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Reaction of Ketenimines with an Oxaziridine and Nitrones

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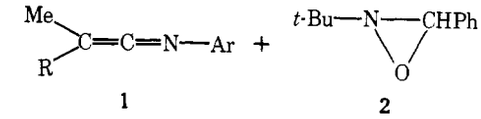
The reaction of the *N*-arylketenimines **1a–d** with the oxaziridine **2** gave the 1:1 adducts, 1,3-diazolidin-4-ones **3**. In the case of the diphenylketenimine **1e**, the oxindole **9** was isolated instead of **3**. No addition reaction was observed in the reaction of *N*-cyclohexylketenimines. Similar results were obtained in the reactions of **1a,d** with the nitrone **12**, but two oxindoles **9** and **13** were formed in the reaction of **1e**. A substituent effect and the difference between **2** and **12** were observed.

Synthetic application of ketenimines has been less developed than that of other heterocumulenes in the field of heterocyclic chemistry.[1]

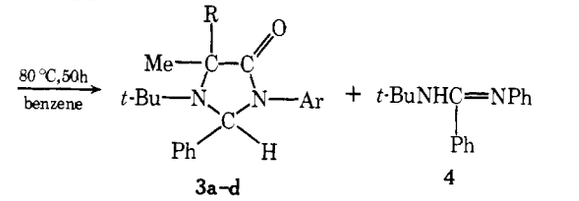
In this paper, the reactions of ketenimines with an oxaziridine and nitrones are described. We reported previously that an isocyanate, a carbodiimide, and an isothiocyanate gave 1:1 adducts in the reactions with 2-*tert*-butyl-3-phenyloxaziridine or *C*-phenyl-*N*-*tert*-butylnitrone, the isomer of the oxaziridine.[2,3] In the reaction with these isomers, on the contrary, a ketene behaved in a different manner from those of the other heterocumulenes.[2,4]

While a ketenimine has one terminal carbon atom like a ketene, the difference between their chemical behavior has been shown in many instances.[1] Most additions to a ketenimine occur on the C=C bond,[1] and Barker and his co-worker reported that *C,N*-diphenylnitrone added to diphenylketene-*N*-*p*-bromophenylimine across the C=C bond.[5] However, our present study revealed that the addition occurs on the C=N bond of ketenimines.



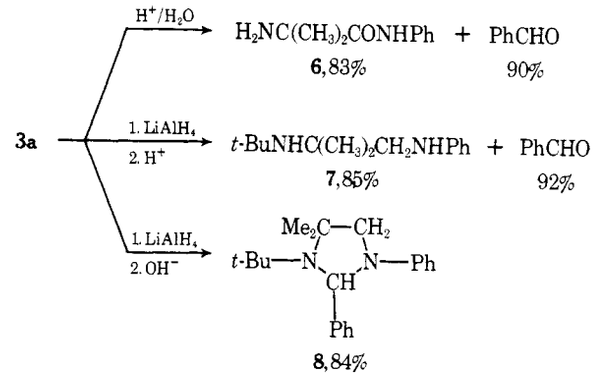
1 **2**

a, R = Me; Ar = Ph
b, R = Me; Ar = *p*-MeC_6H_4
c, R = Me; Ar = *p*-$MeOC_6H_4$
d, R = Ar = Ph



3a–d **4**

+ *t*-BuN=CHPh
5



6, 83% **7**, 85% **8**, 84%

Results and Discussion

Reactions with Oxaziridine. The reaction of dimethylketene-*N*-phenylimine (**1a**) with 2-*tert*-butyl-3-phenyloxaziridine (**2**) gave the 1:1 adduct **3a**, a 1,3-diazolidine derivative, in 40% yield. The dimethylketenimines **1b** and **1c** also gave the 1:1 adducts **3b** and **3c**. In the reaction of phenylmethylketene-*N*-phenylimine (**1d**), however, N^1-*tert*-butyl-N^2-phenylbenzamidine (**4**) and *N*-*tert*-butylbenzaldimine (**5**) were isolated as major products, and the yield of the 1:1 adduct **3d** decreased to 5%.

