mmol) of tetramethylhydrazine[18] in 5 ml of benzene was sealed in tubes under vacuum and heated at 80 ± 3° for 50 hr. The course of the reaction was followed by ir. The resulting solution was evaporated under vacuum to an oil which crystallized. The crystals, 355 mg (1.10 mmol, quantitative), were identified as aziridinecarboxamide **3c** by mp 110–113°, mmp 113–116°, and an ir spectrum identical with that of an authentic sample. Diaziridinone **1c** was totally unchanged on heating in benzene alone for 50 hr at 80°.

A solution of 330 mg (1.02 mmol) of **1c** and 115 μl (88 mg, 1.00 mmol) of tetramethylhydrazine in 5 ml of *t*-butyl alcohol (distilled from sodium metal) was degassed, sealed in a tube, and heated for 6 hr at 80 ± 3°. The resulting solution was evaporated; the crystals, 295 mg (0.92 mmol, 89%), were identified as **3c** by mp 110–113°, mmp 114–116°, and ir spectrum identical with an authentic one. When **1c** was heated alone in *t*-butyl alcohol for 6 hr 20% was consumed. (A band in the 1675–1700-cm^{-1} region appeared which roughly accounted for all the **1c** consumed.)

A solution of 323 mg (1.00 mmol) of **1c** and 88 mg (1.00 mmol) of tetramethylhydrazine in 5.00 ml of acetonitrile (dried over P_2O_5 and distilled on a Teflon spinning-band column) was heated for a total of 18 hr at 80° in one large and several small capillary tubes to produce yellow solutions. A small amount of **1c** was consumed. Approximately the same degree of consumption was observed when **1c** was heated in acetonitrile in the absence of the hydrazine.

Attempted Reaction of Di-*t*-amyldiaziridinone, 1b, with Tetramethylhydrazine.—A solution of 30 μl (23 mg, 0.26 mmol) of tetramethylhydrazine[19] and 45 mg (0.23 mmol) of diaziridinone **1b** in 2.0 ml of benzene was heated at 80° for 18 hr in tubes sealed under vacuum. Analysis of ir spectra indicated no consumption of diaziridinone or appearance of any new bands. No reaction was observed by ir when a solution of equimolar amounts of each component was heated at 80° for 12 hr, without solvent.

Reaction of 1-*t*-Butyl-2-(2-methyl-3-phenyl-2-propyl)diaziridinone, 1d, with Di-*t*-butylhydrazine 2a.—A solution of 0.876 g (3.56 mmol) of **1d**[1a] and 0.573 g (3.98 mmol) of **2a** in 5 ml of benzene was degassed, sealed in tubes, and heated at 80°. Reaction was complete in 2.5 hr. Separation of the crystals and recrystallization from benzene afforded 0.32 g (1.31 mmol, 41%) of 1-*t*-butyl-2-(2-methyl-3-phenyl-2-propyl)urea: mp 164–165°, mmp 163–165°, ir and nmr identical with authentic spectra. Fractional recrystallization of material from the filtrates afforded 0.19 g (0.77 mmol, 24%) of N-*t*-butylcarbamyl-2,2-dimethyl-3-phenylaziridine, **3d**, mp 175–176°, identical in ir and nmr with the synthetic sample. Analysis by nmr of an aliquot of the original solution of products from the reaction showed that 50% urea and 50% **3d** were formed. A parallel experiment with 0.172 g (0.70 mmol) of **1d** and 0.185 g (1.28 mmol) of **2a** in 4 ml of benzene assayed by nmr indicated 47% urea and 53% **3d**.

Reaction of Diaziridinone 1d with 1,2-Dimethylhydrazine.—A solution of 0.29 g (1.18 mmol) of **1d** and 0.24 g (4.0 mmol) of 1,2-dimethylhydrazine was degassed, sealed, and left at 25° for 24 hr. Removal of volatile components left 0.287 g (98% yield) of 1-*t*-butyl-3-(2-methyl-3-phenyl-2-propyl)urea, mp 163–165°, identical in ir and nmr with authentic material. A solution of **1d** (0.015 *M*) and 1.2-dimethylhydrazine (0.033 *M*) in benzene afforded the urea in 87% and **3d** in 13% yield.

Registry No.—1-*t*-Butyl-3-(2-methyl-3-phenyl-2-propyl)urea, 19656-66-7; **1d**, 19656-67-8; 1,2-di-*t*-amylhydrazine, 19713-61-2; 2,2′-dimethyl-2,2 -azobutane, 19694-12-3; **3a**, 19656-68-9; **3b**, 19656-69-0; **3c**, 19656-70-3; **3d**, 19656-77-0.

Diaziridinones. IV.[1] Formation by Condensation of Alkyl Isocyanide with Nitrosoalkane. Evidence for a Carbodiimide N-Oxide

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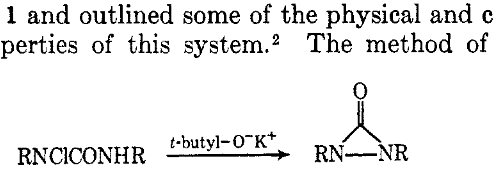
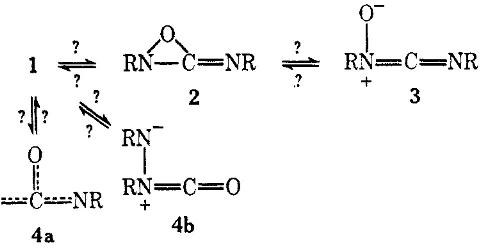
Received August 26, 1968

