Column chromatography of the residue after distillation employing chloroform, ethyl acetate, and methanol as eluents on silica gel gave about 5 g of a light yellow-brown semisolid which crystallized overnight under vacuum. This material was extracted with diethyl ether in a Soxhlet extractor. The resultant colorless solid recrystallized from di-*n*-butyl ether (100:1 ratio of ether to solid heated to 60°) to afford 2.1 g (52%) of colorless needles (some as long as 1.5–2 in.) of pure N-cyanotris(dimethylamino)phosphinimide (XIII), mp 77.8–79°.

Anal. Calcd for $C_7H_{18}N_5P$: C, 41.4; H, 8.9; N, 34.5. Found: C, 41.5; H, 8.8; N, 34.0.

Tris(dimethylamino)difluorophosphorane (XIV). The difluorophosphorane (XIV) was prepared by the procedure described by Firth and co-workers[7] for the preparation of difluorotriphenylphosphorane. A 0.489-g (3×10^{-3} mole) sample of $[(CH_3)_2N]_3P$ and 20 ml of diethyl ether were placed in a 50-ml glass reactor fitted with a Teflon needle valve and a magnetic stirring bar. The reactor was cooled to −196° and degassed and 0.416 g (4×10^{-3} mole) of N_2F_4 was added by condensation. The mixture was warmed very slowly to room temperature and stirred overnight. After removal of the solvent and excess N_2F_4 under partial vacuum, the residue was fractionally distilled to give 0.37 g (61.4%) of tris(dimethylamino)difluorophosphorane (XIV). This material was spectroscopically identical with that obtained from the CF_2N_2–$[(CH_3)_2N]_3P$ reaction described above.

N-Cyanobis(dimethylamino)methoxyphosphinimide (XV). Using the procedure outlined for XIII, 5.05 g (3.36×10^{-2} mole) of $[(CH_3)_2N]_2POCH_3$ and 2.0 g (2.56×10^{-2} mole) of difluorodiazirine in 25 ml of methylene chloride were allowed to react, with stirring, at −78°. The reactor was warmed to room temperature; methylene chloride was removed under partial vacuum. Fractional distillation–condensation through −40 and −196° traps was used to remove the difluorophosphorane by-product (XVI). Distillation of the contents of the −40° trap gave 1.5 g (47.5%) of pure difluorobis(dimethylamino)methoxyphosphorane (XVI), bp 39–40° (4 mm), n^{23}D 1.4069, which was identified by infrared and nmr spectroscopy (Table I).

The residue from the solvent removal and fractionation was dissolved in chloroform, washed with 5% HCl, dried, and purified by column chromatography on silica gel, using chloroform and methanol as eluents. Evaporation of the solvents afforded a 61.5% yield of N-cyanobis(dimethylamino)methoxyphosphinimide (XV) as a colorless, viscous liquid, n^{23}D 1.4797.

Anal. Calcd for $C_6H_{15}N_4OP$: C, 37.9; H, 7.9; N, 29.5. Found: C, 38.0; H, 7.9; N, 29.2.

Triphenyl-N-(5-tetrazoyl)phosphinimide (XVIII). To 1.193 g (3.95×10^{-3} mole) of N-cyanotriphenylphosphinimide (I) in 12 ml of CH_2Cl_2 was added 11 ml of a 0.545 *N* HN_3 solution (6.0×10^{-3} mole) in diethyl ether. The mixture was stirred overnight and filtered and the colorless solid was recrystallized from methanol. The yield of XVIII was 0.702 g (51.5%) melting with decomposition at 225–226°. Unreacted N-cyanoimide was also recovered.

Anal. Calcd for $C_{19}H_{16}N_5P$: C, 66.1; H, 4.7; N, 20.3; mol wt, 345. Found: C, 66.0; H, 4.9; N, 20.1; mol wt, 347.

Tributyl-N-(5-tetrazoyl)phosphinimide (XIX). To a 1.21-g (5.0×10^{-3} mole) sample of N-cyanotributylphosphinimide (III) dissolved in 12 ml of benzene was added 11 ml of a 0.545 *N* solution of HN_3 (6.0×10^{-3} mole) in diethyl ether. The mixture was stirred overnight at room temperature during which a colorless solid precipitated. Filtration (two crops) and recrystallization from ethyl acetate afforded 0.915 g (64.2%) of colorless needles of XIX melting with decomposition at 169–170°.

Anal. Calcd for $C_{13}H_{28}N_5P$: C, 54.7; H, 9.9; N, 24.5; mol wt, 285. Found: C, 54.9; H, 9.9; N, 24.2; mol wt, 300.

O,O,O-Triphenyl N-(5-Tetrazoyl)phosphoroimidate (XX). To 0.35 g (1.0×10^{-3} mole) of triphenyl N-cyanophosphoroimidate (IX), dissolved in 5 ml of benzene, was added 2 ml of a 0.545 *N* HN_3 solution (1.09×10^{-3} mole) in diethyl ether. The reactor was sealed and heated on a steam bath for 18 hr. The colorless precipitate was removed by filtration and recrystallized from ethyl acetate. A 37% yield of the desired tetrazoyl derivative, melting at 162–163°, was obtained.