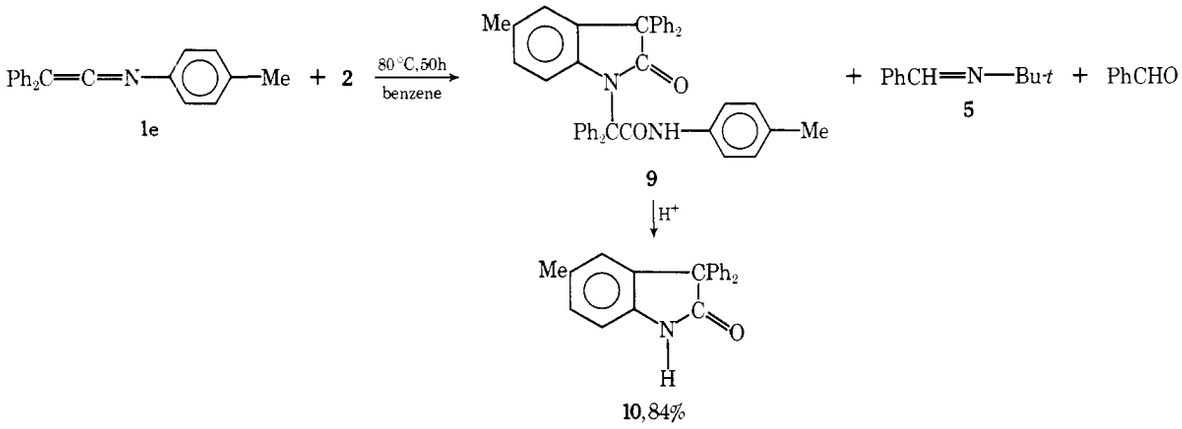
The adduct **3a** exhibited a strong infrared absorption at 1685 cm^{-1}, which was assigned to the carbonyl group. Furthermore, the following chemical evidences provided conclusive proof for the structure of **3a**. Acidic hydrolysis of **3a** gave the anilide **6** and benzaldehyde.[6] After the reaction with lithium aluminum hydride, the addition of hydrochloric acid afforded the acyclic diamine **7** and benzaldehyde, but the alkaline post-treatment gave the 1,3-diazolidine **8**.

On the other hand, diphenylketene-*N*-*p*-tolylimine (**1e**) gave no 1:1 adduct, but the oxindole **9**,[7] benzaldimine **5**, and benzaldehyde were obtained. Benzaldehyde was presumably formed from **5** by hydrolysis. The oxindole **9** was identical with an authentic sample.[8] Hydrolysis of **9** with perchloric acid gave the oxindole **10**.[9]

Table I. Reaction of Ketenimines with an Oxaziridine and Nitrones

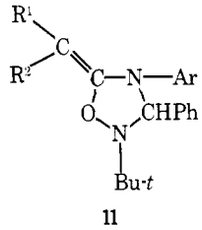
	Ketenimine $R^1R^2C{=}C{=}N{-}R^3$				Product (yield, %)						
	R^1	R^2	R^3	Reactant	3	4	5	9	13	16	PhCHO
1a	Me	Me	Ph	**2**	40						
1b	Me	Me	*p*-MeC_6H_4	**2**	42						
1c	Me	Me	*p*-$MeOC_6H_4$	**2**	60						
1d	Ph	Me	Ph	**2**	5	53	30				
1e	Ph	Ph	*p*-MeC_6H_4	**2**			25	14			45
1g	Me	Me	c-C_6H_{11}	**2**							*a*
1h	Ph	Ph	c-C_6H_{11}	**2**							*a*
1a	Me	Me	Ph	**12**	60						
1d	Ph	Me	Ph	**12**	3	42	40				
1e	Ph	Ph	*p*-MeC_6H_4	**12**			93	10	45		
1f	Ph	Ph	*p*-BrC_6H_4	**15**	33						
1a	Me	Me	Ph	**15**			13[b]			71	

[a] The oxaziridine **2** rearranged to the nitrone **12** quantitatively. [b] PhN=CHPh.



