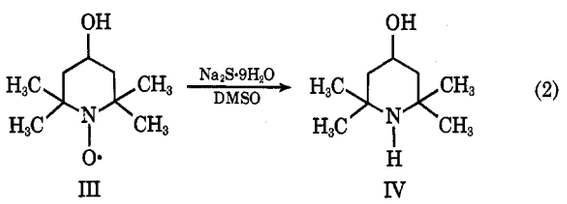
TABLE I
EFFECT OF SULFUR ON THE REACTION OF DI-*tert*-BUTYL NITROXIDE WITH SODIUM SULFIDE NONAHYDRATE IN DMF IN THE LIGHT[a]

Time, hr	% Reaction	(100 Atom % of S[b] Added)
0.5	0	26
1.0	1	100
2.0	8	
4.0	35	
8.0	100	

[a] By vpc. [b] Relative to nitroxide.



III IV (2)

data for the di-*tert*-butyl nitroxide case. While these reductions go in the dark, they proceed more rapidly in the light. For example, in 14 hr the reduction of eq 1 goes only 21% in the dark whereas a duplicate experiment employing two ordinary 20-W fluorescent lights is 83% complete in this time. All this suggests that the sulfide reduction of nitroxides may well be a chain process involving radical intermediates.

Aside from its value as a synthetic and degradative procedure, the reaction of nitroxides with sodium sulfide is of interest because nitroxides are employed as mechanistic probes in a variety of ways.[3] One wonders, therefore, what other nucleophiles will reduce nitroxides. Preliminary experiments in hexamethylphosphoramide reveal that di-*tert*-butyl nitroxide is also destroyed by sodium thiophenoxide at room temperature (ordinary room light); on the other hand, the nitroxide is not affected by sodium azide, sodio malonic ester, sodium nitrite, sodium benzenesulfinate, and the lithium salt of 2-nitropropane.[4]

Experimental Section

Reduction of Di-*tert*-butyl Nitroxide.—Di-*tert*-butyl nitroxide[5] (5.66 g, 39.2 mmol), sodium sulfide nonahydrate (50 g, 208 mmol), and sulfur (1.33 g, 0.0416 g-atom) were stirred under nitrogen in 150 ml of DMF between two 20-W fluorescent light bulbs for 2 hr and the resulting mixture was then poured into *ca.* 200 ml of ice–water. The aqueous phase was saturated with potassium carbonate and extracted with pentane, and the pentane solution was washed with water and dried over anhydrous magnesium sulfate. Distillation gave 3.25 g (65% yield) of pure di-*tert*-butylamine: bp 119–120°; n^{24}D 1.4100; ir (neat) 3.0, 6.8, 7.2, 7.3, 8.2 μ; nmr (CCl_4) δ 0.45 (1 H, broad), 1.18 (18 H); mass spectrum (75 eV) *m/e* (rel intensity) 131 (0.15), 130 (0.38), 129 (M, 3.63), 114 (14.1), 58 (100).

Anal. Calcd for $C_8H_{19}N$: C, 74.34; H, 14.82; N, 10.84. Found: C, 74.50; H, 15.00; N, 10.96.

Reduction of 2,2,6,6-Tetramethylpiperidine Nitroxide (I).—A solution of 5.55 g (35.6 mmol) of 2,2,6,6-tetramethylpiperidine nitroxide[6] (*I*) in 120 ml of DMF was stirred with sodium sulfide nonahydrate (42.7 g, 178 mmol) under N_2 between two 20-W fluorescent lights for 11 hr. On work-up 2.5 g (50% yield) of pure 2,2,6,6-tetramethylpiperidine was isolated: bp 57.5–58.5° (9.5 mm); n^{20}D 1.4451; ir (neat) 3.0, 3.45, 6.9, 7.3, 8.1 μ; nmr (CCl_4) δ 0.6 (1 H), 1.1 (12 H), 1.5 (6 H). A small-scale reaction was greatly accelerated by the addition of 100 atom % of sulfur (relative to I).

