50561-77-8; 3(5)-phenyl-5(3)-methoxydiphenylmethyl-1,2,4-triazole, 50561-78-9; 4(5)-phenyl-5(4)-diphenylpiperidinomethyl-1,2,3-triazole, 50561-79-0; 4(5)-phenyl-5(4)-methoxydiphenylmethyl-1,2,3-triazole, 40759-82-8; pentaphenylpyridine, 40249-26-1; 2-*p*-chlorophenyl-3-phenylquinoline-4-carboxylic acid, 50561-82-5; methyl 3,5-diphenylpyrazole-4-carboxylate, 50561-83-6; 3,5-diphenyl-4-chlorodiphenylmethylpyrazole hydrochloride, 50561-84-7; 3,5-diphenyl-4-methoxydiphenylmethylpyrazole, 50561-85-8; 3,5-diphenyl-4-aminodiphenylmethylpyrazole, 50561-86-9; methyl 3,4-diphenylpyrazole-5-carboxylate, 50561-87-0; 3,4-diphenyl-5-chlorodiphenylmethylpyrazole hydrochloride, 50561-88-1; 3-chlorodiphenylmethyl-1*H*-phenanthro[9,10-*c*]pyrazole, 50561-89-2.

References and Notes

(1) Preliminary results were reported in a communication: E. M. Burgess and J. P. Sanchez, *J. Org. Chem.*, **38**, 176 (1973).
(2) A. Hassner, R. J. Isbister, R. B. Greenwald, J. T. Klug, and E. C. Taylor, *Tetrahedron*, **25**, 1637 (1969).
(3) W. Rohr and H. A. Staab, *Angew. Chem.*, **77**, 1077 (1965); *Angew. Chem., Int. Ed. Engl.*, **4**, 1073 (1965); W. Rohr, R. Swoboda, and H. A. Staab, *Chem. Ber.*, **701**, 349 (1968); R. Gompper and R. Weiss, *Angew. Chem.*, **80**, 277 (1968).
(4) J. H. M. Hill, *J. Org. Chem.*, **32**, 3214 (1967).
(5) J. H. M. Hill and M. A. Battiste, *Tetrahedron Lett.*, 5537, 5541 (1968); A. S. Kende, P. T. Izzo, and P. T. McGregor, *J. Amer. Chem. Soc.*, **88**, 3359 (1966); A. J. Castro, G. Tertzakian, B. T. Nakata, and D. A. Brose, *Tetrahedron*, **23**, 4499 (1967); K. Hafner and K. Pfeiffer, *Tetrahedron Lett.*, 4311 (1968).
(6) A. A. N. Nesmeyanov and M. I. Rybinshaya, *Akad. Nauk SSSR Dokl. Chem.*, **158**, 408 (1964).
(7) F. P. Woerner and H. Reimlinger, *Chem. Ber.*, 103 (1908).
(8) I. Benghiat and E. I. Becker, *J. Org. Chem.*, **23**, 885 (1958).
(9) H. Gilman and R. D. Gorsich, *J. Amer. Chem. Soc.*, **77**, 6380 (1955).
(10) G. Cipens and V. Y. Grinshtein, *Khim. Geterotsikl. Soedin.*, **1**, 624 (1965).
(11) This intermediate was readily available from 3-phenyl-1,2,4-triazole [E. Hoggarth, *J. Chem. Soc.*, 1160, 1163 (1949)] *via* treatment of the 1-benzyl derivative with phenyllithium in THF–ether. The position of alkylation is assumed to follow previous examples: G. Pellizzari and A. Soldi, *Gazz. Chim. Ital.*, **35**, 373 (1905).
(12) H. Behringer and M. Matner, *Tetrahedron Lett.*, 1663 (1966).
(13) As partial structure proof the pyrazines could be hydrolyzed to the precursor carbinols by the action of HCl in aqueous ethanol.
(14) Identified by ir spectral comparison and mixture melting point (where applicable) with an authentic sample.
(15) S. Wawzonek and E. M. Smolin, "Organic Syntheses," Collect. Vol. IV, Wiley, New York, N. Y., 1963, p 387.
(16) W. Pftizinger, *J. Prakt. Chem.*, **56**, 304 (1897).
(17) We wish to thank Dr. Merle Battiste for an authentic sample of this pyridine.
(18) D. W. McNeil, M. E. Kent, P. E. D'Angelo, and E. Hedaya, *J. Amer. Chem. Soc.*, **93**, 3817 (1971).