Anal. Calcd for $C_{19}H_{16}N_5O_3P$: C, 58.0; H, 4.1; N, 17.8; mol wt, 393. Found: C, 57.7; H, 4.4; N, 17.6; mol wt, 391.

Acknowledgments. The author is deeply indebted to Mr. Albert H. Stoskopf, without whose assistance and helpful experimental innovations this work would not have been completed. The author also wishes to express his appreciation to Mr. D. L. Wood for technical assistance, Dr. J. J. McBrady for infrared and nuclear magnetic resonance measurements and interpretation, Mr. P. B. Olson for analytical determinations, and Mr. J. J. Neumayer for molecular weight determinations.

Pivaloylnitrene

G. Thomas Tisue,[1] Siegfried Linke, and Walter Lwowski[2]

Contribution from the Chemistry Department and the Research Center, New Mexico State University, Las Cruces, New Mexico, and the Department of Chemistry, Yale University, New Haven, Connecticut. *Received June 12, 1967*

Abstract: The photolysis of pivaloyl azide gives pivaloylnitrene and *t*-butyl isocyanate. The nitrene behaves similar to carbethoxynitrene; it adds to C=C double bonds, inserts into C–H bonds selectively, and dissociates. With cyclohexene, the yield of nitrene products is 46%, based on azide.

Nitrenes are often invoked as short-lived intermediates in the decomposition of azides, but in many cases it has been difficult to prove that the reaction in question is not one of the undecomposed azide, followed by loss of nitrogen.[3–7] Convincing proof for nitrene intermediates in reactions of decomposing azides has been furnished by creating the same species from a precursor other than the azide. To this end, an α-elimination route was developed for carbalkoxynitrenes[8,9] and the deoxygenation of aromatic nitro and nitroso compounds served in the case of arylni-

---

(1) National Institutes of Health Predoctoral Fellow, 1962–1965.

(2) To whom correspondence should be addressed: Chemistry Department, New Mexico State University, Las Cruces, N. M. 88001.

(3) For a review see R. A. Abramovitch and B. A. Davis, *Chem. Rev.*, **64**, 149 (1964).

(4) P. Walker and W. A. Waters, *J. Chem. Soc.*, 1632 (1962).

(5) P. A. S. Smith and J. H. Hall, *J. Am. Chem. Soc.*, **84**, 480 (1962).

(6) M. F. Sloan, W. B. Renfrow, and D. S. Breslow, *Tetrahedron Letters*, 2905 (1964); D. S. Breslow, T. J. Prosser, A. F. Marcantonio, and C. A. Genge, *J. Am. Chem. Soc.*, **89**, 2384 (1967).

(7) W. Lwowski and T. W. Mattingly, Jr., *ibid.*, **87**, 1947 (1965); *Tetrahedron Letters*, 277 (1962).

(8) W. Lwowski, T. Maricich, and T. W. Mattingly, Jr., *J. Am. Chem. Soc.*, **85**, 1200 (1963).

(9) W. Lwowski and T. J. Maricich, *ibid.*, **87**, 3630 (1965).

trenes.[10-12] The existence of cyanonitrene as a reaction intermediate was shown by the symmetry of the N^{15}-labeled species.[13] From the reactions observed with these "authenticated" nitrenes it develops that a chemical criterion can be applied: the ability of nitrenes to insert into C–H bonds. It is this ability that makes us believe that the species we wish to describe here is pivaloylnitrene, $(H_3C)_3C{-}CO{-}N$, rather than an excited state of pivaloyl azide, $(H_3C)_3C{-}CO{-}N_3$. Our conclusion is strengthened by the general similarity of the reactions of the new species to those of carbethoxynitrene. A preliminary report of some of our work has been published.[14]

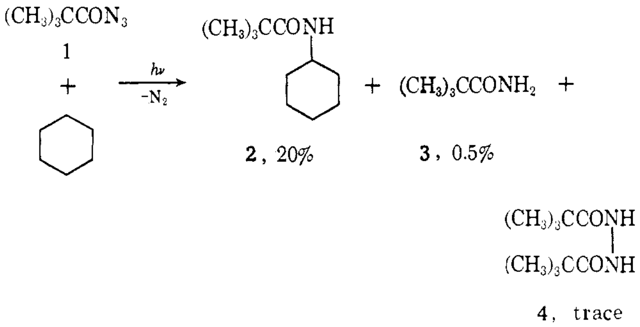
Intramolecular C–H insertions in photodecompositions of carbonyl azides are well known. First observed by Edwards,[15] they have generally been interpreted as nitrene reactions.[3] The geometrical restraints in intramolecular reactions, however, made it impossible to obtain data on the selectivity of such nitrenes.

