uct. Crystallization from benzene gave gold needles, mp 216–218°. The high-resolution mass spectrum gave the empirical formula $C_6H_5N_2O_3Cl$, and revealed the replacement of NH_2 by O, the presence of Cl, and NO_2: ir ($CHCl_3$) 1690 cm^{-1} (C=O).

Supplementary Material Available. GC–mass spectral data for product mixtures from chlorination of **3**, **5**, and **6** (6 pp) will appear following these pages in the microfilm edition of this volume of the journal.

Registry No.—**1**, 504-29-0; **1b**, 1072-98-6; **1c**, 4214-74-8; **2b**, 20712-16-7; **3a**, 56960-76-0; **3b**, 36936-27-3; **3c**, 31430-47-4; **4a**, 31430-41-8; **5a**, 56960-77-1; **5b**, 36936-23-9; **5c**, 22137-52-6; **6a**, 56960-78-2; **6b**, 56960-79-3; **6c**, 56960-80-6; **7**, 21901-29-1; **8**, 22280-62-2; **9**, 56960-81-7; **10**, 56960-82-8; **14**, 56960-83-9.

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Pivaloylnitrene. Reactions with Olefins and Dichloromethane Solvent Effect

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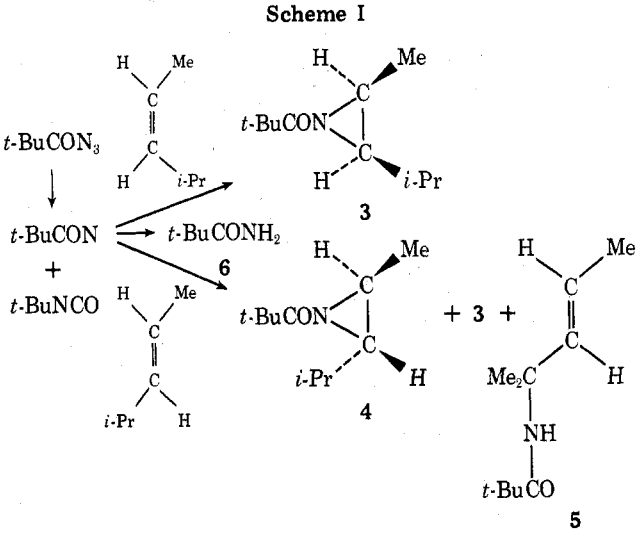
Received August 5, 1975

Pivaloylnitrene, generated photolytically from pivaloyl azide, adds to olefins stereospecifically in its singlet state and stereoselectively in its triplet state. Dichloromethane solvates and stabilizes the singlet nitrene without markedly decreasing its reactivity. Hydrocarbon solvents did not show such a stabilizing effect.

The photolysis of pivaloyl azide, *t*-BuCON$_3$ (**1**), generates pivaloylnitrene, *t*-BuCON (**2**), in about 50% yield, together with about the same yield of *tert*-butyl isocyanate. The latter is formed by an independent, parallel, concerted path[2,3]—the nitrene does not rearrange to *t*-BuNCO at an appreciable rate.[4–6] Of the pivaloylnitrene formed, most can be intercepted by cyclohexene; we obtained a 45% yield of 7-pivaloyl-7-azabicyclo[4.1.0]heptane plus minor yields of other nitrene products by trapping *t*-BuCON with cyclohexene.[2] Including the 41% yield of *t*-BuNCO, the material balance is in the order of 90%. Thus, pivaloylnitrene seemed to be a suitable as well as a representative[2,3] carbonylnitrene for the study of solvent effects and stereochemistry in reactions of singlet and triplet carbonylnitrenes with olefins. Such a study is reported here. A part of our results forms part of a communication,[7] and a small part overlaps with Swern's[6] work on the photolysis (with 254-nm light) of pivaloyl azide in neat *cis*- and *trans*-4-methyl-2-pentene. The results of the few duplicated experiments agree with those of Swern.

Scheme I



Results and Discussion

Photolysis of pivaloyl azide by 254-nm light in the presence of *cis*-4-methyl-2-pentene gave the cis aziridine **3** and traces of pivalamide (**6**). Under the same conditions, *trans*-4-methyl-2-pentene gave both aziridine stereoisomers, **3** and **4**, some **6**, and also the apparent allylic C–H insertion product **5**. The structures of the products **3**, **4**, **5**, and **6** were confirmed by their comparison with authentic samples. Table I shows the yields of the products. The apparent tertiary allylic C–H insertion product **5** was formed only from the trans olefin, and no analogous cis product was found in photolyses in cis olefin or its solutions. This might be due to the greater reactivity of the cis double bond (see below), which intercepts all the nitrene. It could also be due to steric hindrance of the approaching nitrene by the methyl group in the cis olefin, or both factors could combine to render the C–H insertion on C-4 unobservable in the case of the *cis*-4-methyl-2-pentene. Reactions analogous to the formation of the aziridines and of **5** have been observed earlier with cyclohexene as the substrate.[2]