(19) B. M. Trost and R. M. Cory, *J. Amer. Chem. Soc.*, **93**, 5573 (1971).
(20) The formation of such a "homotropylium" cation from cyclooctatetraene in H_2SO_4 has been realized: J. L. Von Rosenberg, Jr., J. E. Mahler, and R. Pettit, *J. Amer. Chem. Soc.*, **84**, 2842 (1962).
(21) G. H. Hitchings, P. B. Russell, and N. Whittaker, *J. Chem. Soc.*, 1019 (1956).
(22) Prepared *via* decarboxylation of the 4-carboxylic acid derived from isatin and 4-chloro-α-phenylacetophenone in a Pfitzinger synthesis.
(23) R. Huisgen, R. G. Grashey, M. Seidel, G. Wallbillich, H. Knupfer, and R. Schmidt, *Justus Liebigs Ann. Chem.*, **653**, 105 (1962).
(24) Parallel arguments have been presented in the thermal conversion of 2-phenylazirine to phenylacetonitrile: J. H. Boyer, W. E. Kruegar, and G. J. Mikol, *J. Amer. Chem. Soc.*, **89**, 5504 (1967); K. Isomura, S. Kobayashi, and H. Taniguchi, *Tetrahedron Lett.*, **No. 31**, 3499 (1968).
(25) The observed photochemical conversion of azirines to nitrile ylides is an interesting contrast to this thermal behavior: A. Padwa, J. Smolanoff, and S. I. Wetmore, *J. Org. Chem.*, **38**, 1333 (1973), and references cited therein.
(26) The conrotation for opening of **40** required by orbital symmetry considerations can avoid the strain of a developing trans bond by inversion at nitrogen: R. B. Woodward and R. Hoffman, "The Conservation of Orbital Symmetry," Verlag Chemie, Weinheim Bergstr., Germany, 1970, p 51.
(27) B. M. Adger, M. Keating, C. W. Rees, and R. C. Storr, *Chem. Commun.*, 19 (1973).
(28) Smolinsky and Chandross obtained **43** from the rearrangement of triphenylcyclopropenyl azide and report its photodecomposition to only diphenylacetylene and benzonitrile. A compound of constitution $C_{42}H_{30}N_2$ with spectral properties similar to those of **27a** was isolated by Smolinsky from this azide rearrangement reaction: E. A. Chandross and G. Smolinsky, *Tetrahedron Lett.*, 19 (1960). More recently Closs and Harrison reported that the photolysis of trimethyl-*v*-triazine gives 2-butyne and acetonitrile: G. L. Closs and A. M. Harrison, *J. Org. Chem.*, **37**, 1051 (1972).
(29) J. van Alphen, *Recl. Trav. Chim. Pays-Bas*, **62**, 485 (1943).
(30) R. Huttel, J. Riedl, H. Martin, and K. F. Franke, *Ber.*, **93**, 1425 (1955).
(31) J. van Alphen, *Recl. Trav. Chim. Pays-Bas*, **62**, 491 (1943).
(32) Melting points are uncorrected and microanalyses were performed by Atlantic Microlab, Inc., Atlanta, Ga. Infrared spectra were obtained using a Perkin-Elmer Model 457 spectrometer fitted with sodium chloride optics. The nmr spectra were determined with a Varian A-60 spectrometer (TMS internal standard) and mass spectra were measured on a Varian M-66 spectrometer. Ultraviolet spectra were obtained from a Cary Model 14 recording spectrophotometer using 1-cm quartz cells.
(33) I. Benghiat and E. I. Beckor, *J. Org. Chem.*, **23**, 885 (1958).
(34) C. R. Hauser and G. G. F. Morris, *J. Org. Chem.*, **26**, 4740 (1961).

