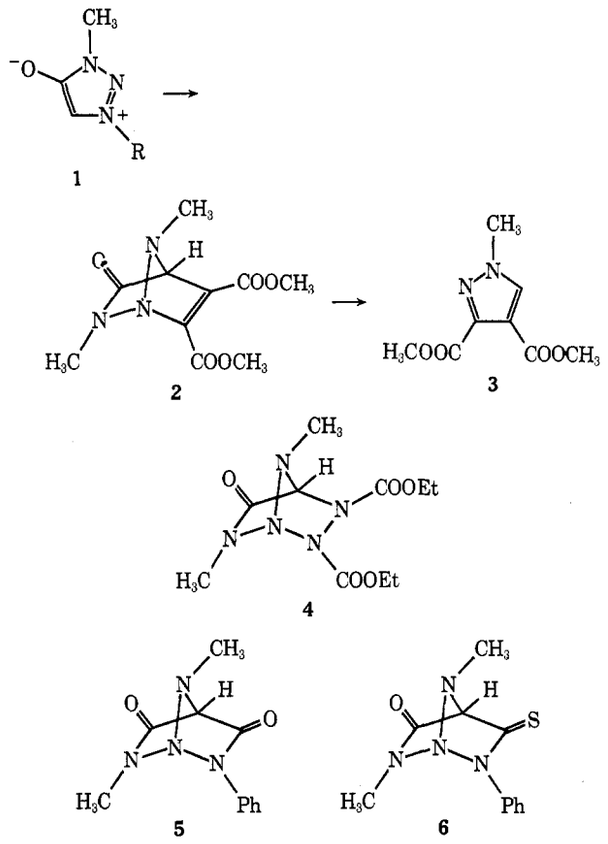

In this case the bridgehead proton at C-4 underwent a large downfield shift to τ −2.5 which can be attributed to the increased deshielding of the thiocarbonyl group.[6]

Experimental Section[7]

Methyl 1-Methylpyrazole-3,4-dicarboxylate (3).—*anhydro*-1,3-Dimethyl-4-hydroxy-1,2,3-triazolium hydroxide[8] and dimethyl acetylenedicarboxylate (equimolar amounts) were refluxed in benzene for 1 hr. The reaction mixture was chromatographed directly on neutral alumina and the ester was eluted with benzene, yield 60%, mp 68–69° (lit.[8] mp 68–69°). This product was identical[9] with an authentic sample.

Ethyl 6,7-Dimethyl-5-oxo-1,2,3,6,7-pentaazabicyclo[2.2.1]-heptane-2,3-dicarboxylate (4).—Equimolar amounts of 1 and ethyl azodicarboxylate were refluxed in xylene for 1 hr. Evaporation of the solvent and trituration of the residue with ether gave a colorless, crystalline product which crystallized from benzene–petroleum ether (bp 40–60°) as colorless, irregular prisms: mp 166–168°; yield 95%; ir (KBr) 3150, 2975 (CH), 1750 (sh), 1725, 1650 cm^{-1} (CO); $\lambda_{max}^{CH_3OH}$ 282 nm (log ϵ 3.86); nmr ($CDCl_3$) τ 8.77 (t, 3, J = 7.0 Hz, CH_2CH_3), 8.73 (t, 3, J = 7.0 Hz, CH_2CH_3), 6.3 (s, 3, NCH_3), 5.95 (s, 3, NCH_3), 5.86 (q, 2, J = 7.0 Hz, CH_2CH_3), 5.78 (q, 2, J = 7.0 Hz, CH_2CH_3), 0.47 (s, 1, 4-CH); mass spectrum m/e (rel intensity) M·+287 (17).

Anal. Calcd for $C_{10}H_{17}N_5O_5$: C, 41.81; H, 5.96; N, 24.38. Found: C, 42.08; H, 5.95; N, 24.10.

2,7-Dimethyl-3,5-dioxo-6-phenyl-1,2,6,7-tetraazabicyclo[2.2.1]-heptane (5).—*anhydro*-1,3-Dimethyl-4-hydroxy-1,2,3-triazolium hydroxide (0.20 g) and phenyl isocyanate (1.0 g) in xylene (5 ml) were refluxed for 10 hr. After cooling, water (5 ml) was added and the next day the solvent was removed under reduced pressure. The solid residue was dissolved in hot benzene and chromatographed on neutral alumina (activity I) and finally eluted with chloroform. It crystallized from benzene as colorless needles: yield 287 mg (70%); mp 167–168°; ir (KBr) 3005 (CH), 1690 cm^{-1} (CO); $\lambda_{max}^{CH_3OH}$ 336 nm (log ϵ 3.76), 312 (4.29); nmr ($CDCl_3$) τ 6.34 (s, 3, NCH_3), 5.74 (s, 3, NCH_3), 2.61 (m, 5, aromatic), −0.23 (broad s, 1, 4-CH); mass spectrum m/e (rel intensity) M·+232 (80).

Anal. Calcd for $C_{11}H_{12}N_4O_2$: C, 56.89; H, 5.21; N, 24.13. Found: C, 57.12; H, 4.99; N, 24.47.