Reaction of *t*-butyl isocyanide with 2-methyl-2-nitrosopropane, **5**, at 70° (1:1, neat) affords di-*t*-butyldiaziridinone, **1a** (90%), di-*t*-butylcarbodiimide, **6a** (10%), and 2-methyl-2-nitropropane, **7**. The ratio of **6a**:**1a** increases with increasing concentrations of nitrosoalkane **5**; products **6a** and **7** are formed in comparable amounts over wide variation in the ratio of reactants. Reaction of *t*-butyl isocyanide with nitrosoalkane **5** in the presence of phenyl isocyanate affords two 1:1:1 adducts, **9** and **10**. Reaction of isopropyl isocyanide and nitrosoalkane **5** affords 1-*t*-butyl-2-isopropyldiaziridinone, **1b**, carbodiimide **6b**, and nitroalkane **7** in the absence of phenyl isocyanate, and affords 1:1:1 adduct **8** in the presence of phenyl isocyanate. The results are discussed in terms of condensation of alkyl isocyanide with nitrosoalkane to afford carbodiimide N-oxide **3**. This intermediate may rearrange (presumably *via* oxaziridinimine **2**) to diaziridinone **1**, may react with nitrosoalkane leading to carbodiimide **6** and nitroalkane **7**, or may react with phenyl isocyanate to afford the 1:1:1 adducts.

We recently described a synthesis (eq 1) of diaziridinones **1** and outlined some of the physical and chemical properties of this system.[2] The method of synthesis was only successful when R was a tertiary alkyl group. In a search for other methods of synthesis of **1** we have considered approaches based on the possibility of ring–chain isomerism in the diaziridinone system (eq 2). If diaziridinones were more stable than forms such as **2**, **3**, or **4**, then compounds of structure **1** might be made *via* syntheses of these other species. Inspection of **2** and **3** reveals the possibility of their formation from an isocyanide and a nitroso compound. This paper describes the results of a study of reaction of 2-methyl-2-nitrosopropane with alkyl isocyanides.[3]



(1)



(2)

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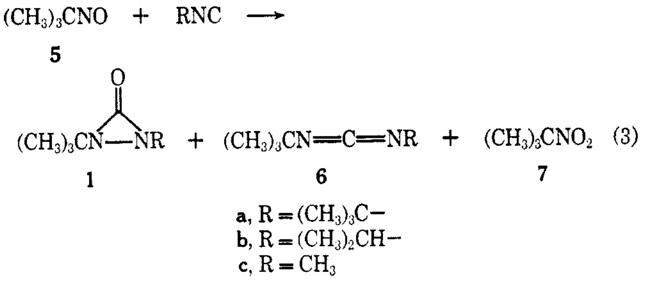
[1] (a) Part III: F. D. Greene, W. R. Bergmark, and J. G. Pacifici, *J. Org. Chem.*, **34**, 2263 (1969); (b) Financial support from the National Science Foundation (Grant No. GP 5527) is gratefully acknowledged.

[2] F. D. Greene, J. C. Stowell, and W. R. Bergmark, *J. Org. Chem.*, **34**, 2254 (1969).

[3] For a report of the reaction of nitrosotrifluoromethane with methyl isocyanide, see S. P. Makarov, *et al.*, *Dokl. Akad. Nauk SSSR*, **142**, 596 (1962).

Results

2-Methyl-2-nitrosopropane **5** reacts with aliphatic isocyanides at moderate temperatures. The main products are diaziridinones **1**, carbodiimides **6**, and nitroalkane **7** (eq 3). The relative yields of products are affected by substituents, concentration, and temperature. Diaziridinone (**1**) corresponds to a 1:1 stoichiometry of nitroso compound and alkyl isocyanide; carbodiimide (**6**) and nitroalkane (**7**), formed in comparable amounts, correspond to a 2:1 stoichiometry of the reactants.



Effect of R in RNC.—Use of *t*-butyl isocyanide with **5** results in good yields of di-*t*-butyldiaziridinone **1a**. From isopropyl isocyanide, diaziridinone **1b** was isolated and characterized although purification was difficult. Neat mixtures of **5** with *sec*-butyl isocyanide or with cyclohexyl isocyanide at 100° yielded approximately equal amounts of diaziridinone and carbodiimide (**1** and **6**, R = *sec*-alkyl) based on spectral data. Under comparable conditions *t*-butyl isocyanide and **5** afforded **1a** and **6a** in the ratio of 10:1. Reaction of methyl isocyanide with **5** afforded **6c** and **7**, with infrared evidence for the presence of diaziridinone **1c**.

The effect of temperature was examined briefly in the reaction of **5** with *t*-butyl isocyanide and with isopropyl isocyanide. An increase in temperature produced an increase in the ratio of diaziridinone to carbodiimide.

A product study as a function of reactant concentrations was made for the reaction of the nitrosoalkane **5** with *t*-butyl isocyanide (Table I).

