R′ = C_6H_{11}).—An amount of 8.06 g of a mixture of cycloadducts, obtained from *p*-toluenesulfonyl isocyanate and dicyclohexylcarbodiimide, is heated in 50 ml of *o*-dichlorobenzene with simultaneous distillation of most of the solvent. Vacuum distillation of the residue yields 4.6 g of *p*-toluenesulfonylcyclohexylcarbodiimide: bp 203–206° (0.3 mm); mp 50–52° (lit.[17] mp 52°); ir ($CHCl_3$) 2151 cm^{-1} ($SO_2N{=}C{=}N$).

(17) Farbenfabriken Bayer A. G., Netherlands Patent Appl. 6,413,827 (1966); *Chem. Abstr.*, **64**, 19506 (1966).

Registry No.—**6**, R = 4-$CH_3C_6H_4$; R′ = C_6H_{11}, 19978-05-3; **6**, R = 4-ClC_6H_4; R = C_6H_{11}, 19978-06-4; **6**, R = 4-$CH_3C_6H_4$; R′ = CH_3, *t*-C_4H_9, 19978-07-5; **8**, R = 4-$CH_3C_6H_4$; R′ = C_6H_{11}, 19978-08-6; **8**, R = 4-ClC_6H_4; R′ = C_6H_{11}, 19978-09-7; **9**, R = 4-$CH_3C_6H_4$; R′ = *i*-C_3H_7, 19978-10-0; **12**, R = 4-$CH_3C_6H_4$; R′ = C_6H_{11}, 19978-11-1; **15**, R = 4-$CH_3C_6H_4$; R′ = C_6H_{11}, 908-18-9.

Diaziridinones (2,3-Diazacyclopropanones). II.[1a] Synthesis, Properties, and Reactions[1b]

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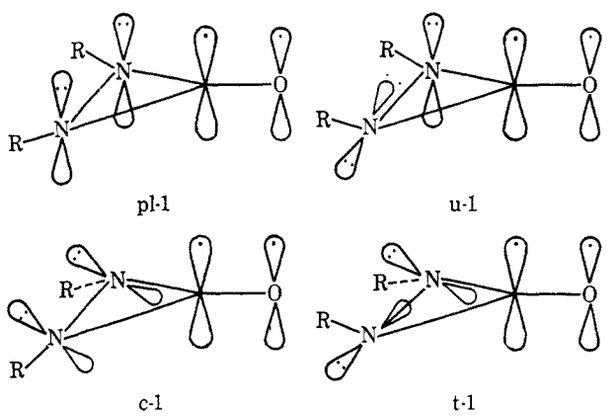
Received August 26, 1968

Reaction of 1-chloro-1,3-di-*t*-alkylurea with potassium *t*-butoxide in *t*-butyl alcohol effects ring closure to a diaziridinone **1**, a new three-membered ring heterocycle. Spectral data indicate a *trans* orientation for the substituents attached to the nitrogen atoms. The diaziridinones are reactive toward acids, only moderately reactive toward a range of nucleophiles, and function as mild oxidizing agents toward thiols, phenols, enols, and some hydrazines. The acids studied include hydrogen chloride, picric acid, benzoic acid, and formic acid with resultant ring opening of diaziridinone and formation of substituted carbazates **8a**, **c–e**. A second method of formation of diaziridinones is found in the regeneration of **1a** by the action of potassium *t*-butoxide on 2,3-di-*t*-butylcarbazyl chloride **8a**. Studies of the action of nucleophiles on di-*t*-butyldiaziridinone include *t*-butoxide, *t*-butyl alcohol, methoxide, and methanol (ring opening to alkyl carbazates **8b** and **8f**), isopropylamine (ring opening to substituted semicarbazide **10**), and hydrazine (ring opening and conversion to carbohydrazide). Di-*t*-butyldiaziridinone is reduced by benzylthiol (or ethanethiol) to 1,3-di-*t*-butylurea and benzyl disulfide (or ethyl disulfide). Diaziridinone **1a** is reduced to the urea rapidly by ascorbic acid and by phenylhydrazine and, more slowly, by phenol and by 2,4,6-tri-*t*-butylphenol. *t*-Butylhydroxylamine reacts with **1a** both by nucleophilic attack at carbonyl carbon with ring opening giving carbazate **17**, and by oxidation–reduction giving di-*t*-butylurea and 2-methyl-2-nitrosopropane. The reactions described here constitute a new method for the formation of a nitrogen–nitrogen bond, hydrazo, and azo compounds. They also provide new routes to substituted carbazates and semicarbazides. Of special interest in the chemistry of diaziridinones is the balance between nucleophilic ring opening with cleavage of the carbonyl carbon–nitrogen bond and oxidation–reduction ring opening with reductive cleavage of the nitrogen–nitrogen bond.

In a search for new methods for the formation of the nitrogen–nitrogen bond, we have examined the effect of strong bases on 1-chloroureas, in analogy to the Favorskii reaction. Reaction occurs, a nitrogen–nitrogen bond *is* formed, and (contrary to our original expectations) the resulting 2,3-diazacyclopropanones (hereafter called diaziridinones)[2] are, in a number of instances, isolable and moderately stable compounds. This paper describes the synthesis, evidence on structure, and a number of reactions of this new class of compounds (Scheme I).[3]

In all cases examined to date, this route has succeeded only when both R and R′ are tertiary alkyl groups. The 1-chloroureas may be isolated and characterized but in general good yields of diaziridinones are obtained without isolation of this species. Diaziridinones may also be prepared by reaction of the 1-chlorourea in pentane with potassium but yields have been lower than by the *t*-butoxide route (Scheme II[4]).

Stereochemistry.—Possible spatial arrangements for the R groups of **1** are shown in pl-1, u-1, c-1, and t-1. In both pl-1 and u-1, a nitrogen lone pair of electrons is in a p orbital conjugated with the carbonyl π system.



The usual delocalization effect in amides is a shift from the value of 1710 cm^{-1} observed in simple ketones to 1650–1690 cm^{-1} (1660–1695 cm^{-1} for ureas). An amide in which delocalization from nitrogen to oxygen is disallowed by the orthogonality of the orbitals, quinuclidone-2,[5] shows carbonyl absorption at 1750 cm^{-1}, ~40 cm^{-1} *higher* than a simple ketone. Cyclo-

(1) (a) Part I: F. D. Greene and J. C. Stowell, *J. Amer. Chem. Soc.*, **86**, 3569 (1964). (b) Financial support from the National Science Foundation (Grant No. GP-5527) is gratefully acknowledged.

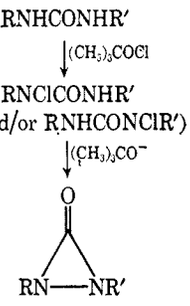
(2) For recent reviews of three-membered ring heterocyclic compounds, see (a) E. Schmitz, "Dreiringe mit Zwei Heteroatomen," Springer-Verlag, Berlin, 1967; (b) I. Lengyel and J. C. Sheehan, *Angew. Chem.*, **80**, 27 (1968); *Angew. Chem. Intern. Ed. Engl.*, **7**, 25 (1968).

(3) The methods are analogous to those used to prepare α-lactams; see ref 2b and H. E. Baumgarten, J. F. Fuerholzer, R. D. Clark, and R. D. Thompson, *J. Amer. Chem. Soc.*, **85**, 3303 (1963).

(4) Nmr values are in parts per million downfield from TMS.

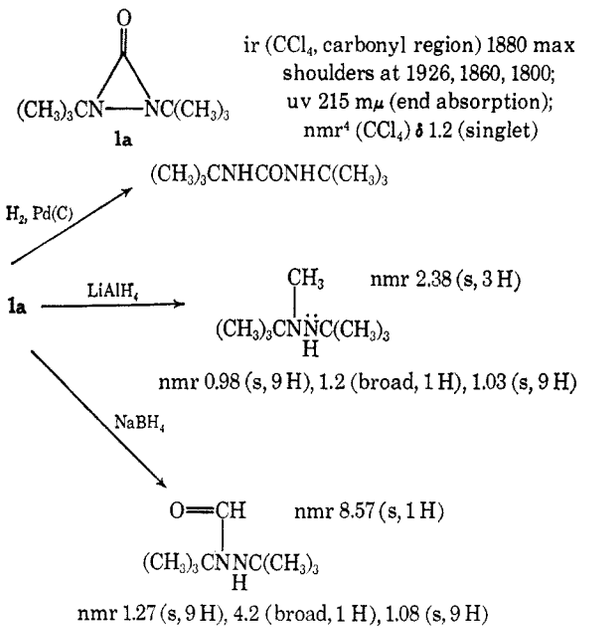
(5) H. Pracejus, M. Kehlen, H. Kehlen, and M. Matschiner, *Tetrahedron*, **21**, 2257 (1965).

