No. CHE9001714 and IREX (International Research and Exchanges Board) for fellowship support to G.V.T.

Registry No. 4, 137627-27-1; 5, 137627-29-3; 6, 137627-30-6; 4-(methylthio)-3-phenyl-2-thioxo-1,3-thiazoline-5-carboxylic acid methyl ester, 125011-68-9.

(8) (a) Engler, E. M.; Patel, V. V. *J. Chem. Soc., Chem. Commun.* **1975**, 671. (b) Lakshmikantham, M. V.; Cava, M. P. *J. Org. Chem.* **1980**, *45*, 2632.

(9) For the sake of simplicity, we suggest the trivial name dithiadiazafulvalene (DTDAF) for 2,2′-bis(thiazolinylidene). Compound 4 would then be 3,3-diphenyl-4,4-bis(methylthio)-5,5-dicarbomethoxy-DTDAF.

2-Methoxyprop-2-yl Hydroperoxide: A Convenient Reagent for the Synthesis of Hydroperoxides and Peracids

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Received August 27, 1991

During the course of studies into hydroperoxide synthesis, we became interested in the nucleophilic introduction of the hydroperoxide group onto an aliphatic backbone. Standard methods for nucleophilic introduction of hydroperoxides require prolonged reaction with concentrated solutions of hydrogen peroxide under strongly basic conditions.[1,2] Based on our earlier results with ketalized hydroperoxides, we reasoned that a half-ketalized hydrogen peroxide such as 1 might rapidly react with alkyl halides under mild conditions to directly afford a protected alkyl hydroperoxide; subsequent unmasking would then cleanly provide the desired alkyl hydroperoxide[3] (Scheme I). We report herein the successful application of this strategy toward the synthesis of aliphatic hydroperoxides and a variety of peracids.

The necessary reagent, 2-methoxyprop-2-yl hydroperoxide (1), is easily generated through ozonolysis of 2,3-dimethylbutene in either MeOH or $MeOH/CH_2Cl_2$.[4] Removal of solvent in vacuo and replacement with the desired reaction solvent affords easily handled solutions of 1.[5] The application of 1 to the synthesis of aliphatic perketals and hydroperoxides is shown in Scheme II. Reaction of 1, an alkyl halide, and CsOH in DMF results in rapid disappearance of the halide and formation of the corresponding perketal.[6] Reactions with primary bromides proceed cleanly to afford moderate to good yields of the corresponding perketals. All perketals are stable to

(1) Williams, H. R.; Mosher, H. S. *J. Am. Chem. Soc.* **1954**, *76*, 2984–87.

(2) Williams, H. R.; Mosher, H. S. *J. Am. Chem. Soc.* **1954**, *76*, 2987–90.

(3) Dussault, P. H.; Sahli, A. S. *Tetrahedron Lett.* **1990**, *33*, 5117–20.

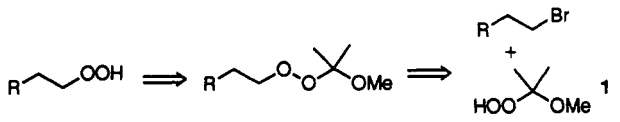
(4) Murray, R. W.; Agarwal, S. K. *J. Org. Chem.* **1985**, *50*, 4698–4702.

(5) We have always limited preparation of 1 to ≤3 g. Peroxides and hydroperoxides are handled and stored at or below room temperature in the presence of 0.1% butylated hydroxytoluene (BHT).

(6) The calculated amounts of 1 are based upon the quantity of dimethylbutene initially subjected to ozonolysis. A requirement for a slight excess of 1 is likely due to loss of material during concentration.

0022-3263/92/1957-1009$03.00/0

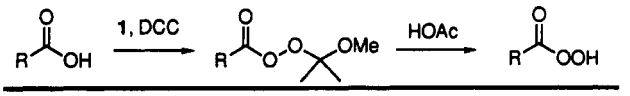
Scheme I



Scheme II. Synthesis of Hydroperoxides

$CH_3(CH_2)_{15}$-Br	76%	$CH_3(CH_2)_{15}$-OOH	70%
$CH_3(CH_2)_{11}$-Br	73%	$CH_3(CH_2)_{11}$-OOH	68%
$CH_3(CH_2)_9$-Br	72%	$CH_3(CH_2)_9$-OOH	65%
(*S*)-2-bromooctane	25%	(*R*)-2-octyl-OOH	75%