Horner, *et al.*,[16,17] studied the photolysis of benzazide in nucleophilic solvents (dimethyl sulfoxide, alcohols, water). He concludes that the photolysis (but not the thermolysis) of benzazide generates benzoylnitrene, which then adds to the nucleophiles or dehydrogenates them. While our work was in progress, Huisgen[18] showed that the photolysis of acetyl azide in benzonitrile and phenylacetylene gives products corresponding to 1,3 addition of acetylnitrene to these solvents: 2-methyl-5-phenyl-1,3,4-oxadiazole and 2-methyl-5-phenyloxazole, respectively. These investigations present evidence for the formation of carbonylnitrenes in the photolysis of carbonyl azides, $R{-}CO{-}N_3$. In the following, we wish to report on the formation of pivaloylnitrene, and its intermolecular reactions: selective insertion into C–H bonds, addition to the C=C double bond of cyclohexene, and fragmentation.

Results and Discussion

Pivaloyl azide (**1**) was decomposed by ultraviolet light (containing 84% of light of 2537 A) in a variety of hydrocarbons, at −10°. All these reactions gave *t*-butyl isocyanate in about 40% yield, as discussed in the accompanying paper.[19] The other products are discussed here.

Cyclohexane and Cyclopentane. Irradiation of **1** in cyclohexane (containing 10 vol % of dichloromethane to prevent freezing) gave products analogous in nature and in relative yields to those formed from carbethoxynitrene and cyclohexane.[7-9] The intramolecular C–H insertion product, 3,3-dimethylazetidin-2-one (**5**), could not be detected, for the vpc trace did not show a peak with the retention time of authentic **5**. Photolysis of **1** in cyclopentane gave entirely analogous results: N-cyclopentylpivalamide was obtained in 13% yield (based on **1** consumed), and pivalamide in 0.5% yield.



Neopentane and Dichloromethane. Photolysis of **1** in neopentane gave only a 0.2% yield of N-neopentylpivalamide (**6**), besides *t*-butyl isocyanate (40%), pivalamide (0.7%), and a nonvolatile oil corresponding to 36% of the weight of the pivaloylnitrene that could theoretically have been generated. The oil showed broad infrared absorptions in the NH (or OH) region, C–H absorption at 2994 cm^{-1}, and broad carbonyl absorption, centered at 1686 cm^{-1}. The nmr spectrum showed only a multiplet centered at δ 1.25. The same oil was produced when **1** was photolyzed in dichloromethane. The gas evolved in all the photolyses contained isobutene; the largest amounts of it were formed in the photolyses in neopentane (13.5% yield) and dichloromethane, where least of the nitrene is trapped.

$$\mathbf{1} \longrightarrow (CH_3)_3CCON \longrightarrow [(CH_3)_3\dot{C}\ \dot{C}NO] \longrightarrow (CH_3)_2C{=}CH_2 + \text{polymer}$$

The isobutene was identified and quantitatively determined through its mercury nitrate complex,[20] which was also prepared from authentic isobutene. The nonvolatile oil seems to be a polymer from isobutene and cyanic acid. The material balance in the photolysis in neopentane is 90%. The fragmentation of most of the nitrene (50% based on **1**, 83% based on **1** minus isocyanate yield) seems to be due to the low reactivity of the neopentane C–H groups with singlet nitrenes, which allows most of the nitrene to fragment, perhaps *via* its triplet form. This fragmentation has an analogy in the gas phase decomposition of carbethoxynitrene, to give cyanate and ethoxy radicals.[21]

2-Methylbutane. When pivaloyl azide was photolyzed in 2-methylbutane, the four isomeric insertion products **7–10** were formed in a total yield of 25%. They were separated by vpc. Dividing their yields by the number of hydrogens available of each type gave the relative reactivities of the various sites on 2-methylbutane. The two different sites of primary C–H bonds had the same reactivity, within the accuracy of our measurements. The relative reactivities of primary, secondary, and tertiary C–H bonds of 2-methylbutane are summarized in Table I and compared with the selectivities of the same C–H bonds toward carbethoxynitrene[9,22] and phenylnitrene.[23] The products **7–10** were identified by independent synthesis.

All three nitrenes share a pronounced preference for insertion into tertiary C–H bonds. This could be interpreted as indicating a partial positive charge on

---

[10] R. J. Sundberg, *Tetrahedron Letters*, 477 (1966); *J. Am. Chem. Soc.*, **88**, 3781 (1966).

[11] R. A. Odum and M. Brenner, *ibid.*, **88**, 2074 (1966).

[12] G. Smolinsky and B. I. Feuer, *J. Org. Chem.*, 31, 3882 (1966).

[13] A. G. Anatassiou, H. E. Simmons, and F. D. Marsh, *J. Am. Chem. Soc.*, 87, 2296 (1965).

[14] W. Lwowski and G. T. Tisue, *ibid.*, 87, 4022 (1965).

[15] J. W. Apsimon and O. E. Edwards, *Proc. Chem. Soc.*, 461 (1961); *Can. J. Chem.*, 27, 1930 (1963).

[16] L. Horner and A. Christmann, *Ber.*, **96**, 388 (1963).

[17] L. Horner, G. Bauer, and J. Dorges, *ibid.*, **98**, 2631 (1965).

[18] R. Huisgen and J. P. Anselme, *ibid.*, **98**, 2998 (1965).

[19] S. Linke, G. T. Tisue, and W. Lwowski, *J. Am. Chem. Soc.*, **89**, 6308 (1967).

