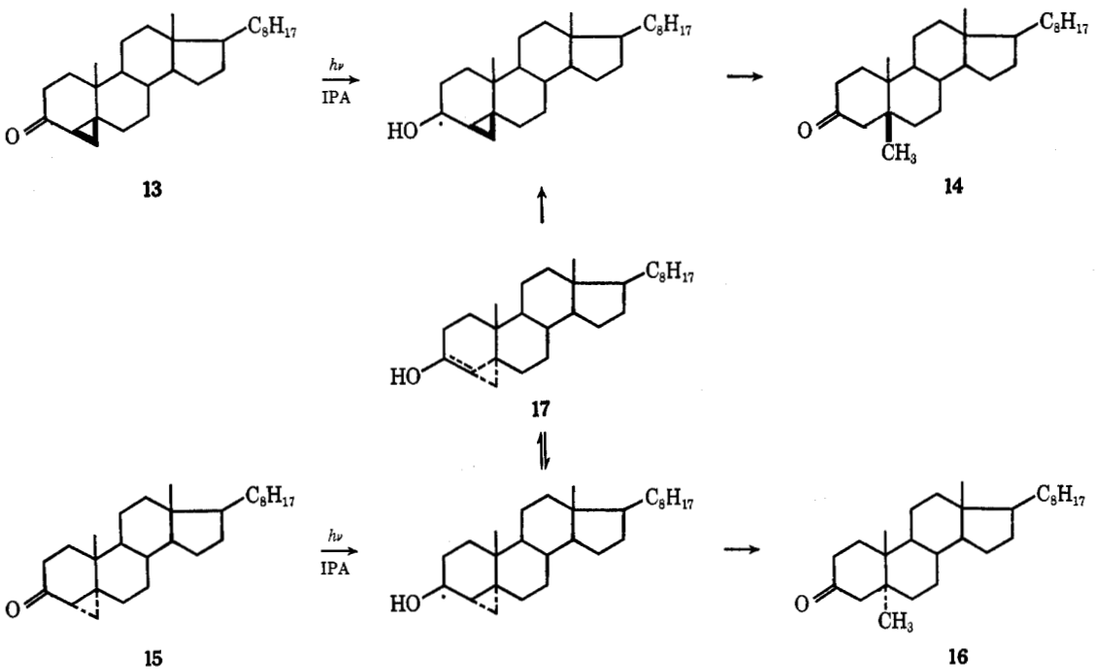

(1)

2.5 hr as described for the 4β,5β isomer **13**, at which time 80% of the starting material had been consumed. The reaction mixture was chromatographed by the Duncan procedure[8] to yield 290 mg of reaction product and 80 mg of starting ketone. The reaction product was recrystallized from absolute ethanol to yield a granular solid, mp 76–132°, mol wt, 400 (mass spectrum).

Anal. Calcd for $C_{28}H_{48}O$: C, 83.93; H, 12.08. Found: C, 83.99; H, 11.91.

The product was analyzed by vpc and found to be composed of 85% of 5β-methylcholestan-3-one (**14**) and 15% of 5α-methylcholestan-3-one (**16**) by coinjection with authentic samples.[9]

Registry No.—**6**, 14845-43-3; **7**, 34562-14-6; **10**, 29750-24-1; **12**, 34562-16-8; **13**, 2429-48-3; **15**, 2602-40-6; isopropyl alcohol, 67-63-0.

Cycloaddition Reactions with *anhydro*-1,3-Dimethyl-4-hydroxy-1,2,3-triazolium Hydroxide[1]

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In a previous communication,[2] *anhydro*-3-aryl-4-hydroxy-1-methyl-1,2,3-triazolium hydroxides (**1**, R = aryl) were reported to undergo cycloaddition reactions with dimethyl acetylenedicarboxylate to the corresponding pyrazole. Reactive olefinic-type dipolarophiles such as ethyl azodicarboxylate also gave 1:1 adducts with the ring system and tetracyanoethylene formed "ene" type substitution products. Particularly noteworthy, however, was the lack of reaction with phenyl isocyanate and phenyl isothiocyanate, even over extended reaction periods.