Scheme III. Synthesis of Peracids



$CH_3(CH_2)_{10}COOH$	92%	$CH_3(CH_2)_{10}CO_3H$	88%
$CH_3(CH_2)_9COOH$	88%	$CH_3(CH_2)_9CO_3H$	87%
(*E*)-PhCH=CHCOOH	70%	(*E*)-PhCH=CHCO$_3$H	48%
$CH_3CH_2CH(Ph)COOH$	65%	$CH_3CH_2CH(Ph)CO_3H$	60%

normal workup, purification, and storage. In all cases, acidic hydrolysis affords the desired hydroperoxides in good overall yield and with excellent purity. Displacement of secondary bromides or iodides proved more troublesome. Our standard conditions resulted in capricious yields while attempted displacements of mesylates, nosylates, or triflates were unsuccessful. The reduced yield of secondary peroxides in displacements of secondary halides is well-precedented in earlier studies.[2] We have found that the use of KOtBu/18-crown-6 in benzene leads to a more reproducible yield (15–25%) of secondary perketal. Displacement at secondary centers proceeds with net inversion. Displacement of (*S*)-2-bromooctane ($[\alpha]_D$ = +39.2 ($CHCl_3$)) affords optically active perketal ($[\alpha]_D$ = −11.0 ($CHCl_3$)).[7,8] Deprotection provides (*R*)-2-octyl hydroperoxide ($[\alpha]_D$ = −4 ($CHCl_3$)).[9] ^1H NMR analysis of the corresponding (−)-2-phenylcyclohexyl perketal, prepared by the method of Porter, indicated that the hydroperoxide was formed in 85% ee.[10]

We reasoned that our general strategy might also provide an extremely mild method for peracid synthesis in which reagent 1 would behave as the equivalent of anhydrous hydrogen peroxide. The results of our experiments are shown in Scheme III. Dicyclohexylcarbodiimide-mediated esterification of 1 with carboxylic acids affords high yields of the 2-methoxypropyl peresters. Subsequent hydrolysis provides peracids uncontaminated with either the carboxylic acid or the diacyl peroxide.[11] The transformation of cinnamic acid to percinnamic acid demonstrates the utility of this method for sensitive substrates. It is unlikely that traditional conditions for peracid synthesis (cinnamoyl chloride/H_2O_2/base) would be compatible with the presence of the enoate group. The methoxypropyl peresters are all stable to flash chromatography and characterization; however, the cinnamic and 2-phenylbutyric peresters begin to decompose within a day. All peresters are cleanly deprotected with wet acetic acid to the corresponding peracids. The identity of each peracid was confirmed by reduction and comparison with the corresponding carboxylic acid.

In conclusion, we have demonstrated that hemiketalized hydrogen peroxide can be used as an easily obtained hydrogen peroxide equivalent for synthesis of hydroperoxides and peracids.

Caution. Although we have not encountered any specific dangers in the course of this work, standard precautions for handling peroxides (avoidance of heat, light, or metal salts, work behind shields, use of a stabilizer)[5] should be followed whenever possible.

Experimental Section

All reagents and solvents were used as supplied commercially, except DMF, which was stored over activated 4-Å sieves. ^1H and ^{13}C NMR spectra were recorded on 200-, 300-, 360-, or 500-MHz spectrometers in $CDCl_3$. Optical rotations were obtained in a 1-dm cell in $CHCl_3$ unless otherwise noted. Elemental analyses were obtained from Desert Analytics, Tucson, AZ. Perketals, hydroperoxides, peracids, and peresters were all stored in the presence of approximately 0.1% butylated hydroxytoluene (BHT). Progress of reactions involving peroxides were monitored by TLC, using an *N,N'*-dimethyl-*p*-phenylenediamine indicator; hydroperoxides and peracids yield an immediate reddish-pink spot while perketals or peresters exhibit a pink or green-red color after mild charring.[12]