Reaction of Oxaziridine with Heterocumulene. A Ketene, Isocyanates, and a Carbodiimide

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Received September 21, 1973

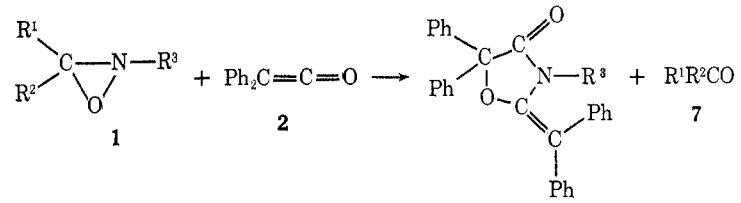
Reactions of oxaziridines **1** with a ketene, isocyanates, and a carbodiimide are studied, and the results are quite different from those of oxiranes, aziridines, or thiiranes. With diphenylketene (**2**), 2-*n*-alkyl- or *sec*-alkyloxaziridines give 3-alkyl-5,5-diphenyl-2-diphenylmethylidene-1,3-oxazolidin-4-ones (**3**), but 2-*tert*-butyloxaziridine **1f** rearranges to *N*-*tert*-butylbenzamide. In the reactions with isocyanates, cycloadditions forming 1,2,4-oxadiazolidin-5-ones **10** are exclusively observed. The reactions similar to that with the ketene **2** occur between 2-*n*-alkyloxaziridines and diphenylcarbodiimide, giving hexahydro-1,3,5-triazine derivatives **17** as a result of hydride shift. The oxaziridine **1f** undergoes 1:1 cycloaddition with the carbodiimide.

Many reactions of three-membered heterocycles containing one heteroatom with heterocumulenes have been reported. Oxiranes react with a ketene, an isocyanate, and a carbodiimide to give dioxolans[1] or γ-lactones,[2] oxazolidinones,[3] and imidazolidinones,[1] respectively; imidazolidinones are also given by the cycloaddition of aziridines to an isocyanate.[4] Thiiranes react with a ketene to afford thiolactones.[5]

On the other hand, the chemistry of three-membered rings containing two heteroatoms has not been so widely studied. In particular, there has been no report on the cycloadditions of such heterocycles to heterocumulenes.

In this study, the reactions of oxaziridines with a ketene, isocyanates, and a carbodiimide are presented. The accompanying report[6] describes the reactions of oxaziridines with sulfur-containing heterocumulenes.

