to obtain several concentrations of reactants. The reactions were carried out in standard volumetric flasks which were placed in a constant-temperature bath. Samples were removed periodically and analyzed for the extent of reaction. The kinetic runs were carried out under conditions in which the relative concentrations of valeryl peroxide and potassium thiocyanate were varied. Second-order kinetics were followed in each case to beyond 80% reaction.

Registry No.—Thiocyanogen, 505-14-6; valeryl peroxide, 925-19-9; potassium thiocyanate, 333-20-0.

Acknowledgment.—We wish to thank the National Science Foundation and the NDEA for financial support.

tert-Alkylnitroso Compounds. Synthesis and Dimerization Equilibria

JOHN C. STOWELL

Department of Chemistry, Louisiana State University in New Orleans, Lake front, New Orleans, Louisiana 70122

Received February 9, 1971

Kahr and Berther[1] showed that sodium tungstate catalyzed hydrogen peroxide oxidation of primary amines containing an α hydrogen gives oximes. With an amine containing no α hydrogen, this oxidation should give the nitroso compound. In this way we have prepared 2-methyl-2-nitrosopropane in 24% yield.[2] This simple one-step preparation from the inexpensive *tert*-butylamine is more convenient than the previous routes such as $KMnO_4$ oxidation of *tert*-butylamine to the nitro compound[3] followed by Zn–HCl reduction to the hydroxylamine[4] and finally bromine oxidation.[5] The nitroso compound has also been prepared on a small scale by oxidation of *tert*-butylamine vapor with solid *m*-chloroperbenzoic acid.[6] The other product of the H_2O_2 oxidation is 2-methyl-2-nitropropane. Using more H_2O_2 the yield of this nitro compound is 70%. This is a rapid and convenient alternative to permanganate oxidation.

$$RNH_2 + H_2O_2 \xrightarrow{Na_2WO_4} RNO \longrightarrow RNO_2$$

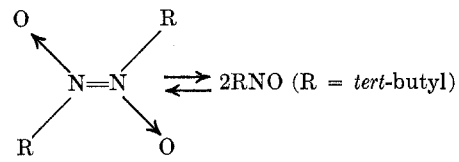
R = *tert*-butyl or 1,1,3,3-tetramethylbutyl

The method functions as well with water-insoluble amines such as 1,1,3,3-tetramethylbutylamine which gives the nitroso compound in 36% yield.

Unhindered aromatic nitroso compounds are monomeric in solution while aliphatic nitroso compounds are dimeric in solution.[7,8] For example, nitrosobenzene is 100% dissociated at 20° in benzene (0.1 *M*) while nitrosocyclohexane is only 0.088% dissociated.[8] The title compounds are exceptions to this. The high steric hindrance of a *tert*-alkyl group favors the monomeric form. For example, we have found that solutions of 2,4,4-trimethyl-2-nitrosopentane in CCl_4 (0.5 *M*) are >99% dissociated by nmr analysis. The equilibrium constants for the *tert*-butyl compound were measured at several temperatures; these and the thermodynamic values are given in Table I.

TABLE I

EQUILIBRIUM CONSTANTS AND THERMODYNAMIC VALUES



K_c = [monomer]²/[dimer]

Temp, °C (±0.5°)	K_c	$\Delta G°$, cal
35.0	4.85	−968
26.5	2.77	−609
20.0	1.92	−381
9.0	1.06	−33
4.0	0.57	309
0.5	0.43	458

$\Delta H° = 11.8 \pm 0.3$ kcal/mol
$\Delta S° = 41.5 \pm 1.0$ cal/(deg mol)

The $\Delta H°$ is 9 kcal/mol smaller than that for nitrosocyclohexane (20.6 kcal/mol),[8] probably due to the steric bulk of the *tert*-butyl group causing a large amount of crowding in the dimer. This is the opposite of the effect of steric hindrance on aromatic compounds. Ortho substitution favors dimerization; for example, nitrosomesitylene is about 69% dimer. This was explained[9] as steric hindrance to resonance in the monomer which destabilizes the monomer with respect to dimerization.

The per cent dissociation was measured by nmr integration. The spectra of the dimers were obtained by rapid scanning of solutions freshly prepared from the crystalline dimers. These solutions were pale blue but after a few minutes they were deep blue and the spectra showed mostly monomer.

2,4,4-Trimethyl-2-nitrosopentane is thermally unstable. Heating a sample at 150° for 10 min causes complete decomposition giving a variety of products including diisobutylenes and the nitro compound.

Experimental Section

2-Methyl-2-nitrosopropane.—A solution of *tert*-butylamine (36.6 g, 0.50 mol) and $Na_2WO_4 \cdot 2H_2O$ (4.0 g) in 50 ml of water was cooled in an ice bath. Hydrogen peroxide (170 g of 21%, 1.0 mol) was added dropwise over 1.3 hr at 15–20° with stirring.[10]

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(10) Stop H_2O_2 addition temporarily whenever 20° is reached. More rapid addition can cause accumulation of H_2O_2, leading to higher temperatures.

Stirring was continued for 30 min more at 20–25°. About 3 g of NaCl was added to break the emulsion and the blue organic layer was separated. This was washed with dilute HCl and dried ($MgSO_4$). Distillation gave 10.2 g (24%) of the dark blue nitroso compound, bp 50–55°, which rapidly solidified to a colorless solid, mp 74–75° (sealed capillary, variable according to how long the sample is in the bath) (lit.[4,5] mp 66–67° or 79–81°). The distillate should be kept in an ice bath until it solidifies, since the heat of dimerization–crystallization can boil off some of the monomer.

Continued distillation gave 21.2 g (41%) of the nitro compound, bp 126–127°.