Table I shows some regularities. The cis olefin gives only cis aziridine, while the trans olefin gives trans and cis aziridines and **5**. Furthermore, the yield of the trans aziridine increases with decreasing olefin concentration, while the yields of **5** and of cis aziridine are nearly constant in the photolyses of trans olefin in various concentrations in dichloromethane solutions. However, caution is in order owing to the photolability of *N*-pivaloylaziridines when using 254-nm light.[2] The aziridines **3** and **4** absorb significantly at 254 nm: **4** has ϵ 414 at 254 nm (λ_{max} 244 nm, ϵ 483) and **3** has ϵ 473 at 254 nm (λ_{max} 247 nm, ϵ 514). With the absorption coefficient of the azide **1** being only about 100 at 254 nm, the danger of photodecomposition of products exists, even when the photolyses are not carried to the point of quantitative nitrogen evolution. Therefore, all subsequent photolyses were carried out using fluorescent uv lamps which emit 83% of their light between 280 and 450

Table I
Photolyses of Pivaloyl Azide with 254-nm Light in the Presence of *cis*- and *trans*-4-Methyl-2-pentene

Olefin	Mol % olefin in CH_2Cl_2	% completion[a]	Aziridine yields,[b] %			Yield of 5, %	Yield of 6, %
			Total	Cis	Trans		
Cis	100	74	25.2	25.2	0	0	Trace
Trans	100	89	8.3	3.9	4.4	11.8	Trace
Cis	50	88	37.8	37.8	0	0	Trace
Trans	10	84	19.4	5.4	14.0	12.0	3.6
Cis	5	82	34.0	34.0	0	0	Trace
Trans	5	86	16.4	3.9	12.5	12.8	3.1

[a] Reaction stopped at this yield of nitrogen evolved. [b] Based on nitrogen evolved (= azide decomposed).

Table II
Photolyses of Pivaloyl Azide with 300-nm light in the Presence of *cis*-4-Methyl-2-pentene and Dichloromethane[a]

Mol % olefin in CH_2Cl_2	% completion	Aziridine yields, %		Yield of 5	Yield of 6
		Cis	Trans		
100	75	40	0	0	0
47	78	38	0	0	0
36	74	48	0	0	0
18	69	45	0	0	0
4.4	99	33	0	0	0
1.3	68	2.1	0	0	0

[a] All yields based on azide decomposed.

Table III
Photolyses of Pivaloyl Azide with 300-nm Light in Dichloromethane Solutions of *trans*-4-Methyl-2-pentene[a]

Mol % olefin	% completion	Aziridine yields, %		Yield of 5, %	Ratio of 3:5	Mol % CH_2Cl_2
		Trans	Cis			
78	79	7.4	5.8	9.7	0.60	22
68	83	7.7	5.8	10.5	0.55	32
57	59	11.0	6.2	9.9	0.63	43
47	29	12.9	5.8	9.0	0.64	53
47	65	13.0	5.0	7.6	0.66	53
47	51	13.0	5.6	9.6	0.58	53
47	75	13.0	5.8	9.4	0.62	53
23	65	16.2	5.1	9.3	0.55	77
23	65	16.2	4.6	8.7	0.53	77
23	65	15.6	5.2	8.7	0.60	77
18	49	15.8	5.9	8.5	0.69	82
12	49	15.1	5.9	8.4	0.70	88
9	56	18.5	6.1	10.3	0.59	91
3	66	20.5	5.4	12.3	0.44	97
1.3	65	16.3	4.1	13.5	0.30	98.7

[a] Yields are based on azide decomposed and would have to be approximately doubled to base them on nitrene produced.

nm, with a peak output near 300 nm. These lamps improved the aziridine yields over those reported in Table I and by Swern.[6]

Table II shows the results of photolyzing pivaloyl azide in *cis*-4-methyl-2-pentene and its dichloromethane solutions. The yield of the cis aziridine peaks at 36 mol % olefin concentration and drops off sharply below 4 mol %, without the formation of a detectable yield of pivalamide (**6**), or of the trans aziridine **4**. As discussed in more detail below, this is consistent with all of the singlet and triplet nitrene reacting with the olefin to form the cis aziridine, or dissociating to HNCO and isobutene (or to corresponding ion or radical pairs), which then form the observed polymer.[2]