Table I
Reaction of Oxaziridine with Diphenylketene

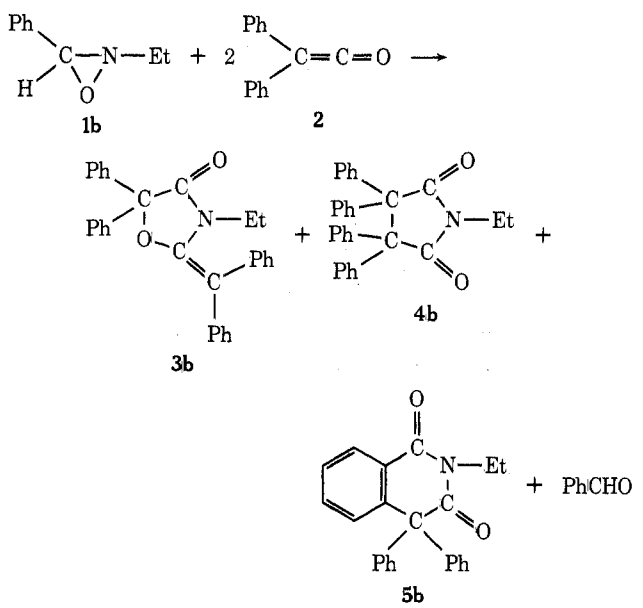


1 2 3 7

Registry no.	Oxaziridine (1)	R¹	R²	R³	Conditions[a] Temp, °C	Time,[b] hr	Registry no. of 3	Yield, % 3	7
3400-12-2	**1a**	C_6H_5	H	CH_3	60	0.5	50484-08-7	24	27[e]
7771-15-5	**1b**	C_6H_5	H	C_2H_5	60	0.5	50484-09-8	38	59
21710-99-6	**1c**	C_6H_5	H	n-C_4H_9	60	0.5	50484-10-1	40	62
7731-32-0	**1d**	C_6H_5	H	i-C_3H_7	80	4.5	50484-11-2	64	43
21711-00-2	**1e**	C_6H_5	H	c-C_6H_{11}	80	1.0	50484-12-3	28	75
7731-34-2	**1f**	C_6H_5	H	t-C_4H_9	80	5.0		c	
21711-01-3	**1g**	C_6H_5	CH_3	n-C_4H_9	60	0.5		80	d
21711-02-4	**1h**	C_2H_5	CH_3	n-C_4H_9	60	0.5		32	d

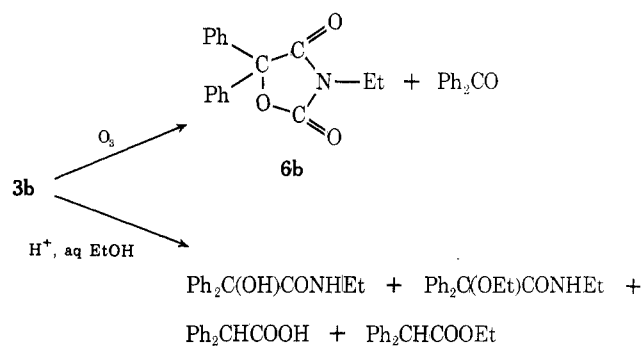
[a] Mole ratio of **1**:**2** was 0.8–1.0; benzene was employed as a solvent. [b] Allowed to react until ir absorption of C=C=O disappeared. [c] *t*-BuNHCOPh (**8**) was obtained in 97% yield. [d] Not determined exactly. [e] Registry no., 100-52-7.

Reaction with Diphenylketene. Reaction of 2-ethyl-3-phenyloxaziridine (**1b**) with diphenylketene (**2**) gave an oxazolidinone derivative **3b** (yield 38%) and small amounts of *N*-ethyltetraphenylsuccinimide (**4b**) and 2-ethyl-4,4-diphenyl-1,3-(2*H*,4*H*)-isoquinolinedione (**5b**) with benzaldehyde (yield 59%). Such a type of reaction has not been found for other three-membered heterocycles.



1b 2 3b 4b 5b

The ir spectrum of the major product **3b** shows strong absorption bands at 1726 and 1630 cm^{-1}, which are assigned to C=O and C=C stretching vibrations, respectively. The minor product **4b** has a very weak ir absorption band at 1765 cm^{-1} and a strong one at 1700 cm^{-1} whose pattern well coincides with those of other five-membered imides. The nmr spectra of **3b** and **4b** show the signals of the ethyl group of the oxazolidinone **3b** appearing at higher fields than those of the imide **4b** (by 0.26 ppm for the triplet due to the methyl protons and by 0.76 ppm for the quartet due to the methylene protons). This shift can be attributed to the phenyl ring located near the ethyl group in the oxazolidinone **3b** and to the two carbonyl groups adjacent to the nitrogen atom of the imide **4b**. That the signal of phenyl rings of **3b** is broad and that of **4b** is very sharp is also consistent with these structures. Further evidence for the structure **3b** was provided by ozonolysis and acidic hydrolysis of **3b**. The former gave benzophenone (85%) and an oxazolidinedione **6b** (40%) and the latter gave *N*-ethyl-2-hydroxy-2,2-diphenylethanamide (69%), *N*-ethyl-2-ethoxy-2,2-diphenylethanamide (23%), diphenylacetic acid (21%), and ethyl diphenylacetate (41%).



