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°), $\delta_{\mathrm{TMS}}^{\mathrm{CCl_4}}$ 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)]; $\delta_{\mathrm{TMS}}^{\mathrm{CCl_4}}$ 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 $\delta_{\mathrm{TMS}}^{\mathrm{CCl_4}}$ 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: $\delta_{\mathrm{TMS}}^{\mathrm{CCl_4}}$ 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]

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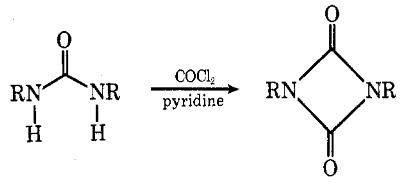
Diaryluretidinediones (1,3-diaryl-1,3-diazetidinediones) are well-known compounds and are readily available by trialkylphosphine-catalyzed dimerization of isocyanates.[2] Little is known of dialkyluretidinediones.[3,4] Treatment of aliphatic isocyanates with the phosphine catalysts gives trimers in good 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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(1) Financial support from the National Science Foundation is gratefully acknowledged.

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at 1730–1760 cm^{-1}, diphenyluretidinedione absorbs at 1775 cm^{-1}, di-*tert*-butyldiazetidinedione absorbs at 1813 cm^{-1},[9] and 2,4-azetidinediones absorb at 1725–1750 cm^{-1}.[10]

It is interesting to note that treatment of *tert*-butylamine with phosgene–pyridine gives *tert*-butyl isocyanate[11] and only small amounts of the urea and the uretidinedione. Treatment of *tert*-butylamine with phosgene in the absence of pyridine gives the urea in good yield. No tri-*tert*-butyl isocyanurate was found in these reactions.

The ring compound is quite stable. At 200° it readily cleaves to give 2 mol of *tert*-butyl isocyanate in high yield.[12] Infrared analysis of a sample which had been heated at 200° showed isocyanate and remaining dimer but no trimer. The convenience of this preparation of *tert*-butyl isocyanate is comparable with other good methods.[13] The ring is rapidly opened by sodium methoxide in methanol to give methyl *N*,*N*′-di-*tert*-butylallophanate.

Photolysis of the di-*tert*-butyluretidinedione gave only *tert*-butyl isocyanate. Di-*tert*-butyldiaziridinone[8a] was not detected[14] and was shown to be stable to the photolysis conditions.

Comparison of the photochemical and mass spectra results are of interest. The principal ions in the mass spectrum are M − 15 (loss of CH_3), M − 15 − 56 (loss of CH_3 and of C_4H_8), and M − 15 − 99 (the base peak, loss of CH_3 and of C_4H_9NCO). These fragmentations are similar to those observed with acyclic ureas.[15] Completely absent are *m/e* 99 (cleavage of molecular ion into two *tert*-butyl isocyanates), 170 (decarbonylation), and 142, 141 (loss of isobutylene, loss of *tert*-butyl).

Experimental Section

Di-*tert*-butyluretidinedione.—A solution of 4.05 g (0.0410 mol) of phosgene in 50 ml of benzene was added dropwise with stirring and ice-bath cooling to 25 ml of pyridine, giving a yellow precipitate. *N*,*N*′-Di-*tert*-butylurea (6.43 g, 0.0373 mol) was added at once, giving a thick yellow mixture. This was stirred for 1 hr at room temperature, during which it became more fluid and the yellow color faded. Water (200 ml) was added and the benzene layer was separated. No solid was present, and infrared analysis showed carbodiimide (2095 and 2130 cm^{-1}) and the uretidinedione. The water layer was extracted with pentane and the combined pentane and benzene solution was extracted with 50 ml of dilute HCl to remove the pyridine and to hydrate the carbodiimide. The precipitated *N*,*N*′-*tert*-butylurea was filtered. The solvent was distilled and the residue taken up in 50 ml of pentane. Filtration gave the remainder of the urea (total 1.70 g, representing a 26% yield of di-*tert*-butylcarbodiimide). The pentane was evaporated and the residue sublimed at 15 mm and 75° to give 3.84 g (52%) of white crystals, mp 87–90°. Recrystallization from a small amount of pentane gave mp 89–90°; ir (CCl_4) 1760 cm^{-1}; nmr (CCl_4) 1.37 (singlet); uv (cyclohexane) 240 nm (ε 96); mass spectrum (70 eV) *m/e* (rel intensity) 198 (M, 2.8), 183 (16.5), 127 (21), 85 (5.9), 84 (100), 70 (4.4), 57 (23), 56 (11.3), 55 (3.8).