The results obtained with *trans*-4-methyl-2-pentene under the same conditions are shown in Table III. Besides *t*-BuNCO, three main products are formed. The yield of the trans aziridine **4** is seen to increase with decreasing olefin concentration in the range from 78 to 3 mol %. The cis aziridine **3** is formed in 5.56 ± 0.45% yield, constant over the same concentration range. The tertiary allylic insertion product **5** also is formed in constant yield: 9.11 ± 0.78% if computed over the olefin concentration range from 78 to 12 mol %, or 9.42 ± 0.82% if computed over the range from 78 to 9 mol %. At 1.3 mol % olefin concentration the yields of both aziridine isomers are down, while that of **5** is up. The drastic differences between the two olefin isomers prompted an attempt to measure their relative reactivities toward *t*-BuCON. Photolysis of *t*-$BuCON_3$ in a 1:1 mixture of *cis*- and *trans*-4-methyl-2-pentene gave a 40% yield of the cis aziridine **3** only. A 9:1 trans:cis olefin mixture gave a 23% yield of **3**, no trans aziridine **4**, and a 0.8% yield of **5**. Given the detectability of a 1% yield of **4**, the rate constant for the formation of cis aziridine (**3**) from the cis olefin must be at least 230 times as large as the rate constant for the formation of the trans aziridine (**4**) from the trans olefin. In contrast to this factor of ≥230, ethoxycarbonylnitrene forms aziridine (stereospecifically) only 1.4 times faster with *cis*- than with *trans*-4-methyl-2-pentene.[8] Since the two nitrenes are quite similar in their general chemical behavior,[2] the difference here must be due to steric reasons. As seen on molecular models, the *t*-BuCO on the nitrogen can avoid all interaction with the alkyl groups on C_2 and C_3 in the cis aziridine **3** only, by assuming the anti configuration on the ring. Such an orientation should be maintained already during the approach of the nitrene to the olefin, and in the transition state. In the trans aziridine **4** (and during its formation), no such orientation is possible; both N invertomers of **4** have pivaloyl–alkyl interactions. Of the olefins, the cis isomer has the higher thermochemical energy, and together with the steric hinderance developed in the two transitions states, the one forming the trans aziridine ends up with a free energy of activation sufficiently larger than that of its cis counterpart to explain the difference in reactivity of the two olefins. Similarly, the diradical *t*-BuCON-ĊHMeCH-*i*-Pr, formed from triplet *t*-BuCON and either cis or trans olefin, should prefer ring closure to the cis aziridine **3**. Thus, we expect the triplet nitrene addition to be stereoselective (if nonstereospecific) and form cis aziridine from either olefin. The hypothesis explains both the high relative reactivity of the cis olefin and the absence of trans aziridine **4** in all reaction mixtures arising from cis olefin, regardless of the experimental conditions.

The 0.8% yield of **5** from a 9:1 trans:cis olefin mixture attests to the presence of triplet pivaloylnitrene, but no trans aziridine was formed. How much of the cis isomer **3** formed in this reaction is due to the reaction of triplet nitrene with cis olefin we do not know. The formation of **3** from the trans olefin is attributed to the triplet nitrene because an open-chain intermediate must intervene to change the configuration at one C atom. This intermediate, by analogy with other nitrene reactions,[8,9] is assumed to be the triplet diradical *t*-BuCONĊHMeCH-*i*-Pr. We also attribute to

the triplet nitrene the formation of 5, because its yield is unaffected by the concentration of CH_2Cl_2 in the reaction mixtures. Singlet C–H insertion yields of similar alkanoylnitrenes have been found to increase drastically with increasing dichloromethane concentration.[7] The formation of 5 seems to involve the abstraction of the tertiary allylic hydrogen of the trans olefin, followed by the combination of the radical pair *t*-BuCONH $\dot{C}Me_2CH$=CHMe. The constant yields of 3 and 5 (Table III) over a wide olefin concentration range suggest that the triplet nitrene forming them is present in constant concentration—it cannot be formed by intersystem crossing (favored where the trapping agent concentration is low). The triplet nitrene must thus be formed directly in the photolysis of the parent azide. Such direct triplet species formation is already known for ethoxycarbonylnitrene[9] and certain carbenes.[10]

The almost threefold yield increase of the thermodynamically disfavored trans aziridine 4 with decreasing concentration of the trans olefin would not be expected in a truly inert medium. Rather, the delay incurred before reactive collision with an olefin molecule would favor competing reactions, such as decomposition or intersystem crossing of the nitrene. This would lower the trans aziridine yield. Intersystem crossing would produce triplet nitrene and increase the yields of 3 and 5, which is not observed. Indeed, the total yield of (singlet and triplet) nitrene products increased with decreasing olefin concentration (increasing dichloromethane concentration) to over 38% at 97 mol % dichloromethane (3% olefin) concentration from 23% at 30 mol % CH_2Cl_2 (70% olefin). (The yields are based on azide decomposed; based on nitrene presumably formed they are about 76 and 46%, respectively.) Thus, it appears that dichloromethane has a singlet nitrene stabilizing effect of the kind predicted by Hoffmann.[11] To test this, we ran photolyses in neopentane instead of dichloromethane solutions. Neopentane is very unreactive toward carbonylnitrenes, possessing only primary C–H bonds. The yield of *N*-neopentylpivalamide from the photolysis of pivaloyl azide in neat neopentane is only 0.2%.[3] Photolyses of *cis*-4-methyl-2-pentene in neopentane solution gave cis aziridine yields of 40.2% at 70 mol % olefin concentration, 21.3% at 25% olefin concentration, and only a trace of cis aziridine at 10% olefin concentration. This is in sharp contrast to the 33% yield of 3 obtained in a 4.4% cis olefin solution in dichloromethane (Table II). As expected from the stereoselectivity argument (above), no trans aziridine 4 was formed.

Using *trans*-4-methyl-2-pentene in neopentane solutions gave complex mixtures, and no quantitative method was found for separating the volatile products from a gummy material very similar to that resulting from photolyzing pivaloyl azide in inert solvents.[3] The yield of volatile products decreased with decreasing olefin concentration, while the ratio of 3:4 remained approximately constant. The mixture was much more complex than that formed in dichloromethane solution, and the yield of singlet products was low.