2-Methoxyprop-2-yl hydroperoxide (1) is obtained by ozonolysis of a −78 °C solution of 2,3-dimethyl-2-butene (10 mmol) in 30 mL of 85:15 CH_2Cl_2/MeOH in the presence of 5–10 mg of $NaHCO_3$. The ozonolysis is stopped when the blue tint of free ozone persists; excess ozone is then purged with a stream of N_2. A small amount of BHT is added (0.01 mmol), and the solution is allowed to warm to room temperature. The major portion of the solvent is removed on a rotary evaporator (water bath temperature ≤ 30 °C!), and the partially concentrated solution is briefly (30 s to 1 min) subjected to high vacuum (0.5 mm) to afford hydroperoxide 1. Although we have found that refrigerated samples of 1 are stable for weeks, the crude oil is typically diluted with the desired reaction solvent and used immediately: R_f = 0.35 (20% EA/hex); ^1H NMR (500 MHz) δ 7.91 (s, 1 H, OOH, broadens and shifts to ca. 9 ppm in high concentrations), 3.30 (s, 3 H), 1.40 (s, 6 H); ^{13}C NMR (125 MHz) δ 104.95, 48.94, 21.91.

Synthesis of Primary Perketals. To a 0 °C solution of bromoalkane (2.5 mmol) in DMF (5 mL) is added CsOH (3.1 mmol) followed by a solution of 2-methoxyprop-2-yl hydroperoxide (3 mmol) in DMF (5 mL). The initially colorless reaction becomes yellow and later brown. Upon consumption of starting material (TLC, typically 1–2 h) the reaction is made basic with 5% NaOH, diluted with 10 mL of H_2O, and extracted with ether (3 × 15 mL). The organic extracts are washed with H_2O (10 mL), dried over Na_2SO_4, and concentrated. Flash chromatography with ethyl acetate/hexane (EA/hex) provides the primary perketals as colorless oils in 65–75% yield.

Synthesis of Secondary Perketals. To a solution of 2-bromooctane (1 mmol), hydroperoxide 1 (1.2 mmol), and 18-crown-6 (1 mmol) in 5 mL of toluene is added potassium *tert*-butoxide (2 mmol) in small portions. After stirring for 8 h, the yellow solution is directly subjected to flash chromatography. Elution with 2.5–5% EA/hex affords 2-methoxypropyl 2-octyl peroxide in 15–25% yield.

Synthesis of Peresters. To a solution of carboxylic acid (1 mmol) in CH_2Cl_2 (6 mL) is added dicyclohexylcarbodiimide (DCC, 1.6 mmol). To the resulting suspension is added dropwise a solution of hydroperoxide 1 (1.2 mmol) in CH_2Cl_2 (2 mL) followed

(7) Synthesized from (*R*)-(−)-2-octanol ($[\alpha]_D$ = −9.5), Aldrich; [lit. $[\alpha]_D$ = −10.38]. Jung, M. E.; Ornstein, P. L. *Tetrahedron Lett.* **1977**, 2659–62.
(8) (*S*)-2-Bromooctane: $[\alpha]_D$ = +43 (MeOH) for (*S*)-(+)-2-bromooctane. Schmidt, S. P.; Brooks, D. W. *Tetrahedron Lett.* **1987**, *28*, 767–8. $[\alpha]_D$ = +44.1 (neat). Hudson, H. R. *Synthesis* **1969**, 112–19.
(9) (*R*)-2-Octyl hydroperoxide: $[\alpha]_D$ = −2.5 (c = 1, $CHCl_3$). Johnson, R. A.; Nidy, E. G.; Merritt, M. V. *J. Am. Chem. Soc.* **1978**, *100*, 7960–66.
(10) Porter, N. A.; Dussault, P.; Breyer, R. A.; Kaplan, J.; Morelli, J. *Chem. Res. Tox.* **1990**, *3*, 236–243.
(11) Rakhimov, A. I.; Androsyuk, E. R. *Zh. Org. Khim.* **1981**, *17*, 1652.
(12) Smith, L. L.; Hill, F. L. *J. Chromatogr.* **1972**, *66*, 101–109.

by 4-(dimethylamino)pyridine (DMAP, 0.1 mmol, 10 mol %). The suspension was stirred for 4–8 h and concentrated in vacuo. The crude residue is taken up in EA/hex and directly subjected to flash chromatography to provide the peresters in 65–90% yield.

Deprotection. The perketal (0.6–1 mmol) is dissolved in a freshly prepared solution of 90% HOAc/10% H_2O (2–5 mL) along with several drops of a 0.1 M ether solution of BHT. After stirring for 0.5–1 h, the reaction is worked up by either of the following methods to afford a 65–75% yield of alkyl hydroperoxide (48–88% for peracids). (A) The reaction is concentrated under high vacuum and directly subjected to flash chromatography. This method is superior for high boiling hydroperoxides and for peracids. (B) The reaction is quenched with 5% $NaHCO_3$ (10 mL), extracted with ether (3 × 10 mL), and dried over Na_2SO_4. After removal of solvent in vacuo, the crude hydroperoxide is purified by flash chromatography.