SCHEME I
SYNTHESIS OF DIAZIRIDINONES



1a, R = R′ = *t*-butyl
b, R = R′ = *t*-amyl
c, R = R′ = *t*-octyl
d, R = R′ = 2-methyl-3-phenyl-2-propyl
e, R = *t*-butyl; R′ = *t*-octyl

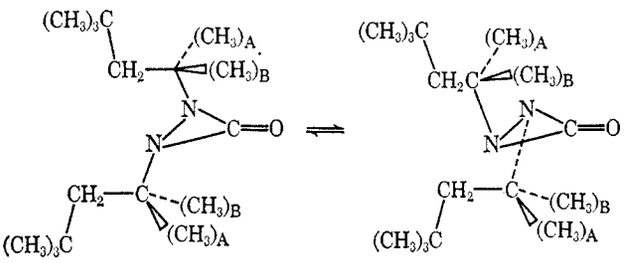
SCHEME II
EVIDENCE ON STRUCTURE, DI-*t*-BUTYLDIAZIRIDINONE



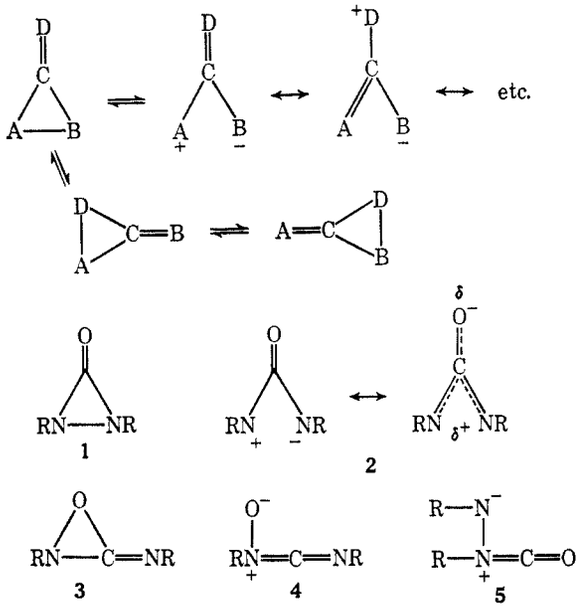
propanones have values of 1813–1840 cm^{-1},[6] aziridinones 1837–1850 cm^{-1},[2b] and diaziridinones 1855–1880 cm^{-1}. These data suggest a decreased amount of nitrogen lone pair delocalization in diaziridinones in comparison with urea, and favor structures c-1 and t-1 over pl-1 and u-1. Structure c-1, with two large groups eclipsed, would be expected to be less stable than t-1.

The dipole moment of di-*t*-butyldiaziridinone measured in benzene solution at 24° is 2.6 D. This may be compared with values of 3.47 D for tetramethylurea,[7] 5.1 D for 1,3-dimethylurea,[7] 2.76 D for cyclobutanone,[7] and 4.78 D for di-*n*-butylcyclopropenone.[8]

Further evidence on stereochemistry is found in the temperature dependence of the nmr spectrum of di-*t*-octyldiaziridinone. Below 30°, the methyl groups on the carbon atoms attached to the nitrogen atoms appear as two equal peaks ($\Delta\delta$ = 7 Hz). On heating to 40°, the doublet coalesces to a single sharp peak, corresponding to a ΔF^* of ~16 kcal/mol. The magnitude of this energy barrier seems too great to be ascribed to hindered rotation around an sp^3 C–N bond. The nmr observations are, however, in accord with interconversion of the two optical antipodes of *trans*-**1** *via* "slow" inversion about both nitrogen atoms.[9] The nmr spectrum of di-*t*-butyldiaziridinone is a sharp singlet, unchanged over the range examined, −40 to +150°.



Reactions of Diaziridinones. General Considerations.—The diaziridinones present several aspects of interest. As a three-ring system possessing an exocyclic multiple bond, a diaziridinone has the possibility of "ring–chain" isomerism[10] and small-ring isomerism (**1**, **2**, **3**, **4**, **5**).[11]



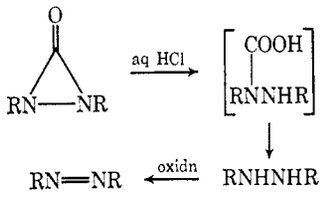
Each of the alternatives **2**–**5** fails in some respects to accommodate the physical and chemical evidence presented in this paper, which strongly favors structure **1** for the ground state of diaziridinones. Detailed consideration of the role these structures (*e.g.*, **2**–**5**) may play in the chemistry of diaziridinones is deferred to a later paper in which reactions requiring their involvement are described. In the reactions outlined

(6) (a) N. J. Turro and W. B. Hammond, *J. Amer. Chem. Soc.*, **88**, 3673 (1965); (b) J. F. Pazos and F. D. Greene, *ibid.*, **89**, 1030 (1967).
(7) A. L. McClellan, "Tables of Experimental Dipole Moments," W. H. Freeman, San Francisco, Calif., 1963.
(8) R. Breslow, T. Eicher, A. Krebs, R. A. Peterson, and J. Posner, *J. Amer. Chem. Soc.*, **87**, 1320, 1326 (1965).
(9) See R. S. Atkinson, *Chem. Commun.*, 676 (1968), and references cited therein; L. W. Reeves, *Advan. Phys. Org. Chem.*, **3**, 187 (1965).
(10) J. G. Burr, Jr., and M. J. S. Dewar, *J. Chem. Soc.*, 1201 (1954); see also A. W. Fort, *J. Amer. Chem. Soc.*, **84**, 2620 (1962), and references therein.
(11) See E. F. Ullman and W. J. Fanshawe, *ibid.*, **83**, 2379 (1961); J. P. Chesick, *ibid.*, **85**, 2720 (1963); J. A. Deyrup and R. B. Greenwald, *Tetrahedron Lett.*, 5091 (1966).

below, however, one should bear in mind the possibility of involvement of these forms.

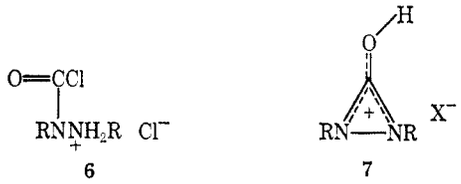
Reactivity.—The diaziridinones studied to date have a tertiary alkyl group on each nitrogen. The compounds are moderately stable to heat and light, generally insensitive to water, only moderately reactive toward a range of nucleophiles, reactive toward acids, and undergo a number of interesting reactions with certain reducing agents. Most of the exploratory work on reactivity has been carried out on di-*t*-butyldiaziridinone.

Effects of Acids.—Diaziridinones undergo facile ring opening with acid. Aqueous hydrochloric acid effects ring opening and decarboxylation (eq 1). The resulting hydrazine has been isolated in 90% yield from di-*t*-butyldiaziridinone. This sequence constitutes a useful route to hydrazines and the corresponding azo compounds, readily obtained by a subsequent oxidation. It may be of special use in the synthesis of unsymmetrical tertiary azo compounds;[12] the symmetrical ones may be prepared by the action of IF_5 on the tertiary alkyl primary amine.[13]



(1)

Treatment of **1a** with dry hydrogen chloride in pentane affords an immediate precipitate. This material is soluble in chloroform and shows two singlets for the *t*-butyl groups in the nmr and a carbonyl band at 1750 cm^{-1} (Nujol) on which grounds it is assigned structure **6**, the hydrochloride of the carbazyl chloride, rather than a protonated diaziridinone **7**. The free

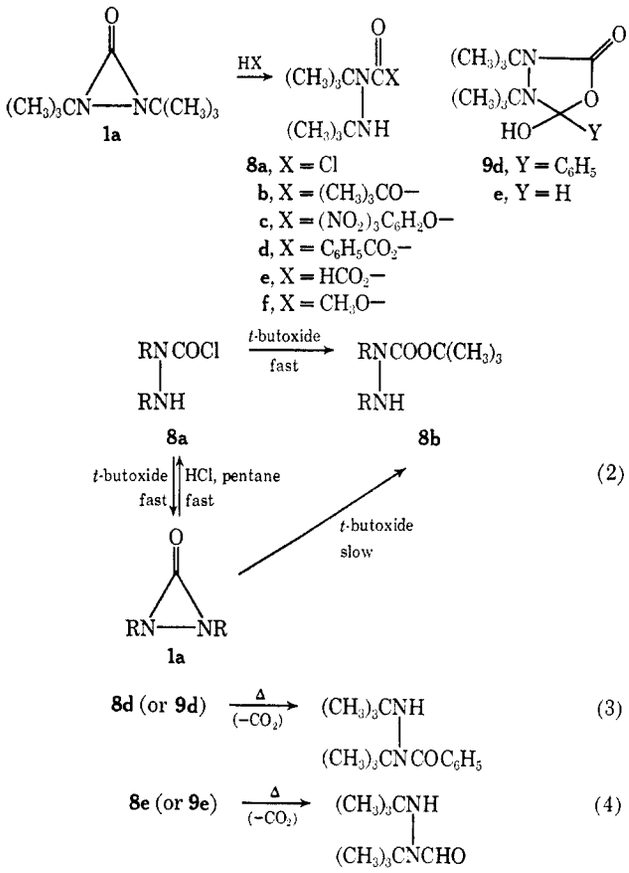


6 **7**

carbazyl chloride, **8a**, is easily obtained from **6**. Treatment of **8a** with *t*-butyl alcohol–potassium *t*-butoxide effects rapid conversion to a mixture of the *t*-butyl carbazate **8b** (25%) and **1a** (45%), eq 2. Here, **8b** is formed directly from **8a** and not from **1a**; reaction of **1a** with *t*-butoxide is a much slower reaction (see next section).

The conversion of the carbazyl chloride to the diaziridinone (eq 2) constitutes a second method of preparation of this ring system.

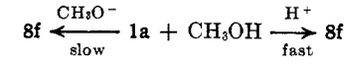
Picric acid effects rapid conversion of **1a** to the picryl carbazate **8c**. Reaction with less acidic phenols such as phenol itself or alkyl-substituted phenols



takes an entirely different course, an oxidation–reduction reaction, and is discussed in a later section of this paper.

Reaction of **1a** with benzoic acid proceeds more slowly than with picric acid, and affords **8d** (or its cyclic tautometric form, **9d**). Upon heating, **8d** (or **9d**) is converted to 1-benzoyl-1,2-di-*t*-butylhydrazine with loss of carbon dioxide (eq 3). In view of the reducing properties of formic acid, its action on **1a** was examined. The reaction proceeds as with benzoic acid.

