Diaziridinones (2,3-Diazacyclopropanones). A Cis-Fused Example. Lone Pair–Lone Pair Destabilization[1a]

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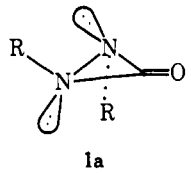
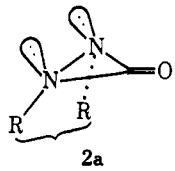
2,2,5,5-Tetramethyl-1,6-diazabicyclo[4.1.0]heptan-7-one (**4**), the first example of a diaziridinone of cis stereochemistry, has been prepared by reaction of the *N*-chloro urea, 1-chloro-4,4,7,7-tetramethyl-1,3-diazacycloheptan-2-one, with either sodium tribenzylmethoxide in tetrahydrofuran or with the potassium salt of the urea 4,4,7,7-tetramethyl-1,3-diazacycloheptan-2-one in dimethoxyethane. Diaziridinone **4** reacts at room temperature with unhindered alcohols by nucleophilic addition and ring opening, with 1,2-disubstituted hydrazines by oxidation–reduction to afford the urea corresponding to **4** and the azo compound corresponding to the hydrazine, and with *p*-nitrophenyl isocyanate to afford the cycloaddition product (a substituted 1,2,4-triazolidine-3,5-dione). Diaziridinone **4** shows a single methyl signal in the NMR, ascribed to rapid interconversion between **4a** and **4b** (eq 3), $\Delta G^{\ddagger} < 5$ kcal/mol. Compound **4** decomposes to carbon monoxide and the azo compound 3,3,6,6-tetramethyl-1,2-diaza-1-cyclohexene ($t_{1/2}$ at 25 °C in CCl_4, 25.1 h; $\Delta H^{\ddagger} = 24.8 \pm 0.4$ kcal/mol; $\Delta S = 1.2 \pm 1.5$ *G*/mol). Comparisons between *cis*-diaziridinone **4** and *trans*-1,2-di-*tert*-butyldiaziridinone indicate that the former is much more reactive than the latter, both in unimolecular reactions (e.g., decarbonylation) and in the bimolecular reactions described above (nucleophilic addition, oxidation–reduction, cycloaddition).

Part A

The synthesis and properties of some *N,N'*-di-*tert*-alkyldiaziridinones (diazacyclopropanones), **1**, have been described.[2] The compounds are thermally rather stable (**1**, R = *tert*-butyl, $t_{1/2} \sim 2$ h at 180 °C), unexpectedly sluggish toward nucleophiles, and show some unusual oxidation–reduction reactions (primarily with hydrogen atom donors such as hydrazines and thiophenols). The physical data (NMR and ir) indicate for the ground state the structure shown in **1a** in which the substituents are trans. Comparison of the carbonyl absorptions (1855–1880 cm^{-1} for diaziridinones, 1837–1850 cm^{-1} for aziridinones, 1813–1840 cm^{-1} for cyclopropanones) indicates a lack of amide-type delocalization of nitrogen lone pair electrons in diaziridinones.

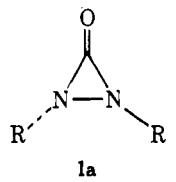


1a

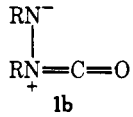


2a

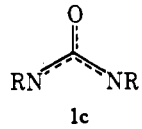
The synthesis and examination of diaziridinones with smaller substituents and of cis diaziridinones (**2a**) has been of interest to us. Such compounds might (a) provide information on the effect of adjacent lone pairs as a function of conformation; (b) indicate whether the low reactivity of **1a** (R = *tert*-alkyl) toward nucleophiles was a steric effect of the substituents or an electronic repulsion effect of the nitrogen lone pairs;[3] (c) provide information on the possible intermediacy of isomeric modifications **1b–e**.[4a] In this paper we report the synthesis of a cis-fused diaziridinone.



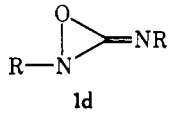
1a



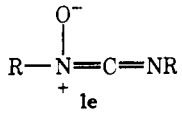
1b



1c



1d

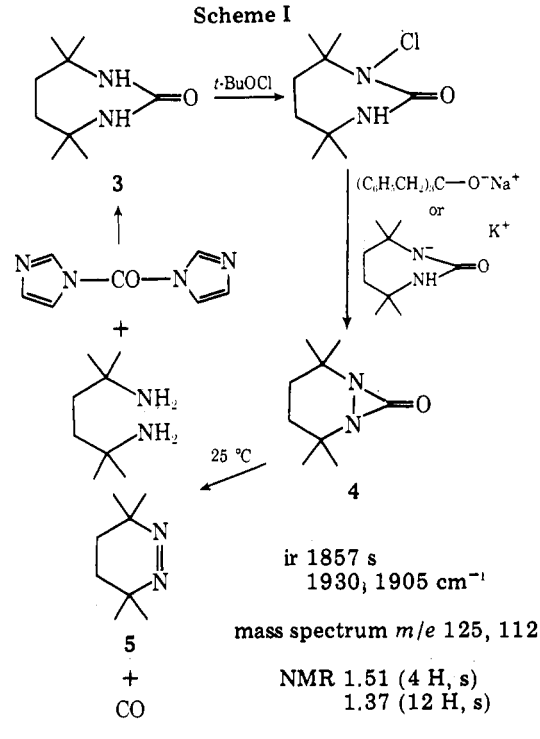


1e

Results

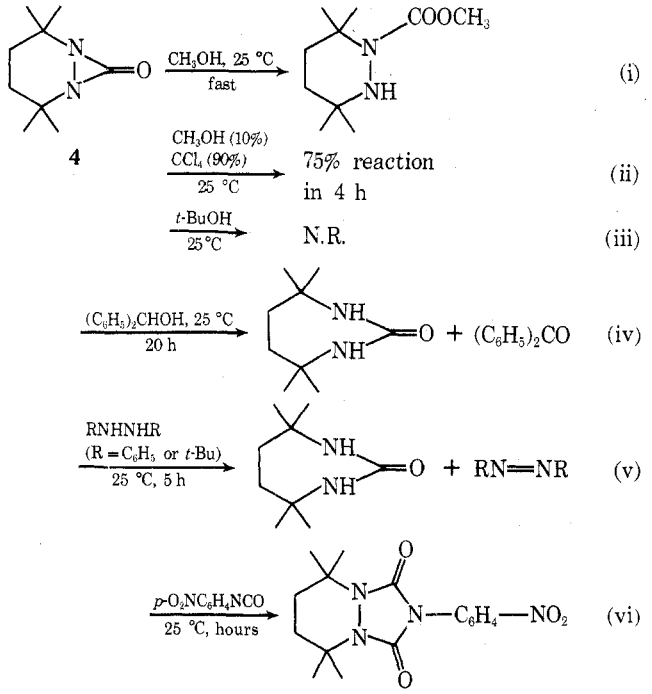
The cis diaziridinone **4**, 2,2,5,5-tetramethyl-1,6-diazabicyclo[4.1.0]heptan-7-one, has been synthesized by the route shown in Scheme I. Choice of base for the conversion of the *N*-chloro urea to diaziridinone **4** was crucial. Use of the hindered base, sodium tribenzylmethoxide, afforded **4** in low, and often variable, yield (15%); use of smaller alkoxides (routinely used for the preparation of di-*tert*-alkyl diaziridinones)[2] afforded carbazates (Scheme II, i). Variation in temperature, solvent, or cation (K^+ instead of Na^+) showed little improvement. Use of the potassium salt of the urea **3** effected the conversion of the *N*-chloro urea to the diaziridinone **4**. The yield was still low but more reproducible than with the tribenzylmethoxide. Of particular interest, this approach has been successful for the synthesis of diaziridinones **1a** in which R = primary and secondary alkyl groups.[4b]

Scheme I



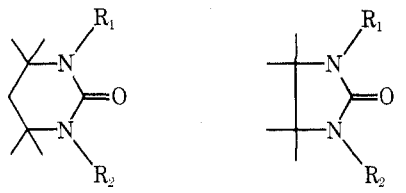
The structural assignment for **4** is based on the physical

Scheme II



data summarized in Scheme I and on the facile decarbonylation of **4** to **5** (3,3,6,6-tetramethyl-1,2-diazacyclohexene).