In Hoffmann's model[11] singlet nitrenes are stabilized by the symmetrical approach of solvent unshared electron pairs to the nitrene. This certainly agrees with our results, as well as with those of Breslow[12] (published simultaneously with our communication[11]), who used hexafluorobenzene. More recently, dichloromethane has been found to stabilize the singlet state of ethoxycarbonylnitrene as well.[13,14]

The use of the cis and trans butenes, rather than the 4-methyl-2-pentenes, promised greater reactivity (less hindrance) of the trans olefin and less reactivity of the allylic, but now primary, C–H bonds. Photolyses of *cis*-2-butene (7)–dichloromethane–pivaloyl azide solutions gave, besides

Table IV
Photolyses of Pivaloyl Azide in Dichloromethane Solutions of *cis*-2-Butene

Mol % olefin	% completion	Yields, % Cis oxazoline 9	Cis aziridine 8	Sum 8 + 9
20	69	1.1	48.9	50.0
15	63	1.2	58.0	59.2
10	72	1.0	53.4	54.4
5	60	1.7	57.9	59.6
3.3	51	6.1	10.8	16.9

t-BuNCO, the cis aziridine 8. VPC analysis of the mixture converted part of the 8 into its ring expansion product 9, *cis-tert*-butyl-4,5-dimethyl-2-oxazoline. This rearrangement occurs, upon VPC, with pure 8 as well, and our ir and NMR spectra of the crude reaction mixture showed 9 to be absent. We therefore regard the sum of the yields of 8 and 9 as the minimum yield of 8 originally formed. The stereospecific rearrangement of *N*-acylaziridines to oxazolines of the same configuration is well known,[15] as is the ring opening of *N*-acyl-2-alkylaziridines to allylamides.[16] In our cases, such a ring opening did not occur during our analytical VPC routine, but 8 was converted to 10 under more drastic VPC conditions.

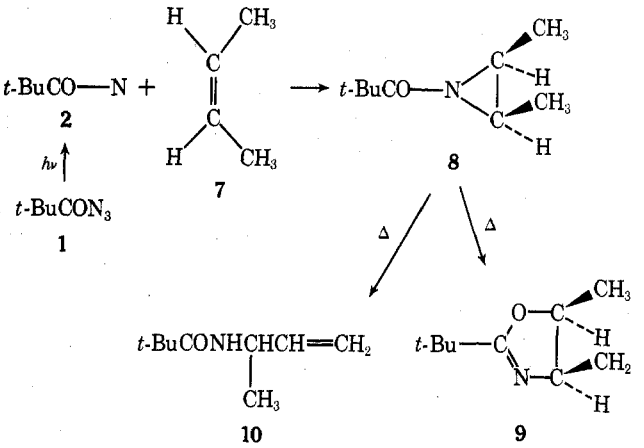


Table IV shows no distinct yield maximum for 8 + 9 in photolyses of 1 in the presence of 5–20% of 7. No trans aziridine 12 or the corresponding oxazoline 13 were found. It seems that the nitrene 2 adds rapidly and almost quantitatively to the olefin, since the yield average obtained (55.8 ± 4.5%) is based on the azide decomposed and represents almost all the nitrene formed. The sudden drop in yields from 5 to 3.3 mol % olefin concentration might not be real but rather the result of some systematic error, such as a solvent impurity. The disproportionate yield of 9 supports this suspicion.

Photolyses using *trans*-2-butene (11) gave rather constant yields of the trans aziridine 12 (and its ring expansion product 13), 31.6 ± 1.4% over an olefin concentration range from 50 to 2 mol % (Table V). Nonstereospecific addition gave 8 in 1.1% yield. Thus, the pivaloylnitrene–dichloromethane adduct or solvate adds stereospecifically to the olefins. The products of nonstereospecific addition are attributed to triplet pivaloylnitrene. Just how large their fraction is, is hard to say. The ratio of aziridine of retained configuration (trans) to that of its cis isomer is much higher than the corresponding ratio 4/(3 + 5) in the experiments using *trans*-4-methyl-2-pentene as the olefin (Table III). Possibly, less triplet is formed in the presence of 2-butene, or less of the triplet nitrene is captured by the *trans*-2-butene, or less of the capture product is converted to recognizable final products.

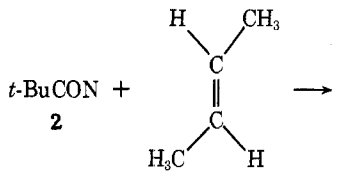
Table V
Photolyses of Pivaloyl Azide in Dichloromethane Solutions of *trans*-2-Butene

Mol % olefin	% completion	Aziridine yields, %		Oxazoline yields, %		Total yields, %	
		Trans	Cis	Trans	Cis	Trans	Cis
50	63	25.0	1.2	5.8	Trace	30.8	1.2
20	56	28.8	0.9	3.2	Trace	32.0	0.9
10	81	25.8	0.9	5.3	0	31.1	0.9
5	88	25.8	1.2	8.0	0	33.8	1.2
2	82	20.8	1.5	9.3	Trace	30.1	1.5

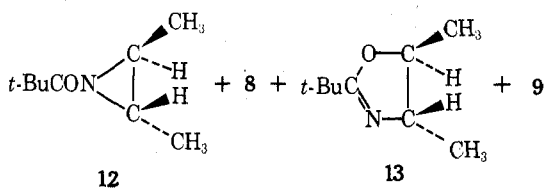
Table VI
Photolyses of Pivaloyl Azide in Cyclopentane Solutions of *cis*-2-Butene