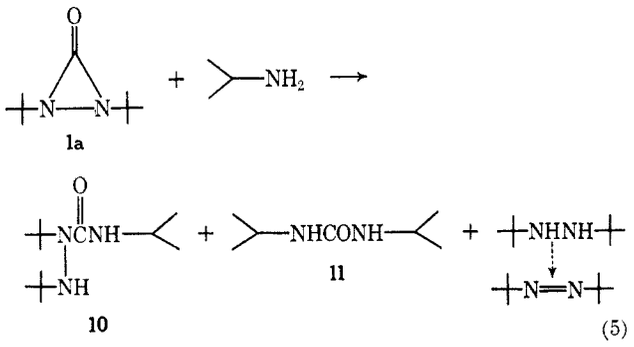
Effect of Nucleophiles. A. Attack at Carbonyl Carbon.—Diaziridinones are rather sluggish toward nucleophilic attack at the carbonyl carbon atom. Reflux for 16 hr in *t*-butyl alcohol containing potassium *t*-butoxide is required to effect 50% ring opening of **1a** to *t*-butyl 2,3-di-*t*-butylcarbazate, **8b**. As expected, reaction with methanol–methoxide is more rapid (complete conversion to the methyl carbazate after 40 min at reflux in 0.4 *M* CH_3ONa–CH_3OH). Far more rapid, however, is the conversion of **1a** to **8f** by acid catalysis in place of base catalysis.



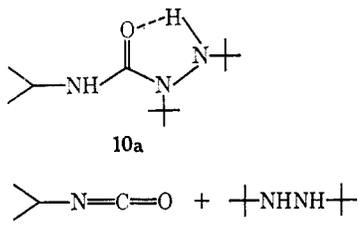
Reaction of **1a** with a few amines has been examined. From the reaction of equimolar amounts of isopropylamine and **1a** at 25° for 96 hr were obtained 1,2-di-*t*-butyl-4-isopropylsemicarbazide, **10** (35%), 1,3-diisopropylurea, **11** (25%), and 2,2′-dimethyl-2,2′-azopropane (from air oxidation of the corresponding hy-

(12) Primary and secondary 1,2-disubstituted hydrazines are accessible from the corresponding azines. A variety of symmetrical 1,2-disubstituted hydrazines also may be prepared *via* the 1,2-dialkyl sulfuric acid diamides: R. Ohme and E. Schmitz, *Angew. Chem.*, **77**, 429 (1965).

(13) T. E. Stevens, *J. Org. Chem.*, **26**, 2531 (1961); S. F. Nelson and P. D. Bartlett, *J. Amer. Chem. Soc.*, **88**, 137 (1966).



drazine liberated in the reaction), eq 5. It is of interest that **10** competes so well with the diaziridinone for isopropylamine. 1-*t*-Butyl-3-isopropylurea, a compound comparable with **10** in the degree of steric hindrance at carbonyl carbon, was inert toward the amine. The greater reactivity of **10** may be associated with intramolecular catalysis *via* **10a**. Alternatively, it may



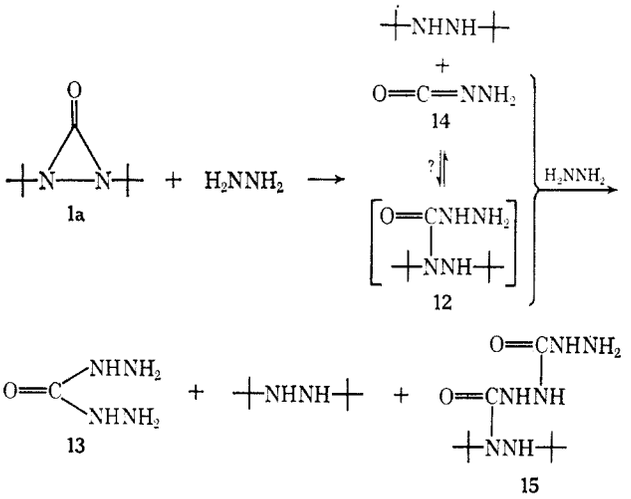
be due to dissociation of **10** into isopropyl isocyanate and 1,2-di-*t*-butylhydrazine, followed by reaction of the isocyanate with the isopropylamine.[14] A choice between these paths might be made by use of a secondary amine in place of isopropylamine, in that the species corresponding to **10** would then lack the NH necessary for dissociation into an isocyanate. However, diethylamine was too unreactive toward the diaziridinone, precluding the desired mechanistic distinction. Under the conditions of the **1a**–isopropylamine reaction, aniline does not react with **1a**.

The slowness of nucleophilic attack at the carbonyl carbon of diaziridinones requires comment. The data relevant to structure provide a strong indication that diaziridinones have stereochemistry t-1. The *trans*-oriented *t*-alkyl groups provide considerable steric hindrance to the carbonyl carbon. Nucleophilic attack at carbonyl carbon is much faster with *trans*-2,3-di-*t*-butylcyclopropanone[6b] than with di-*t*-butyldiaziridinone. Thus, delocalization of nitrogen lone pair electrons to the carbonyl group in t-1, although of diminished value in comparison with acyclic amides and ureas, is still of consequence. A second factor leading to reduced reactivity of the diaziridinone compared with the cyclopropanone may be repulsion between a nitrogen lone pair and the nucleophile as it approaches the carbonyl carbon.

B. Reaction with Hydrazines.—Hydrazines interact with diaziridinones in three ways: (1) nucleophilic attack at carbonyl carbon, (2) oxidation of the hydrazine and reduction of the diaziridinone to the corresponding urea, (3) rearrangement of the diaziridinone to an aziridinecarboxamide (1-carbamoylaziridine). Some information on the first two categories is presented in this paper. The third category (and its relation to the second) is treated in detail in part III of this series.[15]

Reaction of **1a** with hydrazine in a 1:1 molar ratio affords carbohydrazide **13** (23%) and a compound to which is assigned structure **15** (25%), 1-(2,3-di-*t*-butylcarbazyl)carbohydrazide, along with di-*t*-butylhydrazine and unchanged **1a**. Reaction of **1a** with a tenfold excess of hydrazine affords **13** (93%) and di-*t*-butylhydrazine (72%). In neither case was the intermediate **12** obtained. Here also, as with the question of **10** and isopropylamine discussed above, the basis for the apparent reactivity of **12** with hydrazine is not known; the main possibilities are intramolecular catalysis or dissociation to **14** and di-*t*-butylhydrazine.[14] The insolubility of carbohydrazide **13** in the reaction medium is suggestive that formation of **15** from **12** + **14** may be preferred over **13** + **1a** (or **12**) (Scheme III).

SCHEME III



C. Oxidation–Reduction Reactions with Nucleophiles.—In marked contrast to the reaction of hydrazine with di-*t*-butyldiaziridinone **1a**, in which the initial step is simple nucleophilic attack at carbonyl carbon, phenylhydrazine reacts with **1a** to give 1,3-di-*t*-butylurea, benzene, and nitrogen (eq 6). In general, both aliphatic- or aromatic-substituted hydrazines undergo oxidation–reduction reactions with the diaziridinone **1a** rather than nucleophilic attack at carbonyl carbon. This aspect has been examined for a series of diaziridinones.[15]

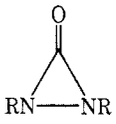
Reaction of **1a** with thiols also involves over-all oxidation–reduction affording urea **16** and disulfide (eq 7, R′ = benzyl and ethyl) rather than nucleophilic ring opening. Reaction of ethanethiol and **1a** in pentane at 25° for 20 days afforded di-*t*-butylurea (33%), diethyl disulfide (34%), and recovered **1a** (54%).

Most phenols also effect reduction of **1a** to the urea (eq 8). As noted earlier, the highly acidic phenol, picric acid, behaves like other acids toward **1a** and effects ring opening (eq 9) to picryl carbazate **8b** with no evidence of reduction of **1a** to the urea. The enediol, ascorbic acid, effects rapid reduction of **1a** to the urea (eq 10).

(14) T. Mukaiyama and Y. Hoshino, *J. Amer. Chem. Soc.*, **78**, 1946 (1956).

(15) F. D. Greene, W. R. Bergmark, and J. G. Pacifici, *J. Org. Chem.*, **34**, 2263 (1969).

The oxidizable nucleophile, *t*-butylhydroxylamine, reacts with **1a** by both oxidation–reduction, giving 2-methyl-2-nitrosopropane in 40% yield and di-*t*-butylurea in 30% yield, and by nucleophilic ring opening, giving a 1:1 adduct assigned structure **17** (eq 11) on the basis of the physical data and its clean pyrolysis (eq 12) to 2,2′-dimethyl-2,2′-azopropane, carbon dioxide, and *t*-butylamine (the latter two react to give *t*-butylammonium *t*-butylcarbamate **18**).

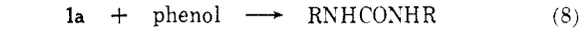


1a, R = *t*-butyl

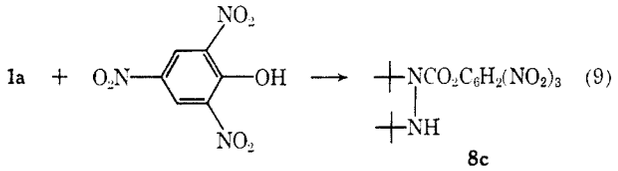
RNHCONHR + C_6H_6 + N_2 (6)

16, R = *t*-butyl

1a + R′SH → RNHCONHR + R′SSR′ (7)



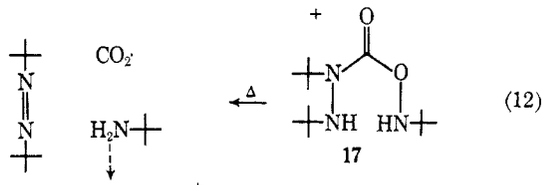
1a + phenol → RNHCONHR (8)



1a + L-ascorbic acid → RNHCONHR (10)

1a + NHOH → RNHCONHR + NO (11)

30% 40%



(12)

18

1a + $(C_6H_5)_2CHOH$ → RNHCONHR + $(C_6H_5)_2CO$ (13)

The possibility of oxidation–reduction with **1a** and an alcohol was examined briefly with benzhydrol. After several days at reflux in benzene, one obtains benzophenone, di-*t*-butylurea, and unchanged **1a** (eq 13). The possible product of nucleophilic attack at carbonyl carbon was not observed. As noted earlier, methanol reacts slowly with **1a** to afford the methyl carbazate **8f**.