2-Methoxyprop-2-yl hexadecyl peroxide (hexadecyl perketal): R_f = 0.50 (10% EA/hex); ^{1}H NMR (360 MHz) δ 3.99 (t, 2 H, J = 6.7, CH_2COO), 3.30 (s, 3 H, OCH_3), 1.60 (m, 2 H, CH_2COOH), 1.38 (s, 6 H, 2 CH_3), 1.24 (bs, 26 H, CH_2), 0.87 (t, 3 H), J = 6.7, CH_3CH_2); ^{13}C NMR (50 MHz) 104.5, 75.2, 49.1, 31.9, 29.7, 29.6, 29.5, 29.45, 29.36, 27.8, 26.1, 22.72, 22.68, 14.1; IR (neat) 2993, 2923, 2854, 1466, 1377, 1367, 1209, 1184, 1155, 1074 cm^{-1}. Anal. Calcd for $C_{20}H_{42}O_3$: C, 72.67; H, 12.81. Found: C, 73.10, H, 12.49.

Hexadecyl hydroperoxide: R_f = 0.28 (10% EA/hex); ^{1}H NMR (360 MHz) δ 7.85 (s, 1 H, OOH), 4.01 (t, 2 H, J = 6.7, CH_2COO), 1.60 (m, 2 H, CH_2COOH), 1.24 (26 H, CH_2), 0.87 (t, 3 H, J = 6.71, CH_3CH_2); ^{13}C NMR (50 MHz) 77.2, 31.9, 29.7, 29.6, 29.5, 29.44, 29.36, 27.6, 25.9, 22.7, 14.1; IR (neat) 3371 (b), 2954, 2917, 2850, 1466, 1377, 908, 734 cm^{-1}.

2-Methoxyprop-2-yl dodecyl peroxide (dodecyl perketal): R_f = 0.54 (10% EA/hex) ^{1}H NMR (200 MHz) δ 3.99 (t, 2 H, J = 6.7, CH_2COO), 3.30 (s, 3 H, OCH_3), 1.60 (m, 2 H, CH_2COOH), 1.38 (s, 6 H, 2 CH_3), 1.24 (bs, 18 H, CH_2), 0.86 (t, 3 H, J = 6.6, CH_3CH_2); ^{13}C NMR (50 MHz) 104.4, 75.1, 49.1, 31.9, 29.6, 29.55, 29.50, 29.4, 29.3, 27.8, 26.1, 22.7, 22.6, 14.0; IR (neat) 2993, 2925, 2854, 1466, 1377, 1367, 1209, 1134, 1157, 1074, 858 cm^{-1}. Anal. Calcd for $C_{16}H_{34}O_3$: C, 70.54; H, 11.84. Found: C, 70.26; H, 12.16.

Dodecyl hydroperoxide: R_f = 0.41 (10% EA/hex); ^{1}H NMR (200 MHz) δ 7.9 (bs, 1 H, OOH), 4.03 (t, 2 H, J = 6.8, CH_2COO), 1.64 (m, 2 H, CH_2COOH), 1.26 (bs, 18 H, CH_2), 0.88 (t, 3 H, J = 6.4, CH_3CH_2); ^{13}C NMR (50 MHz) 77.2, 31.9, 29.62, 29.57, 29.5, 29.4, 29.3, 27.5, 25.9, 22.7, 14.1; IR (neat) 3400 (b), 2924, 2854, 1466, 1377, 1169, 1010, 818 cm^{-1}.

2-Methoxyprop-2-yl decyl peroxide (decyl perketal): R_f = 0.50 (10% EA/hex); ^{1}H NMR (360 MHz) δ 3.99 (t, 2 H, J = 6.8, CH_2COO), 3.30 (s, 3 H, OCH_3), 1.60 (m, 2 H, CH_2COOH), 1.38 (s, 6 H, 2 CH_3), 1.25 (bs, 14 H, CH_2), 0.86 (t, 3 H, J = 6.8, CH_3CH_2); ^{13}C NMR (50 MHz) 104.3, 74.9, 48.9, 31.8, 29.4, 29.3, 29.2, 27.7, 26.0, 22.5, 13.9; IR (neat) 2993, 2925, 2854, 1466, 1377, 1367, 1209, 1184, 1157, 1074 cm^{-1}. Anal. Calcd for $C_{14}H_{30}O_3$: C, 68.25; H, 12.27. Found: C, 69.33; H, 12.19.