The 3-aryl substituent would be expected to have considerable effect on the electron density associated with the nucleus of **1**. The inability of **1** (R = aryl) to form the corresponding methyl ether with methyl iodide whereas the 3-methyl compound **1** (R = CH_3) underwent ready methylation with methyl iodide[3] may be attributed to substituent effect. We have now found that replacement of the 3-aryl substituent with a methyl group facilitates cycloaddition reactions with this ring system and greatly extends the scope of the reaction.

anhydro-1,3-Dimethyl-4-hydroxy-1,2,3-triazolium hydroxide (**1**, R = CH_3) underwent reaction with dimethyl acetylenedicarboxylate in refluxing benzene (1 hr), giving dimethyl 1-methylpyrazole-3,4-dicarboxylate (**3**) in 60% yield, presumably *via* the intermediate **2** which lost methyl isocyanate under the reaction conditions. An equally facile reaction of **1** (R = CH_3) with ethyl azodicarboxylate also occurred, giving ethyl 6,7-dimethyl-5-oxo-1,2,3,6,7-pentaazabicyclo[2.2.1]heptane-2,3-dicarboxylate (**4**) in 95% yield. The assignment of this structure to the cycloadduct is based on analytical and spectral data (see Experimental Section) and is analogous to the structure of the product from **1** (R = aryl) and the ester.

Both phenyl isocyanate and phenyl isothiocyanate gave 1:1 cycloadducts with **1** (R = CH_3). In the former case, structure **5**, 2,7-dimethyl-3,5-dioxo-6-phenyl-1,2,6,7-tetraazabicyclo[2.2.1]heptane, was assigned to the product. The bridgehead proton at C-4 resonated at τ −0.23, broadened slightly by coupling with the bridge NCH_3 group,[2,4] and is at extremely low field consistent with it being deshielded by the carbonyl groups in the 3 and 4 positions. This would appear to exclude from consideration the isomeric 2,7-dimethyl-3,6-dioxo-5-phenyl-1,2,5,7-tetraazabicyclo[2.2.1]heptane formed by reverse addition of the phenyl isocyanate to **1**. Such a reverse addition has been observed with sydnone.[5] The adduct with phenyl isothiocyanate was assigned the analogous structure **6**.

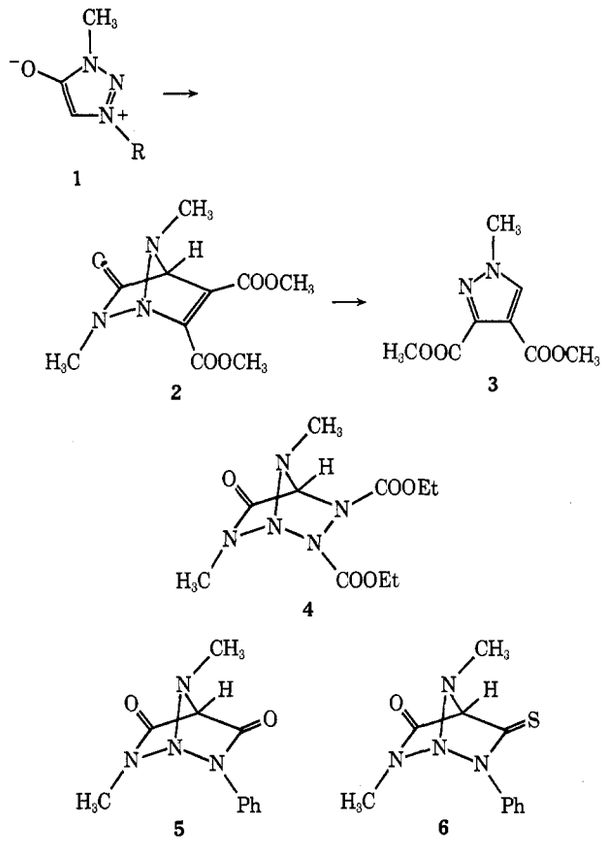
(1) (a) Support of this work by U. S. Public Health Service Research Grant CA 08495, National Cancer Institute, is gratefully acknowledged. (b) Part XVII in the series, Mesoionic Compounds.

(2) K. T. Potts and S. Husain, *J. Org. Chem.*, **35**, 3451 (1970).

(3) M. Begtrup and C. Pedersen, *Acta Chem. Scand.*, **20**, 1555 (1966); M. Begtrup and P. A. Kristensen, *ibid.*, **23**, 2733 (1969).

(4) D. E. Ames and B. Novitt, *J. Chem. Soc. C*, 2355 (1969).

(5) H. Kato, S. Sato, and M. Ohta, *Tetrahedron Lett.*, 4261 (1967).



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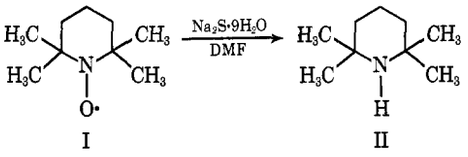
We report the facile reduction of nitroxides to amines. This reduction takes place at room temperature and, despite our relatively cursory study of the matter, the yields of pure products range from 50 to 81%. Thus, the nitroxide I on treatment with sodium sulfide in dimethylformamide for 11 hr gives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