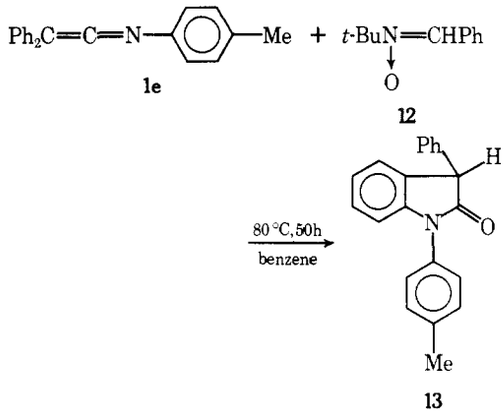
Though *N*-arylketenimines reacted with the oxaziridine **2**, no addition reaction was observed, unexpectedly, for *N*-cyclohexylketenimines. The oxaziridine **2** rearranged to the isomeric nitrone and the ketenimines were recovered quantitatively in the reactions of dimethyl- and diphenylketene-*N*-cyclohexylimines (**1g,h**). The results are summarized in Table I.

The reaction of the oxaziridine **2** can be explained by cycloaddition across the C=N bond of the cumulative system of the ketenimine **1** to form the labile cycloadduct **11**. The final adduct **3** is formed by rearrangement of the intermediate **11**, which gives the amidine **4** by decomposition[10] or the oxindole **9** by elimination of the benzaldimine **5**.

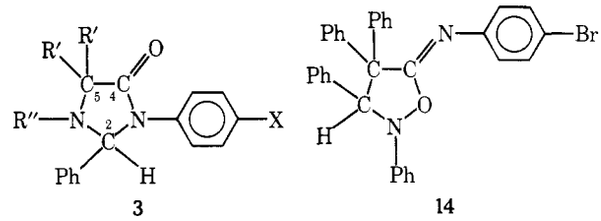


11

Reactions with Nitrones. In the reaction of the ketenimine **1a** or **1d** with *C*-phenyl-*N*-*tert*-butylnitrone (**12**), products were the same as in the case of the isomeric oxaziridine **2** (see Table I), but the reaction of **1e** with **12** gave 1-*p*-tolyl-3-phenyloxindole (**13**) in 45% yield in addition to the products obtained in the reaction of **1e** with **2**. The reaction mode of the nitrone **12** was somewhat different from that of the oxaziridine **2**. Barker had reported that the 1,2-oxazolidine **14** was formed by the addition of *C,N*-diphenylnitrone (**15**) across the C=C bond of diphenylketene-*N*-*p*-bromophenylimine (**1f**).[5] Nevertheless, the formation of 1,3-diazolidines **3** can be accounted for by the addition of **12** to the ketenimine



across the C=N bond followed by rearrangement. Hence, the 1,2-oxazolidine structure **14** appears doubtful. The reaction



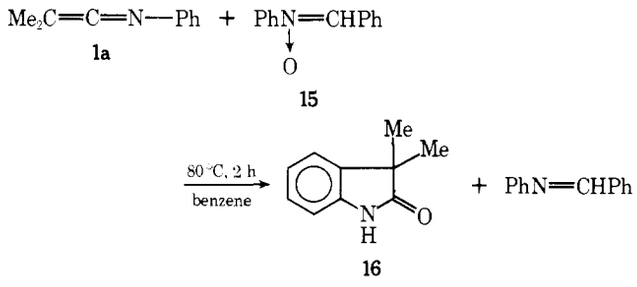
of the ketenimine **1f** and the nitrone **15** was carried out under the reported conditions,[5] and the 1:1 adduct **3f** was obtained in 33% yield. Melting point and infrared and mass spectra of **3f** agreed with the reported data. ^{13}C NMR study on the compound **3f** suggested that a 1,3-diazolidin-4-one structure is more reasonable than a 1,2-oxazolidine structure (Table II).