Table I

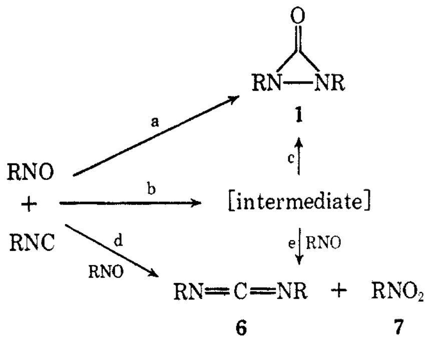
Reaction of 2-Methyl-2-nitrosopropane (5) with *t*-Butyl Isocyanide at 70°, 75 Hr

Reactants, mole fraction		Yield of products, %		
RNO	RNC	Diaziridinone 1a	Carbodiimide 6a	Nitroalkane 7
0.5	0.5	90	10	10
0.05[a]	0.05[a]	50	1	1
0.1	0.9	95	2.7	3.0
0.9	0.1	65	32	35

[a] In chlorobenzene.

Di-*t*-butyldiaziridinone does not react with 2-methyl-2-nitrosopropane, excluding this possible path for formation of carbodiimide and nitroalkane. The diaziridinone is also unreactive with alkyl isocyanides under the reaction conditions. The principal findings (Table I) are as follows: (1) carbodiimide and nitroalkane are formed in comparable amounts over wide variation in ratio of reactants; and (2) the ratio of carbodiimide to diaziridinone is dependent on the concentration of nitrosoalkane. The ratio of **6**:**1** increases with increasing concentration of the nitrosoalkane; *i.e.*, the carbodiimide-forming reaction is of higher order in the nitrosoalkane than is the diaziridinone-forming reaction.

This evidence is suggestive of the possibilities summarized in eq 4. The involvement of an intermediate seemed attractive to us since, indeed, this possibility had been the original basis for trying the experiment. The major possibilities considered for an intermediate were an oxaziridinimine, **2**, and a carbodiimide N-oxide, **3**. The latter appeared to offer the simplest routes to all three products—**1** by intramolecular rearrangement (eq 4, path c) and **6** and **7** by reaction with the nitrosoalkane (eq 4, path e). Consequently, a suitable trapping agent for the suspected intermediate was sought.



(4)

Trapping Experiments.—The necessary aspect appeared to be a 1,3-dipolarophile which would react with **3**, but not with nitrosoalkane, alkyl isocyanide, or diaziridinone. Of a number of possible trapping agents examined, isocyanates appeared to be the best. Control experiments showed that phenyl isocyanate was unreactive toward nitrosoalkane, alkyl isocyanide, and diaziridinone. Also, the rate of disappearance of the reactants was approximately the same in the presence or absence of phenyl isocyanate. However, the product composition was completely altered. Diaziridinone, carbodiimide, and nitroalkane were absent; in their place was a mixture of products, some of which were rather labile. From isopropyl isocyanide, 2-methyl-2-nitrosopropane (**5**), and phenyl isocyanate was isolated a crystalline compound corresponding to a 1:1:1 adduct, **8**. From *t*-butyl isocyanide, nitrosoalkane **5**, and phenyl isocyanate were isolated two 1:1:1 adducts (**9** and **10**) and a third adduct, **11**, of composition $C_{18}H_{19}N_3O_2$ corresponding formally to a 1:1:1 adduct of *phenyl* isocyanide, **5**, and phenyl isocyanate. From the reaction of *t*-butyl isocyanide, nitrosoalkane **5**, and *t*-butyl isocyanate was isolated a 1:1:1 adduct, **12**. Of principal consequence to the present paper is the formation of the 1:1:1 adducts. The number of possible structures is large. Both the structures and the reactions of these adducts pose many questions on which we hope to report at a later date. A summary of information and tentative structural assignments are given in the following section.

Nature of the 1:1:1 Adducts.—Physical data are summarized in Table II. The principal mode of mass spectral fragmentation of the adducts[4,5] involves the

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[4] The full mass spectral data are reported in ref 5.

[5] J. F. Pazos, Doctoral Dissertation, Massachusetts Institute of Technology, Cambridge, Mass., 1967.

TABLE II

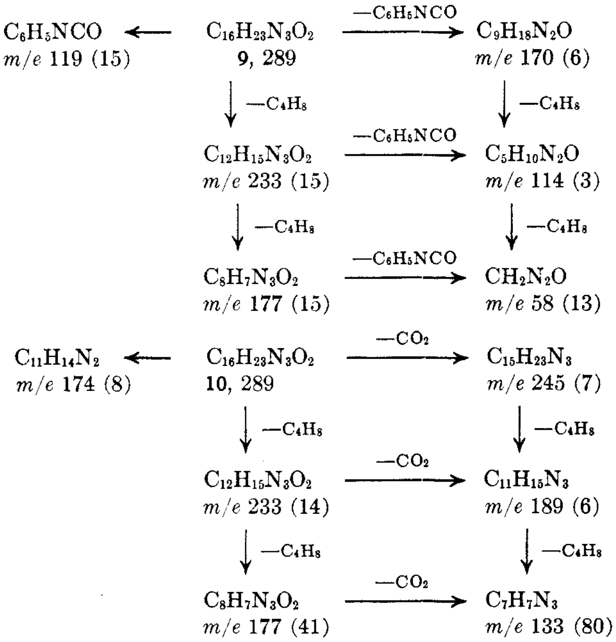
PHYSICAL DATA FOR 1:1:1 ADDUCTS OBTAINED FROM REACTION OF 2-METHYL-2-NITROSOPROPANE WITH ALKYL ISOCYANIDE IN THE PRESENCE OF PHENYL ISOCYANATE