Effect of Trapping Agents.—If diaziridinones underwent ring opening to forms such as **2**, one might hope to capture the resulting 1,3-dipolar species by appropriate dipolarophiles.[16] No evidence for trapped products has been found from experiments in which **1a** was heated in cyclohexene, cyclopentadiene, or norbornylene. Efforts to obtain 1:1 adducts with maleic anhydride or tetracyanoethylene also were unsuccessful. (However, **1a** and TCNE do afford an immediate yellow color in methylene chloride which slowly darkens.) Either the ring-opened species are too hindered to undergo cycloaddition with the reagents used to date, or they are not formed to an adequate extent.

(16) See R. Huisgen, *J. Org. Chem.*, **33**, 2291 (1968), and references cited therein.

Experimental Section

All melting points are corrected. All melting points of 1,3-di-*t*-butylurea were taken in tubes sealed under vacuum. Nuclear magnetic resonance spectra were determined at 60 Mc; signals are reported in parts per million (ppm) downfield from tetramethylsilane. Gas–liquid partition chromatographic analyses (glpc) were performed on Aerograph Models 200 and A-700 (Autoprep) using a helium carrier gas and thermal conductivity detectors with the following columns: column A [a 6 ft × 0.25 in. aluminum tube packed with 20% (w/w) silicone oil "SE-30" on a 60/80 mesh Chromosorb W diatomite support employing a flow rate of 65 cc/min; column B [a 10 ft × 0.25 in. aluminum tube packed with 80/100 Linde Molecular Sieves 5A]; column E [a 4 ft × 0.25 in. aluminum tube packed with 20% (w/w) Apiezon M hydrocarbon grease on a Chromosorb P diatomite base washed to pH 7–8 employing a flow rate of 65 ml/min. All identifications (unless otherwise noted) of glpc components were made by the identity with an authentic sample of both retention time and ir spectrum of a collected sample. All quantitative analyses were made by the internal standardization method unless otherwise noted. Assessment of error was obtained in several of the analytical series by matching two or more standard solutions against each other. Error was found to be ±2%.

Preparation of Diaziridinones.—***t*-Octylamine** had bp 139°, $n^{25}D$ 1.4220 (lit.[17] bp 139°, $n^{25}D$ 1.4222); ***t*-amylamine** had bp 78–79°, $n^{25}D$ 1.3950 (lit.[18] bp 77°, $n^{20}D$ 1.3990). **1,3-Di-*t*-butylurea** was prepared by the action of phosgene on a benzene solution of the amine: mp 243–244° (sealed tube) (lit.[19] mp 242°); ir (CCl_4) 1680, 1650 cm^{-1}. **1,3-Di-*t*-octylurea** was prepared by exchange of *t*-octylamine with urea:[20] mp 150–151° (lit.[20] mp 152°); nmr ($CDCl_3$, all singlets) 1.00 (18 H), 1.30 (12 H), 1.72 (4 H), 4.35 (two NH). **1,3-Bis(2-methyl-3-phenyl-2-propyl)urea** had mp 181–182° (lit.[21] mp 184–185°). ***t*-Butyl isocyanate** had bp 85–86°, $n^{26}D$ 1.3842 (lit.[22] bp 85.5°).

1,3-Di-*t*-amylurea was prepared by a method adapted from one of Pepesch and Schroeder.[23] Recrystallization from ethanol–water gave the urea in 69% yield: mp 220–220.5°; ir ($CHCl_3$) 3425 b, 1675 s, 1505 s, 1380 m, 1375 sh, m, 1360 cm^{-1}; nmr ($CDCl_3$) 0.90 triplet (6 H, J = 7.5 Hz), 1.29 singlet (12 H), 1.75 quartet (4 H, J = 7.5 Hz), 4.30 broad singlet (two NH).

Anal. Calcd for $C_{11}H_{24}N_2O$: C, 65.95; H, 12.08; N, 13.99. Found: C, 65.90; H, 12.28; N, 13.90.

1-*t*-Butyl-3-isopropylurea.—To a stirring solution of 4.28 ml (2.95 g, 0.05 mol) of isopropylamine (Eastman) in 50 ml of dry benzene was added 4.58 ml (3.97 g, 0.04 mol) of *t*-butyl isocyanate. The mixture was stirred 12 hr, solvent evaporated, and the solid was recrystallized (ethanol–water) to give 5.00 g (79%) of long, white needles: mp 203–204°; ir ($CHCl_3$) 1665 cm^{-1} s.

Anal. Calcd for $C_8H_{18}N_2O$: C, 60.71; H, 11.46. Found: C, 60.75; H, 11.71.

1-*t*-Butyl-3-*t*-octylurea [mp 153–154° (lit.[20] mp 154–155°)] was prepared in the same way.

1,3-Di-*t*-butyl-1-chlorourea.—A procedure similar to that used by Chalsty and Israelstam[24] to prepare monochlorourea was applied. 1,3-Di-*t*-butylurea (5.00 g, 0.0290 mol) was dissolved in 25 ml of methanol, and *t*-butyl hypochlorite (3.15 g, 0.0290 mol) was added with stirring. After 15 min of stirring, the methanol was removed on a rotatory evaporator to give an oil. The oil was recrystallized twice at −78° from 20 ml of pentane to give 5.09 g (85%): mp 30–31°; ir (CCl_4) 1690, 1505 cm^{-1}; nmr (CCl_4, all singlets) 1.33 (9 H), 1.43 (9 H), 5.48 (1 H, broad). The compound decomposes at room temperature but may be stored at −20°.

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(18) W. Haaf, *Chem. Ber.*, **96**, 3359 (1963).
(19) A. Bühler and H. E. Fierz-David, *Helv. Chim. Acta*, **26**, 2123 (1943).
(20) N. Bortnick, L. S. Luskin, M. D. Hurwitz, and A. W. Rytina, *J. Amer. Chem. Soc.*, **78**, 4358 (1956).
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(23) V. Papesch and E. F. Schroeder, *J. Org. Chem.*, **16**, 1879 (1951).
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Anal. Calcd for $C_9H_{19}N_2OCl$: C, 52.29; H, 9.26; N, 13.55; Cl, 17.15. Found: C, 52.52; H, 9.25; N, 13.27; Cl, 17.36.

1-Chloro-1,3-di-*t*-octylurea was prepared from 1,3-di-*t*-octylurea and *t*-butyl hypochlorite by the same method:[24] yield 43.5% after two recrystallizations from pentane at −78°; mp 31.5°; ir (CCl_4) 3450 sp, 1690 cm^{-1} s; nmr (CCl_4, all singlets) 1.01 (18 H), 1.35 (6 H), 1.45 (6 H), 1.68 (2 H), 1.90 (2 H).

Anal. Calcd for $C_{17}H_{35}ClN_2O$: C, 64.02; H, 11.08; Cl, 11.13; N, 8.78. Found: C, 64.13; H, 10.90; Cl, 11.14; N, 8.91.

Di-*t*-butyldiaziridinone (1a). A. From Potassium Metal.—Potassium metal (3.0 g, 0.077 g-atom) was dispersed in hot toluene; the toluene was removed under reduced pressure and was replaced with 90 ml of pentane. 1,3-Di-*t*-butyl-1-chlorourea (8.00 g, 0.0387 mol) was added and the mixture was heated to reflux under nitrogen with vigorous stirring for 1.25 hr. The mixture was filtered and the solid washed with pentane. The combined filtrate and washings were distilled to remove the pentane and then the residue was distilled at 0.3 mm and 25° to give 2.75 g (48%): mp 0–1°; $n^{26}D$ 1.4267; d^{29} 0.871 g/ml; ir (CCl_4) 1926 weak, 1880 strong, 1862 strong, and 1800 cm^{-1} weak; nmr (CCl_4) 1.20 (s); uv (end absorption) 215 mμ (ε 1190) (not a maximum).

Anal. Calcd for $C_9H_{18}N_2O$: C, 63.49; H, 10.66; N, 16.45; mol wt, 170.3. Found: C, 63.38; H, 10.74; N, 16.47; mol wt, 178 ± 10 (cryoscopic in cyclohexane).

B. From Potassium *t*-Butoxide. The Preferred Method.—*t*-Butyl hypochlorite, 53.4 ml (48.6 g, 449 mmol), was added dropwise with stirring over a 5-min period to a viscous, creamy suspension of 77.4 g (440 mmol) finely ground 1,3-di-*t*-butylurea in 350 ml of *t*-butyl alcohol distilled from sodium metal. The mixture was protected from the light. At the end of the addition, all the urea had gone into solution. To the clear pale yellow-green solution was added over a 10-min period a solution of potassium *t*-butoxide in *t*-butyl alcohol [prepared from 19.9 g (0.51 g-atom) of potassium metal in 500 ml of *t*-butyl alcohol] under nitrogen. Stirring was continued for 10 min. The mixture was poured into 3 l. of water and extracted with three 500-ml portions of pentane. The combined pentane extracts were extracted with three 1-l. portions of water and dried (K_2CO_3). (The use of $MgSO_4$ and standing for several hours results in some acid-catalyzed addition of *t*-butyl alcohol to **1a** to give carbazate **8b**.) Pentane was removed on a steam bath and the diaziridinone was distilled on a spinning-band column at 58–59° (8 mm): yield 68.6 g, 90%; $n^{26}D$ 1.4266.

Di-*t*-amyldiaziridinone (1b), by method B, gave a 75% yield: bp 66.5–67.5° (8 mm); ir (CCl_4) 1920 sh, 1860 s, none at 1500–1800 nor at 3200–3600, 1460, 1380, 1365, 1075 cm^{-1}; nmr (CCl_4) 0.98 (t, 6 H, J = 7.5 Hz), 1.13 (s, 12 H), 1.60 (q, 4 H; J = 7.5 Hz); $n^{24}D$ 1.4440.

Anal. Calcd for $C_{11}H_{22}N_2O$: C, 66.62; H, 11.18; N, 14.13. Found: C, 66.78; H, 11.21; N, 14.18.