Table II. ^{13}C Chemical Shifts with Respect to Me_4Si ($CDCl_3$ as Solvent)

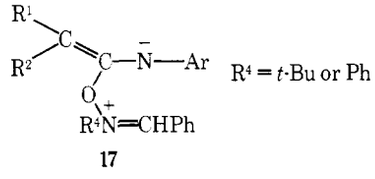
	Substituent			Chemical shift, ppm		
	R′	R″	X	C_2	C_4	C_5
3a	Me	*t*-Bu	H	77.8 (d)	174.8 (s)	64.0 (s)
3f	Ph	Ph	Br	78.2 (d)	170.8 (s)	74.8 (s)

The signal at 170.8 ppm of **3f** can be better assigned to a carbonyl carbon than to an imino or olefinic carbon.[11] The difference between the chemical shifts (C-4) of **3a** and **3f** is due to the mesomeric effect of Br. The C-2 carbons of **3a** and **3f**, whose signals can be determined easily by off-resonance technique, showed almost the same chemical shift. The downfield shift of C-2 carbons of **3** can be explained by the N–C–N linkage rather than by the C–C–N linkage.

In the reaction with *C,N*-diphenylnitrone (**15**), the ketenimine **1a** gave 3,3-dimethyloxindole (**16**) instead of a 1:1 adduct **3**. The similar reaction of **15** with bis(trifluoromethyl) ketene-*N*-phenylimine has been reported by Del'tsova and his co-workers.[12]



The difference between the oxaziridine **2** and the nitrone **12** should be taken into account for the reaction with the ketenimines. The reaction proceeds via the acyclic intermediate **17**, which gives rise to **3**, **9**, and **16** through **11** according



to their substituents. A similar intermediate to **17** has already been proposed in the reaction of a nitrone with a ketene.[13] When R^1 is a phenyl group, the oxindole **13** is formed by nucleophilic attack of the anionic nitrogen atom to the phenyl ring followed by elimination of an aldimine.

In the reaction with nitrones, the formation of the 1:1 adducts and the oxindoles is dependent on the substituents of the reactants. In this respect, chemical behavior of ketenimines resembles that of ketenes.[4] However, ketenimines showed a completely different reaction manner from that of ketenes in the reaction with oxaziridine **2**.

Experimental Section

All melting points were determined on a Yanagimoto micromelting point apparatus and were uncorrected. IR, NMR, and mass spectra were obtained on a JASCO IR-E spectrometer, JEOL LNM-3H-60 and JNM-PS-100 spectrometers, and a Hitachi RMU-6E spectrometer, respectively. The resulting benzaldehyde and benzaldimines were identified and determined by GLC using a 10% Apiezon L on Diasolid L (60–80 mesh, 4 mm × 2 m) column.

Unless noted otherwise, IR and NMR spectra were taken in Nujol mulls and in deuteriochloroform solutions, respectively. The mass spectra were obtained at 70 eV.

All reactions were carried out under nitrogen atmosphere in a 50-ml four-necked flask equipped with a reflux condenser, a dropping funnel, a thermometer, and a magnetic stirrer.

The reactions were ceased after heating to reflux for 50 h, when the characteristic absorption of the ketenimine disappeared.

Materials. Ketenimines **1** were prepared from corresponding amides according to the reported procedures.[14,15] 2-*tert*-Butyl-3-phenyloxaziridine (**2**) was prepared by oxidation of *N*-*tert*-butylbenzaldimine with perbenzoic acid.[16] *N*-*tert*-Butyl-*C*-phenylnitrone (**12**) and *C,N*-diphenylnitrone (**15**) were prepared from the oxaziridine **2**, and benzaldehyde and *N*-phenylhydroxylamine, respectively.[17,18]