	8	9	10	11	12
Mp, °C	85.5–86	80–88 dec	70–71.5	105–106	104–106
Ir (CCl_4), cm^{-1}	1815 (2), 1715 (3)	1775 (1), 1700 (5)	1815 (2), 1716 (3)	1810 (vs), 1690 (vs)	1790 (s), 1700 (vs)
Nmr (CCl_4), ppm	1.13 (s, 9 H), 1.23 (d, 6 H), 3.87 (septuplet, 1 H), 7.3 (m, 5 H)	1.32 (s, 9 H), 1.40 (s, 9 H), 7.25 (d, 5 H)	1.27 (s, 9 H), 1.34 (s, 9 H), 7.1–7.6 (m, 5 H)	1.55 (s, 9 H), 6.4–6.9 (m, 5 H), 7.05 (s, 5 H)	1.25 (s, 9 H), 1.34 (s, 9 H), 1.55 (s, 9 H)
Uv, λ, mμ (ε) (isooctane)	238 (11, 380)	243 (11,960) 276 sh (1,715), 284 sh (935)	238 (11,320)	263 (6,540) plateau on end absorption	End absorption
Mass spectrum[a] ion, m/e (relative intensity)	275, 260 (3), 231 (13), 219 (100), 177 (18), 175 (37), 160 (13), 133 (82), 119 (17), 118 (12), 105 (27), 104 (35), 92 (58), 77 (72), 57 (76)	289 (0.7), 245 (zero), 233 (15), 218 (8), 177 (15), 170 (6), 119 (15), 114 (3), 93 (7), 91 (11), 84 (15), 83 (15), 58 (13), 57 (100)	289, 245 (7), 233 (14), 189 (6), 177 (41), 174 (8), 133 (80), 119 (8), 118 (7), 105 (10), 93 (22), 91 (20), 83 (26), 77 (26), 57 (100)	309 (18), 265 (7), 253 (100), 209 (48), 208 (85), 207 (18), 194 (7), 134 (10), 118 (40), 109 (115), 92 (44), 77 (46), 65 (15), 57 (48)	269, 213 (7), 157 (19), 142 (34), 135 (10), 133 (8), 113 (12), 101 (29), 98 (40), 89 (12), 74 (7), 68 (11), 58 (42), 57 (100)

[a] References 4 and 5.

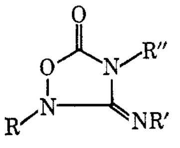
loss of isobutylene (McLafferty rearrangement). For adducts **8**, **10**, and **11**, loss of carbon dioxide is observed both as a primary process and as a secondary process (after loss of one or more isobutylene units). Fragments of composition corresponding to isopropylphenylcarbodiimide, *t*-butylphenylcarbodiimide, and diphenylcarbodiimide also are obtained from **8**, **10**, and **11**, respectively. Adduct **9** (isomeric with **10**) shows loss of isobutylene but no primary loss of carbon dioxide. It also affords a positive ion at M − C_6H_5NCO. Adduct **10** shows no ion at M − C_6H_5NCO. The positive ions corresponding to C_6H_5NCO and $(CH_3)_3CNCO$ are much larger from **9** than from **10**. The main mass spectral fragmentation patterns for **9** and **10** are summarized in Scheme I.

SCHEME I



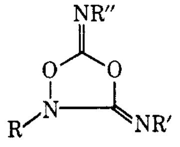
Adduct **9** could only be isolated when the reaction was carried out at 40° and worked up after 10% reaction. It decomposed in 10 min at 100°. Thermal decomposition of **9** in dilute solution afforded **10**, diaziridinone **1a**, and phenyl isocyanate. When excess phenyl isocyanate was added to a solution of **9** in acetonitrile before heating, no diaziridinone was formed.

Adducts **8**, **10**, and **11**, similar in ir, uv, and mass spectral fragmentation patterns, are tentatively assigned structure A, the substituted 3-imino-1,2,4-oxadiazolinone-5. Adduct **9** is tentatively assigned structure B, the substituted 2,5-diimino-1,3,4-dioxazolidine.



A

8, R = $(CH_3)_3C$; R′ = $(CH_3)_2CH$; R″ = C_6H_5
10, R = $(CH_3)_3C$; R′ = $(CH_3)_3C$; R″ = C_6H_5
11, R = $(CH_3)_3C$; R′ = C_6H_5; R″ = C_6H_5



B

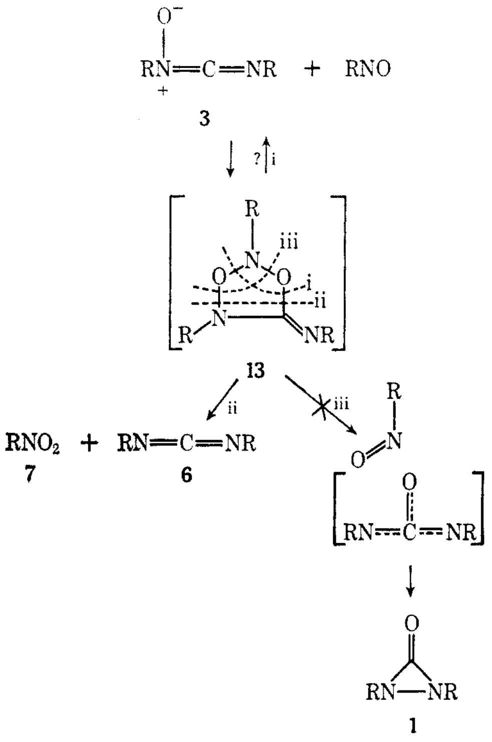
9, R = $(CH_3)_3C$; R′ = $(CH_3)_3C$; R″ = C_6H_5

$C_2N_3O_2RR'R''$
12, R = R′ = R″ = $(CH_3)_3C$
(structure unassigned)

Conclusions from Trapping Experiments.—The absence of diaziridinone **1**, carbodiimide **6**, and nitroalkane **7** from the product mixture when nitrosoalkane reacts with alkyl isocyanide in the presence of phenyl isocyanate, coupled with the absence of an effect of isocyanate on rate, provides compelling evidence for an intermediate. This evidence excludes the formation of diaziridinone by a direct bimolecular reaction of nitrosoalkane and alkyl isocyanide (Scheme I, path a). It also excludes the formation of nitroalkane and carbodiimide by a direct termolecular reaction (Scheme I, path d).