[20] G. Denigès, *Compt. Rend.*, **126**, 1043 (1898); C. D. Hurd and A. R. Goldsby, *J. Am. Chem. Soc.*, **56**, 1815 (1934); C. E. Starr, Jr., and T. Lane, *Anal. Chem.*, 21, 572 (1949).

[21] D. W. Cornell, R. S. Berry, and W. Lwowski, *J. Am. Chem. Soc.*, 87, 3626 (1965).

[22] W. Lwowski and T. J. Maricich, *ibid.*, **86**, 3164 (1964).

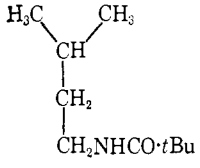
[23] J. H. Hall, J. W. Hill, and H. C. Tsai, *Tetrahedron Letters*, 2211 (1965).

Table I. Reactivities of Pivaloylnitrene and Other Nitrenes toward the C–H Bonds in 2-Methylbutane

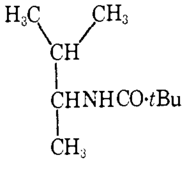
Parent azide	Type of C–H bond: Tertiary	Secondary	Primary
$EtOCON_3$[22]	34 (±5%)[a]	9 (±10%)	1
$C_6H_5N_3$[23]	140–280	>7	1
$(CH_3)_3CON_3$	160 (±25%)[b]	8.6 (±10%)	1

[a] The relative errors appear in parentheses. [b] The small vpc peaks of the primary insertion products were broad, thus rendering integration difficult and giving rise to the large relative errors.

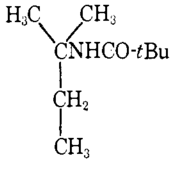
carbon in the transition state of the insertion. It has been found, however, that carbethoxynitrene inserts readily into the bridgehead C–H bonds of norbornane.[24]



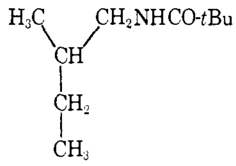
7



8



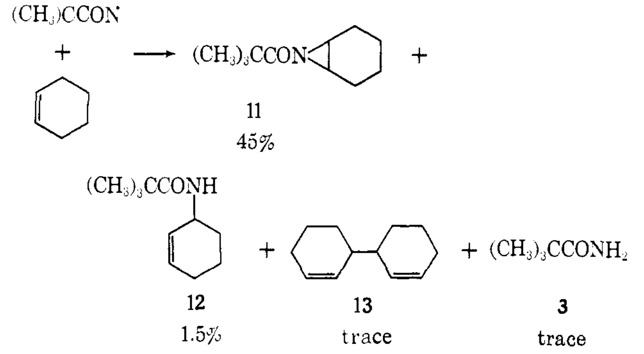
9



10

These bonds are only a little less reactive than the (averaged) other C–H bonds in norbornane, and one must conclude that only little, if any, positive charge is created on the carbon, in the transition state. The data available correlate reasonably well with the C–H bond strengths, rather than with the stability of the corresponding carbonium ions.

Cyclohexene. Photolysis of **1** in cyclohexene again gave products analogous to those obtained with carbethoxynitrene. Apart from a 41% yield of isocyanate, the products are shown below.



The aziridine **11** absorbs light at 2537 A with an extinction coefficient of 347, while **1** has an extinction coefficient of about 100 at this principal wavelength of irradiation. The aziridine **11** is destroyed photolytically, and gives a 63% yield of nonvolatile matter, 8% of **12**, and 19% of **3**. The yields given above are from a run carried to 30% of completion. They are based on nitrogen evolved and would be higher by a factor of 1.5 if the isocyanate yield were taken into account as derived from a nonnitrene path.[19] The allylic amide **12** might, in part or all, come from the photolysis of **11** rather than from allylic insertion. The nonallylic isomer of **12** was not found, although a 0.3% yield would have been detected. At temperatures approaching 200°, the aziridine **11** is converted (in the gas chromatograph) to N-pivaloylcyclohexanonimine (**14**).

Thermolysis. At about 28°, **1** decomposed to over 90% in 6 hr. Such thermolysis in cyclohexene, cyclohexane, and 2-methylbutane did not give any of the intermolecular products obtained in the photolyses.

Experimental Section

General. Infrared spectra were recorded on Perkin-Elmer 421 and Beckman IR 8 instruments, nmr spectra on Varian A-60 and A-60A spectrometers, and ultraviolet spectra on a Cary Model 14 instrument. Melting and boiling points are uncorrected. The photolyses were carried out in Rayonet Photochemical Reactors, and the temperature in the irradiation vessel was maintained by means of a cold finger immersed in the photolysate, cooling being provided by a Forma refrigerated circulation bath. Gas chromatography was done on Varian-Aerograph A-90 units. Quantitative analyses by vapor phase chromatography (vpc) were carried out by calibrating the detector response for the compound in question by injecting known volumes of standard solutions and aliquots of the reaction mixtures. The peak areas were determined planimetrically. Tests for decomposition of samples during vpc analysis were made by collecting all the effluent in a Dry Ice trap, and reinjecting. If no new vpc peaks appeared, and the infrared spectrum of the sample had not changed, decomposition was regarded as absent.