Reaction of Dimethylketene-*N*-phenylimine (1a) with the Oxaziridine 2. A mixture of the ketenimine **1a** (2.9 g, 20 mmol) and the oxaziridine **2** (3.5 g, 20 mmol) in benzene (25 ml) was allowed to react at 80 °C for 50 h. The solvent was evaporated in vacuo and the residue was chromatographed (Al_2O_3, benzene–hexane) to give 2.6 g (40%) of 1-*tert*-butyl-2,3-diphenyl-5,5-dimethyl-1,3-diazolidin-4-one (**3a**). Recrystallization of **3a** from hexane yielded colorless needles: mp 93–94 °C; IR 1685 cm^{-1} (C=O); NMR δ 1.13 (s, 9, *t*-Bu), 1.58 (s, 3, Me), 1.75 (s, 3, Me), 5.79 (s, 1, CH), 6.9–7.2 (m, 10, aromatic protons); mass spectrum *m/e* 322 (M^+, calcd 322), 307 (M^+ – Me), 251 (307 – $Me_2C{=}CH_2$), 245 (M^+ – Ph), 189 (245 – $Me_2C{=}CH_2$).

Anal. Calcd for $C_{21}H_{26}N_2O$: C, 78.22; H, 8.13; N, 8.69. Found: C, 78.14; H, 8.23; N, 8.98.

Reaction of Dimethylketene-*N*-*p*-tolylimine (1b) and the Oxaziridine 2. From 3.2 g (20 mmol) of the ketenimine **1b** and 3.5 g (20 mmol) of the oxaziridine **2**, 2.9 g (42%) of 1-*tert*-butyl-2-phenyl-3-*p*-tolyl-5,5-dimethyl-1,3-diazolidin-4-one (**3b**) was obtained. The product **3b** was purified by pot distillation (100–120 °C, 1 mm) to afford colorless, viscous liquid: IR (neat) 1706 cm^{-1} (C=O); NMR δ 1.12 (s, 9, *t*-Bu), 1.58 (s, 3, Me), 1.76 (s, 3, Me), 2.53 (s, 3, Me), 5.74 (s, 1, CH), 7.0–7.3 (m, 9, aromatic protons); mass spectrum *m/e* 336 (M^+, calcd 336).

Anal. Calcd for $C_{22}H_{28}N_2O$: C, 78.53; H, 8.39; N, 8.33. Found: C, 78.27; H, 8.31; N, 8.69.

Reaction of Dimethylketene-*N*-*p*-anisylimine (1c) and the Oxaziridine 2. From 3.5 g (20 mmol) of the ketenimine **1c** and 3.5 g (20 mmol) of the oxaziridine **2**, 4.2 g (60%) of 1-*tert*-butyl-2-phenyl-3-*p*-anisyl-5,5-dimethyl-1,3-diazolidin-4-one (**3c**) was isolated and purified by pot distillation (90–120 °C, 1 mm) to give colorless solid (no attempts at recrystallization of the product were successful): mp 30–31.5 °C; IR (neat) 1698 cm^{-1} (C=O); NMR δ 1.15 (s, 9, *t*-Bu), 1.55 (s, 3, Me), 1.70 (s, 3, Me), 3.60 (s, 3, MeO), 5.68 (s, 1, CH), 6.4–6.9 (m, 4, aromatic protons), 7.0–7.2 (m, 5, aromatic protons); mass spectrum *m/e* 352 (M^+, calcd 352).

Anal. Calcd for $C_{22}H_{28}N_2O_2$: C, 74.96; H, 8.01; N, 7.95. Found: C, 74.91; H, 7.95; N, 7.87.

Reaction of Phenylmethylketene-*N*-phenylimine (1d) and the Oxaziridine 2. The reaction of the ketenimine **1d** (3.1 g, 15 mmol) and the oxaziridine **2** (2.7 g, 15 mmol) gave 0.29 g (5%) of 1-*tert*-butyl-2,3,5-triphenyl-5-methyl-1,3-diazolidin-4-one (**3d**), 2.0 g (53%) of N^1-*tert*-butyl-N^2-phenylbenzamidine (**4**), and 0.73 g (30%) of *N*-*tert*-butylbenzaldimine (**5**). Recrystallization of the amidine **4** from benzene–hexane yielded colorless needles: mp 131–133 °C; IR 3360 (NH), 1610 cm^{-1} (C=N); NMR δ 1.53 (s, 9, *t*-Bu), 4.3–4.5 (broad, 1, NH), 6.5–7.2 (m, 10, aromatic protons); mass spectrum *m/e* 252 (M^+, calcd 252), 196 (M^+ – $Me_2C{=}CH_2$), 180 $(Ph{=}CPh)^+$.