Di-*t*-octyldiaziridinone (1c), by method B, had $n^{26.2}D$ 1.4562; ir (CCl_4) 1870 s, b, none at 3100–3700, 1470, 1395 w, 1380 m, 1370 m, 1345 w, 1060 cm^{-1} m; nmr (CCl_4) 1.02 (S, 18 H), 1.58 (s, 4 H), and at 20.0° a broad doublet centered at 1.20 (12 H) with a separation of about 3 Hz; at 40° this doublet coalesces to a broad singlet at 1.20 which continues to sharpen with further rise in temperature; at 0° the doublets show a 7 Hz separation.

Anal. Calcd for $C_{17}H_{34}N_2O$: C, 72.28; H, 12.13; N, 9.92. Found: C, 72.57; H, 12.18; N, 9.71.

Bis(2-methyl-3-phenyl-2-propyl)diaziridinone (1d), by method B, had mp 43–44° (from pentane), ir (CCl_4) 1855 s; nmr (CCl_4) 1.10 (s, 12 H), 2.80 (s, 4 H), 7.13 (s, 10 H).

Anal. Calcd for $C_{21}H_{26}N_2O$: C, 78.22; H, 8.13; N, 8.69. Found: C, 78.30; H, 8.11; N, 8.62.

***t*-Butyl-*t*-octyldiaziridinone (1e)**, by method B, gave a 71% yield: bp 50–50.5° (0.1 mm); $n^{24.4}D$ 1.4450; nmr at 90° (benzene) 1.06 (s, 9 H), 1.18 (s, 9 H), 1.21 (s, 6 H), and 1.64 (s, 2 H); nmr at −16° (CCl_4) 1.07 (s, 9 H), 1.15, 1.20, 1.24 (singlets, a total of 15 H), and 1.62 (s, 2 H); ir ($CHCl_3$) 1855 cm^{-1} (s).

Anal. Calcd for $C_{13}H_{26}N_2O$: C, 68.98; H, 11.58; N, 12.38. Found: C, 69.04; H, 11.50; N, 12.39.

Dipole Moment of Di-*t*-butyldiaziridinone (1a).—The dipole moment of di-*t*-butyldiaziridinone was determined by the heterodyne beat method with an oscilloscope detector.[25] A value of 2.63 D was obtained with measurements at 24.0° from four benzene solutions from which the following mole fractions, densities, and dielectric constants were recorded: (a) 0.00937, 0.8725, 2.282; (b) 0.0195, 0.8734, 2.501; (c) 0.0421, 0.8730, 2.715; (d) 0.0577, 0.8737, 2.921.

Hydrogenation of Di-*t*-butyldiaziridinone.—The diaziridinone (26.7 mg, 0.157 mmol) was hydrogenated at 1 atm in 3 ml of ethyl acetate using 50 mg of 5% palladium-on-carbon catalyst. Filtration followed by evaporation of the ethyl acetate gave 25.9 mg (95.6%) of 1,3-di-*t*-butylurea, mp 240–242°, infrared spectrum identical with that of authentic material.

Lithium Aluminum Hydride Reduction of Di-*t*-butyldiaziridinone.—Di-*t*-butyldiaziridinone (1.00 g, 5.87 mmol) was added dropwise to a suspension of 0.60 g (0.016 mol) of lithium aluminum hydride in 50 ml of ether. The mixture began to reflux, and heat was applied to maintain refluxing for 30 min. A slight excess of water was added and the mixture was filtered. The solid was washed with ether, and the combined washings and filtrate were evaporated to give 0.90 g of clear oil. This was distilled at 0.3 mm and 25° to afford 0.794 g (85%) of 1,2-di-*t*-butyl-1-methylhydrazine, about 98% pure by gas chromatography. A sample, collected at 95°, showed $n^{25}D$ 1.4254; nmr (CCl_4) 0.98 (9 H), 1.03 (9 H), 1.2 (1 H, broad), 2.38 (s, 3 H).

Anal. Calcd for $C_9H_{22}N_2$: C, 68.29; H, 14.01; N, 17.70. Found: C, 68.24; H, 14.28; N, 18.02.

Sodium Borohydride Reduction of Di-*t*-butyldiaziridinone.—Sodium borohydride (151 mg, 4.00 mmol) and di-*t*-butyldiaziridinone (500 mg, 2.94 mmol) were heated at reflux in 2 ml of absolute ethanol for 1 hr. Water (3 ml) was added and refluxing was continued for 0.5 hr. This was added to 10 ml of water and extracted with ether. The extract was dried ($MgSO_4$) and evaporated to give a white solid. This was sublimed at 0.2 mm and 25° to yield 0.313 g (61.7%) of 1,2-di-*t*-butyl-1-formylhydrazine, mp 38–41°. Four successive sublimations raised the melting point to 42–43°: ir (CCl_4) 1670 cm^{-1}; nmr (CCl_4) 1.08 (s, 9 H), 1.37 (s, 9 H), 4.2 (1 H, broad), 8.57 (s, 1 H).

Anal. Calcd for $C_9H_{20}N_2O$: C, 62.75; H, 11.70; N, 16.26; O, 9.29. Found: C, 62.87; H, 11.82; N, 16.04; O, 9.50.

Reaction of Di-*t*-butyldiaziridinone with Hydrogen Chloride.—Hydrogen chloride gas was bubbled into a solution of 1.00 g (5.86 mmol) of di-*t*-butyldiaziridinone in 50 ml of pentane for 10 min, giving a white precipitate. Water (5 ml) was added and the white precipitate dissolved. The pentane layer was separated, dried ($MgSO_4$), and evaporated to give 0.80 g (66%) of 2,3-di-*t*-butylcarbazyl chloride, ir (CCl_4) 1745 cm^{-1}. A sample distilled at 0.3 mm and 50° gave nmr 1.2 (s, 9 H), 1.43 (s, 9 H), 4.04 (1 H, broad), and a positive silver nitrate test. The acid chloride slowly decomposes to a white solid at room temperature.

A solution of the acid chloride (100 mg, 0.483 mmol) in 1 ml of carbon tetrachloride was treated with 400 mg (4.30 mmol) of aniline at room temperature giving an immediate precipitate. This was washed with water and recrystallized from ethanol–water to give 50 mg of diphenylurea: mp 241–242° (lit. mp 238–239°); ir (Nujol) 1640, 1590, 1540 cm^{-1}.

Reaction of 2,3-Di-*t*-butylcarbazyl Chloride with Potassium *t*-Butoxide.—2,3-Di-*t*-butylcarbazyl chloride (0.760 g, 3.68 mmol) was added dropwise to a solution of potassium *t*-butoxide prepared from 0.250 g (6.40 mg-atom) of potassium metal and 20 ml of *t*-butyl alcohol (distilled from sodium). After 10 min of stirring, the mixture was poured into 50 ml of water and extracted with pentane. The extract was washed with water, dried ($MgSO_4$), and evaporated to give a clear oil. An infrared spectrum showed carbonyl absorptions for only di-*t*-butyldiaziridinone and *t*-butyl 2,3-di-*t*-butylcarbazate. Distillation of the oil at 0.3 mm and 25° gave 0.20 g (45%) of the diaziridinone containing a small amount of the carbazate. Further distillation using a heat lamp gave 0.218 g (24%) of the carbazate (see following section) containing a small amount of the diaziridinone.

***t*-Butyl 2,3-Di-*t*-butylcarbazate.**—Di-*t*-butyldiaziridinone (0.50 g, 2.93 mmol) was added to a solution of potassium *t*-butoxide prepared from 0.30 g (7.68 mg-atom) of potassium metal and 25 ml of *t*-butyl alcohol (distilled from sodium) and heated to reflux for 16 hr. An infrared spectrum of the reaction solution showed carbonyl bands of about equal intensity for the diaziridinone and the carbazate. The *t*-butyl alcohol was removed on a rotary evaporator and the residue was extracted with ether. Evaporation of the ether left a residue which was distilled at 0.2 mm and 25° to give 0.284 g of a mixture of *t*-butyl alcohol, the

(25) D. P. Shoemaker and C. W. Garland, "Experiments in Physical Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1962.

diaziridinone, and the carbazate. The residue of this distillation was extracted with pentane, and the extract evaporated and distilled at 0.2 mm under a heat lamp to afford 0.192 g of *t*-butyl 2,3-di-*t*-butylcarbazate. A sample, collected by glpc at 135°, had $n^{26}D$ 1.4320; ir (CCl_4) 1690 cm^{-1}; nmr (CCl_4) 1.02 (s, 9 H), 1.31 (s, 9 H), 1.48 (s, 9 H), 3.95 (1 H, broad).

Anal. Calcd for $C_{13}H_{28}N_2O_2$: C, 63.89; H, 11.55; N, 11.47. Found: C, 64.09; H, 11.49; N, 11.63.

1,2-Di-*t*-butylhydrazine. A. From *t*-Butyl 2,3-Di-*t*-butylcarbazate (8b).—To 9.40 g (38.4 mmol) of *t*-butyl 2,3-di-*t*-butylcarbazate was added with stirring 20 ml of 36% HCl (aqueous). Bubbling occurred for 30 min. The solution was stirred for an additional 30 min, made basic with sodium hydroxide solution (20% aqueous), and extracted four times with pentane (total pentane, 225 ml). The combined pentane extracts were washed with water and dried (K_2CO_3). Removal of the pentane yielded 5.01 g (91%) of crude 1,2-di-*t*-butylhydrazine. Glpc analysis at 150° (column E) indicated that pentane and 2,2'-dimethyl-2,2'-azopropane were impurities. Di-*t*-butylhydrazine purified by glpc has nmr (CCl_4) 1.15 ppm (singlet); ir (CCl_4) 3200–2400 b, 1475 m, 1450 m, 1385 m, 1365 m, 1210 m cm^{-1}; $n^{27.5}D$ 1.4122.

