for several months without noticeable decomposition or handling problems.

Tetra-*n*-butylammonium cyanide was purchased from Fluka and dried [60 °C (0.2 torr)] for 24 h prior to use. Solutions of this reagent were prepared in dry CH_3CN.

Preparation of MTM Ethers. A typical procedure follows: To a cold (−78 °C), stirred solution of menthol–MOM ether **8** (1 mmol) in 8.8 mL of dry CH_2Cl_2, under argon, was added a CH_2Cl_2 solution of dimethylboron bromide (1.73 M, 1.16 mL). The reaction mixture was stirred at −78 °C for 1 h and then treated with diisopropylethylamine (2.5 mmol) and a solution of methanethiol in CH_2Cl_2 (10 M, 0.3 mL). After 1 h at −78 °C the mixture was cannulated into a stirred mixture of THF (5 mL) and saturated aqueous $NaHCO_3$ (5 mL). Ether (50 mL) was then added. The organic layer was separated, washed with saturated aqueous $NaHCO_3$, water, and brine, and dried over $MgSO_4$. Removal of solvent and purification by flash chromatography gave pure menthol–MTM ether **9** (91%): IR (neat) 2955, 2920, 1061, 1050 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.76–1.12 (m, 3 H), 0.79 (d, J = 6.8 Hz, 3 H), 0.88 (d, J = 8.2 Hz, 3 H), 0.90 (d, J = 6.5 Hz, 3 H), 1.23 (m, 1 H), 1.35 (br m, 1 H), 1.57–1.71 (m, 2 H), 2.02–2.30 (overlapping m, 2 H), 2.14 (s, 3 H), 3.38 (ddd, J = 10.5, 10.5, 4.1 Hz, 1 H), 4.62 (d, A part of AB, J = 11.8 Hz, 1 H), 4.68 (d, B part of AB, J = 11.8 Hz, 1 H); MS m/e (relative intensity) 216 (2), 169 (26), 139 (38), 83 (100), 61 (10). Anal. Calcd for $C_{12}H_{24}OS$: C, 66.61; H, 16.78. Found: C, 66.47; H, 16.81.

Preparation of *O,S*-Acetals. In a typical procedure these compounds were prepared essentially as outlined above. After the addition of diisopropylethylamine and the appropriate thiol the reaction mixtures were stirred at −78 °C for only 15 min. Workup using 10% aqueous K_2CO_3 in place of saturated aqueous $NaHCO_3$ (vide supra) and purification yielded the desired *O,S*-acetals.

Preparation of Cyanomethyl Ethers. A typical procedure follows: To a cold (−78 °C), stirred solution of dodecanol–MOM ether **6** (0.5 mmol) in 1.9 mL of dry CH_2Cl_2, under argon, was added a solution of dimethylboron bromide (1.56 M, 0.64 mL) in CH_2Cl_2. After 1 h at −78 °C, solvent and excess reagent were removed under vacuum (0.25 torr, −78 °C to room temperature). The resultant material was dissolved in 2.5 mL of CH_2Cl_2, cooled to −78 °C, and then treated with a solution of *n*-Bu_4NCN (1.0 M, 1.5 mL) in CH_3CN. Stirring was continued at −78 °C for 1 h and room temperature for 1 h. Saturated aqueous $NaHCO_3$ (5 mL) and ether (50 mL) were then added. The organic layer was washed with saturated aqueous $NaHCO_3$, water, and brine and dried over $MgSO_4$. Concentration and purification by flash chromatography gave pure cyanomethyl ether **37** (84%): IR (neat) 2923, 2855, 1111 cm^{-1} (the CN absorption was not observed, see ref 22); ^1H NMR ($CDCl_3$) δ 0.88 (br t, 3 H), 1.22–1.40 (m, 18 H), 1.56–1.66 (m, 2 H), 3.58 (t, J = 6.0 Hz, 2 H), 4.24 (s, 2 H). Anal. Calcd for $C_{14}H_{27}ON$: C, 74.61; H, 12.08. Found: C, 74.80; H, 12.25.

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Registry No. **6**, 34458-41-8; **7**, 87770-95-4; **8**, 91898-14-5; **9**, 99054-41-8; **10**, 91898-15-6; **11**, 87770-94-3; **12**, 99054-42-9; **13**, 99054-38-3; **14**, 99054-43-0; **15**, 99054-39-4; **16**, 59304-70-0; **17**, 91898-33-8; **18**, 99054-44-1; **19**, 99054-40-7; **20**, 99096-76-1; **21**, 99054-58-7; **22**, 18824-63-0; **23**, 99054-46-3; **24**, 99054-45-2; **25**, 99054-47-4; **26**, 54815-13-3; **27**, 99054-48-5; **28**, 99054-49-6; **29**, 91898-23-6; **30**, 99054-50-9; **31**, 91928-35-7; **32**, 99054-51-0; **33**, 25632-03-5; **34**, 50438-51-2; **35**, 91898-11-2; **36**, 99054-52-1; **37**, 70282-70-1; **38**, 99054-53-2; **39**, 99054-54-3; **40**, 99054-55-4; **41**, 99054-56-5; **42**, 99054-57-6; Me_2BBr, 5158-50-9; *i*-Pr_2NEt, 7087-68-5; MeSH, 74-93-1; Br_4NCN, 10442-39-4; EtSH, 75-08-1; PhSH, 108-98-5; 4-(benzyloxy)-3-methoxybenzyl methyl sulfide, 99054-59-8.