Efforts to prepare diaziridinones from cyclic ureas **6** and **7** were unsuccessful. Syntheses of the ureas and their *N*-chloro



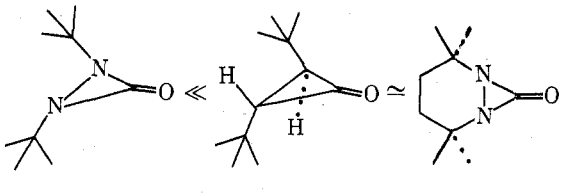
6 **7**

a, $R_1 = R_2 = H$
b, $R_1 = H$; $R_2 = Cl$
c, $R_1 = R_2 = Cl$

and *N,N'*-dichloro derivatives are described in the Experimental Section.

Reactions of Diaziridinone 4. Two aspects of interest are the effect of heat on **4** (consideration of the single methyl and methylene absorptions in the NMR, and the facile decarbonylation) and the effect of attacking agents (nucleophiles, reductants, etc.). In both areas, comparison with *trans*-di-*tert*-butyldiaziridinone is revealing.

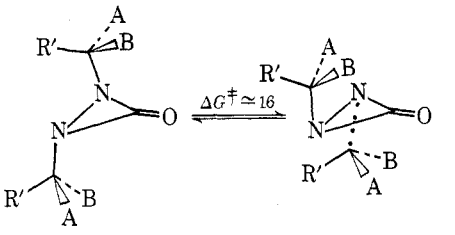
The reactions of **4** (Scheme II) include nucleophile addition and ring opening, oxidation–reduction, and "cycloaddition", paralleling related reactions of **1a** (R = *tert*-butyl).[2] In all cases rates are faster for **4** than for **1a** [e.g., requiring a temperature 100 °C higher for **1a** (R = *tert*-butyl) than for **4**]. Particular attention is directed to the facile reduction of **4** by hydrogen transfer from benzhydrol (eq iv)[2] and from hydrazines (eq v).[2] Methanolysis (eq 1) provides a point of comparison of cis and trans diaziridinones with a related trans cyclopropanone: cis diaziridinone **4** and *trans*-di-*tert*-butylcyclopropanone are of comparable (and high) reactivity



(1)

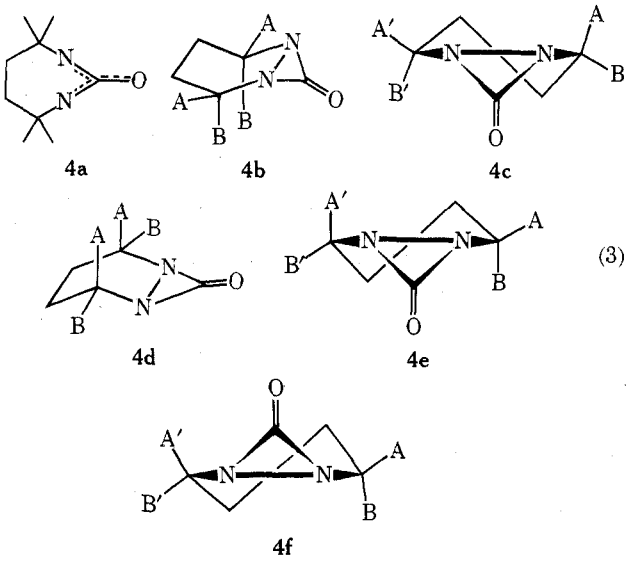
toward methanol; *trans*-di-*tert*-butyldiaziridinone is much less reactive.[3]

Thermal Behavior of 4. The NMR of **4** shows single methyl and methylene peaks. In comparison, *trans*-di-*tert*-octyldiaziridinone shows separate methyl peaks at 0 °C which coalesce at 35 °C, a $\Delta G^{\ddagger}$ of 16 kcal/mol for equilibration of the magnetic environments of the A and B methyl groups (eq 2).[2]



(2)

There are several possibilities for **4**: (1) the molecule has structure **4a**; (2) the molecule has structure **4b** or **4c** and has accidental equivalence of the methyls (and of the methylene hydrogens); (3) the molecule is rapidly inverting, e.g., between **4b** and **4d** or **4c** and **4f** (eq 3). The close similarity in the ir



4a **4b** **4c**

(3)

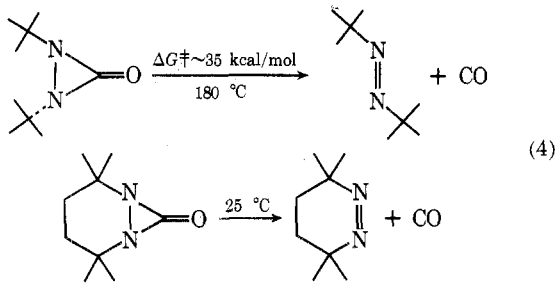
4d **4e**

4f

carbonyl region of **1** and **4** strongly indicates that both possess the diaziridinone ring system, thereby excluding **4a**. The half-chair forms (**4c, 4e, 4f**) are expected to be more stable than the boat forms (**4b, 4d**) by analogy to cyclohexenes.[5] The possibility of accidental equivalence of the methyls in **4c** (or **4b**) is discounted on the following grounds. The spectrum remains two sharp singlets (one for the methyls, one for the methylenes) in several solvents over a broad temperature range: CCl_4 from 0 to 30 °C, CD_3CN from −10 to 30 °C, CH_2Cl_2 from −90 to 30 °C, CCl_2F_2 from −120 to 0 °C, benzene 25 °C. The change from CCl_4 to C_6D_6 results in a modest upfield shift for the methyl resonance (from 1.37 ppm to 1.13) and a larger shift for the methylene (from 1.51 to 1.06), associated with greater anisotropic shielding of the methylene. Preservation of accidental equivalences in two sets of signals in the change from CCl_4 to C_6D_6 is very unlikely. This leaves the third possibility, i.e., **4c, 4e,** and **4f** (or **4b** and **4d**) in rapid equilibrium (eq 3). Efforts to observe a splitting at low temperature in the NMR of **4** were not successful. In CCl_2F_2–CF_3Br (1:1) the spectrum remains two singlets down to −150 °C although considerably broadened at that temperature. Below −150 °C further broadening occurs but with no indication of splitting into different peaks. Clearly, a coalescence peak is not reached even at −150 °C, indicating that the barrier to interconversion of **4a** and **4b** is less than 5–6 kcal/mol, approximately 10 kcal/mol less than the barrier for di-*tert*-octyldiaziridinone.

On standing at room temperature, 4 undergoes quantitative decarbonylation, Scheme I ($t_{1/2}$ at 25 °C in CCl_4 is 25 h). The kinetics of the thermal decomposition were followed by Fourier transform ^1H NMR. [This technique has advantages for kinetics measurements over the usual continuous wave NMR: (a) the greater signal-to-noise ratios, permitting smaller sample size and lower concentrations; (b) the high resolution without "ringing" bands, permitting accurate integration even for absorbances close in chemical shift (an aspect of particular importance in the present study).] Decarbonylation is first order in 4. Results are summarized in Table I.

Diaziridinone 4 decomposes much more readily than di-*tert*-butyldiaziridinone (**1a**). Decomposition of the latter requires several hours at 180 °C and affords a mixture of products[6a] including carbon monoxide and di-*tert*-butyldiazine. A minimum estimate for the free energy of activation for decarbonylation is thus approximately 35 kcal/mol (eq 4).