Anal. Calcd for $C_8H_{20}N_2$: C, 66.60; H, 13.97; N, 19.42. Found: C, 66.52; H, 13.83; N, 19.61.

B. From Di-*t*-butyldiaziridinone (1a).—A total of 21.0 ml (18.3 g, 107.5 mmol) of **1a** was added portionwise to 850 ml of 4.2% aqueous HCl. Stirring was continued for 30 min after CO_2 evolution ceased and a clear, homogeneous solution resulted (total time about 2 hr). All further operations were performed under a nitrogen atmosphere. The solution was made pH 12 by addition of saturated aqueous NaOH and extracted quickly with two 250-ml portions of ether; the ether solution was dried (K_2CO_3), solvent was removed, and the residue was distilled on a spinning-band column, affording 14 g, bp 137–138°, yield 90%, which was immediately transferred into tubes which were sealed under vacuum.

The use of a large volume of dilute acid was important; when 60 ml of 36% aqueous HCl was used in the above procedure only a low yield of the hydrazine was recovered (23%).

Reaction of Benzoic Acid and Di-*t*-butyldiaziridinone.—Benzoic acid (0.716 g, 5.86 mmol) and di-*t*-butyldiaziridinone (1.00 g, 5.86 mmol) were dissolved in 15 ml of benzene and heated at reflux under nitrogen for 1 hr. All of the diaziridinone was consumed as shown by infrared analysis. The benzene was removed on a rotary evaporator to afford an oil. Addition of 3 ml of pentane caused crystallization of a white solid which was filtered and washed with pentane. This gave 0.473 g (28%) of **8–9d**, mp 145–147° dec. Three recrystallizations from ether gave mp 152–154° dec; ir (CCl_4) 1655 cm^{-1}; nmr (CCl_4) 1.08 (s, 9 H), 1.6 (s, 9 H), 7.45 (m 5 H), 11.8 (1 H, broad).

Anal. Calcd for $C_{16}H_{24}N_2O_3$: C, 65.72; H, 8.27; N, 9.58. Found: C, 65.69; H, 8.37; N, 9.42.

The pentane washings and filtrate were combined and cooled to −20° to afford 0.367 g (25%) of white needles, mp 62–69°. Sublimation at 55° and 0.2 mm afforded 1-benzoyl-1,2-di-*t*-butylhydrazine: mp 72–74°; ir (CCl_4) 1650 cm^{-1}; nmr (CCl_4) 1.04 (s 9 H), 1.11 (s, 9 H), 4.89 (broad, 1 H), 7.5 (m, 5 H).

Anal. Calcd for $C_{15}H_{24}N_2O$: C, 72.54; H, 9.74; N, 11.28. Found: C, 72.49; H, 9.84; N, 11.40.

The last pentane filtrate contained at least two unidentified compounds with infrared absorptions at 1700 and 1760 cm^{-1}.

Another reaction heated at reflux for 5 hr afforded an 87% yield of 1-benzoyl-1 2-di-*t*-butylhydrazine and none of the compound of mp 152–154°. A reaction heated at reflux for 30 min afforded a 42% yield of the compound of mp 152–154°.

Reaction of Formic Acid with Di-*t*-butyldiaziridinone.—A solution of 0.67 ml (0.82 g 17.6 mmol) of formic acid (Baker reagent) in 15 ml of ether was added dropwise over a 2-hr period to a stirring, ice-bath cooled solution of 3.44 ml (3.00 g, 17.6 mmol) of diaziridinone 1a in 15 ml of ether. The stirring was continued for 12 hr while the ice bath was allowed to melt and warm to room temperature. A white precipitate was collected by filtration, washed, and dried: yield 2.20 g; mp 136° dec with gas evolution. Removal of the ether afforded an additional 1.10 g isolated as above, mp 139° dec (gas evolution). Recrystallization of the first fraction ($CHCl_3/CCl_4$) afforded 985 mg, mp 146° dec (gas evolution), identified as formyl 2,3-di-*t*-butylcarbazate (**8e**): ir ($CHCl_3$) 3400–3000 b, 2875 m, 2730 m, 2590 m, 1685 s, 1305 s, 1340 m, 1180 cm^{-1} m; nmr ($CDCl_3$, all singlets) 1.51 (18 H), 8.15 (1 H), 12.2 (1 H). Total yield of carbazate **8e** was 3.30 g (86.3%). The assignment of structure **8e** is preferred over **9e** on the basis of nmr and ir evidence: the single CH proton appears at 8.15 ppm which is reasonable for a formate -CHO, but not for the -CHOH of **9e**. Characteristic -CHO combination bands also appear in the ir region at 2875 and 2730 cm^{-1}.

Anal. Calcd for $C_{10}H_{20}N_2O_3$: C, 55 53; H, 9.32; N, 12.96. Found: C, 55.63; H, 8.99; N, 13.26.

The filtrate obtained after removal of all the ether contained diaziridinone **1a**. After 48 hr under high vacuum a mixture of two components (tlc on silica gel) remained with ir (film) 1775 s and 1715 cm^{-1} s. When the above reaction was carried out without solvent or cooling, an exothermic reaction took place with the liberation of gas. The resulting solid–liquid mixture was separated into a pentane-insoluble fraction, 982 mg, mp 123–125° dec, with gas evolution, which was identified as crude formyl 2,3-di-*t*-butylcarbazate, **8e**, by tlc on silica gel and by ir. Distillation of the pentane-soluble fraction at 25° and 0.02 mm afforded 691 mg of 1-formyl-1,2-di-*t*-butylhydrazine.

Pyrolysis of Formyl 2,3-Di-*t*-butylcarbazate (8e).—A solution of 792 mg (3.66 mmol) of carbazate **8e** in 20 ml of benzene and 20 ml of toluene was refluxed for 15 hr. Gas was given off. After removal of the toluene and benzene the residue was heated to 160° for 1 hr and then sublimed at 0.02 mm at 50° to yield 408 mg (59%) of pure 1-formyl-1,2-di-*t*-butylhydrazine: mp 42.5–43.5°; mmp 42.5–43.5°; ir spectrum identical with that of the authentic sample.

Picryl 2,3-Di-*t*-butylcarbazate (8c).—Picric acid (0.500 g, 2.94 mmol) was dissolved in 70 ml of anhydrous ether and di-*t*-butyldiaziridinone (0.670 g, 2.94 mmol) was added dropwise, causing an immediate darkening of the yellow color. The ether was evaporated to give a yellow solid. Recrystallization from 10 ml of carbon tetrachloride gave 1.00 g (85.5%), mp 144–148°. Two more recrystallizations afforded yellow plates: mp 147–149° dec; ir (CCl_4) 1750, 1610, 1555 cm^{-1}; nmr (CCl_4) 1.19 (s, 9 H), 1.44 (s, 9 H), 3.95 (broad, 1 H), 8.95 (s, 2 H).

Anal. Calcd for $C_{15}H_{21}N_5O_8$: C, 45.11; H 5.30; N 17.54. Found: C, 44.90; H, 5.18; N, 17.29.

Methyl 2,3-Di-*t*-butylcarbazate. A. Base-Catalyzed Preparation.—A solution of sodium methoxide (prepared from 0.23 g, 10 mg-atoms of sodium and 25 ml of methanol) and 1.00 g (5.88 mmol) of di-*t*-butyldiaziridinone was heated at reflux for 1 hr. After 40 min of reflux only a trace of the diaziridinone was detectable by infrared. Methanol was removed on a rotary evaporator until the volume was 10 ml and this was poured into 60 ml of water. The resulting mixture was extracted with four 20-ml portions of pentane and then the combined pentane extracts were washed with four 30-ml portions of water. The pentane solution was dried ($MgSO_4$) and evaporated to afford 0.979 g of clear oil (82%) approximately 98% pure by glpc at 135°. This oil was purified by glpc to give 0.640 g of methyl 2,3-di-*t*-butylcarbazate: $n^{25}D$ 1.4291; ir (CCl_4) 1700 cm^{-1}; nmr (CCl_4) 1.03 (s, 9 H), 1.31 (s, 9 H), 3.69 (s, 3 H), 3.94 (1 H, broad).

Anal. Calcd for $C_{10}H_{22}N_2O_2$: C, 59.37; H, 10.96; N, 13.85. Found: C, 59.15; H, 10.78; N, 14.13.

B. Acid-Catalyzed Preparation.—A solution of 250 mg (1.47 mmol) of di-*t*-butyldiaziridinone in 25 ml of methanol (distilled from sodium methoxide) was heated at reflux under nitrogen for 2 hr. An infrared spectrum showed only slight decomposition of the diaziridinone. Concentrated sulfuric acid (5 mg) was added and, after 5 min at reflux, no diaziridinone remained (by infrared). The methanol was removed on a rotary evaporator and the residual clear oil was dissolved in 8 ml of pentane. The pentane solution was washed with three 4-ml portions of water and then evaporated leaving 200 mg (67%) of oil. This was purified by glpc at 135° to afford 118 mg of methyl 2,3-di-*t*-butylcarbazate.

Reaction of Di-*t*-butyldiaziridinone with Methanol.—Diaziridinone, 0.25 g (1.5 mmol), was dissolved in 20 ml of methanol. Infrared analysis indicated that the diaziridinone was consumed in 43 hr at room temperature. The excess methanol was removed under vacuum to leave a clear, colorless oil, 0.31 g (1.5 mmol, 100%), crude methyl 2,3-di-*t*-butylcarbazate (**8f**) by glpc (column E, 155°) with methanol as its only impurity. Distillation (25°, 0.02 mm) left only a 0.2-mg residue.