Pivaloyl azide (1) has been described in the literature,[25] but the preparation of **1** from sodium azide and pivaloyl chloride is much superior to the method reported in ref 25. Pivaloyl chloride (redistilled, Eastman P 2817) (12.1 g, 0.1 mole) dissolved in 40 ml of ether was dropped over a period of 0.5 hr into a vigorously stirred, ice-cooled solution of 7.8 g (0.12 mole) of sodium azide in 35 ml of water. After stirring at 0° for another 3 hr, the layers were separated, the aqueous layer was extracted twice with 20 ml of cold ether, and the ether solutions was dried over $MgSO_4$ at 0°. The residue from the ether solution was distilled three times in a short-path distillation apparatus at 0.3 mm pressure from a pot immersed in ice into a trap cooled by Dry Ice. The colorless azide solidified at the Dry Ice temperature, yield 9.5–10.5 g (75–83%); infrared spectrum (CCl_4), N_3 at 2137, CH at 2994, C=O at 1712 cm^{-1}. The thermal instability of **1** prevented elemental analysis. Reaction of **1** with aniline gave the known[26] pivalanilide, mp 129–131°, in nearly quantitative yield. *Caution:* pivaloyl azide, like other acyl azides of low molecular weight, has been observed to explode without warning at room temperature. All operations involving neat or concentrated solutions of **1** should be carried out with great caution and always behind a shield. The vapors of **1** are quite toxic, and (in some persons) even brief exposure causes rapid pulse, nausea, vertigo, and severe headache.

N-Alkylpivalamides were prepared by dissolving 1 g of the parent amide in 5 ml of dry pyridine and adding dropwise a solution of 1.5 g of pivaloyl chloride in 5 ml of dry pyridine. After the exothermic reaction, the mixture was allowed to stand for 2 hr at room temperature. The mixture was poured into 25 ml of water, and the amides were obtained by filtration or by extraction with ether, followed by gas chromatography.

N-Cyclohexylpivalamide showed the following physical properties: mp 125–125.5° (from hexane); infrared spectrum, NH at 3460, C=O at 1663 cm^{-1}.

Anal. Calcd for $C_{11}H_{21}NO$: C, 72.13; H, 11.47; N, 7.65. Found: C, 72.09; H, 11.58; N, 7.82.

N-Cyclopentylpivalamide had mp 128–130° (from heptane); infrared spectrum, NH at 3470 and 3375, C=O at 1660 cm^{-1}.

Anal. Calcd for $C_{10}H_{19}NO$: C, 71.05; H, 11.24; N, 8.28. Found: C, 70.95; H, 11.12; N, 8.29.

N-Neopentylpivalamide had mp 88–89° (from hexane); infrared spectrum (CCl_4), NH at 3480, C=O at 1665 cm^{-1}.

---

[24] W. Lwowski and J. O. Reed, unpublished results.

[25] A. Bühler and H. E. Fierz-David, *Helv. Chim. Acta*, **26**, 2131 (1943).

[26] G. Schroeter, *Ber.*, **44**, 1206 (1911).

Anal. Calcd for $C_{10}H_{21}NO$: C, 70.18; H, 12.28; N, 8.19. Found: C, 70.16; H, 12.11; N, 8.17.

Isomeric (2-methylbutyl)pivalamides were prepared by dissolving 0.05 mole of the appropriate amine in 5 g of triethylamine and 25 ml of tetrahydrofuran, and adding dropwise with stirring at 0° a solution of 8.55 g (0.05 mole) of pivaloyl chloride in 25 ml of tetrahydrofuran. The mixture was kept overnight, filtered, and 10% aqueous hydrochloric acid was added to the cloud point. These solutions were twice extracted with 50-ml portions of ether, the ether extracts were washed with aqueous sodium carbonate and water, dried, treated with activated carbon, filtered, and concentrated. The residue was recrystallized twice or sublimed twice.

N-(3-Methylbutyl)pivalamide (7) showed a yield of 74%, mp 68–69° (twice sublimed); infrared spectrum, NH at 3475, C=O at 1660 cm^{-1}; nmr spectrum (CCl_4), singlet at δ 1.15 superimposed on multiplet at δ 0.76 to 1.14 (18 protons), multiplet δ 2.89–3.43 (2), NH broad at δ 6.65 (1).

Anal. Calcd for $C_{10}H_{21}NO$: C, 70.18; H, 12.28; N, 8.19. Found: C, 70.06; H, 12.33; N, 8.23.

2-Pivaloylamido-3-methylbutane (8) showed the following physical properties: yield 94%; mp 101–103° (twice sublimed); infrared spectrum in CCl_4, NH at 3470, C=O at 1660 cm^{-1}; nmr spectrum, *t*-butyl at δ 1.17 superimposed on a multiplet δ 0.74–2.30 (19), multiplet at δ 3.29–4.24 (1), NH at δ 4.05 (broad).

Anal. Found: C, 70.28; H, 12.31; N, 8.19.