Anal. Calcd for $C_{17}H_{20}N_2$: C, 80.91; H, 7.99; N, 11.10. Found: C, 81.33; H, 7.77; N, 11.15.

The diazolidine **3d** was recrystallized from benzene–hexane to afford colorless needles: mp 154–156 °C; IR 1680 cm^{-1} (C=O); NMR δ 0.91 (s, 9, *t*-Bu), 2.25 (s, 3, Me), 5.77 (s, 1, CH), 6.9–7.2 (m, 15, aromatic protons); mass spectrum *m/e* 384 (M^+, calcd 384), 251 $(t\text{-BuNCPh}{=}NPh)^+$.

Anal. Calcd for $C_{26}H_{28}N_2O$: C, 81.21; H, 7.34; N, 7.29. Found: C, 81.40; H, 7.27; N, 7.56.

Hydrolysis of the Diazolidine 3a. To a solution of 0.5 g (1.4 mmol) of **3a** in 20 ml of ethanol, 3 ml of 2 N HCl was added. The mixture was heated to reflux for 5 h, and then extracted (ether) to give 0.1 g (90%) of benzaldehyde. The inorganic layer was neutralized (NaOH) and extracted (ether). The ethereal extract was concentrated in vacuo to give 0.25 g (83%) of 2-amino-2-methylpropananilide (**6**), which was recrystallized (benzene–hexane) to afford colorless needles: mp 58.5–60.0 °C; IR 3280 (NH), 1670 cm^{-1} (C=O); NMR δ 1.43 (s, 6, 2 Me), 1.61 (s, 2, NH_2), 6.9–7.6 (m, 5, aromatic protons), 9.8–10.0 (broad, 1, NH); mass spectrum *m/e* 178 (M^+, calcd 178).

Anal. Calcd for $C_{10}H_{14}N_2O$: C, 67.38; H, 7.92; N, 15.72. Found: C, 67.34; H, 8.00; N, 15.54.

Reduction of 3a with $LiAlH_4$. A. To a suspension of 100 mg of $LiAlH_4$ in 30 ml of ether, 0.50 g (1.4 mmol) of **3a** in 10 ml of ether was added dropwise with cooling. The mixture was stirred for 1 h at room

temperature and then heated to reflux for 2 h. The mixture was treated with 1 N HCl and was extracted (ether) to give 0.12 g (92%) of benzaldehyde. The inorganic layer was neutralized (NaOH) and extracted (ether). Evaporation of ether yielded 0.31 g (85%) of *N*-(2-*tert*-butylamino-2-methylpropyl)aniline (**7**), which was purified by sublimation to afford colorless needles: mp 54–55 °C; IR 3350 cm^{-1} (NH); NMR δ 0.7–0.9 (broad, 1, NH), 1.17 (s, 9, *t*-Bu), 1.25 (s, 6, 2 Me), 2.83 (d, 2, J = 4 Hz, CH_2), 4.5–4.7 (broad, 1, NH) 6.5–7.3 (m, 5, aromatic protons); mass spectrum m/e 220 (M^+, calcd 220).

Anal. Calcd for $C_{14}H_{24}N_2$: C, 76.31; H, 10.98; N, 12.71. Found: C, 76.59; H, 11.29; N, 12.62.