Reaction of Di-*t*-butyldiaziridinone (1a) with Isopropylamine.—Isopropylamine (Eastman), 1.04 g (17.6 mmol), and 3.00 g (17.6 mmol) of **1a** were allowed to react for 96 hr at room temperature under dry nitrogen. Repeated trituration and recrystallization of the resulting liquid–solid mixture at −20°

with pentane (50 ml) afforded two fractions. The less soluble, high melting material, 584 mg (3.78 mmol, 43%) (mp 181–188°) was identified as 1,3-diisopropylurea by mp 189–191° (after recrystallization from methanol–benzene) (lit.[26] mp 192°), mmp 189–191°, and an ir spectrum identical with an authentic one. The low melting, more soluble fraction, 1.406 g (6.14 mmol, 35%), mp 93–95°, was subjected to repeated low temperature recrystallization from pentane: needles; mp 93–94°; ir (CCl_4) 3440 b, 2250 w, 1670 s, 1450 m, 1175 m, 1495 s, 1360, 1380 cm^{-1}; nmr (CCl_4) 0.94 (d, 6 H), J = 6.2 Hz), 0.95 (s, 9 H), 1.07 (s, 9 H), 3.88 (m, 1 H, J = 6.2 Hz). From this spectral evidence and the evidence presented below, the compound was assigned structure **10**, 1,2-di-*t*-butyl-4-isopropylsemicarbazide.

Anal. Calcd for $C_{12}H_{27}N_3O$: C, 62.84; H, 11.87; N, 18.32; mol wt, 229.3. Found: C, 63.10; H, 11.83; N, 18.54; mol wt, 237 ± 10 (vapor osmometer in benzene).

The pentane filtrates from above were subjected to glpc analysis at 138° on column E. The following components were identified: 2,2′-dimethyl-2,2′-azopropane (assayed 11.5%, 2.03 mmol), **1a**, and the thermal decomposition products of semicarbazide **10**. (Under the conditions of the analysis semicarbazide **10** produced two peaks (of intensity indicating high conversion) which were identified as 1,2-di-*t*-butylhydrazine and isopropyl isocyanate.) Further observations indicated the equilibrium of **10** with the isocyanate and hydrazine. Compound **10** exhibits a weak peak at 2250 cm^{-1} (in CCl_4 solution) characteristic of isopropyl isocyanate. The compound has a sharp odor (isocyanate) and a pure sample sublimes readily at room temperature with the sublimate being less pure than the original sample. When isopropylamine was used in excess in this experiment the yield of the urea was enhanced at the expense of the semicarbazide **10**; 3.87 g (22.7 mmol) of **1a** in 10.0 g (169 mmol) of isopropylamine for 43 hr gave 2.568 g (16.7 mmol, 73.5%) of the urea and 0.565 g (2.46 mmol, 10.8%) of semicarbazide **10**.

When 1-*t*-butyl-3-isopropylurea was subjected to the reaction conditions above (excess isopropylamine) for 43 hr, no reaction occurred; only starting urea was recovered, mp 203–205°.

Reaction of Di-*t*-butyldiaziridinone with Hydrazine.—A solution of 3.44 ml (3.00 g, 17.6 mmol) of **1a** and 6.70 ml (5.60 g, 176 mmol) of anhydrous hydrazine (Eastman, $n^{25}D$ 1.4672) in 80 ml of *t*-butyl alcohol (distilled from sodium) was allowed to stand at room temperature under a dry nitrogen atmosphere. A small amount of heat was given off at first and a crystalline precipitate appeared which after 12 hr was collected by filtration, washed, and dried to give 1.114 g. An additional 342 mg was obtained by evaporation of the alcohol–hydrazine filtrate. The combined precipitates, identified as carbohydrazide **13**, 1.456 g (92.5%), had mp 155–158° [mmp 153.5–156°, authentic sample (Aldrich) 153.5–156°] and an ir spectrum identical with an authentic one. Analysis by glpc (column A, 112°) indicated 71.5% (12.4 mmol) di-*t*-butylhydrazine in the original filtrate.

A solution of 3.05 g (17.6 mmol) of 1,3-di-*t*-butylurea, 6.70 ml (5.60 g, 176 mmol) of hydrazine, and 80 ml of *t*-butyl alcohol was allowed to stand for 12 hr at room temperature under nitrogen. No precipitate was observed. Evaporation of the solvent and dilution with water afforded a total of 3.04 g (100% recovery) of the urea, mp 237–239°, mmp 239–240°.

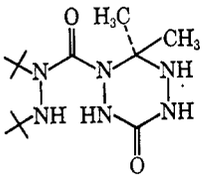
A solution of 3.44 ml (3.00 g, 17.6 mmol) of diaziridinone **1a**, 0.67 ml (0.56 g, 17.6 mmol) of hydrazine, and 20 ml of *t*-butyl alcohol after 12 hr at 25° afforded a precipitate, 364 mg (4.04 mmol), 46% of carbohydrazide **13**, mp 148° dec (recrystallization from methanol–water gave 199 mg, mp 152–155°, mmp 153.5–156°, and an ir identical with an authentic one.) Removal of the *t*-butyl alcohol from the filtrate under vacuum left a solid–liquid mixture, which was separated by filtration. The solid phase (after drying at 0.02 mm) appeared to be a ternary mixture of carbohydrazide **13** and two other components by tlc on silica gel. The liquid phase was largely unchanged **1a** (by ir) which also showed additional carbonyl absorption at 1650 cm^{-1}.

When 15 ml of ether was used as a solvent for the preceding experiment a precipitate of 1.45 g was obtained of which 510 mg was chromatographed over 20 g of neutral alumina (activity grade I). Elution with methanol afforded a nearly pure component (by tlc) which was obtained pure by recrystallization from $CHCl_3$, 200 mg (0.77 mmol represents 2.2 mmol, 25%) of a compound, mp 240° dec, R_f 0.7 on silica gel tlc with CH_3OH eluent, which is assigned as 1-(2,3-di-*t*-butylcarbazyl)carbohydrazide, **15**: ir ($CHCl_3$) 3385 (very broad and strong), 1670 (strong); 1450–1500 complex, 1385 w, 1360 cm^{-1} m; nmr (CD_3OD) 1.10 (s, 9 H), 1.38 (s, 9 H), 4.76 (broad, singlet, OH of CD_3OH representing the six NH's of **15**).

Anal. Calcd for $C_{10}H_{24}N_6O_2$: C, 46.13; H, 9.29; N, 32.28; mol wt, 260.34. Found: C, 45.86; H, 9.06; N, 32.31; mol wt, 240 (vapor osmometer, ethanol solvent).

A condensation product of carbohydrazide **15** and acetone was obtained from a solution of **15** in acetone as a white crystalline substance, mp 171°, assigned **19** (although the data do not exclude other structures such as **20**) by ir ($CHCl_3$) 3375 b, 1660 s, 1690 cm^{-1} sh; nmr ($CDCl_3$, all singlets) 1.15 (9 H), 1.42 (9 H), 1.73 (3 H), 1.99 (3 H), 3.8 (NH's). [This compound was not present (tlc) in the mixture before contact with acetone.]

Anal. Calcd for $C_{13}H_{28}N_6O_2$: C, 51.98; H, 9.39; N, 27.98; mol wt, 300.40. Found: C, 51.88; H, 9.32; N, 27.72; mol wt, 291 (osmotic in ethanol).



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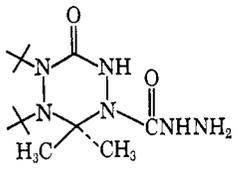

20

Reaction of Di-*t*-butyldiaziridinone with Phenylhydrazine.—A solution of **1a**, 1.72 ml (1.50 g, 8.8 mmol), and phenylhydrazine, 0.87 ml (0.95 g, 8.8 mmol; Eastman, mp 19–20°), in 35 ml of dry ether was prepared and rapidly stirred at 0° in an apparatus to measure gas evolution. Upon mixing a bright orange color developed. Gas evolved which was identified by gas–solid partition chromatography (column B, 140°) as nitrogen, 90%. In 31 min half of the nitrogen was evolved. Evolution was nearly linear with time for the first three-fourths of the reaction. After cessation of nitrogen evolution (4.5 hr) the liquid phase of the remaining solid–liquid mixture was found by glpc (column A, 56°) to contain 83.0% benzene. The solid phase was collected as fine, white needles by filtration and washed with 10 ml of ether. Evaporation of the ether afforded a solid–liquid mixture which when triturated with 10 ml of ether afforded additional white precipitate. Removal of the ether and repetition of the trituration procedure several times with 10-ml portions of pentane afforded a combined holding of 1.57 g (100%), 1,3-di-*t*-butylurea, identified by mp 241–242°, mmp 241–242°, and an ir spectrum identical with an authentic spectrum. The 230-mg residue proved to be a mixture of several components as demonstrated by tlc on silica gel (six were distinguishable using EtOAc). One of the components had the same color and R_f value as azobenzene. Separation of these components on neutral alumina was unsuccessful.

Very slow portionwise addition (over a 2-hr period) of an ether solution of phenylhydrazine to an ether solution of **1a** at 25° and addition in reverse order produced colored solutions which did not exhibit any fading with time.

Reaction of 2,4,6-Tri-*t*-butylphenol with Di-*t*-butyldiaziridinone.—2,4,6-Tri-*t*-butylphenol [Aldrich Chemical Co., mp 128–131° (lit. mp 131°) after recrystallization from isooctane], 0.52 g (2 mmol), and **1a**, 0.17 g (1 mmol), were dissolved in 7 ml of benzene (dried by azeotroping any water present), and sealed under vacuum after several degassings. The clear, colorless solution became pale blue after 5 min of heating at 100°; after 45 min an intense blue color was noted. After 20 hr at 100°, crystals had separated and the solution was a green color. The tube was opened and the crystals were isolated, washed, and dried: 14 mg (8.1%) of 1,3-di-*t*-butylurea identical with authentic material.

A solution of 17 mg (1 mmol) of **1a** and 52 mg (2 mmol) of 2,4,6-tri-*t*-butylphenol in 700 μl of benzene was degassed in a quartz tube and sealed under vacuum. After 2 days at room temperature an intense blue color was observed with the precipitation of fine needles. An intense esr spectrum was observed: a single sharp line, ascribed to the 2,4,6-tri-*t*-butylphenoxyl free radical, **14** (a single line at concentrations greater than 10^{-3} M).[27]

(26) A. W. Hofmann, *Ber.*, **15**, 756 (1882).