2-Pivaloylamido-2-methylbutane (9) showed the following physical properties: yield 97%; melting point after two sublimations 74.5–75.5°; infrared spectrum in CCl_4, NH at 3465, C=O at 1660 cm^{-1}; nmr spectrum in CCl_4, 20 protons at δ 0.62–1.95, NH broad at δ 5.42 (1).

Anal. Found: C, 70.15; H, 12.16; N, 8.31.

1-Pivaloylamido-2-methylbutane (10) gave an 85% yield, melting point after two sublimations, 63–64°; infrared spectrum in CCl_4, NH at 3480, C=O at 1660 cm^{-1}; nmr spectrum in CCl_4, *t*-butyl at δ 1.23 superimposed on a multiplet at δ 0.68–1.92 (total 18), multiplet at δ 2.84–3.25, NH at δ 7.38 (broad, 1).

Anal. Found: C, 70.37; H, 12.39; N, 8.31.

Pivalamide (3) was prepared from pivaloyl chloride and ammonia in ether; mp 154° (lit.[27] 155°); infrared spectrum in KBr, NH_2 at 3400 and 3200, C=O at 1655 cm^{-1}; infrared spectrum in $CHCl_3$, NH at 3571 (sharp), 3546 (sharp), and 3195 (broad), C=O at 1664 cm^{-1}.

N,N′-Dipivaloylhydrazine (4) was prepared from hydrazine and pivaloyl chloride in pyridine, as described above; mp 215–217° (subl); infrared spectrum in KBr, NH at 3280 (broad), C=O at 1645 cm^{-1}; infrared spectrum in $CHCl_3$, NH at 3472 (sharp), and 3290 (broad), C=O at 1621 cm^{-1}.

N-(Cyclohex-2-enyl)pivalamide (12) was prepared from 3-aminocyclohexene[7] and an equimolar amount of pivaloyl chloride in ether, in the presence of 1 equiv of triethylamine. Triethylammonium chloride was filtered off and the residue from the filtrate was sublimed at 50–60° (5×10^{-2} mm). This yielded 86% of the theoretical quantity of a white solid: mp 79–81°; infrared spectrum in CCl_4, NH at 3470 (sharp) and 3037 (broad), C=O at 1670 cm^{-1}; nmr spectrum in CCl_4, *t*-butyl at δ 1.26 (8), multiplet at δ 1.34–2.26 (6), δ 4.40 (broad, 1), multiplet δ 5.29–5.97 (2), multiplet δ 6.27–6.67 (1).

Anal. Calcd for $C_{11}H_{19}NO$: C, 72.92; H, 10.49; N, 7.73. Found: C, 72.72; H, 10.49; N, 7.92.

N-(Cyclohex-3-enyl)pivalamide was prepared following the general procedure above (acylation of the amine in pyridine) from 4-aminocyclohexene (see below). Chromatography on alumina and elution with pentane gave crystals: mp 84°; infrared spectrum in CCl_4, NH at 3497 (sharp) and 3401 (broad), CH at 3058, 2976, CO at 1664 cm^{-1}.

Anal. Calcd for $C_{11}H_{19}NO$: C, 72.92; H, 10.49; N, 7.73. Found: C, 72.82; H, 10.68; N, 7.47.

4-Aminocyclohexene. Cyclohexene-4-carboxylic acid chloride[7] (0.05 mole) was dissolved in 40 ml of benzene and 4 g of activated sodium azide was added. The stirred mixture was heated to reflux for 6 hr, after which time no more nitrogen was evolved. The solution was heated to reflux with 25 ml of concentrated hydrochloric acid, then evaporated to dryness, and the residue dissolved in water. After extraction with ether, the water solution was made basic, and the amine was extracted with ether. The dried ether solution gave 3.6 g (66%) of the amine, bp 72–77° (50 mm), $n^{23}\mathrm{D}$ 1.4921.

7-Pivaloyl-7-azabicyclo[4.1.0]heptane (11). By the method of Hassner,[28] 7-azabicyclo[4.1.0]heptane was prepared in 74% yield. Pivaloyl chloride (2.28 g) was added to a cooled solution of this aziridine (1.8 g) in 75 ml of pentane and 1.9 g of triethylamine. After 1 hr, the triethylammonium salt was filtered off; the residue from the pentane solution was subjected to vpc on a 2-m 20% neopentyl glycol sebacate on Anachrom ABS 50–60 mesh column at 132°. Under these conditions no isomerization occurred. The product showed no NH in the infrared spectrum; the carbonyl frequency occurs at 1680 cm^{-1}. The nmr spectrum in CCl_4 shows the *t*-butyl singlet at δ 1.18 superimposed on a multiplet at δ 1.00–2.09 (total 17), and the hydrogens at C-1 and C-6 at δ 2.54 (multiplet, 2); ultraviolet spectrum (in hexane), maxima at 2533 A (ϵ 347) and 2030 A (ϵ 4670). The yield was 70% of the theoretical.

Anal. Calcd for $C_{11}H_{19}NO$: C, 72.92; H, 10.49; N, 7.73. Found: C, 73.27; H, 10.77; N, 7.74.