Mol % olefin	% completion	Yields, %		
		Cis oxazoline 9	Cis aziridine 8	Sum 8 + 9
20	67	0.8	54.1	54.9
15	71	1.1	54.6	55.7
15	75	0	58.8	58.8
5	65	1.9	59.6	61.5

To single out a dichloromethane solvent effect, the 2-butene–pivaloyl azide photolyses were also run in a hydrocarbon solvent. Since, in principle, it could be true that neopentane, rather than dichloromethane, is the "special" solvent, we used the structurally rather different cyclopentane. While it reacts more readily with pivaloylnitrene than does neopentane, the olefins could still be expected to compete well with the C–H insertion into the solvent. Photolysis of pivaloyl azide in pure cyclopentane gave a maximum yield of 13% of *N*-cyclopentylpivalamide,[3] less when the cyclopentane concentration was lowered. Photolyses of **1** in cyclopentane solutions of *cis*-2-butene (**7**) gave results very similar to those obtained in dichloromethane, an average 58% yield of **8** + **9**. That indicates a practically quantitative



11



12 **13**

interception of the nitrene, at a rate much faster than that of any competing process (Table VI). Photolyses of **1** in cyclopentane solutions of the trans olefin **11** again produced a strong contrast of results, both in comparison with the cis olefin–cyclopentane runs, and with the trans olefin–dichloromethane runs. As shown in Table VII, photolyses in cyclopentane solutions of **11** gave about the same yields of the cis aziridine as found in dichloromethane solutions. The trans aziridine **12**, however, is formed in much lower yields and its formation could no longer be observed at 5 and 2 mol % concentrations of **11**, concentrations at which 34 and 30% yields were formed in dichloromethane. At 5 and 2 mol % **11** in cyclopentane, the reactions mixtures became intractable for quantitative analysis. The diminished aziridine yields in cyclopentane solutions cannot be explained by a removal of singlet nitrene due to C–H insertion into cyclopentane. *N*-Cyclopentylpivalamide is formed in a maximum yield of 12–13% in pure cyclopentane,[3] which thus is not reactive enough to compete effectively with the olefin. This is confirmed by the data in Table VI and VII, which show no such competitive effect. Our VPC analysis procedure was not suitable for measuring the yield of *N*-cyclopentylpivalamide, but a modest yield of it was isolated and identified spectrally. Interestingly, the yield of nonstereospecific addition products (Table VII) remains reasonably constant between 70 and 10 mol % *trans*-2-butene concentration (av 1.03 ± 0.2), the same value as in dichloromethane solution (av 1.1 ± 0.2).

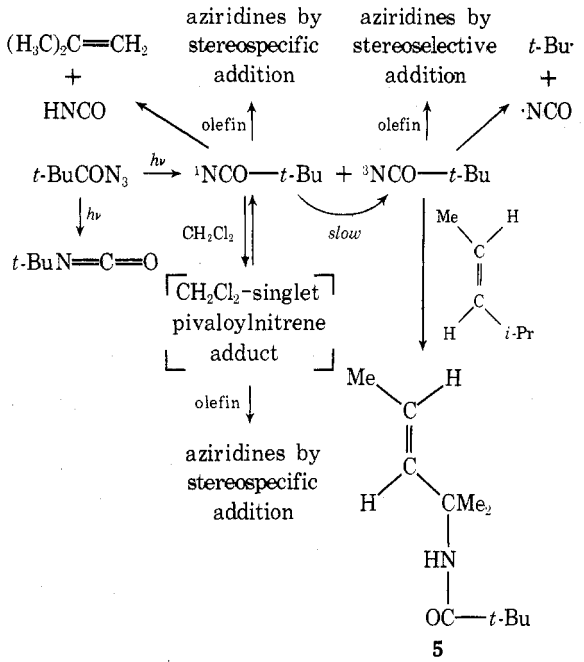
Conclusions

The experimental results agree with Scheme II. Photolysis of pivaloyl azide (**1**) produced pivaloylnitrene (**2**), a part of which is formed directly in the triplet state. This triplet nitrene adds nonstereospecifically to olefins and attacks the tertiary allylic C–H of *trans*-4-methyl-2-pentene to give **5**. Given sufficient steric hindrance, such as in the 4-methyl-2-pentenes, the addition of the triplet nitrene to the C=C double bond is highly stereoselective, producing the cis aziridine from both cis and trans olefins. Thus, the triplet products are not directly apparent in reactions with the cis olefin. In reactions with *trans*-4-methyl-2-pentene the triplet products are the cis aziridine **3** and the formal allylic insertion product **5**, produced in about 18% total yield. In reactions with *trans*-2-butene, only about 1% triplet products are actually detected. This might be due to a loss of triplet nitrene (^{3}NCO-*t*-Bu → HNCO + $Me_2C{=}CH_2$) because of a less reactive substrate, or it could be due to lesser direct formation of triplet nitrene in the photolysis process, as compared to solutions containing the 4-methyl-2-pentene. Intersystem crossing seems to become important only at very low olefin concentrations. The main paths for disappearance of singlet pivaloylnitrene are bimolecular reactions with olefins and dissociation to HNCO and isobutene.[2,3] A powerful "singlet stabilizing" effect is