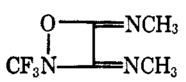
For the structure of the intermediate, we favor the carbodiimide N-oxide, **3**, on the basis of the high reactivity toward 1,3-dipolarophiles. Covalent structure **2** cannot be excluded for the trappable intermediate, but it would not appear to be a reactive "dipolar species." (Compare also nitrones and oxaziridines in cycloaddition reactivity.)[6,7]

We return now to the question of mode of formation of carbodiimide **6** and nitroalkane **7** (eq 3). These products, formed in equal amounts, might arise by single oxygen transfer from **3** to nitrosoalkane **5**. An attractive alternative (eq 5) is 1,3-dipolar cycloaddition of **3** and nitrosoalkane yielding **13**. Decomposition of **13** by retrocycloaddition path ii would give **6** and **7**. An alternate mode of decomposition, path iii, formally *could* lead to **1**. However, the variation in product composition with changes in reactant concentrations (Table I) indicates that the formation of products **6** and **7** is of higher order in nitrosoalkane than the formation of **1**. Thus, path iii would not appear to be an important route to **1**.



(5)

The reaction of nitrosotrifluoromethane with methyl isocyanide[3] affords an adduct of composition $2CH_3NC + 1CF_3NO$ to which structure **14**, 2-trifluoromethyl-3,4-di(methylimino)-1,2-oxazetidine, has been assigned on the basis of its pyrolysis (400°) to methyl isocyanate and N-methyl-N′-trifluoromethylcarbodiimide. Adduct **14** may be formed by capture of an intermediate carbodiimide N-oxide by methyl isocyanide rather than by the nitrosotrifluoromethane.



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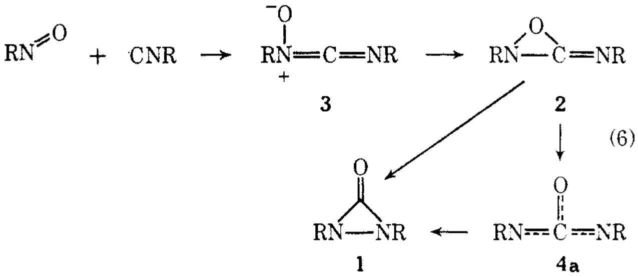
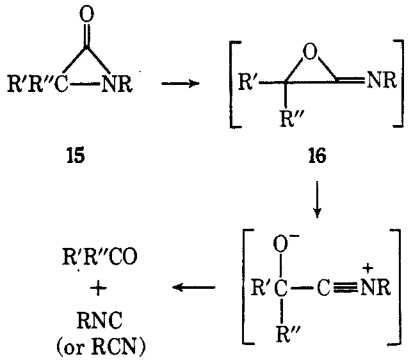
It is of interest to consider the over-all conversion of nitrosoalkane and alkyl isocyanide to diaziridinone (eq 6). As indicated above, we favor **3** for the trappable intermediate. Its isomerization to **1** would appear to require proceeding *via* **2**. At this time we have no evidence to indicate whether **2** has a finite existence or represents an energy maximum (the former seems more likely to us). Conversion of **2** to **1** may proceed directly or *via* a species such as **4a**.



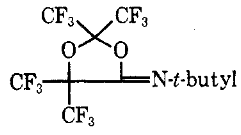
(6)

Efforts to approach **3** from **1** have been unsuccessful. Di-*t*-butyldiaziridinone may be heated with phenyl isocyanate for prolonged periods with no evidence of formation of adducts **9** or **10**. Other efforts to trap a ring-opened form of a diaziridinone have been unsuccessful.[2] Also, thermal decomposition of diaziridinones[5] does not afford nitrosoalkane, isocyanide, or nitrile (the expected thermal rearrangement product of an isocyanide).

The structurally related class, aziridinones **15**,[8] shows rather different behavior. Efforts to prepare these compounds from aldehydes or ketones and isocyanides have been unsuccessful. On the contrary, even under mild conditions some aziridinones decompose to ketones and isocyanides, presumably *via* the sequence of eq 7.[8] An important difference between **17** and **3** lies in the poorer accommodation of charges in the former compared with the latter. However, when R′ and R″ are perhaloalkyl, reaction appears to proceed in the reverse direction; *e.g.*, hexafluoroacetone reacts with *t*-butyl isocyanide to afford the iminodioxolane, **18**, in a formal sense the product of reaction of **17** with another molecule of hexafluoroacetone.[9]



(7)



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[6] R. Huisgen, R. Grashey, and J. Sauer in "The Chemistry of the Alkenes," S. Patai, Ed., Interscience Publishers, New York, N. Y., 1964, Chapter 11.

[7] E. Schmitz, "Dreiringe mit Zwei Heteroatomen," Springer-Verlag, Berlin, 1967.