B. After the reduction under the same conditions, the mixture was treated with 2 N NaOH and was extracted (ether) to give 0.41 g (84%) of 1,2-diphenyl-3-*tert*-butyl-4,4-dimethyl-1,3-diazolidine (**8**). The product **8** was purified by pot distillation (100 °C, 1 mm) to give colorless, viscous liquid: IR (neat) no characteristic absorption; NMR δ 1.13 (s, 9, *t*-Bu), 1.15 (s, 3, Me), 1.27 (s, 3, Me), 3.15 (d, 1, J = 9.0 Hz, CHH), 3.45 (d, 1, J = 9.0 Hz, CHH), 5.80 (s, 1, CHPh), 6.5–7.5 (m, 10, aromatic protons); mass spectrum m/e 308 (M^+, calcd 308).

Anal. Calcd for $C_{21}H_{28}N_2$: C, 81.77; H, 9.15; N, 9.08. Found: C, 81.71; H, 9.39; N, 9.16.

Reaction of Diphenylketene-*N*-*p*-tolylimine (1e) and the Oxaziridine 2. The same treatment of 4.2 g (15 mmol) of the ketenimine **1e** and 2.7 g (15 mmol) of the oxaziridine **2** afforded 0.95 g (45%) of benzaldehyde, 0.45 g (25%) of **5**, and 0.62 g (14%) of 1-(*p*-tolylcarbamoyldiphenylmethyl)-3,3-diphenyl-5-methyloxindole (**9**). The crystallization of the oxindole **9** from benzene–hexane gave colorless granules, mp 245–246 °C (lit.[8] 249–251 °C), which showed no depression by mixing with an authentic sample. The spectral data agreed well with those of the authentic sample.

Hydrolysis of the Oxindole 9. The oxindole **9** (0.45 g) was refluxed in 20 ml of ethanol containing 2 ml of 40% $HClO_4$ for 25 h. Removal of the solvent yielded 5-methyl-3,3-diphenyloxindole (**10**, 3.9 g, 84%).[9] Recrystallization of **10** from ethanol gave colorless needles, whose melting point and spectral data agreed with those of an authentic sample.[8]

Reactions of the Ketenimines 1g,h with the Oxaziridine 2. After the same treatment of 2.5 g (17 mmol) of dimethylketene-*N*-cyclohexylimine **1g** and 3.0 g (17 mmol) of the oxaziridine **2**, no change in the IR spectrum of the reaction mixture was observed. The additional heating to reflux for 22 h did not affect the reaction. The reaction mixture was chromatographed (Al_2O_3, benzene–hexane) to give 2.76 g (92%) of *N*-*tert*-butyl-*C*-phenylnitrone (**12**) and 2.45 g (86%) of *N*-cyclohexyl-2-methylpropionamide. The amide was recrystallized (benzene–hexane) to give colorless needles, mp 121–122 °C, which showed no depression by mixing with an authentic sample prepared from isobutanoyl chloride and cyclohexylamine.

The same result was obtained from the reaction of diphenylketene-*N*-cyclohexylimine (**1h**) with the oxaziridine **2**. From 4.1 g (15 mmol) of **1h** and 2.6 g (15 mmol) of **2**, 2.2 g (87%) of the nitrone **12** and 3.4 g (88%) of *N*-cyclohexyldiphenylacetamide were obtained.

Reaction of the Ketenimine 1a with *N*-*tert*-Butyl-*C*-phenylnitrone (12). The reaction of 1.45 g (10 mmol) of **1a** with 1.77 g (10 mmol) of **12** gave 1.93 g (60%) of the diazolidine **3a**.

Reaction of the Ketenimine 1d with the Nitrone 12. The reaction of 3.1 g (15 mmol) of **1d** with 2.7 g (15 mmol) of **12** gave 0.17 g (3%) of the diazolidine **3d**, 1.58 g (42%) of **4**, and 1.1 g (40%) of **5**.