Decyl hydroperoxide: R_f = 0.36 (10% EA/hex); ^{1}H NMR (360 MHz) δ 7.85 (s, 1 H, 00H), 4.01 (t, 2 H, J = 6.6, CH_2COO), 1.60 (m, 2 H, CH_2COOH), 1.25 (bs, 14 H, CH_2), 0.87 (t, 3 H, J = 6.8, CH_3CH_2); ^{13}C NMR (50 MHz) 77.2, 31.9, 29.5 (2 C), 29.4, 29.3, 27.5, 25.9, 22.7, 14.1; IR (neat) 3389 (b), 2925, 2854, 1466, 1377, 1036 cm^{-1}.

2-Methoxyprop-2-yl 2(*R*)-octyl peroxide (2-octyl perketal): R_f = 0.6 (10% EA/Hex); $[\alpha]_D$ = −11.0 (c = 1, $CHCl_3$); ^{1}H NMR (360 MHz) δ 4.06 (m, 1 H, CHOOH), 3.29 (s, 3 H, OCH_3), 1.6 (m, 2 H, CH_2COOH), 1.38 (s, 6 H, 2 CH_3), 1.27 (b, 8 H, CH_2), 1.2 (d, 3 H, J = 6.1, CH_3CH), 0.87 (t, 3 H, J = 6.9, CH_3CH_2-); ^{13}C NMR (125 MHz) 104.3, 79.8, 49.1, 34.6, 31.8, 29.4, 25.5, 23.0, 22.8, 22.6, 18.7, 14.0; IR (neat) 2931, 2858, 1464, 1377, 1367, 1209, 1184, 1144, 1074, 839 cm^{-1}.

(*R*)-(−)-2-Octyl hydroperoxide: R_f = 0.3 (10% EA/hex); $[\alpha]_D$ = −4 (c = 0.5, $CHCl_3$); ^{1}H NMR (500 MHz) δ 7.66 (s, 1 H, OOH), 4.06 (m, 1 H, CHOOH), 1.6 (m, 2 H, CH_2COOH), 1.27 (8 H, CH_2), 1.2 (d, 3 H, J = 6.0, CH_3CH), 0.87 (t, 3 H, J = 6.9 CH_3CH_2); ^{13}C NMR (75 MHz) 81.7, 34.0, 31.7, 29.3, 25.3, 22.6, 18.1, 14.0; IR (neat) 3390 (b), 2954, 2924, 2854, 1568, 1466, 1375, 1146, 1116, 1092 cm^{-1}.

Formation of the *trans*-2-Phenylcyclohexyl Perketal. To a solution of 3 mg of 2-octyl hydroperoxide in 100 μL of CH_2Cl_2 is added 5 μL of (−)-*trans*-2-phenylcyclohexyl 2-propenyl ether[10] and a trace of PPTS. The solvent is removed with a stream of N_2, and the crude mixture is filtered through a 1-g plug of silica gel with EA/hex to remove 2-phenylcyclohexanol. Comparison of the ^{1}H NMR spectrum (300 or 500 MHz) of the crude product with a spectrum obtained after ketalization with racemic enol ether allows determination of the diastereomer ratio through comparison of the methyl singlets at δ 0.50 and 0.48 ppm.

Peroxydodecanoic acid, 2-methoxyprop-2-yl ester (lauric perester): R_f = 0.72 (20% EA/hex) ^{1}H NMR (360 MHz) δ 3.32 (s, 3 H, OCH_3), 2.30 (t, 2 H, J = 7.5, CH_2CO), 1.65 (app p, 2 H, CH_2CH_2CO), 1.45 (s, 6 H, 2 CH_3), 1.24 (16 H, CH_2), 0.87 (t, 3 H, J = 6.8, CH_3CH_2); ^{13}C NMR (50 MHz) 170.6, 106.7, 49.7, 31.8, 31.0, 29.51, 29.49, 29.3, 29.2, 29.1, 28.9, 24.9, 22.6, 22.4, 14.0; IR (neat) 2995, 2924, 2854, 1782, 1369, 1219, 1134, 1090, 1068, 822 cm^{-1}; exact mass calculated for $C_{16}H_{32}O_4K$ (M^+ + K) 327.1940, found 327.1927.