Table VII
Photolyses of Pivaloyl Azide in Cyclopentane Solutions of *trans*-2-Butene

Mol % olefin	% completion	Aziridine yields, %		Oxazoline yields, %		Total yields, %	
		Trans	Cis	Trans	Cis	Trans	Cis
70	65	10.1	0.9	3.0	Trace	13.1	0.9
50	62	16.1	1.2	4.4	Trace	20.5	1.2
20	57	15.2	0.8	3.2	Trace	18.4	0.8
20	64	15.0	1.4	3.9	Trace	18.9	1.4
15	67	13.2	1.1	3.2		16.4	1.1
10	70	5.8	0.8	3.7		9.5	0.8

Scheme II



exerted by dichloromethane, but not by neopentane or cyclopentane. The effect is most clearly seen in reactions of trans olefins, rather than in those of the more reactive cis olefins, which intercept efficiently even the unstabilized singlet pivaloylnitrene. We assume the existence of a singlet nitrene–dichloromethane solvate or complex, in equilibrium with the "free" nitrene. This complex is much longer lived than the "free" nitrene but is still capable of reacting with C=C double bonds, much in the manner of the "free" nitrene. Our earlier work[7] shows that the complex is also capable of reacting with C–H bonds. The nature of the complex and the requirements for a solvent to form "singlet stabilized" solvates or complexes remain to be investigated.

Experimental Section

Hydrocarbons used were Phillips pure grade (99% minimum purity). The dichloromethane was MCB spectroquality grade. *cis*- and *trans*-4-methyl-2-pentene were distilled before use and stored under nitrogen.

Pivaloyl azide (1) was prepared from *t*-BuCOCl and NaN_3.[2] It starts to decompose above 0°, might explode without warning, and its vapor is toxic.

2-Isopropyl-3-methyl-*N*-*tert*-butylcarbonylaziridines (cis, 3, and trans, 4) were prepared by Hassner's method.[17] The diastereomeric **2-*N*-ethoxycarbonylamino-3-iodo-4-methylpentanes** were obtained by adding 0.1 mol of the olefin at −10° over 30 min to a slurry of 0.1 mol of iodine and 0.13 mol of freshly prepared silver cyanate in 200 ml of ether. After addition and stirring at room temperature for 5 hr, the solutions were filtered, then concentrated to half their volumes. Absolute ethanol (200 ml) was added and the mixtures heated to reflux for 4 hr, then concentrated to 75 ml and poured onto ice. Thorough extraction into ether, drying, and removal of solvent gave oils. The yield from the cis olefin was 68%, from the trans olefin 60%. To obtain the aziridines, 0.07 mol of the appropriate 2-*N*-ethoxycarbonylamino-3-iodo-4-methylpentane in 600 ml of ethanol was heated to reflux with 30 g of KOH for 3 hr. Water (100 ml) was added to the cooled solution and the mixture was extracted exhaustively with ether. The dried ether solution was concentrated to 500 ml, and 0.09 mol of triethylamine and then dropwise 0.07 mol of pivaloyl chloride were added. The concentrated (125 ml) solution was washed with water, dried, and distilled. The cis aziridine **3**, bp 47–48° (0.3 mm), was obtained in 41% yield: ir spectrum C=O at 1680 cm^{-1} (neat); NMR *i*-Pr as two doublets, 6 H, at δ 0.94 and 1.06, split by the methine H, J = 6 Hz, and due to the chirality of the adjacent ring carbon;[18,19] ring CH_3 d, δ 1.30, integrated together with *t*-Bu, s, δ 1.22, 12 H; isopropyl CH m, δ 2.0–2.2, 1 H, ring hydrogens m, δ 2.2–2.7, 2 H; mass spectrum P *m/e* 183 (6%), 98 (86%) (P − *t*-BuCO), 70 (89%), 57 (100%) (*t*-Bu). Anal. Calcd for $C_{11}H_{21}NO$: C, 72.08; H, 11.52; N, 7.64. Found for **3**: C, 71.95; H, 11.72; N, 7.57. Found for **4**: C, 71.99; H, 11.76; N, 7.82.

The trans aziridine **4** was obtained in 23% yield: ir C=O at 1670 cm^{-1} (neat); NMR isopropyl CH_3's δ 0.90 and 1.02, two doublets, 6 H; *t*-Bu, s, δ 1.21, integrated with ring CH_3 at δ 1.28, 12 H; *i*-Pr CH m, δ 2.0–2.2, 1 H; ring H's δ 2.3–2.7, m, 2 H. The mass spectrum is similar to that of **3**, P *m/e* 183 (15%), 70 (100%).