Reaction of the Ketenimine 1e and the Nitrone 12. From the reaction mixture of 2.83 g (10 mmol) of the ketenimine **1e** and 1.77 g (10 mmol) of the nitrone **12**, 1.49 g (93%) of **5** was obtained by distillation (42–45 °C, 5 mm). The residue was chromatographed (Al_2O_3, benzene) to give 0.30 g (10%) of the oxindole **9** and 1.34 g (45%) of 1-*p*-tolyl-3-phenyloxindole (**13**). The oxindole **13** was recrystallized (benzene–hexane) to afford colorless needles: mp 168–170 °C; IR 1725 cm^{-1} (C=O); NMR δ 2.39 (s, 3, Me), 4.72 (s, 1, CH), 6.7–7.2 (m, 13, aromatic protons); mass spectrum m/e 299 (M^+, calcd 299), 270 (M^+ – CHO), 194 ($PhC{=}NC_6H_4Me)^+$.

Anal. Calcd for $C_{21}H_{17}NO$: C, 84.25; H, 5.72; N, 4.68. Found: C, 84.41; H, 5.74; N, 4.68.

Reaction of Diphenylketene-*N*-*p*-bromophenylimine (1f) and *C,N*-Diphenylnitrone (15). A mixture of 1.74 g (5 mmol) of the ketenimine **1f** and 0.98 g (5 mmol) of the nitrone **15** in ether was heated to reflux for 20 h. Collection of the precipitate afforded 0.89 g (33%) of 1,2,5,5-tetraphenyl-3-*p*-bromophenyl-1,3-diazolidin-4-one (**3f**), which was recrystallized from ethanol to give colorless needles: mp 214–216 °C; IR 1685 cm^{-1} (C=O); NMR δ 6.5–7.5 (m, aromatic protons and CH); mass spectrum m/e 546 and 544 (M^+), 469 and 467 (M^+ – Ph), 347 (M^+ – p-$BrC_6H_4N{=}C{=}O$), 257 ($Ph_2C{=}NPh)^+$, 180 ($PhC{=}NPh)^+$.

Anal. Calcd for $C_{33}H_{25}N_2OBr$: C, 72.66; H, 4.62; N, 5.14. Found: C, 72.47; H, 4.47; N, 5.18.

Acidic hydrolysis of **3f** with $HClO_4$ or HBr in refluxing ethanol was not successful and the diazolidine **3f** was recovered.

Reaction of the Ketenimine 1a and the Nitrone 15. To a solution of 2.9 g (20 mmol) of the ketenimine **1a** in benzene, 3.9 g (20 mmol) of the nitrone **15** (in benzene) was added dropwise at 80 °C, and the mixture was kept refluxing for 2 h. From the reaction mixture, 0.5 g (13%) of *N*-phenylbenzaldimine was distilled away (100 °C, 2 mm). The residue was chromatographed (Al_2O_3, benzene–ethanol) to give 2.1 g (71%) of 3,3-dimethyloxindole **16**, which was recrystallized (benzene–hexane) to give colorless plates: mp 151–152 °C; IR 3120 (NH), 1705 (C=O), and 1660 cm^{-1}; NMR δ 1.42 (s, 6, 2 Me), 6.8–7.2 (m, 4, aromatic protons), 9.7–9.9 (broad, 1, NH); mass spectrum m/e 161 (M^+, calcd 161), 146 (M^+ – Me), 132 (M^+ – CHO), 128 (146 – H_2O).

Anal. Calcd for $C_{10}H_{11}NO$: C, 74.51; H, 6.88; N, 8.69. Found: C, 74.22; H, 6.63; N, 8.75.

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Registry No.—**1a**, 14016-34-3; **1b**, 18779-86-7; **1c**, 14016-32-1; **1d**, 32907-79-2; **1e**, 5110-45-2; **1f**, 29376-76-9; **1g**, 14251-68-4; **1h**, 24932-57-8; **2**, 7731-34-2; **3a**, 60687-68-5; **3b**, 60687-69-6; **3c**, 60687-70-9; **3d**, 60687-71-0; **3f**, 60687-72-1; **4**, 50484-26-9; **6**, 20049-03-0; **7**, 60687-73-2; **8**, 60687-74-3; **9**, 6834-59-9; **12**, 3376-24-7; **13**, 60687-75-4; **15**, 1137-96-8; **16**, 19155-24-9.

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