N-Pivaloylcyclohexanonimine (14) is formed from **11** upon heating, *i.e.*, vpc analysis at higher injector and column temperatures than described above. On the neopentyl glycol sebacate column, an injector temperature of 250° and column temperature of 195° led to almost complete conversion to **14**, a colorless oil that rapidly turns brown on the air at room temperature. Structure assignment was based on the mode of formation, the infrared spectrum (no NH, no olefinic CH, C=O at 1650 cm^{-1}), analysis (N, 7.92), and the nmr spectrum, which contains neither signals attributable to aziridine C–H groups (δ 2.54 in **11**) nor those expected in the isomeric oxazoline[29] (expected at δ 4.7–5.4). Instead, the nmr spectrum shows the *t*-butyl signal at δ 1.17 superimposed on the ring-CH_2 signals (broad, δ 1.0–1.9) and no other signals.

Photolyses. The reaction substrate (50 ml) was cooled to −10° and a stream of dry nitrogen bubbled through for 10 min. Pivaloyl azide (1.95 g, 2 ml) was then added and a cooling finger was inserted in the cylindrical irradiation vessel (made of silica). Coolant from a refrigerated circulator was pumped through the cold finger, and the irradiation vessel was mounted along the center axis of the Rayonet photochemical reactor (of Southern New England Ultraviolet Co.). The progress of the photolysis was followed by measuring the nitrogen evolved and by taking samples for infrared spectra. The gas evolved amounted to about 105% of the theoretical yield of nitrogen and contained isobutene. Photolysis of 2-ml samples of **1** took about 12 hr. After completion, excess substrate and *t*-butyl isocyanate were removed *in vacuo*. The residue was transferred to a 10-ml volumetric flask, diluted to 10 ml, and analyzed by vpc. Two different columns were usually employed for each of the amides. For both, the detector responses were calibrated with authentic material. The analyses agreed closely, and the average figures are given in the Results and Discussion section above. The products were identified by comparison of their retention times and their infrared spectra with those of the authentic materials.

The following columns were used: A, 200 × 0.6 cm, 20% cyanosilicone XF 1150 on Anakrom ABS 50–60 mesh; B, 150 × 0.6 cm, 20% silicone rubber SE-30 on Chromosorb W; C, 200 × 0.6 cm, 20% silicone GE SF 96 on Anakrom ABS; D, 225 × 0.6 cm, 5% Carbowax 6000 on Chromosorb W; E, 200 × 0.6 cm, 20% neopentyl glycol sebacate NPGSE on Anakrom ABS, 50–60 mesh.

Photolysis of 1 in Cyclohexane. Standard procedure but a mixture of 45 ml of cyclohexane and 5 ml of dichloromethane was used to prevent freezing. Analysis was performed on columns A (160°), B (146°), and C (165°).

In another run, photolysis at 0°, in pure cyclohexane, was followed by work-up by column chromatography (acid-washed alumnia Merck, eluent 1:1 petroleum ether–benzene, changing to pure benzene). The **2** so isolated had an infrared spectrum indistinguishable from that of an authentic sample and had a correct elemental analysis (C, 72.31; H, 11.28; N, 7.81). The yield was 11%, and the mixture melting point was undepressed at 124.5–125.5°.

Photolysis of 1 in cyclopentane was performed using standard procedure with analysis on columns A (159°), B (146°), C (156°), and D (125°).

Photolysis of 1 in neopentane was performed using standard procedure with analysis on columns A (160°) and B (146°). For the isobutene assay see below.

---

[27] Haller and E. Bauer, *Compt. Rend.*, **148**, 129 (1909).

[28] A. Hassner and C. Heathcock, *Tetrahedron*, **20**, 1037 (1964).

[29] *Cf.* M. A. Weinberger and R. Greenhalgh, *Can. J. Chem.*, **41**, 1938 (1963).

Table II

Irradiation time, hr	Nitrogen evolution, % theoret	Yields of reaction products, % theoret based on N_2 **11**	**12**	**3**
1	30.2	44.8	1.7	0.4
		44.9	1.2	
2	52.5	44.9	1.8	0.3
		43.4	1.9	
3.5	75	39.8	1.9	0.5
		40.7	2.0	
5	86	35.8	2.5	0.8
		36.7	2.3	
7	98.5	29.9	3.6	1.0
		30.2		
12	100	14.2	6.3	2.5
		13.9		
24	107	Trace	6.8	2.8
			6.8	

Photolysis of 1 in dichloromethane was performed using standard procedure. The yields of *t*-butyl isocyanate and pivalamide (**3**) were 43 and 0.4%, respectively. Chromatoquality (Matheson Coleman and Bell) dichloromethane was used. For the infrared and nmr spectra of the nonvolatile residue see the Discussion section above.

Isobutene was determined gravimetrically through its mercuric nitrate complex.[20] In a typical experiment 1.95 g of pivaloyl azide was irradiated in 50 ml of neopentane, as above. The evolving gas, after passing through the Dewar condenser on top of the irradiation tube, was bubbled through a sintered-glass dispersing tube into 200 ml of an acidified mercuric nitrate solution. When the nitrogen evolution had ceased, cooling was stopped, and the neopentane was allowed to evaporate, its vapor passing through the mercuric nitrate solution (neopentane by itself did not give a precipitate). After standing for 5 hr, the precipitate was collected and weighed, yield 2.58 g, corresponding[20] to 116 mg of isobutene, or 13.5% yield based on azide, or 13.5/0.6 = 22.5% based on nitrene.