2-Methyl-2-nitropropane.—A solution of *tert*-butylamine (36.6 g, 0.50 mol), $Na_2WO_4 \cdot 2H_2O$ (4.0 g), and 25 ml of water was cooled in an ice bath. Hydrogen peroxide (255 g of 21%, 1.50 mol) was added dropwise over a 2-hr period with stirring. The first 100 g was added at 15–20°,[10] 100 ml of methanol was then added, and the H_2O_2 addition was continued at 25–35°. This was stirred for an additional hour at 25°. The organic layer was separated and the water layer was extracted with three 25-ml portions of ether. The combined organic layer and extract was dried ($MgSO_4$) and distilled to afford 35.9 g (70%), bp 126–127° (lit.[3] bp 126–127°), $\delta_{TMS}^{CCl_4}$ 1.60.

2,4,4-Trimethyl-2-nitrosopentane.—Hydrogen peroxide (0.40 mol, 65 g of 21%) was added over a 30-min period to a mixture of 2.0 g of $Na_2WO_4 \cdot 2H_2O$, 25 ml of water, and 25.9 g (0.20 mol) of 1,1,3,3-tetramethylbutylamine with stirring. A temperature of 18–22° was maintained by occasional ice bath cooling. The blue mixture was stirred for an additional 3.5 hr at 18–22°. The organic layer was separated with 25 ml of pentane and then extracted with excess dilute HCl. The blue organic layer was then dried (K_2CO_3) and distilled to give 10.24 g (36%) of the nitroso compound, bp 90–92° (130 mm), a blue liquid which slowly crystallized. Pressing the pale blue crystals on filter paper gives white solid, mp 63–65° (lit.[5] mp 63–64°).

Continued distillation gave 2,4,4-trimethyl-2-nitropentane (6.57 g, 21%): bp 80–85° (15 mm) [lit.[11] bp 83–86° (18 mm)]; $\delta_{TMS}^{CCl_4}$ 0.95 (9 H), 1.60 (6 H), 1.98 (2 H).

A sample of the crystalline nitroso dimer was dissolved in CCl_4 (pale blue solution) in an nmr tube and scanned rapidly. The dimer showed $\delta_{TMS}^{CCl_4}$ 0.96 (9 H), 1.52 (6 H), 2.06 (2 H). Within a few minutes the solution was deep blue and no trace of the dimer was detectable. The spectrum now showed only monomer: $\delta_{TMS}^{CCl_4}$ 0.82 (9 H), 1.04 (6 H), 2.34 (2 H).

Equilibrium Measurement.—A solution of 0.0563 g of 2-methyl-2-nitrosopropane per gram of CCl_4 was analyzed by nmr integration using a variable-temperature probe. The solution was held at each temperature until a constant peak ratio was obtained. The molar concentrations were calculated using a correction for the density of CCl_4 at each temperature.[12] The $\Delta H°$ was obtained by a least-squares treatment.

Temp, °C	Wt % monomer	Temp, °C	Wt % monomer
35.0	76.5	9.0	51.1
26.5	67.6	4.0	40.9
20.0	61.5	0.5	36.8

The signal assignments were made as follows. A sample of the crystalline dimer was dissolved in CCl_4 in an nmr tube (pale blue solution) and rapidly scanned. This gave a large peak at δ 1.51 (dimer). After a few minutes this peak was small and the peak at δ 1.20 became the larger (monomer) and the solution became deep blue.[13]

Registry No.—2-Methyl-2-nitropropane, 917-95-3, 31107-20-7 (dimer); 2-methyl-2-nitropropane, 594-70-7; 2,4,4-trimethyl-2-nitrosopentane, 31044-98-1; 2,4,4-trimethyl-2-nitropentane, 5242-78-9.

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Di-*tert*-butyluretidinedione[1]

JOHN C. STOWELL*

Department of Chemistry, Louisiana State University in New Orleans, Lakefront, New Orleans, Louisiana 70122

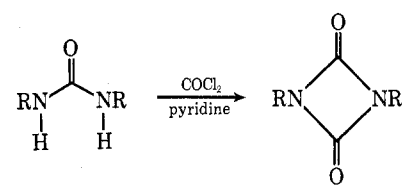
FREDERICK D. GREENE AND WILLIAM R. BERGMARK

Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

Received April 7, 1971

Diaryluretidinediones (1,3-diaryl-1,3-diazetidinediones) are well-known compounds and are readily available by trialkylphosphine-catalyzed dimerization of isocyanates.[2] Little is known of dialkyluretidinediones.[3,4] Treatment of aliphatic isocyanates with the phosphine catalysts gives trimers in good yield.[5] At low conversion small amounts of aliphatic isocyanate dimers may be formed along with the trimers.[3]

We have prepared an aliphatic uretidinedione by a different route. Treatment of *N,N'*-di-*tert*-butylurea with pyridine–phosgene[6] gives the ring compound in 50–60% yield.



R = *tert*-butyl

Previous workers have found that phosgenation of ureas under various conditions gave a variety of products including isocyanates, chloroformamidines, and allophanoyl chlorides.[7] An allophanoyl chloride is a likely intermediate; a recent report describes the preparation of uretidinediones (a series of diaryl and the dimethyl derivative) from allophanoyl chlorides.[4] In our case the choice of *tert*-butyl substituents, which are known to stabilize small rings,[8] allowed synthesis in one operation from the urea. The only by-product was the easily removable carbodiimide.[8c]

Di-*tert*-butyluretidinedione gives one peak in the nmr at δ 1.37 and shows a carbonyl absorption in the infrared at 1760 cm^{-1}. For comparison, β-lactams absorb

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