6,7-Dimethyl-5-oxo-2-phenyl-1,2,6,7-tetraazabicyclo[2.2.1]-heptane-3-thione (6) was prepared as above using phenyl isothiocyanate. The yellow product was eluted using benzene–chloroform (1:1) and crystallized from benzene–petroleum ether as yellow needles: yield 258 mg (59%); mp 148–150°; ir (KBr) 2900 (CH), 1670 cm^{-1} (CO); $\lambda_{max}^{CH_3OH}$ 340 nm (log ϵ 4.39), 240 (3.94); nmr ($CDCl_3$) τ 6.28 (s, 3, NCH_3), 5.47 (s, 3, NCH_3), 2.5 (m, 5, aromatic), −2.5 (broad s, 1, 4-CH); mass spectrum m/e (rel intensity) M·+248 (100).

Anal. Calcd for $C_{11}H_{12}N_4SO$: C, 53.22; H, 4.87; N, 22.57. Found: C, 53.65; H, 4.82; N, 22.44.

Registry No.—**1** (R = CH_3), 13273-71-7; **4**, 34407-45-9; **5**, 34407-46-0; **6**, 34407-47-1.

(6) K. T. Potts and R. Armbruster, *J. Org. Chem.*, **36**, 1846 (1971); R. Hull, *J. Chem. Soc. C*, 1777 (1968).

(7) Spectral characterization of products was carried out on the following instrumentation: ir, Perkin-Elmer Model 337 spectrophotometer; uv, Cary Model 14 spectrophotometer; nmr, Varian A-60, T-60, and HA-100 spectrometers using TMS as internal standard; mass spectra, Hitachi Perkin-Elmer RMU-6E mass spectrometer using the direct inlet probe at about 165°. All evaporations were done under reduced pressure using a rotavap apparatus and melting points were taken in capillaries, Microanalyses are by Instranal Laboratories, Inc., Rensselaer, N. Y.

(8) K. T. Potts and U. P. Singh, *Chem. Commun.*, 66 (1969).

(9) Criteria for product equivalency were superimposable infrared spectra, not more than 1° depression in mixture melting point, and identical R_f values.

Reduction of Nitroxides to Amines by Sodium Sulfide

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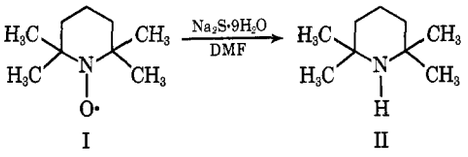
We report the facile reduction of nitroxides to amines. This reduction takes place at room temperature and, despite our relatively cursory study of the matter, the yields of pure products range from 50 to 81%. Thus, the nitroxide I on treatment with sodium sulfide in dimethylformamide for 11 hr gives a 50% yield of the tetramethylpiperidine II. Reduction also occurs



(1)

smoothly in dimethyl sulfoxide; the nitroxide III is reduced to the amine IV in 81% yield. Our third example is the conversion of di-*tert*-butyl nitroxide to di-*tert*-butylamine (65% yield).[1,2]

These reductions have several interesting characteristics. They exhibit an induction period and they are accelerated by elementary sulfur. Table I records

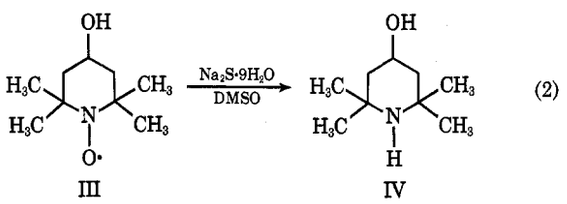
(1) This is the best route to di-*tert*-butylamine. Compare F. Klages and H. Sitz, *Ber.* **92**, 2606 (1959); N. C. Deno, R. Fishbein, and J. C. Wyckoff, *J. Amer. Chem. Soc.*, **93**, 2066 (1971).

(2) The use of zinc (or iron) and refluxing hydrochloric acid has been reported to convert nitroxides to amines in a few isolated cases; the yields are 35% or less [N. C. Deno, private communication; H. Wieland and K. Roth, *Ber.*, **53**, 210 (1920)]. Recently, the catalytic hydrogenation, over Raney nickel, of di-*tert*-butyl nitroxide to di-*tert*-butylamine (60% yield) was reported by E. G. Rozantsev and R. S. Burmistrova, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 2364 (1968).

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.

Acknowledgment.—We thank Eli Lilly and Company and the National Science Foundation for generous support.

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(6) R. Briere, H. Lemaire, and A. Rassat, *Bull. Soc. Chim. Fr.*, 3273 (1965).

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.

(3) R. H. Hales, J. S. Bradshaw, and D. R. Pratt, *J. Org. Chem.*, **36**, 314 (1971).

(4) J. S. Bradshaw and R. H. Hales, *ibid.*, **36**, 318 (1971).

(5) J. S. Bradshaw, J. A. South, and R. H. Hales, *ibid.*, in press.

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

(7) M. R. V. Sahyun and D. J. Cram, *Org. Syn.*, **45**, 89 (1965).

(8) C. Frisell and S. D. Lawesson, *Org. Syn.*, **41**, 91 (1961).