Supplementary Material Available: Full characterization data (IR, ^1H NMR, mass spectral, chemical analysis) for all new compounds (5 pages). Ordering information is given on any current masthead page.

Applications of Di-*tert*-butyliminoxyl Radical to Organic Synthesis. Oxidation of Amines to Imines[1]

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Most iminoxyl radicals can be observed only in the form of transients by EPR spectroscopy. However, the highly hindered di-*tert*-butyliminoxyl radical (**1**) is sufficiently long-lived for it to be isolated as a volatile, blue liquid.[2,3] In inert solvents it decays with bimolecular kinetics to yield an O–C coupled dimer.[2]

$$\underset{\mathbf{1}}{t\text{-}Bu_2C{=}NO\cdot} \qquad \underset{\mathbf{2}}{t\text{-}Bu_2C{=}NOH}$$

In preliminary studies[2,4] it was shown that **1** abstracts hydrogen from a variety of organic compounds. We have previously studied the di-*tert*-butyliminoxyl-mediated oxidation of a variety of phenols at room temperature and found the radical to be an efficient reagent for the synthesis of quinones and related oxidation–addition compounds.[5] The reduction of the radical regenerates the parent oxime **2**, which can be separated from the reaction medium and reconverted into **1**.

Both in the former and present study it was advantageous to have an inexpensive and efficient synthesis of **1**. In the original study,[2,4] oxime **2** was oxidized to **1** with silver oxide in benzene. We now report a very straightforward approach that makes use of ceric ammonium nitrate to perform the oxidation of **2** in methanol in a few minutes at room temperature. The radical **1**, which gives a blue solution, can be used directly in methanol, extracted into pentane or hexane, or recovered neat after evaporation of the solvent. We have consistently obtained yields around 80% of **1** with this method, as long as an exact 1:1 molar ratio of starting reagents is present, since ceric ion also destroys the radical. The blue color of the radical is due to a weak absorption extending from about 530 to beyond 800 nm and can be used for spectrometric quantitation.

We have explored the feasibility of a direct, room-temperature dehydrogenation of primary and secondary amines with **1** to give the corresponding imines. In general, the literature procedures[6] for dehydrogenation of amines to imines do not have a wide scope and usually require strong conditions.

We report here the direct conversion of primary and secondary amines to imines with **1** in pentane or hexane under mild conditions. Due to the high inherent reactivity of most imines, in the initial attempts it was chosen to transform the imines in situ to the 2,4-dinitrophenylhydrazine derivatives of the corresponding carbonyl compounds.[7] *N*-Benzylmethylamine (**3**) was then chosen to carry out a detailed HPLC study of the reaction since the derived imine, *N*-benzylidenemethylamine (**4**) is commercially available and suitable as a reference compound in product analysis. The results are summarized in Table I.

For the cases when the 2,4-dinitrophenylhydrazine derivative isolation was used, the reported reaction time

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Table I. Oxidation of Amines with Di-*tert*-butyliminoxyl

	amine	product	reacn time, h	temp, °C	yield,[b] % DNP[a]	yield,[b] % HPLC[c]
1	Ph_2CHNH_2	$Ph_2C{=}NH$	4.0	25	79	
2	$PhCH(CH_3)NH_2$	$PhC(CH_3){=}NH$	8.5	25	42	
3	$PhCH_2NHCH_2Ph$	$PhCH{=}NCH_2Ph$	3.5	25	78	
4	$PhCH_2NH_2$	$PhCH{=}NH$	5.3	25	68	
5	$PhCH_2NH_2$	$PhCH{=}NH$	3.0	25		ca. 83[d]
6	**3**	**4**	5.0	25	43	
7	**3**	**4**	4.0	25		64
8	**3**	**4**	0.5	69		49
9	**3**	**4**	24.0	−5		76
10	**3**	**4**	16.0	25		43

[a] Isolated as the 2,4-dinitrophenylhydrazone. Reactions carried out in pentane. [b] Yields are referred to the starting amine. Two equivalents of radical per equivalent of amine. [c] Reactions for HPLC analysis were carried out in hexane, except for entry 10, in which acetonitrile was used. [d] Imine **4** used as reference.

refers to the moment when the blue to blue-green color of the radical in solution was no longer visible. Notably, the oxime **2** did not interfere with the conversion of the imine to the 2,4-DNP derivative.