(4)

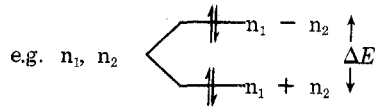
4 **5**

$\Delta G^{\ddagger}$ 180 °C (calcd, Table I) ~25 kcal/mol

In summary, both the barriers to "inversion" (eq 2 and 3) and to decarbonylation (eq 4) are approximately 10 kcal/mol smaller for the cis diaziridinone 4 than for the trans diaziridinone **1**. The analysis in the following section is suggestive that in both processes the smaller barriers for **4** may be ascribed, perhaps in large measure, to ground state destabilization associated with the less favorable cis arrangement of the nitrogen lone pairs in **4** than the 120° lone pair–lone pair dihedral angle in **1a**.

The Problem of Adjacent Lone Pairs. Major questions here are the degree of interaction of lone pairs situated on adjacent atoms and total energy as a function of conformation. Theoretical,[7] microwave,[8] NMR,[9] photoelectron spectroscopic,[10] and thermochemical studies[11] provide some information on these questions. Theoretical analyses on hydrazine show a preferred conformation at a lone pair–lone pair dihedral angle $\theta = 90°$.[7] The calculated energies relative to the level for $\theta = 90°$ are (in kcal/mol) 12.2 for $\theta = 0°$, 3.6 for $\theta = 180°$, 1 for $\theta = 120°$. A microwave study on hydrazine indicates the preferred conformation at $\theta = 90°$ and a barrier to rotation of 3 kcal/mol.[8] This number may be too small and has been questioned.[9]

Photoelectron spectroscopy provides a clear indication of lone-pair n_1–lone pair n_2 interactions, and in favorable cases provides a measure of the degree of interaction, ΔE, for the $n_1 + n_2$ vs. the $n_1 - n_2$ levels (eq 5). The interaction is strongly



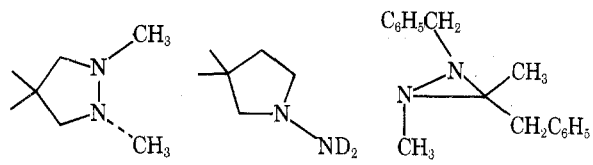
(5)

dependent on the dihedral angle θ (least for $\theta = 90°$, greatest for $\theta = 0$ and 180°).[10a] The largest interaction between adjacent lone pairs might be expected when the pairs are in parallel p orbitals. Strong interaction is seen, by PES, between lone pairs in sp^3 orbitals (e.g., hydrazines)[10a] and in sp^2 orbitals (azo compounds, both cis and trans).[10b] Both "through space" and "through bond" interactions may be important.[10c] The PES data, while providing a good index of lone pair–lone pair interactions, are uninformative on *total* energy differences between conformations as a function of θ (e.g., hydrazines) or between isomers (e.g., cis and trans azo compounds). These total energy differences could be obtained from thermochemical data. Few such data are available for the analysis of the effect of adjacent lone pairs. A recent study on a series of azo compounds (trans acyclic and cis cyclic) indicates that the trans azo linkage is more stable than the cis (in a 1,2-diazacyclohexene-1) by 8 kcal/mol. The rates of decomposition of a series of azo compounds show activation energies that are lower for cis than for trans, also attributed to ground state destabilization from lone pair–lone pair interactions, more unfavorable in cis azo compounds than in trans by ~7 kcal/mol.[12]

Table I. Kinetics Data for Thermal Decomposition of Cis Diaziridinone 4

	CCl_4	CD_3CN (90%)–CCl_4 (10%)
$k_{25\,°C}$	$7.66 \pm 0.07 \times 10^{-6}\ s^{-1}$	$4.26 \pm 0.08 \times 10^{-6}\ s^{-1}$
$k_{50.05\,°C}$	$2.11 \pm 0.03 \times 10^{-4}\ s^{-1}$	$1.28 \pm 0.03 \times 10^{-4}\ s^{-1}$
$\Delta G^{\ddagger}_{298\,K}$	24.4 kcal/mol	24.8 kcal/mol
$\Delta H^{\ddagger}$	24.8 ± 0.4 kcal/mol	25.4 ± 0.6 kcal/mol
$\Delta S^{\ddagger}$	1.2 ± 1.5 *G*/mol	2.5 ± 2.5 *G*/mol

Studies by NMR of conformational changes in hydrazines and related systems have provided some information on lone pair–lone pair interactions.[9] Analysis is frequently complicated by occurrence of both rotational and nitrogen inversion barriers. Comparisons of the type shown by Lehn and Wagner[13a] (**8** and **9**) and by Mannschreck and Seitz (**10**)[13b] are of interest.



8 **9** **10**

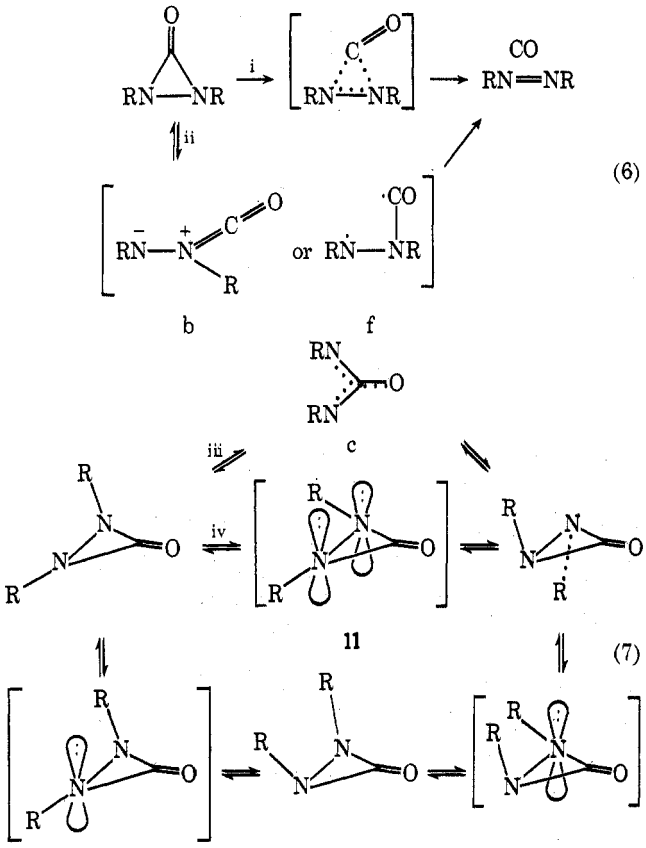
$\Delta G^{\ddagger}$ kcal/mol 11.1 8.5 27

In summary, comparisons of the type described above are suggestive that a cis diaziridinone may be less stable than a trans diaziridinone, perhaps by several kcal/mol; the 10 kcal/mol greater reactivity of **4** compared with **1** in decarbonylation and in equilibration of the magnetic environments may be largely due to ground state destabilization of a cis diaziridinone compared to a trans diaziridinone, but other strain effects may also play a role in compound **4**. Additional examples of cis diaziridinones would be helpful.

Part B

What can be said about the mechanisms of the two processes, equilibration of the magnetic environments and decarbonylation, and do the two processes proceed along common paths? On the grounds described in the preceding paragraph, the transition states both for decarbonylation and for equilibration of the magnetic environments of the methyl groups for cis diaziridinone **4** should reflect a major reduction in the lone pair–lone pair interactions.