Peroxydodecanoic acid (lauric peracid): R_f = 0.36 (10% EA/hex); ^{1}H NMR (360 MHz) δ 2.41 (t, 2 H, J = 7.5, CH_2COO), 1.67 (m, 2 H, CH_2CH_2CO), 1.25 (16 H, CH_2), 0.87 (t, 3 H, J = 6.8, CH_3CH_2); ^{13}C NMR (50 MHz) 174.6, 31.9, 29.54, 29.51, 29.32, 29.29, 29.0, 28.9, 24.6, 22.6, 14.1; IR (neat) 3263, 3203, 2952, 2917, 2870, 2846, 1753, 1734(s), 1466, 1419 cm^{-1}; exact mass calculated for $C_{15}H_{30}O_4Na$ (M^+ + Na) 297.2043, found 297.2033.

Peroxyundecanoic acid, 2-methoxyprop-2-yl ester: R_f = 0.44 (10% EA/hex); ^{1}H NMR (360 MHz) δ 3.32 (s, 3 H, OCH_3), 2.31 (t, 2 H, J = 7.5, CH_2CO), 1.66 (m, 2 H, CH_2CH_2CO), 1.45 (s, 6 H, 2 CH_3), 1.25 (14 H, CH_2), 0.87 (t, 3 H, J = 6.8, CH_3); ^{13}C (50 MHz) 170.5, 106.6, 49.6, 31.8, 30.9, 29.4, 29.3, 29.1, 29.0, 28.9, 24.9, 22.5, 22.3, 13.9; IR (neat) 2996, 2927 (s), 2856, 1781 (s), 1466, 1380, 1371, 1218, 1133, 821 cm^{-1}.

Peroxyundecanoic acid: R_f = 0.38 (10% EA/hex); ^{1}H NMR (360 MHz) δ 2.40 (t, 2 H, J = 7.5, CH_2CO), 2.09 (bs, 0.5 H, CO_3H), 1.69 (app pentet, 2 H, J = 7, CH_2CH_2CO); 1.25 (14 H, CH_2), 0.87 (t, 3 H, J = 6.5, CH_3); ^{13}C (50 MHz) 174.6, 31.9, 30.4, 29.5, 29.33, 29.25, 29.0, 28.9, 24.6, 22.7, 14.1; IR (neat) 3261, 3203, 2954, 2917 (s), 2846, 1752, 1733 (s), 1467, 1419 cm^{-1}.

3-Phenyl-2-peroxypropenoic acid, 2-methoxyprop-2-yl ester (cinammic perester): R_f = 0.40 (10% EA/hex); ^{1}H NMR (200 MHz) δ 7.94 (d, 1 H, J = 16.2, PhCH=), 7.50–7.39 (5 H, Ph), 6.44 (d, 1 H, J = 16, =CH), 3.37 (s, 3 H, OCH_3), 1.50 (s, 6 H, 2 CH_3); ^{13}C (50 MHz) 164.5, 146.1, 133.8, 130.6, 128.7, 128.0, 112.8, 106.9, 49.6, 22.3; IR (neat) 2995, 1757 (s), 1635, 1306, 1219, 1149, 1105 (s), 1066, 820, 761 cm^{-1}; exact mass calculated for $C_{13}H_{16}O_4Na$ (M^+ + Na) 259.0949, found 259.0930.

3-Phenyl-2-peroxypropenoic acid (cinnammic peracid): R_f = 0.33 in 10% ethyl acetate/hexane; ^{1}H NMR (200 MHz) δ 7.95 (d, 1 H, J = 16, PhCH=), 7.50–7.39 (5 H, Ph), 6.45 (d, 1 H, J = 16, =CH); ^{13}C (250 MHz) 167.5, 144.89, 134.3, 130.3, 128.9, 128.1, 117.7; IR (neat) 2995, 1718 (s), 1637, 1328, 1315, 1275, 1203, 1171 (s), 768 cm^{-1}.