After prolonged handling at ambient temperatures, the radical solution shows (HPLC) the presence of the dimer[8] and di-*tert*-butyl ketone,[8] but this in no way affects the outcome of the reactions as determined from control experiments.

The use of a more polar solvent or high temperatures does not improve the yields. Indeed, the best yields are obtained at low temperature in nonpolar solvents. Several control experiments indicated (HPLC) that, during and after the period of time needed to complete the reaction **3** → **4**, there was no noticeable reaction between **3** and **4**, **2** and **4**, or **1** and **4**. Also, after several hours of standing at room temperature in the dark, practically no change was detected by HPLC in the reaction mixture of **3** → **4**. These observations will prove of value for any use of solutions of the imines in subsequent transformations.[9]

Experimental Section

All the amines were commercially available materials and were used without further purification. HPLC was performed using a size exclusion column (IBM Corp), 250 × 7.0 mm, type M, poly(styrene/divinylbenzene) with mixed hexanes as mobile phase and refractive index difference detection.

Di-*tert*-butyl Ketoxime (2). The procedure of Mendenhall and Ingold[2] was followed to prepare the oxime in 81% yield. Sublimation under reduced pressure afforded pure material, mp 158 °C (lit.[10] mp 157.5–158 °C).

Di-*tert*-butyliminoxyl (1). The parent oxime **2** (0.738 g, 4.98 mmol) was dissolved in 35 mL of methanol and 2.758 g (4.98 mmol) of 99% cerium(IV) ammonium nitrate dissolved in 15 mL of methanol was quickly added with rapid stirring. The resulting blue solution was stirred for an additional 15 min, after which it was poured into a separatory funnel along with 40 mL of water and 15 mL of pentane. The layers were separated, the water phase was extracted with an additional 10 mL of pentane, and the organic phases were combined and dried over anhydrous sodium sulfate. The concentration of di-*tert*-butyliminoxyl in the deep blue solution obtained was determined spectrophotometrically at 800 nm (ϵ 4.7[2]), which indicated an 82.8% yield of the radical. When not in use, this stock solution was stored at −15 °C. After 1 month of occasional use, the maximum decay of the radical was about 12%.[11]

Reactions of 1 with Amines. (a) The typical procedure through which the imines were in situ converted to the 2,4-DNP derivatives is exemplified here for the case when diphenylmethylamine was used: To an oven dried, 50 mL three-necked flask equipped with a magnetic stirrer and nitrogen inlet was added 6.0 mL of a 0.135 M solution of **1** (0.81 mmol) in pentane followed by 73 μL (0.405 mmol) of 96% diphenylmethylamine (Aldrich). After 4 h of stirring at room temperature the blue color of the radical was no longer present, and the reaction mixture was immediately used in the next step.

2,4-Dinitrophenylhydrazone of Benzophenone. The above reaction mixture was poured into a freshly prepared ethanol solution of 2,4-dinitrophenylhydrazine reagent,[12] and an orange precipitate formed instantaneously. The mixture was heated to boiling for an additional 10 min and allowed to cool, and the precipitate was filtered, washed with aqueous methanol, and dried. The solid weighed 0.115 g (79%), mp 240–241 °C (lit.[12] mp 238–239 °C).

(b) For reactions where HPLC analysis was needed, the required amount of radical was taken from the stock solution in pentane, and after careful evaporation of the solvent under reduced pressure and low temperature, it was redissolved in hexane to run the main reaction in the same way as described above at the chosen temperature. Authentic samples of all the intervening compounds were used in both the qualitative assesments and yield calculations. For the control experiments, **3** + **4**, **2** + **4**, and **1** + **4**, the same overall reaction times were allowed before performing the analyses.

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Registry No. **1**, 2406-25-9; **2**, 7754-22-5; **3**, 103-67-3; **4**, 622-29-7; Ph_2CHNH_2, 91-00-9; $PhCH(CH_3)NH_2$, 98-84-0; $PhCH_2NHCH_2Ph$, 103-49-1; $PhCH_2NH_2$, 100-46-9; $Ph_2C{=}NNHDNP$, 1733-62-6; $PhC(CH_3){=}NNHDNP$, 1677-87-8; $PhCH{=}NNHDNP$, 1157-84-2; $PhCH{=}NH$, 16118-22-2.

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(7) Small-scale Reactions of **1** with di-*n*-butylamine and *n*-hexylamine failed to provide measurable amounts of 2,4-DNP derivatives under identical conditions. Aliphatic imines are prone to polymerize and to react with amines.[6]

(8) The rate constant, $2k_t$, for dimerization of **1**, at 24 °C, in benzene is[2] $(2.1 \pm 0.1) \times 10^{-5}$ M^{-1} s^{-1}. Decomposition of **1** at room temperature gives ultimately di-*tert*-butyl ketone as the main product.[2]

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(11) The vacuum distillation procedure to separate the neat radical from its dimer has been described elsewhere.[2]

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