Decarbonylation, involving cleavage of the C–N bonds, might proceed in two ways: synchronously by a nonlinear cheleotropic process,[14] or stepwise via species b or f (eq 6). Conversion of diaziridinone to azo compound and carbon monoxide by the former path implies a transition state in which the lone pair–lone pair interaction is intermediate between that of reactant and product. The heats of formation for the products of decarbonylation (eq 4) indicate 8.3

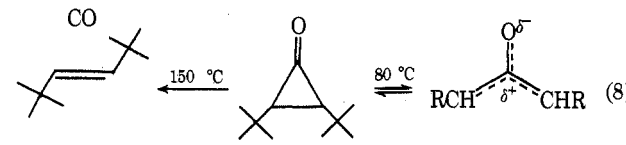


(6)

(7)

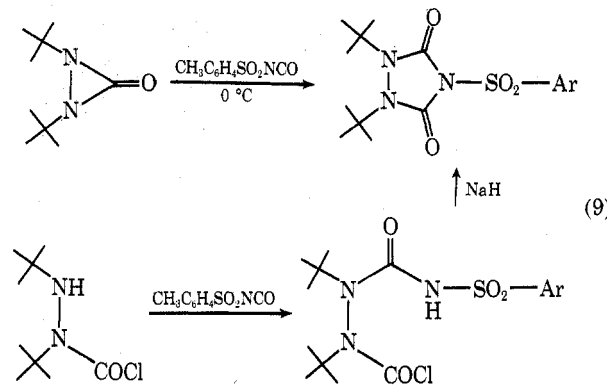
kcal/mol of strain in **5**,[11] ascribed primarily to lone pair–lone pair interactions. Thus decarbonylation by the cheletropic path would not account for the 10 kcal/mol difference in activation energy between 1 and 4. Decarbonylation via b or f of eq 6 (in a variety of geometries) could afford the apparently needed reduction in lone pair–lone pair interactions between ground state and transition state.[15] Equilibration of the magnetic environments of the methyl groups in di-*tert*-octyldiaziridinone, $\Delta G^{\ddagger} = 16$ kcal/mol (eq 2),[2] could be achieved by path ii of eq 6 or by paths iii (N–N cleavage), iv (one-step, double N inversion), or v (two-step, single N inversion) of eq 7. Barriers to inversion in acyclic amines are ~5 kcal/mol vs. 17–20 kcal/mol in aziridines.[16] This increase in barrier height is ascribed to angle strain and is comparable to the increase in ring strain (~13 kcal/mol) in a methylenecyclopropane compared with a cyclopropane. Inversion barriers also increase in molecules possessing adjacent heteroatoms, e.g., diaziridine **10**,[13b] ascribed, in part, to unfavorable lone pair–lone pair interactions as a nitrogen is made planar. Calculations indicate a strong preference (>35 kcal/mol)[13b] for nitrogen inversion in **11** proceeding singly (as in path v of eq 7) rather than doubly (as in path iv of eq 7).[17] Thus, angle considerations, lone pair–lone pair interactions (**11** in eq 7 may also be viewed as an "antiaromatic" system), and steric effects all indicate that path iv will not be important. The barrier for path v of eq 7 may be viewed as that for a diaziridine (e.g., **11**, $\Delta G = 27$ kcal/mol) minus the amide resonance associated with making one nitrogen planar (~10 kcal/mol), i.e., 17 kcal/mol vs. the observed barrier of 16 kcal/mol. *Rough* estimates of the energy changes associated with paths ii of eq 6 and iii and v of eq 7 provide no basis for excluding any of these possibilities. Thus for acyclic diaziridinones equilibration (e.g., of the magnetic environments of the methyls in di-*tert*-octyldiaziridinone, eq 2) may be by paths ii, iii, or v.

The very low barrier (<5 kcal/mol) associated with **4** permits the rejection of the nitrogen inversion paths (iv and v of eq 7) for this system: a stepwise, single N inversion process would involve a highly strained transition state resembling a trans diaziridinone fused to a six-membered ring; a one-step, double N inversion process is rejected for **4** on the grounds indicated above for **1a** and **11**. Thus the "equilibration" associated with **4** is ascribed to breaking of a C–N bond (path ii of eq 6) or the N–N bond (path iii of eq 7). Economy of mechanism might lead one to prefer C–N cleavage since the decarbonylation *must* involve these bonds. However, ring opening of **4a** to **4c** (see eq 3) is an allowed process. A related situation of bond changes is found in the racemization (80 °C) and decarbonylation (150 °C) of (+)-*trans*-di-*tert*-butylcyclopropanone for which the evidence favors C_2–C_3 cleavage for the racemization, C_1–C_2 cleavage for decarbonylation (eq 8).[6]



(8)

Efforts to trap potential intermediates such as b or f (eq 6) or c (eq 7, path iii) have afforded several 1:1 adducts; efforts to *prove* the presence of intermediates have been unsuccessful (i.e., in no case has it been possible to demonstrate an independence of adduct formation on concentration of the trapping agent). Urazoles have been obtained from reaction of *p*-nitrophenyl isocyanate with **4** (25 °C, Scheme II, vi) and with di-*tert*-butyldiaziridinone (100 °C). Di-*tert*-butyldiaziridinone also reacts instantly at 0 °C with *p*-toluenesulfonyl isocyanate and with chlorosulfonyl isocyanate to form urazoles (eq 9). The structure of the former adduct was proved by synthesis.



(9)

Experimental Section

4,4,7,7-Tetramethyl-1,3-diaza-2-cycloheptanone (3). A 2-l. Morton flask equipped with two 500-ml pressure-equalizing addition funnels and a fast mechanical stirrer was flamed out under nitrogen. Dry THF (400 ml) was introduced into the flask and heated to just below the boiling point. A solution of 2,5-dimethyl-2,5-diaminohexane (13.84 g, 0.096 mol, Aldrich Chemical Co.) in dry THF (total volume 350 ml) was added to one funnel, and a solution of 1,1′-carbonyldiimidazole[18] (15.50 g, 0.096 mol) in THF (total volume 350 ml) was added to the other funnel. Simultaneous slow addition with rapid stirring under nitrogen was completed in 8 h. After standing overnight the solvent was evaporated. The residue was shaken with 250 ml of water. The resulting solid was collected by filtration, washed with water, air dried, dissolved in 250 ml of THF, and filtered to remove polymer. Evaporation of the THF and sublimation at 150 °C and 0.01 mm provided 6.50 g (40%) of a white solid, **3**, mp 168–170 °C. A resublimed sample had mp 170–171 °C; ir ($CHCl_3$) 3395 (m), 2970 (m), 1645 (vs), 1460 (m), 1445 (m), 1410 (m), 1385 (m), 1365 (m), 1280 (m), 1145 cm^{-1} (m); NMR ($CDCl_3$) 4.45 (b, 2 H), 1.68 (s, 4 H), 1.28 ppm (s, 12 H); mass spectrum *m/e* (rel intensity) 171 (0.5), 170 (M^+, 4), 156 (2), 155 (18), 141 (0.5), 140 (1.5), 113 (2), 112 (18), 107 (2), 95 (13), 58 (100), 55 (13), 42 (25), 41 (26).

Anal. Calcd for $C_9H_{18}N_2O$: C, 63.49; H, 10.65; N, 16.46. Found: C, 63.33; H, 10.90; N, 16.08.

The residue from the sublimation, 2.00 g, was assumed to be low polymer of **3** on the basis of the physical data: mp 250 °C dec; ir ($CHCl_3$) 3430 (m, b), 1680 (s, b), 1520 (s, b), 1385 (m), 1365 (m), 1245 cm^{-1} (s); NMR ($CDCl_3$) 4.00 (b), 1.76 (b), 1.21 ppm (b); mass spectrum *m/e* (rel intensity) 341 (3), 340 (M^+, 10), 312 (2), 287 (4), 265 (5), 264 (5), 186 (3), 171 (5), 170 (13), 156 (5), 155 (41), 149 (17), 95 (13), 70 (10), 58 (100), 57 (10), 56 (10), 42 (25), 41 (20). The mass spectrum appears to show only the dimer of **3**, 4,4,7,7,11,11,14,14-octamethyl-1,3,8,10-tetrazatetradecane-2,9-dione; higher analogues may not have had enough volatility to be seen. This polymeric material could be cracked in 60–75% yield to the monomer at 300 °C.

1-Chloro-4,4,7,7-tetramethyl-1,3-diazacycloheptan-2-one. Tetramethyldiazacycloheptanone (0.023 g, 0.135 mmol) was dissolved in 2 ml of methylene chloride. To this stirred solution was added *tert*-butyl hypochlorite (0.030 g, 0.27 mmol); the reaction was protected from light. After 4 h the solvent was evaporated affording a slightly yellow solid: mp 80 °C dec; ir ($CHCl_3$) 3400 (m), 1680 (s), 1450 cm^{-1} (w); NMR ($CDCl_3$) 5.00 (b, 1 H), 1.80 (m, A_2B_2, 4 H), 1.40 (s, 6

H), 1.26 ppm (s, 6 H). This reaction failed when THF was the solvent.