The same procedure was used with cyclopentane and cyclohexene as solvents. After the photolyses were complete, the solutions were heated to 40–50° and the vapors were bubbled through the mercuric nitrate solution. Photolysis in cyclopentane gave a 6.3% yield of isobutene (based on azide); photolysis in cyclohexene gave only traces of isobutene. This agrees with the contention that the isobutene is a product of the nitrene, which is more completely trapped in cyclopentane, and almost totally trapped in cyclohexene.

Photolysis of 1 in 2-Methylbutane. "Chromatoquality" (MCB) 2-methylbutane was saturated with nitrogen. About 35 ml of it was cooled to −15° in the irradiation apparatus of Figure 1, and 2.80 g (0.022 mole) of pivaloyl azide was added from a syringe equipped with a 6-in. needle. Stirring was started, and after some time for thermal equilibration, irradiation was begun. Methanol–water of −15° was circulated through the cold finger. After 74% of the theoretical volume of nitrogen had evolved, the solvent was removed *in vacuo*, and the residue was taken up in a little tetrahydrofuran. Vpc analysis on a 600 × 0.6 cm column containing 10% cyanosilicone XF 1150 on 50–60 mesh Firebrick at 150° separated the four pivaloylamides **7**, **8**, **9**, and **10** from each other as well as from the other products. The compounds were identified by their retention times as well as by collecting them and comparing their infrared spectra with those of the authentic compounds. Collecting all the materials together, and reanalyzing them, showed that no decomposition or change of product ratios occurred. The detector response was calibrated by injecting known amounts of the authentic materials. The response was the same for **7**–**10** within ±10%. The compounds emerged from the column in the sequence **9**, **8**, **7**, **10**, and the peaks of the two primary insertion products, **7** and **10**, were rather broad, making planimetry difficult. Since these peaks also overlapped some, they were determined together, and their sum was taken as the basis for the calculation of the relative reactivities in Table I.

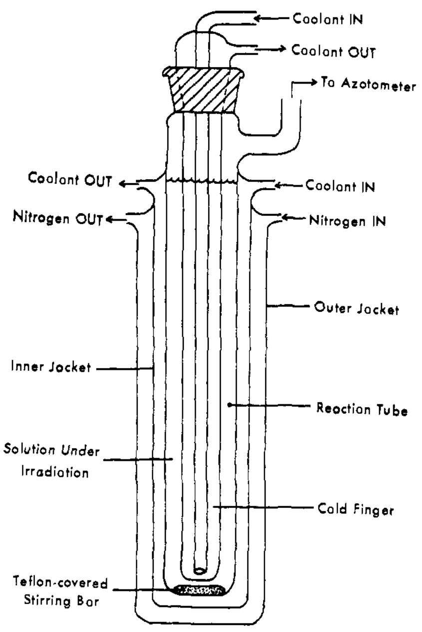


Figure 1.

Photolysis of 1 in Cyclohexene. Carefully purified cyclohexene[7] was used in the general procedure. The following columns were suitable for analysis: 7-pivaloyl-7-azabicyclo[4.1.0]heptane (**11**), columns B (at 146°), C (at 164°), and E (at 132°); for 3,3′-bis-(cyclohexenyl) (**13**), columns B (at 146°), C (at 164°), and D (at 125°); for N-(cyclohex-2-enyl)pivalamide (**12**), columns B (at 146°), C (at 165°), and D (at 152°). Prolonged irradiation decreased the yield of **11** (based on nitrogen evolved), led to the formation of polymer, and slightly increased the yields of **12** and **3**, as shown in Table II.

Photolysis of 7-Pivaloyl-7-azabicyclo[4.1.0]heptane (11). A solution of 0.95 g of **11** in 25 ml of dichloromethane was irradiated under standard conditions for 24 hr at −10°. The yellow solution was evaporated and the residue was analyzed by vpc. Yields of 8 and 19% of the theoretical were found of pivalamide (**3**) and of **12**, respectively, on columns B and C. Many small peaks were seen in the vpc traces; together they amounted to approximately a 10% yield (assuming a response of the detector similar to that for **3** or **12**). The rest of the material was not volatile.

Thermolyses[30] were conducted at 28° in 2-methylbutane and cyclohexene, and at reflux temperature (76° in Las Cruces) in cyclohexane. The standard analysis procedures were used, but failed to show any of the intermolecular products obtained in the photolyses. Thermolysis of **1** in cyclohexene gave traces of 3,3′-biscyclohexenyl and of di-*t*-butylurea.

Acknowledgments. We are greatly indebted to the National Institutes of Health and to the National Science Foundation for support of this work.

(30) The rate of thermolysis of pivaloyl azide has been measured in Professor Huisgen's laboratory as 4.92 × 10^{-5} sec^{-1} at 60° (G. Müller, Thesis, Universität München, 1962).