3b 6b

$Ph_2C(OH)CONHEt$ + $Ph_2C(OEt)CONHEt$ +

$Ph_2CHCOOH$ + $Ph_2CHCOOEt$

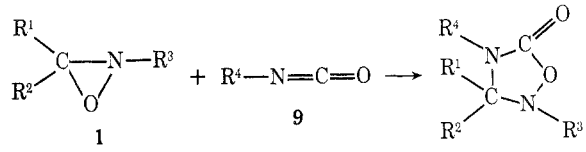
The ozonolysis product **6b** shows two strong ir absorption bands at 1812 and 1728 cm^{-1}. As for nmr spectra, the chemical shifts of the ethyl protons of **6b** are nearly equal to those of the imide **4b**.

In this reaction, another minor product **5b** was isolated; elemental analysis and the mass spectrum show that the compound was formed with loss of two hydrogens from a 1:1 adduct of the oxaziridine **1b** and the ketene. Absorptions characteristic of imido carbonyl groups are found in the ir spectrum (1706 and 1658 cm^{-1}). The nmr spectrum indicates substitution on a phenyl ring and the pattern of the signal of H-8, a complex multiplet at δ 8.2–8.3, is completely consistent with the computed one for H-6 of benzocyclobuten-1-ol.[7]

The thermal rearrangement of **3b** to **4b** was not observed when the compound **3b** was heated directly above 180° for 25 hr or in refluxing solvents (xylene or chloroform) for a long period.

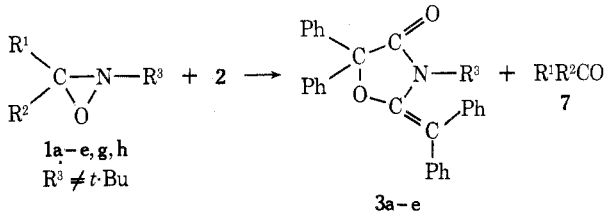
Other 2-*n*-alkyl- or *sec*-alkyloxaziridines, **1a,c–e,g,h,** similarly reacted with the ketene **2** to give oxazolidinone derivatives **3** and ketones (or aldehydes) **7**. Substituents on the oxaziridine carbon do not change the course of the reaction but do influence the yield of oxazolidinones **3**.[25] The results are shown in Table I.

Table II
Reaction of Oxaziridine with Isocyanates



	Oxaziridine (1)			Isocyanate (9)	Conditions					
	R^1	R^2	R^3	R^4	Mole ratio 1:9	Solvent	Temp, °C	Time,[a] hr	Registry no.	Yield, %
1c	C_6H_5	H	n-C_4H_9	C_6H_5[f]	1.0	C_6H_6	85	25[b]	50484-14-5	36
1d	C_6H_5	H	i-C_3H_7	C_6H_5	1.2	C_6H_6	85	13	50484-15-6	95
1d	C_6H_5	H	i-C_3H_7	C_6H_5	0.5	$C_6H_5OCH_3$	81	25		53
1d	C_6H_5	H	i-C_3H_7	C_6H_5	0.5	CH_3CN	75	12		5[c]
1d	C_6H_5	H	i-C_3H_7	n-C_4H_9[g]	1.4	C_6H_6	90	17	50506-96-2	24
1f	C_6H_5	H	t-C_4H_9	C_6H_5	1.0	C_6H_6	80	2	2289-83-0	94
1i[e]	$-(CH_2)_5-$		COC_6H_5	C_6H_5	1.0	$C_6H_5CH_3$	115	7		*d*

[a] Allowed to react until ir absorption of $-N=C=O$ (*ca.* 2300 cm^{-1}) disappeared. [b] In a sealed tube. [c] Unreacted **1d** was recovered (88%) and most of the unreacted isocyanate was recovered in trimeric form. [d] Rearranged to dioxazoline **15** in 60% yield. [e] Registry no., 50484-16-7. [f] Registry no., 103-71-9. [g] Registry no., 111-36-4.