2,2,5,5-Tetramethyl-1,6-diazabicyclo[4.1.0]heptan-7-one (4). A. A solution of sodium tribenzylmethoxide was prepared by heating at reflux for 24 h under nitrogen a solution of tribenzylcarbinol[19] (0.674 g, 2.23 mmol) in 25 ml of dry THF with sodium hydride [0.115 g (57% dispersion), 2.70 mmol; washed twice with 15 ml of THF]. 1-Chloro-4,4,7,7-tetramethyl-1,3-diaza-2-cycloheptanone prepared from the urea (0.400 g, 2.35 mmol) and *tert*-butyl hypochlorite (0.50 g, 4.5 mmol) was dissolved in 15 ml of THF. To this solution, stirred under nitrogen, was added by cannula the solution of sodium tribenzylmethoxide in 15 min; a fine white precipitate formed during the addition. The solvent was removed at aspirator pressure. The residue was washed with 20 ml of pentane, and the pentane evaporated to give a viscous liquid whose ir spectrum had a strong carbonyl band at 1860 cm^{-1}. The product was collected by sublimation at 0.01 mm through a 5-mm U-tube collector cooled at −78 °C. A colorless, crystalline solid collected in the tube just above the cooling bath, and a yellow liquid collected at the bottom. The colorless solid, 37 mg (14%), was found to be pure diaziridinone **4**: mp 30 °C; ir (CCl_4) 2980 (s), 1930 (m), 1905 (m), 1857 (vs), 1460 (m), 1390 (m), 1370 (m), 1130 (m), 1100 (m), 1080 cm^{-1} (m); NMR (CCl_4) 1.51 (s, 4 H), 1.37 ppm (s, 12 H); NMR (C_6D_6) 1.13 (s, 12 H), 1.06 ppm (s, 4 H); mass spectrum *m/e* (rel intensity) 125 (2), 113 (1), 112 (11), 69 (8), 57 (23), 56 (100), 55 (12), 41 (43), 39 (12). The yellow liquid was found to consist mainly of 3,3,6,6-tetramethyl-1,2-diazacyclohexene (**5**), ir 1560 (m), 1465 (m), 1455 (m), 1380 (m), 1360 (m), 1340 cm^{-1} (m), and a small amount of diaziridinone **4**; in addition weak unidentified absorbances were noted at 2250, 1780, 1735, and 1710 cm^{-1}. the yields for this reaction are variable.

B. The potassium salt of 4,4,7,7-tetramethyl-1,3-diaza-2-cycloheptanone was prepared from the urea (168 mg, 0.99 mmol) and potassium hydride (39 mg, 0.98 mmol) in 10 ml of DME; the salt formed rapidly and was largely insoluble. 1-Chloro-4,4,7,7-tetramethyl-1,3-diaza-2-cycloheptanone, prepared from the urea (168 mg, 0.99 mmol) and *tert*-butyl hypochlorite (142 mg, 1.3 mmol), was dissolved in 7 ml of DME and added by cannula to the urea salt stirred under nitrogen. Within a few minutes all the anion had dissolved, and a new fine white precipitate formed. The solvent was evaporated at aspirator pressure. Sublimation (3 h) at 0.001 mm through a U-tube collector cooled at −78 °C afforded again colorless crystals of diaziridinone **4** (38 mg, 23%) in the tube just above the cooling bath, and a small amount of yellow liquid, azo compound **5** (5 mg), at the bottom of the tube; the products were identified by ir and NMR. When the scale of the reaction was doubled the yield of diaziridinone was 15%.

Thermal Decomposition of 2,2,5,5-Tetramethyl-1,6-diazabicyclo[4.1.0]heptan-7-one (4). Product Study. When samples of diaziridinone **4** were heated, or allowed to stand at room temperature for extended periods, they were transformed quantitatively into a fragrant yellow liquid, 3,3,6,6-tetramethyl-1,2-diazacyclohexene (**5**): ir (CCl_4) 2960 (s), 1560 (w), 1465 (m), 1455 (m), 1380 (m), 1360 (m), 1340 (m), 850 cm^{-1} (m); NMR (CCl_4) 1.45 (s, 4 H), 1.25 ppm (s, 12 H); mass spectrum *m/e* (rel intensity) 112 (3), 84 (10), 70 (6), 69 (13), 57 (27), 56 (76), 55 (20), 43 (25), 42 (20), 41 (100), 40 (10), 39 (40). The ir and NMR spectra were identical with those already reported for this compound.[20] Decomposition of a sample of diaziridinone **4** in a sealed capillary, and mass spectral analysis of the contents established the presence of carbon monoxide (*m/e* calcd, 27.9946; obsd, 27.9946) and azo compound **5** (*m/e* calcd, 140.1313; obsd, 140.1313) and the absence of carbon dioxide and cyclic hydrazine 3,3,6,6-tetramethyl-1,2-diazacyclohexane (possible products of hydrolysis and decarboxylation of diaziridinone **4**).

Kinetics Method. Preparation of Samples. Carbon tetrachloride was distilled from P_2O_5 and then K_2CO_3. Acetonitrile-d_3 was distilled from P_2O_5. The NMR tubes were washed with basic detergent, repeatedly rinsed with distilled water, acetone, and methylene chloride, placed in a drying oven at 125 °C for 24 h, and flame dried under nitrogen immediately before use. To each of three NMR tubes was added 35 μl of a carbon tetrachloride solution of the diaziridinone (ca. 29%). Carbon tetrachloride (300–400 μl) was added to two of the tubes. Acetonitrile-d_3 (300 μl) was added to the third. The samples were degassed by four consecutive freeze–pump–thaw cycles, and sealed under vacuum.

A 20-s warm-up period was allowed each time the tube was submerged in the constant-temperature bath. Quenching of the reaction was accomplished by submerging the tube in a dry ice–2-propanol bath. The interval time was taken at the point at which the tube was submerged.

The reaction was followed by NMR. The Fourier transform spectra were determined at 60 MHz and −5 to 0 °C using a Perkin-Elmer Model R-20B spectrometer interfaced with a Digilab FTS/NMR-3 data system.[21] The significant pulsing parameters were irradiation frequency, 60015150 Hz; band width, 400 Hz; nutation angle, ca. 40°; transform size, 4096 points; computer resolution, 0.196 Hz; time between pulses, 5.10 s; number of pulses per spectrum, 60 (decomposition in CCl_4); 120 (decomposition in CD_3CN). Observed resolution varied between 0.3 and 0.5 Hz. The integrals were calculated by the computer and recorded on fine-lined (1 mm spacing) spectral paper. Integrals were standardized and normalized by having the computer set the total integral of the two diaziridinone resonances plus the two product resonances in each spectrum equal to the same value, 240 mm. The results are summarized in Table I.