Reduction of 2,2,6,6-Tetramethyl-4-piperidinol Nitroxide (III).—This nitroxide[6] (3.70 g, 21.4 mmol) and sodium sulfide nonahydrate (26.4 g, 110 mmol) were stirred in 75 ml of DMSO under nitrogen while exposed to the fluorescent lights. After 63 hr the reaction mixture was poured into ice–water and continuously extracted with pentane. After washing with water and drying the solvent was removed and the crude product was chromatographed on acid-washed alumina. Vacuum sublimation gave 2.57 g (81% yield) of white crystals: mp 127.5–128.5°, and a mixture melting point with authentic 2,2,6,6-tetramethyl-4-piperidinol (mp 128–128.5°) was undepressed; ir ($CHCl_3$) 3.0, 3.4, 6.9, 7.3, 8.2 μ; nmr (CCl_4) δ 0.8 (0.5 H), 1.0 (0.5 H), 1.15 (6 H), 1.2 (6 H), 1.8 (2 H), 2.0 (2 H), 4.0 (1 H). A small-scale reaction in DMF was greatly accelerated by the addition of 100 atom % of sulfur (relative to III).

Registry No.—II, 768-66-1; IV, 2403-88-5; di-*tert*-butylamine, 21981-37-3.

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A Convenient Method for the Preparation of Naphthyl Ethers and Sulfides[1]

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We have recently reported the reactions of the monohalonaphthalenes with alkoxide[3,4] and mercaptide[5] bases in dimethyl sulfoxide (DMSO). The products of these reactions were the alkylnaphthyl ethers[3,4] and sulfides.[5]

Aromatic ethers in general are easy to prepare. The appropriate naphthol is treated with an alkyl halide in the presence of sodium hydroxide.[6] *tert*-Butyl ethers cannot be prepared in this manner. Sahyun and Cram first reported the preparation of *tert*-butylphenyl ether by treating bromobenzene with *tert*-butoxide in DMSO.[7] Bromonaphthalene cannot be used to prepare *tert*-butylnaphthyl ethers because a mixture of *tert*-butyl-1- and 2-naphthyl ethers are obtained in this reaction.[4] Fluoronaphthalene, on the other hand, reacted to yield only the one ether product.[3] Pure *tert*-butylnaphthyl ethers can also be prepared by treating the naphthyl Grignard reagent with *tert*-butyl perbenzoate.[8]

The reaction was carried out by adding the DMSO, *tert*-butyl alcohol, potassium *tert*-butoxide, and 2-fluoronaphthalene in that order to the reaction vessel at 70°

(1) This work was supported by the Research Division, Brigham Young University.

(2) National Defense Education Act Fellow, 1967–1970.

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(6) See, for example, D. M. Musser and H. Adkins, *J. Amer. Chem. Soc.*, **60**, 664 (1938).

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and stirring for 14 hr. These conditions gave the maximum yield of *tert*-butyl-2-naphthyl ether (38%) while keeping the yield of 2-naphthol to a minimum (27%). The naphthol is a degradation product of the *tert*-butylnaphthyl ether.[4] An excellent yield of purified *n*-butyl-2-naphthyl ether (84%) was obtained at 150° using this process.

The alkylnaphthyl sulfides are not as readily available. One preparative method is the acid-catalyzed reaction of naphthol and a mercaptan.[9] In our reaction, 2-bromonaphthalene was added to a mixture of DMSO, *n*-butyl mercaptan, and sodium methoxide and the resulting solution was refluxed for 1 hr. *n*-Butyl-2-naphthyl sulfide was obtained in a 58% yield. This reaction has been carried out on 1- and 2-fluoronaphthalene as well as 1- and 2-bromonaphthalene using both *n*-butyl and *tert*-butyl mercaptans.[5]

Experimental Section

Materials.—2-Fluoronaphthalene was obtained from P. C. R. Inc. 2-Bromonaphthalene and dimethyl sulfoxide (DMSO) were obtained from J. T. Baker Chemical Co. The DMSO was passed through silica gel and stored over Linde 4A, 1/16-in. molecular sieves before using. Sodium methoxide (Olin Matheson Co.) and potassium *tert*-butoxide (M. S. A. Research Corp.) were kept in sealed containers. 1-Butanethiol was purchased from Aldrich Chemical Co. and stored over molecular sieves.