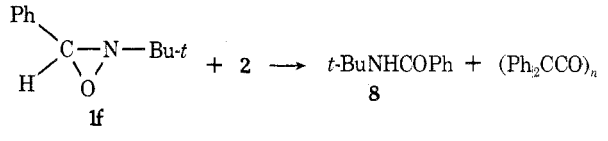


1a–e,g,h
$R^3 \neq t$-Bu

3a–e

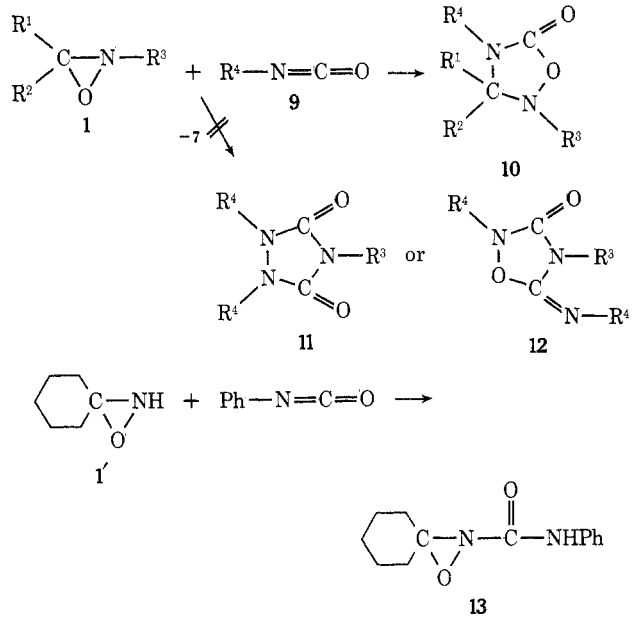
The tetraphenylsuccinimide, which was mistakenly reported to be the major product in a preliminary report,[8] is not a well-known compound[9] and the imide **4b**, the by-product, may be the only N-substituted tetraphenylsuccinimide except for its azomethine derivative.[9b]

Oxazolidinone formation was not observed when 2-*tert*-butyloxaziridine **1f** was treated with diphenylketene; instead **1f** rearranged to *N*-*tert*-butylbenzamide (**8**) quantitatively.



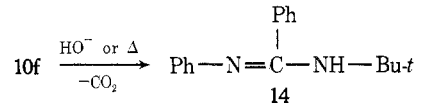
1f

Reaction with Isocyanates. Reaction of oxaziridines with isocyanates **9** did not yield triazolidinediones **11** or



oxadiazolidiones **12.** The reaction gave a 1:1 cycloadduct, an oxadiazolidinone **10**, and was independent of the *N*-alkyl substituent. For the N-unsubstituted oxaziridine **1′**, it has been reported that the oxaziridine acts as an active hydrogen compound and gives 2-aminoformyloxaziridine **13.**[10] The results are listed in Table II.

The ir spectrum of oxadiazolidinone **10** shows an absorption band at *ca.* 1740 cm^{-1} and the spectrum of **10f** was identical with that of an authentic sample prepared from α-phenyl-*N*-*tert*-butylnitrone and phenyl isocyanate.[11] The fragmentation in the mass spectrum also well explains the structure of **10.** Alkaline hydrolysis and pyrolysis of the oxadiazolidinone **10f** gave *N*-*tert*-butyl-*N*′-phenylbenzamidine (**14**).