(*RS*)-2-Phenylperoxybutanoic acid, 2-methoxyprop-2-yl ester (2-phenylbutyric perester): R_f = 0.47 (10% EA/hex); ^{1}H NMR (360 MHz) δ 7.3 (m, 5 H, Ph), 3.49 (t, 1 H, J = 7.2, PhCH), 3.27 (s, 3 H, OCH_3), 2.15 and 1.87 (m, 1 H, CH_2CH_2COO, ABXY) 1.41 and 1.36 (s, 3 H, CH_3), 0.94 (t, 3 H, J = 7.3, CH_3CH_2); ^{13}C NMR (50 MHz) 171.1, 137.9, 128.6, 127.9, 127.9, 107.0, 50.5, 49.8, 26.9, 22.5, 22.4, 12.1; IR (neat) 2968, 2943, 1776, 1371, 1219, 1151, 1124, 1062, 822, 698 cm^{-1}.

(*RS*)-2-Phenylperoxybutanoic acid: R_f = 0.37 (10% EA/hex); ^{1}H NMR (360 MHz) δ 11.4 (b, 1 H, CO_3H), 7.33 (5 H, Ph), 3.49 (t, 1 H, J = 7.2, PhCH), 2.15 and 1.87 (m, 1 H, PhCH_2, ABXY), 0.94 (t, 3 H, J = 7.3, CH_3CH_2); ^{13}C NMR (50 MHz) 175.0, 136.7, 128.8, 127.9, 49.9, 26.7, 11.9; IR (neat) 3276 (b), 2966, 2933, 1753, 1454, 1134, 1068, 698 cm^{-1}.

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Registry No. 1, 10027-74-4; $CH_3(CH_2)_{15}Br$, 112-82-3; $CH_3(CH_2)_{11}Br$, 143-15-7; $CH_3(CH_2)_9Br$, 112-29-8; $CH_3(CH_2)_{10}COOH$, 143-07-7; $CH_3(CH_2)_9COOH$, 112-37-8; (*E*)-PhCH=CHCOOH, 140-10-3; (*RS*)-$CH_3CH_2CH(Ph)COOH$, 7782-29-8; $CH_3(CH_2)_{16}O$-

OH, 4439-43-4; $CH_3(CH_2)_{11}OOH$, 3229-98-9; $CH_3(CH_2)_9OOH$, 4225-91-6; (*R*)-2-octyl-OOH, 68570-62-7; $CH_3(CH_2)_{10}CO_3H$, 2388-12-7; $CH_3(CH_2)_9CO_3H$, 676-08-4; (*E*)-PhCH=CHCO$_3$H, 137846-29-8; (*RS*)-$CH_3CH_2CH(Ph)CO_3H$, 137846-30-1; CsOH, 21351-79-1; H_2O_2, 7722-84-1; 2,3-dimethyl-2-butene, 563-79-1; (*S*)-2-bromooctane, 1191-24-8; 2-methoxyprop-2-yl hexadecyl peroxide, 137846-21-0; 2-methoxyprop-2-yl dodecyl peroxide, 137846-22-1; 2-methoxyprop-2-yl decyl peroxide, 137846-23-2; 2-methoxyprop-2-yl 2(*R*)-octyl peroxide, 137846-24-3; 2-methoxyprop-2-yl peroxydodecanoate, 137846-25-4; 2-methoxyprop-2-yl peroxyundecanoate, 137846-26-5; 2-methoxyprop-2-yl (*E*)-3-phenyl-2-peroxypropenoate, 137846-27-6; 2-methoxyprop-2-yl (*RS*)-2-phenylperoxybutanoate, 137846-28-7; (-)-*trans*-2-phenylcyclohexyl 2-propenyl ether, 116102-43-3; 2(*R*)-octyl 2-[(*trans*-(-)-2-phenylcyclohexyl)oxy]prop-2-yl peroxide, 126873-59-4.

Supplementary Material Available: ^{13}C NMR spectra for all perketals, hydroperoxides, peresters, and peracids and ^1H NMR spectra of *trans*-(-)-2-phenylcyclohexyl perketal (18 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