***trans*-2,2-Dimethyl-3-pentenoic acid**[20] was prepared and its trans stereochemistry[21] further confirmed by the strong ir absorptions at 972 cm^{-1} (both in the acid and its ethyl ester). The acid was converted to its amide by standard procedures.[22,23] The amide showed ir absorptions at 3385, 3200, 3020, 2962, 1650, 1622, and 969 cm^{-1}. It was subjected to standard Hofmann rearrangement conditions to give a 30% yield of ***trans* 2-methyl-3-penten-2-amine,** which showed ir absorptions at 3350, 3020, 1675, and 971 cm^{-1}. The amine was immediately acylated by treating a solution of 0.30 g (3 mmol) in 50 ml of anhydrous ether with 3 mmol of triethylamine and 3 mmol of pivaloyl chloride. A 96% yield (0.53 g) of ***trans*-*N*-2′-(2′-methyl-3-pentenyl)-2,2-dimethylpropanamide (5)** was obtained: mp 67.5–68.5°; ir absorptions at 3335, 3030, 1635, and 958 cm^{-1} (KBr); NMR spectrum *t*-Bu at δ 1.17 s, 9 H; 2-methyls δ 1.42 s, 6 H; allylic methyl δ 1.68, d, 3 H; olefinic and NH, m, δ 5.45–5.85, 3 H; mass spectrum P *m/e* 183 (100%), 168 (69%) (P − CH_3), 126 (14%) (P − MeC), 83 (40%) (P − *t*-BuNHCO), 57 (35%) (*t*-Bu).

Anal. Calcd: C, 72.08; H, 11.55; N, 7.64. Found: C, 72.69; H, 11.61; N, 7.08.

Photolyses of Pivaloyl Azide in Dichloromethane Solutions of *cis*- and *trans*-4-Methyl-2-pentene. A silica photolyses tube was charged with 14.6 ml (116 mmol) of the olefin, 1.0 ml (7.72 mmol) of pivaloyl azide, and sufficient dichloromethane to obtain the desired concentrations. Coolant of −10° was pumped through a cooling finger in the center of the tube, which was suspended along the axis of a Rayonet photochemical reactor equipped with RPR 254- or 300-nm lamps. The progress of the photolyses was followed by monitoring the nitrogen evolution. After the photolyses, solvent, excess olefin, and *tert*-butyl isocyanate were removed in vacuo at 0°. The residue was diluted to 5 ml with chloroform, and aliquots were analyzed. VPC on a 6 ft × 0.25 in. phenylsilicone OV-17 column at 110° separated **5** from **3** + **4**. Quantitative results were obtained by planimetry of the trace and calibrating the instrument with pure authentic samples. The aziridine mixture (**3** + **4**) was pure by NMR and elemental analysis. The ratio **3**:**4** was determined by NMR, using the isopropyl CH_3 signals. This method was checked with artificial mixtures of known composition, the agreement being ±3% of the real value. The aziridines **3** and **4** were separated by peak center cutting using VPC on a preparative scale, for comparison with the authentic samples. The yield of *t*-BuNCO was determined by converting it to *N*-*n*-butyl-*N*′-*tert*-butylurea and determining this by VPC under the same conditions as described above. The *t*-BuNCO yield varied between 40 and 42%, based on azide decomposed. The ratio **3**:**4** was monitored in a run (50 mol % trans olefin) by withdrawing samples at 20, 35, 50, and 65% completion. The fraction of **4** in **3** + **4** was 0.705 ± 0.03.

Photolyses of pivaloyl azide in neopentane solutions of *cis*- and *trans*-4-methyl-2-pentene were done like those in dichloromethane, except that, after sweeping with nitrogen, the appropriate quantity of neopentane was condensed in the dry ice cooled reaction vessel. Analyses were done as above, except that in the runs using trans olefin an aliquot of the residue was injected directly onto a 4 ft × 0.25 in. column of 15% Ucon Polar 50HB2000 on 50/60 mesh Anakrom ABS at 112°.

***trans*-2,3-Dimethyl-1-(2′,2′,-dimethylpropanoyl)aziridine (12).** *trans*-2,3-dimethylaziridine[24] was acylated with pivaloyl chloride and triethylamine in ether in 93% yield. The ir spectrum showed bands at 2960 (s), 2923 (s), and 1665 cm^{-1}; NMR, a singlet at δ 1.28 and a doublet at δ 1.25 integrated as 15 H, a multiplet δ 2.1–2.5 as 2 H; mass spectrum P *m/e* 155 (5%), 140 (5%) (P − CH_3), 98 (24%) (P − *t*-Bu), 70 (P − *t*-BuCO), 57 (100%) (*t*-Bu^+).

Anal. Calcd for $C_9H_{17}NO$: C, 69.64; H, 11.04; N, 9.02. Found: C, 69.81; H, 11.31; N, 9.18.

***cis*-2,3-Dimethyl-1-(2′,2′-dimethylpropanoyl)aziridine (8)** was prepared in 96% yield like the trans isomer from the aziridine.[24] The NMR spectrum had 15 H at δ 1.20 (d) and 1.23 (s) and a multiplet of 2 H at δ 2.2–2.6; mass spectrum P *m/e* 155 (3%), 140 (3%), 98 (17%), 57 (100%).

Anal. Calcd for $C_9H_{17}NO$: C, 69.64; H, 11.04; N, 9.02. Found: C, 69.81; H, 11.31; N, 9.18.