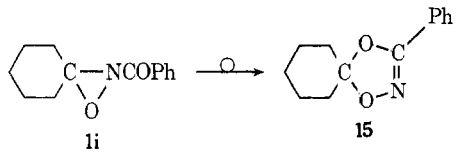


14

Lability of the oxaziridine may have lowered the yield of the product **10c** in the case of 2-*n*-butyloxaziridine **1c.**

The use of polar solvents did not change the product in these reactions, but the yields of **10c** and **10d** decreased with an increase in polarity of solvents. Polar solvents seem to prohibit the addition of an oxaziridine to the isocyanate and to promote, rather, the trimerization of the isocyanate. In anisole, 2-ethyloxaziridine **1b**, less stable than *N*-isopropyloxaziridine **1d**, gave no adduct.

The *N*-acyloxaziridine **1i** did not form any product with the isocyanate **9** but instead isomerization to dioxazoline **15**[12] was observed.



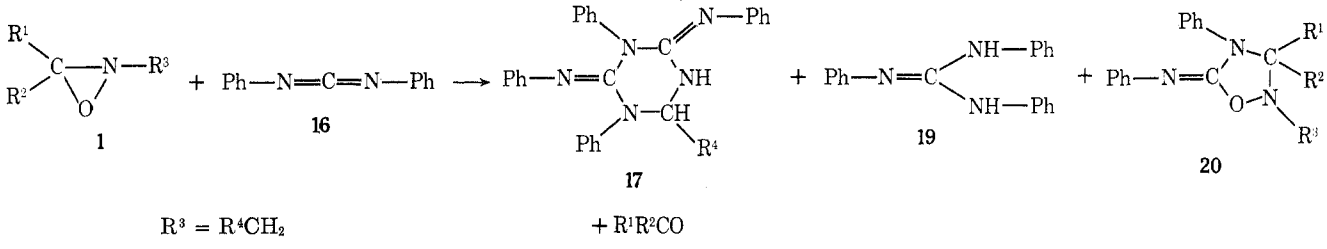
1i **15**

The use in one instance of *n*-butyl isocyanate in place of phenyl isocyanate also gave, when treated with **1d**, the oxadiazolidinone **10′d.**

Reaction with Carbodiimide. The reactions of *N*-*n*-alkyloxaziridines **1a–c,g,h** with diphenylcarbodiimide (**16**) gave hexahydro-1,3,5-triazine derivatives **17a–c** unexpectedly and ketones (Table III).

The ir spectrum of the hexahydro-1,3,5-triazine **17b** shows characteristic absorption bands at 1660, 1622 (C=N), 3400, and 1581 cm^{-1} (NH). The nmr spectrum of the compound **17b** has a doublet (δ 1.84, J = 6.0 Hz, 3 H),

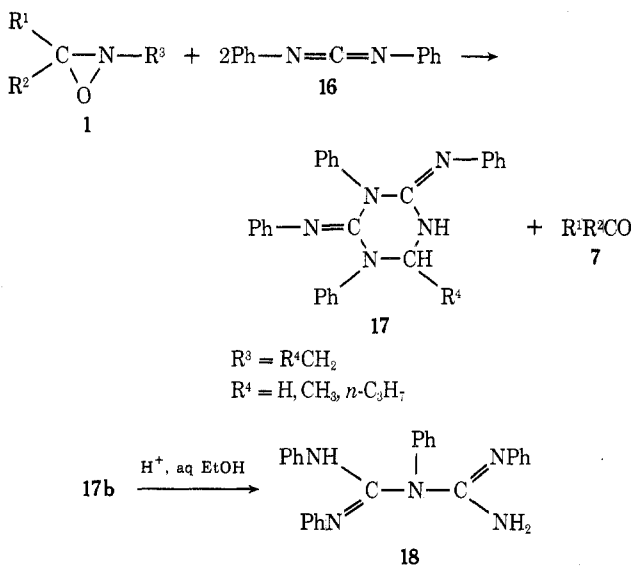
Table III
Reaction of Oxaziridine with Diphenylcarbodiimide