Reactions of 2,2,5,5-Tetramethyl-1,6-diazabicyclo[4.1.0]heptan-7-one (Cis-Diaziridinone 4). See Scheme II. A. With *p*-Nitrophenyl Isocyanate. A solution of freshly sublimed *p*-nitrophenyl isocyanate (4 mg, 0.024 mmol) and 2,2,5,5-tetramethyl-1,6-diazabicyclo[4.1.0]heptan-7-one (**4**, 5 mg, 0.03 mmol) in 100 μl of CCl_4 was allowed to stand at room temperature (reaction was complete after 24 h). The solvent was evaporated and the crude product triturated with CH_2Cl_2; evaporation of the CH_2Cl_2 gave a yellow solid, ir (CCl_4) 1815, 1775, 1715–1685 cm^{-1}. Analysis by TLC indicated two products. Purification was accomplished by TLC on Baker-flex silica gel plate, CH_2Cl_2 eluent. The major product, which had the higher R_f, was assigned the urazole structure 2,2,5,5-tetramethyl-8-*p*-nitrophenyl-1,6,8-triazabicyclo[4.3.0]nonane-7,9-dione (Scheme II, eq vi) on the basis of the physical data: mp 98–107 °C; ir (CCl_4) 1775 (m), 1715 (s), 1595 (m), 1528 (s), 1500 (s), 1400 (m), 1335 cm^{-1} (s); NMR (CCl_4) 7.86 (m, 4 H), 1.70 (s, 4 H), 1.53 ppm (s, 12 H); mass spectrum *m/e* (rel intensity) 333 (14), 332 (M^+, 72), 317 (3), 307 (12), 306 (53), 292 (4), 291 (20), 264 (15), 263 (100), 238 (6), 237 (50), 222 (2), 221 (2), 179 (6), 164 (3), 154 (4), 153 (42), 149 (18), 141 (22), 139 (10), 138 (8), 127 (12), 125 (8), 113 (3), 112 (3), 111 (42), 110 (12), 99 (26), 90 (10), 69 (62), 57 (16), 56 (40), 55 (34), 43 (20), 42 (16), 41 (50), 39 (10). Only a small amount of the second product was obtained: ir (CCl_4) 1815 (m), 1335 (s), 1260 cm^{-1} (m).

Solutions of **4** in CCl_4 showed no reaction with phenyl isocyanate or with dimethyl acetylenedicarboxylate after 10 h at 25 °C.

B. With Ethanol. A solution of 1 μl of diaziridinone **4**, 5 μl of absolute ethanol, and 20 μl of carbon tetrachloride at 25 °C showed slow disappearance of the diaziridinone carbonyl band at 1860 cm^{-1}; after 24 h about 5% of the diaziridinone remained. New carbonyl bands were observed at 1690 and 1650 cm^{-1}.

C. With Methanol. A solution of 5 mg of diaziridinone **4**, 40 μl of absolute methanol, and 400 μl of carbon tetrachloride at 25° showed (ir) approximately 10% of the diaziridinone still present after 4 h; new carbonyl bands were observed at 1690 and 1650 cm^{-1}; a moderate band at 1560 cm^{-1} indicated the presence of azo compound **5**.

D. With Benzhydrol. A solution of 0.5 mg of diaziridinone **4** and 1 mg of benzhydrol in 25 μl of CCl_4 at 25 °C showed (ir) disappearance of the carbonyl band at 1860 cm^{-1} and appearance of two new bands at 1665 (benzophenone) and 1650 cm^{-1} (4,4,7,7-tetramethyl-1,3-diaza-2-cycloheptanone, **3**). The reaction was essentially complete after 20 h. Analysis by TLC, on both alumina and silica gel, confirmed the presence of benzophenone and cyclic urea **3**. No other product was detected.

E. With Hydrazobenzene. A solution of hydrazobenzene (1 mg) and diaziridinone **4** (0.5 μl) in 20 μl of $CHCl_3$ showed (ir) disappearance of the diaziridinone carbonyl at 1860 cm^{-1} and appearance of the carbonyl of 3,3,7,7-tetramethyl-1,3-diaza-2-cycloheptanone at 1645 cm^{-1} (time for 50% reaction, 3000 s). Analysis by TLC showed that **3** and azobenzene were present.

F. With *N,N'*-Di-*tert*-butylhydrazine. A solution of *N,N'*-di-*tert*-butylhydrazine (0.5 μl) and diaziridinone **4** (0.5 μl) in 20 μl of CCl_4 showed (ir) disappearance of the diaziridinone carbonyl at 1860 cm^{-1} and appearance of the carbonyl of 3,3,7,7-tetramethyl-1,3-diaza-2-cycloheptanone at 1650 cm^{-1} (time for 50% reaction, 500 s). Analysis by TLC confirmed the presence of cyclic urea **3**.

Reaction of Di-*tert*-butyldiaziridinone with Isocyanates. A. With *p*-Toluenesulfonyl Isocyanate.[22] Addition of a solution of the isocyanate (1 equiv) in pentane to a solution of the diaziridinone (1 equiv) in pentane at 0 °C resulted in immediate reaction. Analysis by TLC and NMR indicated one major and two (or more) minor products. Removal of the solvent and recrystallization from hexane afforded the major product, 1,2-di-*tert*-butyl-4-*p*-toluenesulfonyl-1,2,4-triazolidine-3,5-dione, in good yield: mp 121–122 °C; ir ($CHCl_3$) 1785 (m), 1740 (vs), 1285 (s), 1170 cm^{-1} (s); NMR ($CDCl_3$) 1.19 (s, 18 H), 2.47 (s, 3 H), 7.25–8.25 ppm (m, 4 H); shown to be identical with an authentic sample (see below).

Anal. Calcd for $C_{17}H_{25}N_3O_4S$: C, 55.53; H, 6.82; N, 11.43. Found: C, 55.38; H, 6.89; N, 11.51.

B. With *p*-Nitrophenyl Isocyanate. A solution of di-*tert*-butyldiaziridinone (0.65 g, 3.8 mmol), *p*-nitrophenyl isocyanate (0.60 g, 3.6

mmol), and 5 ml of isooctane was heated at 100 °C. A yellow precipitate slowly formed and the reaction was followed by ir. After 48 h all the diaziridinone had been consumed. Evaporation of the solvent gave a yellow powder: ir ($CHCl_3$) 1790, 1775, 1730, 1665 cm^{-1}. A portion of the product was purified by preparative TLC (alumina, CH_2Cl_2). The main product, which possessed the highest R_f, was recrystallized from THF–heptane to give colorless needles, assigned the urazole structure, 1,2-di-*tert*-butyl-4-*p*-nitrophenyl-1,2,4-triazolidine-3,5-dione, on the basis of the physical data: mp 158–159.5 °C; ir ($CHCl_3$) 1775 (w), 1730 (s), 1595 (w), 1525 (m), 1495 (m), 1390 (m), 1375 (m), 1345 cm^{-1} (m); NMR ($CDCl_3$) 7.97 (A_2B_2, $\Delta\nu$ 39 Hz, J = 9 Hz, 4 H), 1.37 ppm (s, 18 H); mass spectrum *m/e* (rel intensity) 334 (M^+, 1.5), 280 (1), 279 (5), 278 (25), 263 (3), 248 (2), 224 (2), 223 (7), 222 (50), 192 (4), 176 (2), 165 (2), 149 (7), 115 (9), 57 (100), 41 (30), 29 (25), 28 (15).

2,3 Di-*tert*-butylcarbazyl Chloride. Phosgene (0.95 g, 9.5 mmol) in 20 ml of anhydrous ether was added by cannula to a stirred solution under nitrogen of 1,2-di-*tert*-butylhydrazine (1.30 g, 9.0 mmol) and triethylamine (0.95 g, 9.0 mmol), in 200 ml of ether. A copious precipitate was observed on completion of the addition. Filtration followed by evaporation of the filtrate, and trituration with 20 ml of pentane, filtering, and evaporation of the pentane afforded 1.60 g (86%) of a fragrant, faintly yellow liquid: ir (CCl_4) 3440 (w), 3350 (w), 1745 cm^{-1} (s); NMR (CCl_4) 1.20 (s, 9 H), 1.43 (s, 9 H), and 4.02 ppm (b, 1 H). This material is identical with that obtained by reaction of di-*tert*-butyldiaziridinone with dry HCl. In the absence of moisture it decomposes slowly to a white solid: ir (CCl_4) 3500–2500 (m), 1700 (m, b), 1710 cm^{-1} (s, b).