(27) E. Muller, K. Ley, K. Scheffler, and R. Mayer, *ibid.*, **91**, 2682 (1958).

Reaction of Di-*t*-butyldiazirdinone with Phenol.—A solution of 3.00 g (17.6 mmol) of **1a** and 1.66 g (17.6 mmol) of phenol (mp 42–42.5°) in 40 ml of benzene was refluxed for 44 hr under nitrogen. White needles, 2.428 g (80%), were collected by filtration, washed, dried, and identified as 1,3-di-*t*-butylurea. Refluxing the filtrate for an additional 24 hr resulted in recovery of a polymeric material (rubbery, insoluble by swelled in benzene, nonmelting).

Reaction of Di-*t*-butyldiaziridinone with L-Ascorbic Acid.—A solution of 3.10 g (17.6 mmol) of L-ascorbic acid (mp 189–190.5°) and 3.00 g (17.6 mmol) of **1a** in 12 ml of dimethylformamide became yellow and deposited needles after 1 min. After 12 hr at room temperature the needles were collected by filtration and washed with water. A total of 25 ml of water was added to the filtrate to precipitate additional crystals. After drying, the total amount, 1.403 g (45%), was identified as 1,3-di-*t*-butylurea, mp 241–242°, mmp 241–242°, and an ir spectrum identical with an authentic one. Attempts to convert any dehydroascorbic acid to a 2,4-dinitrophenylhydrazone derivative were unsuccessful.[28]

Reaction of Di-*t*-butyldiaziridinone with Benzohydrol.—A solution of 3.24 g (17.6 mmol) of benzhydrol (mp 66–67°) and 3.00 g (17.6 mmol) of **1a** in 35 ml of benzene was refluxed under nitrogen for 10 days. After cooling, needles were collected, washed, and dried to give 437 mg of 1,3-di-*t*-butylurea, identified by mp 240–241.5°, mmp 240.5–242°, and an ir spectrum identical with an authentic one. The filtrate was composed of **1a**, benzhydrol, and benzophenone by tlc analysis. Removal of the benzene and heating the residue for 48 hr at 100° afforded an oil–solid mixture of **1a**, benzhydrol, and benzophenone. The latter was characterized as the semicarbazone derivative, 823 mg (3.42 mmol, 19.5% yield of benzophenone); recrystallization from benzene–isooctane gave mp 163–165.5°, mmp 162.5–165°, and authentic benzophenone semicarbazone mp 162–164.5° (lit.[29] mp 164–165°) with an ir spectrum identical with that of authentic semicarbazone.

Reaction of Di-*t*-butyldiaziridinone with Ethanethiol.—Ethanethiol (Eastman), 2.19 g (35.2 mmol), was distilled under a nitrogen atmosphere iuto a flask with 3.00 g (17.6 mmol) of **1a** in 10 ml of pentane. The resulting solution was allowed to stand for 20 days at ambient temperature. After this time the contents of the flask were solid with a mat of long, fine needles, which were collected by filtration, washed with pentane, and dried: yield 1.00 g (33%), identified as 1,3-di-*t*-butylurea, by mp 236–238°, mmp 240–241°, and an ir spectrum identical with an authentic one. The pentane filtrate was subjected to glpc analysis at 130° (column E); only two components were observed: starting **1a**, 54%, and diethyl disulfide, 34%.

Reaction of Di-*t*-butyldiaziridinone with Benzylthiol.—A solution of 1.15 ml (1.00 g, 5.88 mmol) of **1a** and 1.38 ml (1.46 g, 11.76 mmol) of benzylthiol (Eastman) in 50 ml of benzene was refluxed for 24 hr under nitrogen which was sufficient to consume 30% **1a** (determination by ir). The solution was reduced to about one-fourth the original volume and refluxed an additional 48 hr. Fine needles were filtered from the cooled solution. The filtrate, a pink solution, was reduced to an oil–solid mixture under vacuum, filtered, and the solid was washed with pentane. The combined solid fractions, 537 mg, were identified as 1,3-di-*t*-butylurea. The oil on fractional crystallization from methanol gave two crystalline fractions both with mp 68–155°, total weight 912 mg. Trituration of the solid with benzene, filtration, and evaporation of the benzene afforded 848 mg (59%) of plates identified as benzyl disulfide by mp 68.5–73°, mmp 68–74°, authentic sample (Eastman) mp 68–74° (lit.[30] mp 69–70°), and an ir spectrum identical with that of an authentic sample. Upon removal of solvent from the methanol filtrate a residue of 254 mg was obtained which when triturated with hexane gave 111 mg of the urea (mp 239–240°, mmp 240–241°). Total recovery of the urea was 648 mg (64%).

(28) J. Kenyon and N. Munro, *J. Chem. Soc.*, 158 (1948).
(29) W. Borshe and C. Merkwitz, *Ber.*, **37**, 3180 (1904).
(30) O. Hinsberg, *ibid.*, **41**, 632 (1908).

Reaction of 1-*t*-Butylhydroxylamine and D-*t*-butyldiaziridinone.—1-*t*-Butylhydroxylamine[31] was recrystallized from a dried (K_2CO_3) solution to give crystals, mp 58–60° (lit.[31] mp 64–65°). The 1-*t*-butylhydroxylamine, 1.56 g (17.6 mmol), and 3.00 g (17.6 mmol) of diazirdinone **1a** were dissolved in 20 ml of benzene and refluxed 1.5 hr under a nitrogen atmosphere. The solution at this time was a very bright blue. Analysis by glpc (column A, 58°) revealed a single peak, 2-nitroso-2-methylpropane,[31] 41.3% (7.29 mmol). The remaining solution was filtered and the precipitate washed with benzene to give after drying 0.818 g of di-*t*-butylurea, identified by mp 239.5–240.5°, mmp 240.5–241.5°, and identity of ir spectrum. The filtrate and washings were reduced to an oil–solid mixture by evaporation under vacuum. An additional 43 mg of urea was recovered from the mixture by filtration (total yield, 861 mg, 4.99 mmol, 28.4%). The oil was distilled at 0.02 mm to give a fraction with bp 58–59°, 2.269 g (8.75 mmol, 49.4%), identified as (*t*-butylamino) 2,3-di-*t*-butylcarbazate, **17**, by ir (CCl_4) 3210 (sharp), 1695 s, 1475 m, 1390 m, 1370 m, 1305 s, 1200 cm^{-1} m; nmr (CCl_4, all singlets) 1.04 (9 H), 1.13 (9 H), 1.33 (9 H), 3.93 (broad, 1 H), 7.25 (broad, 1 H).

Anal. Calcd for $C_{13}H_{29}N_3O_2$: C, 60.19; H, 11.27; N, 16.20. Found: C, 60.17; H, 11.34; N, 16.20.

A small amount of diaziridinone **1a** remained unchanged under these conditions—2.3% by ir analysis employing standard solutions.

Pyrolysis of (*t*-butylamino) 2,3-di-*t*-butylcarbazate, 17 [1-*t*-butyl-O-(2,3-di-*t*-butylcarbazyl)hydroxylamine], was carried out by heating a neat sample, 1.037 g (4.02 mmol), at 155–175° for 1 hr in a microdistillation apparatus with a gas volume measuring device. During the pyrolysis gas was evolved, pale yellow liquid distilled into the receiver, and white solid collected in the condenser. Only a trace of dark material remained in the pot at the end of the pyrolysis. The white solid was removed, washed with 25 ml of pentane, dried, and identified as 180 mg (1.03 mmol, 51.3% yield) of *t*-butylammonium *t*-butylcarbamate,[32] **18**, identical with an authentic sample prepared by treating *t*-butylamine with an excess of Dry Ice. Compound **18** decomposes (sealed tube) at 121–130°, mixture at 121–130°, and the authentic sample at 121–130°. The yellow liquid was identified as 2,2′-dimethyl-2,2′-azopropane by its display of a single major peak on glpc (column A, 58°) with a retention time and ir spectrum of a collected sample identical with authentic material. Quantitative determination gave an assay of 30.8% (1.24 mmol). The gas evolved was identified as 1.99 mmol (99%) of carbon dioxide by its precipitation of barium carbonate from a barium hydroxide solution. The low yields reported for the azo compound and **18** most likely reflect the mechanical difficulties in separation of the components. No blue color attributable to 2-nitroso-2-methylpropane was noted. Glpc analyses indicated a trace amount of di-*t*-butylhydrazine (identification by retention time only.) These results further establish structure **17** and exclude the alternative hydroxysemicarbazide structure for the product from reaction of 1-*t*-butylhydroxylamine with di-*t*-butyldiaziridinone.

Registry No.—1,3-Di-*t*-amylurea, 19656-71-4; 1-*t*-butyl-3-isopropylurea, 19656-72-5; 1,3-di-*t*-butyl-1-chlorourea, 19656-73-6; 1-chloro-1,3-di-*t*-octylurea, 19694-13-4; **1a**, 19656-74-7; **1b**, 19656-75-8; **1c**, 19656-76-9; **1d**, 19694-14-5; **1e**, 19656-84-9; 1,2-di-*t*-butyl-1-methylhydrazine, 19656-85-0; 1,2-di-*t*-butyl-1-formylhydrazine, 19656-86-1; **8b**, 19713-62-3; 1,2-di-*t*-butylhydrazine, 13952-69-7; 1-benzoyl-1,2-di-*t*-butylhydrazine, 19656-88-3; **8c**, 19656-89-4; **8e**, 19694-15-6; **8f**, 19694-16-7; **10**, 19656-90-7; **15**, 19694-17-8; **17**, 19694-18-9.

(31) W. D. Emmons, *J. Amer. Chem. Soc.*, **79**, 5739 (1957).
(32) M. B. Jensen, *Acta Chem. Scand.*, **11**, 499 (1957).