Preparation of *tert*-Butyl-2-naphthyl Ether.—A mixture of DMSO (140 g, 1.8 mol) and 30.5 g (0.41 mol) of *tert*-butyl alcohol was heated to 70° in a 500-ml, three-necked, round-bottom flask equipped with a magnetic stirrer, thermometer, reflux condenser, and addition funnel. Potassium *tert*-butoxide (31.0 g, 0.28 mol) was added and the mixture was stirred until all the base dissolved. 2-Fluoronaphthalene (20.0 g, 0.14 mol) dissolved in 20 g of DMSO (total DMSO in the reaction mixture = 160 g, 2.05 mol) was rapidly added and the resulting mixture was stirred at 70° for 14 hr. The reaction mixture was then added to 50 ml of ice water and extracted four times with 200-ml portions of ether. The combined ether extracts were washed with aqueous sodium hydroxide and dried over anhydrous magnesium sulfate. The filtered ether extract was distilled to give 4.67 g (23%) of starting 2-fluoronaphthalene, bp 75–90° (1 mm), and 8.2 g (38%, based on amount of starting material actually used) of *tert*-butyl-2-naphthyl ether, bp 95–105° (1 mm), $n^{22}D$ 1.5740 (lit.[10] $n^{22}D$ 1.5724). The infrared spectrum of this compound was the same as that previously reported.[10]

The aqueous reaction mixture was acidified to pH 1 with concentrated hydrochloric acid and extracted with ether. The ether extracted yielded 4.25 g (27%) of 2-naphthol.

Prepartion of *n*-Butyl-2-naphthyl Ether.—This reaction was carried out in the same manner as the above reaction except that potassium metal (10.1 g, 0.28 mol) was dissolved in 51 g (0.69 mol) of *n*-butyl alcohol to make the base-alcohol portion of the reaction mixture. A dark yellow solid (26.03 g) was obtained after the ether extract was evaporated. Five grams of this material was recrystallized twice from a 90% aqueous alcohol solution to yield 4.5 g of *n*-butyl-2-naphthyl ether, mp 33.5–34.5° (lit.[11] mp 33–35°). The total yield of purified ether would be 22.4 g (84%).

Preparation of *n*-Butyl-2-naphthyl Sulfide.—Twenty grams (0.096 mol) of 2-bromonaphthalene in 44 g of DMSO was added to a mixture of 70 g of DMSO, 43.6 g (0.48 mol) of 1-butanethiol, and 15.7 g (0.29 mol) of sodium methoxide at reflux temperature (110°) in the same apparatus as reported above. The reaction mixture was worked up as in the *tert*-butyl-2-naphthyl ether reaction to yield 12.12 g (58%) of *n*-butyl-2-naphthyl sulfide, bp 147–152° (1 mm), $n^{25}D$ 1.6205 (lit.[5] $n^{25}D$ 1.6195). The infrared spectrum for this compound was the same as that previously reported.[5]

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Registry No.—*tert*-Butyl-2-naphthyl ether, 15052-11-6; *tert*-butyl alcohol, 75-65-0; 2-fluoronaphthalene, 323-09-1; *n*-butyl-2-naphthyl ether, 10484-56-7; *n*-butyl alcohol, 71-36-3; *n*-butyl-2-naphthyl sulfide, 5286-43-1; 2-bromonaphthalene, 580-13-2; 1-butanethiol, 109-79-5.

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Lead Tetraacetate Oxidation of Guanylhydrazones. A Novel Rearrangement

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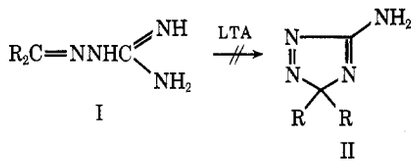
Nitrogen-containing heterocyclic compounds have been synthesized by the oxidative cyclization of ketone or aldehyde semicarbazones, acylhydrazones, *N*-alkylsemicarbazones, thiosemicarbazones, and carbohydrazones.[1]

By analogy, lead tetraacetate oxidation of a guanylhydrazone I should have led to the formation of a triazole derivative II.



I II

Addition of molar quantities of lead tetraacetate to a dichloromethane solution of acetophenone guanylhydrazone[2] resulted in 35% yield of a compound which showed a molecular ion at *m/e* 144. Increasing the quantity of lead tetraacetate to 2 equiv gave a nearly quantitative yield. The infrared spectrum of this compound showed an intense band at 2200 cm^{-1}, in accordance with the structure III shown in Scheme I. Similarly, the nmr spectrum showed only the two signals for the methyl and the phenyl groups at 2.77 and 7.72 ppm, respectively.

Treatment of this compound with dilute boiling HCl followed by extraction with chloroform gave a liquid which was shown to be acetophenone. Evaporation to dryness of the aqueous layer gave a solid which had an identical infrared spectrum with that of a sample of cyanamide which had been treated with acetophenone and hydrochloric acid as above.

The oxidative conversion of guanylhydrazones into cyanimino derivatives is visualized as proceeding through the sequence shown in Scheme I.

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