Synthesis of Some Ethylindeno[1,2,3-*cd*]pyrenes

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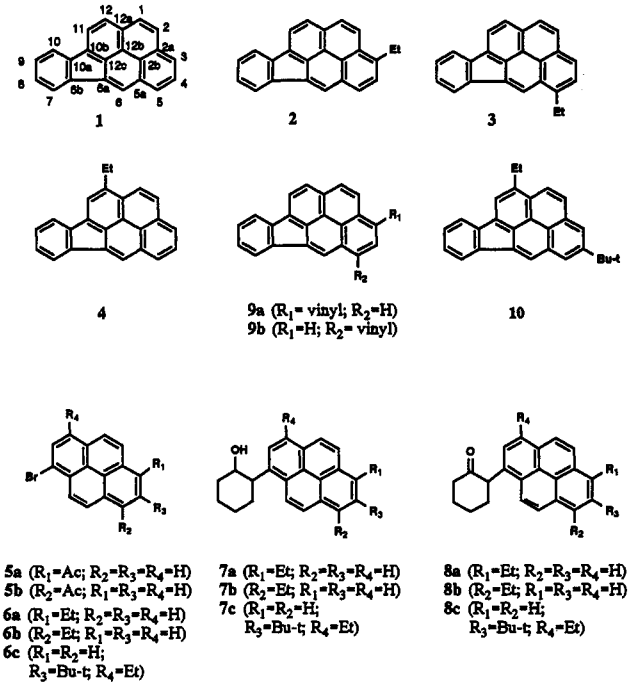
Indeno[1,2,3-*cd*]pyrene (**1**), a polycyclic aromatic compound (PAC) which possesses a fluoranthene framework, is an ubiquitous environmental pollutant that is generated by the combustion of fossil fuels and thus is present in direct emission sources like diesel exhaust.[1-3] Hydrocarbon **1** has also been shown to be both a mutagen and a carcinogen.[2,3] However, relatively little is known about its chemical and biological properties. For example, the results of Dewar-PI calculations predict that the reaction of **1** with electrophiles should yield products of C(3)- or C(5)-substitution.[4] Yet both bromination and Friedel–Crafts acetylation of **1** have yielded, predominantly, products of C(12) substitution, as the NMR spectra of the products have shown.[5] Additionally, the nitration of **1** by both acetyl nitrate and nitrogen dioxide have afforded the 12-nitro derivative[6] rather than the 8- or 9-nitro derivative.[7]

Here is described the synthesis of 3-ethyl- (**2**), 5-ethyl- (**3**) and 4-*tert*-butyl-12-ethylindeno[1,2,3-*cd*]pyrene (**10**) by the method of Cho and Harvey.[1] The ^1H and ^{13}C NMR spectroscopic characteristics were compared with those of the parent compound **1**. In addition, the results provide evidence of what sites of **1** are reactive toward electrophilic substitution.

Scheme I



Results and Discussion

Various bromoethylpyrenes were chosen as precursors of **2** and **3**. Thus, the Friedel–Crafts acetylation of 1-bromopyrene gave, as reported,[8] a ca. 2:3 mixture of 6- (**5a**) and 8-acetyl-1-bromopyrene (**5b**) (Scheme I). Attempts to separate the two isomers on a preparative scale were not successful. Therefore, the mixture was directly subjected to Wolff–Kishner reduction. Recrystallization of the mixture of products afforded pure 1-bromo-8-ethylpyrene (**6b**) (ca. 20%). What remained in the mother liquor was a mixture (ca. 1:1) of 1-bromo-6-ethylpyrene (**6a**) and **6b**.

Treatment of **6b** with, successively, BuLi and cyclohexene oxide yielded the corresponding substituted cyclohexanol **7b**. Similar treatment of the mixture of **6a** and **6b** described above and recrystallization of the mixture of products gave **7a**. The cyclohexanones **8a** and **8b** were obtained by the pyridinium dichromate (PDC) oxidation of **7a** and **7b**, respectively. The cyclodehydration of each ketone gave a mixture of hydrocarbons,[9] which was subjected to dehydrogenation without further purification.

The first attempt to prepare **2** from the products from the cyclodehydration of **8a**, by treatment with DDQ, gave only small amounts of **2** and 3-vinylindeno[1,2,3-*cd*]pyrene (**9a**). Similar treatment of the products from the cyclodehydration of **8b** gave **3** (in low yield) and its 5-vinyl analogue **9b**. A second attempt, which employed trityl trifluoroacetate (TTFA)[10] as the dehydrogenating reagent, was somewhat more successful. Byproducts like vinyl derivatives were not detected by TLC. However, isolating **2** (or **3**) from the dark green reaction mixture proved to be fairly difficult. A last attempt at aromatization, by Pd/C-catalyzed dehydrogenation, was more successful, although the yield of **2** depended on the reaction time.

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