1,2-Di-*tert*-butyl-4-*p*-toluenesulfonyl-1,2,4-triazolidine-3,5-dione. A solution of 2,3-di-*tert*-butylcarbazyl chloride (0.477 g, 2.30 mmol) and *p*-toluenesulfonyl isocyanate (0.446 g, 2.26 mmol) in 10 ml of dry hexane was refluxed for 14 h. Infrared spectra showed weakening of the isocyanate band plus appearance of a new one at 1715 cm^{-1}. Sodium hydride [0.090 g (57%), 2.1 mmol] was added and the solution refluxed for 6 days. The hexane was evaporated leaving white crystals and an oil. This was extracted with 30 ml of pentane, followed by 25 ml of boiling hexane. Evaporation of the pentane afforded mainly *p*-toluenesulfonamide. Evaporation of the hexane afforded 0.078 g (10%) of essentially pure urazole: mp 120–122 °C, shown to be identical by mixture melting point and ir spectra with the product of reaction of di-*tert*-butyldiaziridinone and *p*-toluenesulfonyl isocyanate (see above).

2,2,4,4-Tetramethylglutaric Acid. Isobutyric acid (88.0 g, 1.00 mol) (dried over $MgSO_4$) was added, slowly at first, to lithium wire (7.12 g, 1.01 mol) in 800 ml of dry THF.[23] The mixture was refluxed for 36 h, during which time the lithium was consumed and a white precipitate formed. To this mixture under nitrogen, cooled in an ice bath, was added by cannula 1 mol of lithium diisopropylamide [made from diisopropylamine (102 g, 1.01 mol) and 1 mol of *n*-butyllithium (Ventron) in hexane]. The precipitate dissolved during the addition. After stirring for 3 h diiodomethane (130 g, 0.485 mol) was added with cooling; the reaction is exothermic. The mixture was stirred for 21 h at room temperature and heated at reflux for 5 h. The reaction mixture was evaporated to a volume of 500 ml and then poured into 400 ml of ice and acidified with 180 ml of concentrated hydrochloric acid. This was extracted five times with 250-ml portions of ether. The combined ether was dried ($MgSO_4$) and evaporated to give crystals with highly colored impurities. Recrystallization from water gave 39.3 g (43%) of colorless crystals: mp 187–189 °C (lit.[24] 185–186 °C); ir ($CHCl_3$) 3500–2500 (b), 1715 cm^{-1} (s); NMR ($CDCl_3$) 1.86 (s, 2 H), 1.30 ppm (s, 12 H).

2,2,4,4-Tetramethylglutaryl Dichloride. The procedure followed was adapted from Cason and Reist's preparation of glutaryl dichloride.[25] Thionyl chloride (80 g, 0.68 mol) was added to 2,2,4,4-tetramethylglutaric acid (10.00 g, 0.53 mol) and 0.15 ml of pyridine. After the vigorous initial reaction had subsided, the mixture was heated at reflux for 4 days. The solvent was evaporated and the residue sublimed at 30 °C and 0.005 mm to give 9.12 g (76%) of a white solid which had mp 38–39.5 °C; ir (CCl_4) 1810 (s), 1785 (vs), 1765 (m), 940 (m), 900 (w), 865 (m), 850 cm^{-1} (s); NMR (CCl_4) 2.34 (s, 2 H), 1.33 ppm (s, 12 H).

Anal. Calcd for $C_9H_{14}Cl_2O_2$: C, 48.02; H, 6.27. Found: C, 47.95; H, 6.19.

4,4,6,6-Tetramethyltetrahydro-2-pyrimidone (6a) was prepared in three consecutive steps starting with 2,2,4,4-tetramethylglutaryl dichloride. To a solution of sodium azide (23 g, 0.35 mol) in 75 ml of water, cooled in ice and rapidly stirred, was added slowly by pipet 2,2,4,4-tetramethylglutaryl dichloride (5.00 g, 22.3 mmol) in 15 ml of THF. After stirring for 100 min, 100 ml of water was added and the resulting solution extracted four times with 75 ml of benzene. The combined benzene solution was dried ($MgSO_4$). A small aliquot was evaporated to give 2,2,4,4-tetramethylglutaryl diazide: ir (CCl_4) 2135 (vs), 1710 (s), 1170 (s), 1135 (m), 1035 (s), 1005 cm^{-1} (m); NMR (CCl_4) 1.94 (s, 2 H), 1.13 ppm (s, 12 H). The azide solution was slowly heated to the boiling point of benzene, then refluxed for 1 h; gas evolution began at 65 °C. The benzene was evaporated to give 2,4-dimethyl-2,4-pentyl diisocyanate. A sample purified by GC had ir (CCl_4) 2250 (vs), 1225 (w), 1180 cm^{-1} (m); NMR (CCl_4) 1.71 (s, 2 H), 1.47 ppm (s, 12 H); mass spectrum *m/e* (rel intensity) 168 (1), 127 (3), 85 (6), 84 (100), 83 (3), 76 (4), 56 (12), 55 (3), 54 (2), 53 (1), 42 (5), 41 (6), 40 (2), 39 (3).

Anal. Calcd for $C_9H_{14}N_2O_2$: C, 59.32; H, 7.74; N, 15.37. Found: C, 59.10; H, 7.54; N, 15.09.

The crude diisocyanate was dissolved in 250 ml of THF containing 5 ml of water and refluxed for 3 days. The solvent was evaporated and the resulting solid dried for 1 h at 90 °C and 20 mm. Sublimation at 130 °C and 0.01 mm gave 3.05 g of a white powder, mp 213–216 °C. This was dissolved in 200 ml of methylene chloride, extracted four times with 15-ml portions of saturated $NaHCO_3$ solution, and evaporated to give 2.65 g (76%) of 4,4,6,6-tetramethyltetrahydro-2-pyrimidone (**6a**), mp 216–219 °C. Sublimation at 100 °C and 0.005 mm gave analytically pure material: mp 219–220.5 °C; ir ($CHCl_3$) 3420 (w), 1655 (s), 1480 (m), 1460 cm^{-1} (m); NMR ($CDCl_3$) 5.15 (b, 2 H), 1.69 (s, 2 H), 1.28 ppm (s, 12 H); mass spectrum *m/e* (rel intensity) 156 (M^+, 3), 142 (10), 141 (25), 99 (4), 98 (28), 85 (5), 84 (70), 63 (23), 62.5 (7), 59 (8), 58 (58), 57 (33), 56 (28), 55 (8), 43 (7), 42 (100), 41 (33), 40 (5), 39 (14).

Anal. Calcd for $C_8H_{16}N_2O$: C, 61.51; H, 10.33; N, 17.92. Found: C, 61.28; H, 10.10; N, 17.70.

General Method for the Preparation of *N*-Chloro Ureas. The urea to be chlorinated was dissolved or suspended in a minimal amount of methylene chloride (typically 5–10 ml per gram of urea) containing 1 equiv of *tert*-butyl hypochlorite. After several hours (protected from light) the solvent was evaporated at aspirator pressure and the crude product placed under 0.005 mm vacuum for 10 min in order to remove any residual *tert*-butyl alcohol. An excess of *tert*-butyl hypochlorite should be avoided with the cyclic ureas as dichlorination may occur.

For preparation of the *N,N'*-dichloro ureas, longer reaction times and a severalfold excess of *tert*-butyl hypochlorite were used. Dichlorination was not observed with *N,N'*-di-*tert*-butylurea.

1-Chloro-4,4,6,6-tetramethyltetrahydro-2-pyrimidone (6b) was prepared from 4,4,6,6-tetramethyltetrahydro-2-pyrimidone (0.205 g, 1.31 mmol) and *tert*-butyl hypochlorite (0.150 g, 1.37 mmol) in 5 ml of methylene chloride by the above procedure: 0.253 g (~100%) of white crystals; mp 135–138 °C; ir (CCl_4) 3210 (m), 2960 (m), 1680 (s), 1390 (m), 1365 (m), 1190 cm^{-1} (w); ir ($CHCl_3$) 3410 (m), 1660 cm^{-1} (s); NMR ($CDCl_3$) 5.00 (b, 1 H), 1.96 (s, 2 H), 1.40 (s, 6 H), 1.30 ppm (s, 6 H); mass spectrum *m/e* (rel intensity) 192 (M^+, 1), 190 (M^+, 2), 177 (3), 176 (1), 175 (10), 157 (2), 142 (5), 141 (4), 134 (6), 133 (1), 132 (17), 125 (2), 98 (15), 97 (17), 94 (10), 58 (65), 57 (25), 56 (63), 55 (20), 42 (100), 41 (50), 39 (22).