Preparation of 2-*tert*-Butyl-4,5-dimethyl-4,5-dihydrooxazoles, Cis (9) and Trans (13). Iodine-catalyzed rearrangement of the cis aziridine 8, using Heine's method,[25] gave a 5:1 mixture of 9 and 13. Thermal rearrangement of 8 and 12 was completely stereospecific with retention of geometry. The ir spectra of both showed a strong band at 1660 cm^{-1}. The NMR spectrum of 9 (cis) has methyl signals at δ 1.21 (s), 1.18 (s), and 1.12 (s), together 15 H. The ring methine protons form multiplets at δ 3.8–4.35 (1 H, C-4) and 4.35–5.0 (1 H, C-5), with splitting between the methine protons. The trans compound 13 shows much cleaner ring methine proton signals, multiplets at δ 3.4–3.85 (C-4) and 3.85–4.3 (C-5) with no discernible splitting between them. Splitting as well as relative chemical shifts agree with previous work.[26] The trans isomer 13 has methyl signals at δ 1.21 (s), 1.17 (s), and 1.27, together 15 H; mass spectrum (9) P *m/e* 155 (89%), 140 (100%) (P − CH_3), 111 (40%) (P − CH_3CHO), 57 (63%) (t-Bu^+). The trans isomer 13 has a very similar mass spectrum, with the base peak at *m/e* 111.

Anal. Calcd for $C_9H_{17}NO$: C, 69.64; H, 11.04; N, 9.02. Found for 9: C, 69.84; H, 11.33; N, 9.09. Found for 13: C, 69.43; H, 11.16; N, 8.99.

***trans*-*N*-1′-(2′-Butenyl)-2,2-dimethylpropanamide** (*trans*-1-pivaloylamino-2-butene, 14) was prepared by acylation (as above) of *trans*-2-buten-1-amine.[27] No 14 was found in our photolysis reaction mixtures: ir (neat) 3330, 2955, 1645, 1531, 968 cm^{-1}; NMR δ 1.20, s, 9 H (t-Bu); 1.70, d, 3 H; 3.80, t, 2 H; 5.4–5.7, m, 3 H; mass spectrum P *m/e* 155 (36), P − H at 154 (85%), 138 (24%), 124 (71%), 57 (100%).

Anal. Calcd for $C_9H_{17}NO$: C, 69.64; H, 11.04; N, 9.02. Found: C, 69.79; H, 11.23; N, 9.04.

***N*-3′-(1-Butenyl)-2,2-dimethylpropanamide** (*N*-pivaloyl-3-amino-1-butene, 15) was prepared by acylation of 3-amino-1-butene.[27] No 15 was found in our photolysis reaction mixtures: ir (KBr) 3300, 2950, 1620, 1516, 1204, 908 cm^{-1}; NMR δ 1.23 (s) and 1.26 (d), together 12 H, a series of multiplets δ 4.0–6.2, 5 H; mass spectrum P *m/e* 155 (21%), 140 (13%), 72 (12%), 58 (100%).

2,2-Dimethyl-1-(2′,2′-dimethylpropanoyl)aziridine (16) was prepared by standard acylation of 2,2-dimethylaziridine.[28] No 16 was found in our photolysis reaction mixtures: ir (neat) 2960 and 1675 cm^{-1}; NMR δ 1.24, s, 9 H; 1.33, s, 6 H; 2.17, s, 2 H.

Anal. Calcd for $C_9H_{17}NO$: C, 69.64; H, 11,04; N, 9.02. Found: C, 69.48; H, 11.33; N, 9.19.

Photolyses of Pivaloyl Azide in Solutions of *cis*- and *trans*-2-Butene. In a nitrogen-flushed photolysis tube, 6.5 g (0.12 mol) of the butene was condensed using dry ice as coolant. Then 1.00 ml (7.72 mmol) of pivaloyl azide and the desired quantity of dichloromethane or cyclopentane were added. Coolant of −15° was circulated through the cooling finger in the center of the tube, which was suspended coaxially in a Rayonet photochemical reactor. The photolyses were conducted and worked up as described above, but a 10 ft × 0.25 in. aluminum column containing 15% cyanosilicone QF-1 on 50/60 mesh Anakrom ABS was used at 112°. The detector was calibrated with authentic samples. The amount of rearrangement of the aziridines 8 and 12 depended on the history of the column.

Acknowledgment. We are greatly indebted to the National Science Foundation for support of this work.

Registry No.—1, 4981-48-0; 2, 18677-63-9; 3, 56930-40-6; 4, 56930-41-7; 5, 56930-42-8; 6, 754-10-9; 7, 590-18-1; 8, 56930-43-9; 9, 56930-44-0; 11, 624-64-6; 12, 56930-45-1; 13, 56930-46-2; 14, 56930-47-3; 15, 56930-48-4; 16, 56930-49-5; 2-*N*-ethoxycarbonylamino-3-iodo-4-methylpentane isomer 1, 56930-50-8; 2-*N*-ethoxycarbonylamino-3-iodo-4-methylpentane isomer 2, 56930-51-9; *trans*-2,2-dimethyl-3-pentenoic acid, 56930-52-0; *trans*-2,2-dimethyl-3-pentenamide, 56930-53-1; *trans*-2-methyl-3-penten-2-amine, 31978-79-7; pivaloyl chloride, 3282-30-2; *cis*-4-methyl-2-pentene, 691-38-3; *trans*-4-methyl-2-pentene, 674-76-0; *trans*-2,3-dimethylaziridine, 930-20-1; *cis*-2,3-dimethylaziridine, 930-19-8; *trans*-2-buten-1-amine, 56930-04-2; 3-amino-1-butene, 34375-90-1; 2,2-dimethylaziridine, 2658-24-4.

References and Notes

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