[8] I. Lengyel and J. C. Sheehan, *Angew. Chem.*, **80**, 27 (1968).

[9] W. J. Middleton, D. C. England, and C. G. Krespan, *J. Org. Chem.*, **32**, 948 (1967).

In the presence of acids, reaction occurs between isocyanides and aldehydes (or ketones) affording α-acyloxyamides (the Passerini reaction).[10] That reaction does not require, nor is it likely to involve, species such as **16** or **17** as *discrete* intermediates. Some evidence in support of species such as **17**, **16**, and **15** is found in the reactions of ketones and isocyanides in the presence of boron trifluoride.[11a,b] Isolation of both isomeric forms, **15** and **16**, has been reported for R = *t*-butyl, R′ = 1-adamantyl, R″ = H. Both compounds decompose to R′CHO and RNC; **16** undergoes the change at room temperature, **15** at 140° (presumably *via* **16**).[11c]

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 D [a 10 ft × 0.25 in. glass column packed with 20% Carbowax 20 on Chromosorb W (washed to pH 8) diatomite support]; column E [a 5 ft × 0.25 in. stainless steel tube packed with 20% SE-30 silicone oil on 60/80 mesh Chromosorb W]. 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.

Alkyl isocyanides were prepared by published methods[12,13] (the former[12] gave better results, and handling of the isocyanides was reduced to a minimum): methyl isocyanide,[12b] ir 2165 cm^{-1}; isopropyl isocyanide, bp 87° (lit.[13] bp 87°); *t*-butyl isocyanide, bp 91° (lit.[13] bp 91°). The isocyanides were obtained in 99% purity, analyzed by glpc on column E.

N-*t*-Butylhydroxylamine.—To a mixture of 2-methyl-2-nitropropane[14] (199.5 g, 1.94 mol) and a solution of ammonium chloride (83.2 g in 3.2 l. of water) cooled to 10° with an ice bath was added 274 g of zinc in small portions over 1 hr, never letting the temperature rise above 20°. The mixture was stirred 1 additional hr at 0° and 30 min at room temperature. The reaction mixture was filtered and the solid was washed with 1 l. of boiling water. The filtrate was made basic with sodium hydroxide, and potassium carbonate (1.36 kg) was added. The aqueous layer was extracted with three 500-ml portions of ether. The ether was dried ($MgSO_4$) and evaporated, yielding 118 g (68%) of *t*-butylhydroxyamine: mp 60–62° (lit.[15] mp 64–65°).

2-Methyl-2-nitrosopropane was prepared by the method of Emmons,[15] mp 66–67° when heated at 2°/min (lit.[15] mp 79–81°), not changed by recrystallization or sublimation, and 99% pure by glpc analysis (column E).

Anal. Calcd for C_4H_9NO: C, 55.14; H, 10.41. Found: C, 55.00; H, 10.44.

Di-*t*-butylcarbodiimide had bp 60° (17 mm) [lit.[16] bp 51° (10 mm)]; ir 2090, 2125 cm^{-1}.

1-*t*-Butyl-2-isopropyldiaziridinone, 1b, from Isopropyl Isocyanide and 2-Methyl-2-nitrosopropane.—A sealed tube containing 0.2 g (2.3 mmol) of 2-methyl-2-nitrosopropane and 0.2 g (2.9 mmol) of isopropyl isocyanide was heated at 130° for 20 min. The ir spectrum of the crude reaction mixture indicated absorption at 1870 (diaziridinone), at 2100, 2130, (carbodiimide), and at 1540, 1350 cm^{-1} (nitroalkane). The material was distilled (trap to trap) and gas chromatographed (column D) at 45° and 20 lb of helium pressure. Collection of the major peak gave pure diaziridinone **1b**: ir (CCl_4) 1900 sh, 1880 s, 1850 cm^{-1} sh; nmr (CCl_4) δ 1.03 (singlet with shoulder at 1.1, 15 H), 2.82 (septuplet, 1 H).

Anal. Calcd for $C_8H_{16}N_2O$: C, 61.50; H, 10.32; N, 17.93. Found: C, 61.86; H, 10.31; N, 17.92.

Reaction of Methyl Isocyanide with 2-Methyl-2-nitrosopropane.—A tube containing 0.0169 g (0.194 mmol) of 2-methyl-2-nitrosopropane, 0.0044 g (0.107 mmol) of methyl isocyanide, and 0.0078 g of *t*-butylbenzene (glpc standard) was sealed and heated to 100° for 3 hr. The reaction mixture was analyzed by glpc on column E. The principal products, N-*t*-butyl-N′-methylcarbodiimide[16] (retention time at 100°, 6.2 min) and 2-methyl-2-nitropropane[14] (retention time at 100°, 4.4 min), were collected and identified by ir: yields, 60 ± 5% carbodiimide and 45 ± 5% *t*-$BuNO_2$. Examination by ir of a reaction of methyl isocyanide and the nitrosoalkane, **5** (in a ratio of 1.5:1), heated at 121° for 18 min showed weak absorption at 1860, attributed to N-methyl-N′-*t*-butyldiaziridinone **1c**.