Anal. Calcd for $C_{10}H_{18}N_2O_2$: C, 60.57; H, 9.15; N, 14.13. Found: C, 60.37; H, 9.14; N, 14.14.

***tert*-Butyl Isocyanate.**—Di-*tert*-butyluretidinedione (1.00 g) was placed in a distilling flask with a boiling stone and heated at 200°. For about 30 min the colorless liquid isocyanate distilled (0.95 g, 95%): ir (neat) 2251 cm^{-1}, nmr (CCl_4) 1.37 (singlet).

Photolysis of Di-*t*-butyluretidinedione.—A solution of 452 mg (2.28 mmol) of the uretidinedione in 4.0 ml of cyclohexane in a quartz tube was placed in a quartz flask filled with methylene chloride (to cut out radiation below 230 mm) and irradiated with a Hanovia mercury lamp for 25 hr. Glc and infrared analysis showed *tert*-butyl isocyanate (11%) and unchanged starting material (88%). Di-*tert*-butyldiaziridinone[8a] was not detected.

Control Experiment on Irradiation of Di-*t*-butyldiaziridinone.—A solution of 0.808 g of the diaziridinone[8a] in 20 ml of cyclohexane was irradiated for 20 hr under the conditions described above. The course of the photolysis was followed by ir, which showed an undiminishing diaziridinone carbonyl band and the appearance at the end of two very small bands, one at 2250 cm^{-1} assignable to *tert*-butyl isocyanate and one at 1680 cm^{-1}. Fine needles, 18 mg (2% yield), mp 240–241°, of di-*tert*-butylurea were collected by filtration and identified by mixture melting point and infrared spectrum.

Methyl *N*,*N*′-Di-*tert*-butylallophanate.—Di-*tert*-butyluretidinedione (1.00 g, 5.05 mmol) was dissolved in 10 ml of methanol, and about 50 mg of sodium was added. After 5 min the solution was poured into 100 ml of water. The resulting precipitate was filtered, washed with water, and dried to give 0.396 g (34%) of white solid. Recrystallization from cyclohexane followed by sublimation at 0.15 mm and 40° gave mp 132–133°; nmr (CCl_4) 1.32 (9 H), 1.40 (9 H), 3.65 (3 H), 5.2 (1 H, broad); ir (CCl_4) 1710, 1730, 3423 cm^{-1}.

Anal. Calcd for $C_{11}H_{22}N_2O_3$: C, 57.36; H, 9.63; N, 12.17. Found: C, 57.05; H, 9.57; N, 12.06.

Registry No.—Di-*tert*-butyluretidinedione, 30885-14-4; *tert*-butyl isocyanate, 1609-86-5; methyl *N*,*N*′-di-*tert*-butylallophanate, 30885-16-6.

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On the Dehydration of Bicyclo[2.2.1]-2-heptanols in the Mass Spectrometer

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The mass spectra of bicyclo[2.2.1]-2-heptyl derivatives have been reported in a number of papers. The behavior under electron impact was studied in order to find methods for structure elucidations[1] and also in connection with the investigation of some well-known reactions in the gas phase and solutions as Wagner–Meerwein rearrangement,[2] retro-Diels–Alder reaction,[3] and the classical–nonclassical controversy. In these studies deuterium labeling was often necessary to get precise information regarding the fragmentation in the mass spectrometer and structures of obtained fragments. Kwart and Blazer[3] recently published an

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