1-Chloro-4,4,5,5-tetramethyl-2-imidazolidone (7b) was prepared from 4,4,5,5-tetramethyl-2-imidazolidone[26] (0.312 g, 2.20 mmol) and *tert*-butyl hypochlorite (0.242 g, 2.21 mmol) in 12 ml of methylene chloride by the above procedure: 0.375 (97%) of white crystals; mp >100 °C dec; ir (CCl_4) 3200 (m, b), 1730 cm^{-1} (s); NMR (CCl_4) 7.05 (b, 1 H), 1.25 (s, 6 H), 1.19 ppm (s, 6 H).

1,3-Dichloro-4,4,5,5-tetramethyl-2-imidazolidone (7c) was prepared from 4,4,5,5-tetramethyl-2-imidazolidone[26] (142 mg, 1.00 mmol) and *tert*-butyl hypochlorite (300 mg, 2.75 mmol) in 2 ml of methylene chloride by the above procedure: 211 mg (100%) of a white, crystalline solid; mp 92–96 °C; ir (CCl_4) 1775 (s), 1735 (sh), 1385 (m), 1375 (m), 1275 cm^{-1} (m); NMR (CCl_4) 1.24 ppm (s).

Anal. Calcd for $C_7H_{12}N_2OCl_2$: C, 39.78; H, 5.73. Found: C, 40.04; H, 5.93.

1,3-Dichloro-4,4,7,7-tetramethyl-1,3-diaza-2-cycloheptanone was prepared from 4,4,7,7-tetramethyl-1,3-diaza-2-cycloheptanone (81 mg, 0.48 mmol), dissolved in 1 ml of *tert*-butyl hypochlorite and allowed to stand for 48 h protected from light. Removal of solvent afforded 112 mg (100%) of a white, crystalline solid: mp 88–91 °C; ir (CCl_4) 1705 (s), 1455 (m), 1385 (m), 1365 (m), 1275 (m), 1250 (m), 1140 (m), 1120 cm^{-1} (m); NMR (CCl_4) 1.35 (s, 12 H), 1.88 ppm (s, 4 H); mass spectrum *m/e* (rel intensity) 242 (M^+, 0.5), 240 (M^+, 3), 238 (M^+, 5), 225 (0.5), 223 (2), 149 (3), 148 (19), 147 (6), 146 (60), 112 (11), 111 (9), 110 (9), 96 (9), 95 (28), 93 (26), 92 (77), 84 (23), 70 (31), 69 (50), 68 (11), 67 (11), 58 (60), 57 (12), 56 (70), 55 (65), 54 (12), 53 (11), 43 (19), 42 (77), 41 (100), 40 (15), 39 (40).

Anal. Calcd for $C_9H_{16}N_2OCl_2$: C, 45.19; H, 6.74. Found: C, 45.51; H, 6.89.

1,3-Dichloro-4,4,6,6-tetramethyltetrahydro-2-pyrimidone (6c)

was prepared from 4,4,6,6-tetramethyltetrahydro-2-pyrimidone (27 mg, 0.17 mmol) and *tert*-butyl hypochlorite (150 mg, 1.4 mmol) in 1 ml of methylene chloride: 39 mg (100%) of a white, crystalline solid; mp 90 °C dec; ir (CCl_4) 1705 (s), 1385 (w), 1370 (w), 1290 (m), 1215 cm^{-1} (m); NMR (CCl_4) 1.39 (s, 12 H), 2.15 ppm (s, 2 H).

1,3-Dichlorotetrahydro-2-pyrimidone. Tetrahydro-2-pyrimidone (Aldrich, 1.00 g, 10.0 mmol) and *tert*-butyl hypochlorite (3 ml) in 25 ml of methylene chloride were allowed to stand for 14 h protected from light. The solvent was evaporated to give 1.75 g (~100%) of a white solid: mp 68–70 °C; ir (CCl_4) 1710–1715 (s), 1475 (m), 1395 (m), 1270 (m), 1200 (m), 1165 cm^{-1} (m); NMR (CCl_4) 2.38 (t, J = 6 Hz, 4 H), 1.00 ppm (quintet, J = 6 Hz, 2 H). Samples were observed to decompose spontaneously and exothermically.

Attempted Preparation of Diaziridinones from 6 and 7. Reaction of 1-chloro-4,4,6,6-tetramethyltetrahydro-2-pyrimidone with the potassium salt of 4,4,6,6-tetramethyltetrahydro-2-pyrimidone in DME, or with the potassium salt of 1,1-diethyl-3-*tert*-butylurea in DME, or with sodium tribenzylmethoxide in THF provided no ir evidence even for the transient existence of a diaziridinone. Addition of 1 equiv of bromine to a suspension of 2 equiv of the potassium salt of tetramethyltetrahydropyrimidone in DME gave an immediate precipitation of potassium bromide, and after workup 80% recovery of the urea.

During the reaction of 1,3-dichloro-4,4,6,6-tetramethyltetrahydro-2-pyrimidone with potassium hydride in THF, and with potassium triethylmethoxide in THF, transient weak carbonyl bands were observed at 1915 and 1865 cm^{-1}.

Reaction of the chloro urea with potassium dispersion in benzene was immediate and vigorous; a moderate carbonyl band was seen at 1865 and a weaker one at 1915 cm^{-1}. These absorptions disappeared before isolation could be attempted.

No reaction was observed by ir between 1-chloro-4,4,5,5-tetramethyl-2-imidazolidone and potassium *tert*-butoxide in ether.

Registry No.—**3**, 58816-12-9; **3** dimeric derivative, 59169-67-4; **3** potassium salt, 58816-14-1; **4**, 58816-15-2; **5**, 19403-24-8; **6a**, 58816-16-3; **6b**, 58816-17-4; **6c**, 58816-18-5; **7a**, 3964-19-0; **7b**, 58816-19-6; **7c**, 58816-20-9; 2,5-dimethyl-2,5-diaminohexane, 23578-35-0; 1,1′-carbonyldiimidazolo, 530-62-1; 1-chloro-4,4,7,7-tetramethyl-1,3-diazacycloheptan-2-one, 58816-21-0; *p*-nitrophenyl isocyanate, 100-28-7; 2,2,5,5-tetramethyl-8-*p*-nitrophenyl-1,6,8-triazabicyclo[4.3.0]nonane-7,9-dione, 58816-22-1; ethanol, 64-17-5; methanol, 67-56-1; benzhydrol, 91-01-0; hydrazobenzene, 122-66-7; *N,N′*-di-*tert*-butylhydrazine, 13952-69-7; *p*-toluenesulfonyl isocyanate, 4083-64-1; 1,2-di-*tert*-butyl-4-*p*-toluenesulfonyl-1,2,4-triazolidine-3,5-dione, 58816-23-2; 1,2-di-*tert*-butyl-4-*p*-nitrophenyl-1,2,4-triazolidine-3,5-dione, 58816-24-3; 2,3-di-*tert*-butylcarbazyl chloride, 58816-25-4; 2,2,4,4-tetramethylglutaric acid, 1189-82-8; isobutyric acid, 79-31-2; 2,2,4,4-tetramethylglutaryl dichloride, 58816-26-5; 2,4-dimethyl-2,4-pentyl diisocyanate, 58816-27-6; 1,3-dichloro-4,4,7,7-tetramethyl-1,3-diaza-2-cycloheptanone, 58816-28-7; 1,3-dichlorotetrahydro-2-pyrimidone, 58816-29-8; tetrahydro-2-pyrimidone, 1852-17-1; 2,2,4,4-tetramethylglutaryl diazide, 58816-30-1; di-*tert*-butyldiaziridinone, 19656-74-7.

References and Notes

(1) (a) Supported, in part, by Public Health Service Research Grant CA-16592 from the National Cancer Institute. (b) National Science Foundation Predoctoral Fellow.

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