Product Study for the Reaction of 2-Methyl-2-nitrosopropane and *t*-Butyl Isocyanide.—The reactions were run in sealed tubes. Purified chlorobenzene (better than 99% by glpc) was used as an internal standard. Standard solutions for all reactions (with approximate concentrations expected for the products) were prepared from the pure compounds, di-*t*-butyldiaziridinone,[2] di-*t*-butylcarbodiimide,[16] and 2-methyl-2-nitropropane.[14] Standard solutions with concentrations of di-*t*-butyldiaziridinone (**1a**) near the expected value were used because of the nonlinearity of the response factor of diaziridinone with concentration. The analyses were made on column E by temperature programming (6°/min; flow, 60 ml/min; initial temperature, 25°). The temperatures at which the components were observed are given in parentheses: *t*-Bu-NO (30°), *t*-Bu-NC (40°), *t*-Bu-NO_2 (62°), di-*t*-butylcarbodiimide (105°), di-*t*-butyldiaziridinone (113°). The results are summarized in Table I.

Reaction of Phenyl Isocyanate, 2-Methyl-2-nitrosopropane, and *t*-Butyl isocyanide. A. At 40° for 140 Hr.—2-Methyl-2-nitrosopropane (10.0 g, 0.115 mol), *t*-butyl isocyanide (9.0 g, 0.108 mol), and phenyl isocyanate (13.0 g, 0.109 mol) were heated at 40° for 140 hr in a tightly stoppered vessel. Examination of the crude mixture by ir indicated strong absorption at 1810, 1700, and much weaker absorption at 1775 cm^{-1}. The crude mixture was then heated to 100° for 5 min after which no 1775-cm^{-1} absorption remained. After evaporation of the volatile material, 10.6 g of oil remained. Fractional crystallization from hexane afforded two compounds, **11** and **10**. Compound **11** was less soluble in hexane and was the first material to crystallize. Purification was accomplished by one further recrystallization, affording 1.851 g of pure **11**: mp 105–106°; physical data are reported in Table II.

Anal. Calcd for $C_{18}H_{19}N_3O_2$: C, 69.88; H, 6.19; N, 13.58. Found: C, 70.11; H, 6.20; N, 13.27.

Although ir indicated **10** was the main component left in the reaction mixture, repeated recrystallizations were needed to isolate a pure sample. Final purification by fractional sublimation under high vacuum at 60° afforded compound **10** as a white crystalline solid, mp 70–71.5°; physical data are reported in Table II.

Anal. Calcd for $C_{16}H_{23}N_3O_2$: C, 66.41; H, 8.01; N, 14.52. Found: C, 66.18; H, 8.06; N, 14.34.

B. At 40° for 30 Hr.—2-Methyl-2-nitrosopropane (3.014 g, 0.0346 mol), *t*-butyl isocyanide, (2.999 g, 0.036 mol), and phenyl isocyanate (0.6466 g, 0.0054 mol) were heated at 40° for 30 hr in a stoppered vessel. Analysis of the crude reaction mixture by glpc (column E) indicated no diaziridinone **1a** and very little phenyl isocyanate present. The ir of the crude mixture showed absorption at 1775 and 1700, but no bands at 1810 cm^{-1}. The volatile materials were evaporated under high vacuum at room temperature. The residual oil (1.251 g) was crystallized from hexane affording 0.341 g (1.8 mmol, 33%) of **9** (dec pt 77–88°). Recrystallization from pentane afforded 0.126 g of material of **9**, dec pt 80–88°; physical data are reported in Table II.

Anal. Calcd for $C_{16}H_{23}N_3O_2$: C, 66.41; H, 8.01; N, 14.52. Found: C, 66.70; H, 8.17; N, 14.56.

Thermal Decomposition of 9.—Solutions of **9** (1%) in carbon tetrachloride, isooctane, chloroform, and acetonitrile were sealed and heated for 10 min at 100°. The prominent bands in the ir

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(10) See I. Hagedorn and U. Eholzer, *Chem. Ber.*, **98**, 936 (1965), and references cited therein.

(11) (a) T. Saegusa, N. Taka-ishi, and H. Fujii, *Tetrahedron*, **24**, 3795 (1968); (b) H.-J. Kabbe, *Angew. Chem. Intern. Ed. Engl.*, **7**, 389 (1968); (c) K. Bott, *Tetrahedron Lett.*, 3323 (1968)

(12) (a) J. Casanova, Jr., R. E. Schuster, and N. D. Werner, *J. Chem. Soc.*, 4280 (1963); (b) R. E. Schuster, J. E. Scott, and J. Casanova, Jr., *Org. Syn.*, **46**, 75 (1966).

(13) I. Ugi and R. Meyr, *Chem. Ber.*, **93**, 239 (1960).

(14) N. Kornblum, *Org. Reactions*, **12**, 133 (1962).

(15) W. D. Emmons, *J. Amer. Chem. Soc.*, **79**, 5739, 6522 (1957).

(16) E. Schmidt, W. Striewsky, and F. Hitzler, *Ann.*, **560**, 222 (1948); E. Schmidt and M. Seefelder, *ibid.*, **571**, 83 (1951).

at 1775 and 1700 cm^{-1} of **9** were replaced by absorption at 2250 (isocyanate), at 1870 (diaziridinone **1a**), and at 1810 and 1710 cm^{-1} (**10**). In carbon tetrachloride and isooctane, **10** predominated. In chloroform and acetonitrile, **1a** predominated. From the acetonitrile reaction diaziridinone **1a** was also observed as the major component by glpc, and identified by collection and comparison with authentic material. Addition of phenyl isocyanate to the acetonitrile solution of **9** before heating completely inhibited diaziridinone formation.

Reaction of Isopropyl Isocyanide, 2-Methyl-2-nitrosopropane, and Phenyl Isocyanate.—Isopropyl isocyanide (0.0291 mol), 2-methyl-2-nitrosopropane (0.0279 mol), and phenyl isocyanate (0.0321 mol) were placed in a pressure bottle and heated to 100° for 5 hr and 40 min. Upon cooling crystallization occurred. The volatile materials were removed under high vacuum. The solid residue (6 g) was fractionally crystallized from hexane, affording 1 g (0.003 mol, 11% yield) of pure **8**, mp 85.5–86°; physical data are reported in Table II.

Anal. Calcd for $C_{15}H_{21}N_3O_2$: C, 65.43; H, 7.69; N, 15.26. Found: C, 65.58; H, 7.78; N, 15.13.

Reaction of *t*-Butyl Isocyanide, 2-Methyl-2-nitrosopropane, and *t*-Butyl Isocyanate.—A tube containing 2.010 g (0.023 mol) of 2-methyl-2-nitrosopropane, 2.643 g (0.032 mol) of *t*-butyl isocyanide, and 4.660 g (0.047 mol) of *t*-butyl isocyanate was degassed, sealed under vacuum, and heated for 118 hr at 65°. After breaking the seal, the crude mixture was trap-to-trap distilled (25°, 0.01 mm) leaving 1.803 g of nonvolatile material. The ir of the crude residue indicated some diaziridinone **1a**, but very strong absorption was present at 1700 and 1790. The material was dissolved in hexane and crystallized at −10° affording 0.498 g (0.00185 mol, 8% yield) of **12**, mp 104–106°; physical data are reported in Table II.

Anal. Calcd for $C_{14}H_{27}N_3O_2$: C, 62.42; H, 10.11; N, 15.60; mol wt, 269. Found: C, 62.13; H, 10.06; N, 15.64; mol wt, 266 (osmotic in chloroform).

Control Experiments. Attempted Reaction of 2-Methyl-2-nitrosopropane with Di-*t*-butyldiaziridinone, 1a.—A sealed tube contained 26.2 mg (0.15 mmol) of diaziridinone **1a** and 13.7 mg (0.16 mmol) of 2-methyl-2-nitrosopropane was heated at 100° for 33 hr. Comparison of the ir before and after heating indicated no change had occurred.

Attempted Reaction of Methyl Isocyanide with Di-*t*-butyldiaziridinone.—Methyl isocyanide (4.5 mg, 0.11 mmol) and di-*t*-butyldiaziridinone (8 mg, 0.047 mmol) were sealed in a capillary and heated at 100° for 2 hr. Analysis by ir indicated that no reaction had occurred.

Attempted Reaction of Phenyl Isocyanate with Di-*t*-butyldiaziridinone, 1a.—Phenyl isocyanate (0.381 g, 3.204 mmol) and di-*t*-butyldiaziridinone, **1a** (0.422 g, 2.484 mmol), were mixed and an aliquot was sealed in a capillary tube. The tube was heated to 100° for 5.5 hr. Comparison of ir before and after heating indicated that no reaction had taken place.

Attempted Reaction of Phenyl Isocyanate with 2-Methyl-2-nitrosopropane.—Phenyl isocyanate (0.643 g, 5.41 mmol), 2-methyl-2-nitrosopropane (0.247 g, 2.84 mmol), and chlorobenzene (1.29 g) were sealed and heated for 9 hr at 100°. Analysis on column E indicated 2.02 mmol (71%) of nitroso-*t*-butane and 5.14 mmol (95%) of phenyl isocyanate.

Attempted Reaction of Phenyl Isocyanate with *t*-Butyl Isocyanide.—Phenyl isocyanate (0.624 g, 5.33 mmol), *t*-butyl isocyanide (0.254 g, 3.06 mmol), and chlorobenzene (1.173 g) were sealed and heated for 9 hr at 100°. Analysis on column E indicated 2.60 mmol (85%) of *t*-butyl isocyanide and 5.33 mmol (100%) of phenyl isocyanate.

Reaction of 2-Methyl-2-nitrosopropane and *t*-Butyl Isocyanide in the Presence and Absence of Phenyl Isocyanate. Solution A.—2-Methyl-2-nitrosopropane (0.183 g, 2.103 mmol), *t*-butyl isocyanide (0.190 g, 2.90 mmol), and phenyl isocyanate (0.738 g, 6.205 mmol) were diluted to 2 ml with chlorobenzene (0.925 g).

Solution B.—2-Methyl-2-nitrosopropane (0.184 g, 2.105 mmol) and *t*-butyl isocyanide (0.190 g, 2.90 mmol) were diluted to 2 ml with chlorobenzene (1.646 g).

Aliquots of solutions A and B were sealed in capillary tubes and heated to 100°. Tubes were taken out at intervals and analyzed by glpc (column E) for *t*-BuNO, *t*-BuNC, and diaziridinone, **1a**. The error in the analysis of *t*-BuNO and *t*-BuNC was ±10% owing to the short retention times and small areas. Within this limit of error, the rate of disappearance of *t*-BuNO and *t*-BuNC was not affected by the presence of phenyl isocyanate. Analysis after 4.5 hr gave the following percentages (in parentheses): solution A—*t*-BuNO (50), *t*-BuNC (60), and Dz (0.7); solution B—*t*-BuNO (35), *t*-BuNC (45), and Dz (45).

Registry No.—**1b**, 19656-61-2; **8**, 19656-62-3; **9**, 19656-64-5; **10**, 19656-63-4; **11**, 19656-65-6.

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