	Oxaziridine (1)			Conditions			Yield, %			
	R^1	R^2	R^3	Mole ratio 1:16	Temp, °C	Time,[a] hr	17	19	20	7
1a	C_6H_5	H	CH_3	0.5	110	1.5	61[b,f]			97
1b	C_6H_5	H	C_2H_5	0.5	110	1.0	88[c,g]			*e*
1c	C_6H_5	H	*n*-C_4H_9	1.0	100	1.5	58[d,h]			76
1c	C_6H_5	H	*n*-C_4H_9	0.5	110	1.5	85[d]			92
1g	C_6H_5	CH_3	*n*-C_4H_9	0.5	110	1.5	100[d]			79[i]
1h	C_2H_5	CH_3	*n*-C_4H_9	0.5	110	1.5	52[d]			78[j]
1d	C_6H_5	H	*i*-C_3H_7	0.5	110	3.0		56[k]		*e*
1f	C_6H_5	H	*t*-C_4H_9	1.0	115	3.0			72[l]	

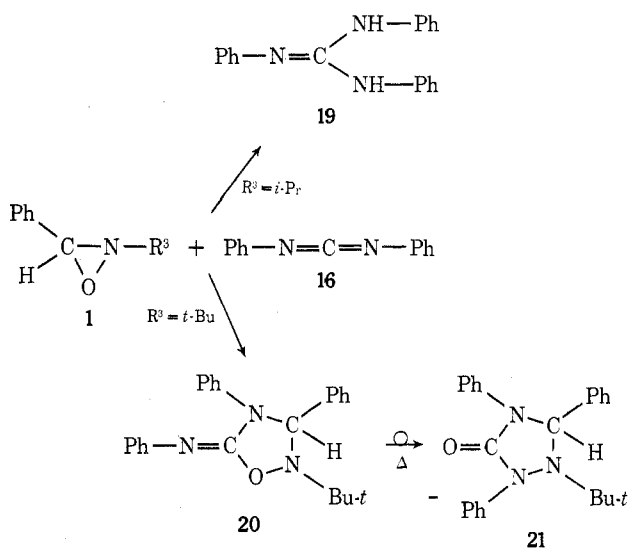
[a] Allowed to react until ir absorption of –N=C=N– disappeared. [b] R^4 = H. [c] R^4 = CH_3. [d] R^4 = *n*-C_3H_7. [e] Not determined exactly. [f] Registry no., 50484-19-0. [g] Registry no., 50600-52-7. [h] Registry no., 50600-53-8. [i] Registry no. 98-86-2. [j] Registry no., 78-93-3. [k] Registry no., 101-01-9. [l] Registry no., 35105-50-1.

a quartet (δ 5.14, J = 6.0 Hz, 1 H), and a broad singlet at δ 4.8–5.3 that rapidly disappears upon addition of deuterium oxide, and these signals are assigned to the methyl, the methine, and the amino protons, respectively. In the mass spectrum of **17b** (R^4 = CH_3), the fragment ion peak corresponding to the elimination of a methyl group from the molecular ion appears at m/e 416 with the absence of the fragment corresponding to the elimination of an ethyl fragment. In addition, acidic hydrolysis of **17b** gave 1,2,3,4-tetraphenylbiguanide (**18**).



The effect of C substituents on the yields of **17** was similar to that in the reaction with the ketene.

When the N substituent was an isopropyl group (**1d**), *N,N',N''*-triphenylguanidine (**19**) was obtained as the product and not the expected hexahydrotriazine. 2-*tert*-Butyloxaziridine **1f** gave a 1:1 cycloadduct, oxadiazolidine **20**, which is identical with the product of the reaction between α-phenyl-*N*-*tert*-butylnitrone and diphenylcarbodiimide.[13] As the oxadiazolidine **20** readily rearranges to the triazolidinone **21** upon heating,[13] the formation of **21** was observed at higher temperatures. With *N,N'*-dicyclohexylcarbodiimide (**16'**), however, the oxaziridine **1f** gave no adduct but rearranged to α-phenyl-*N*-*tert*-butylnitrone, and the carbodiimide **16'** was recovered quantitatively.



Discussion

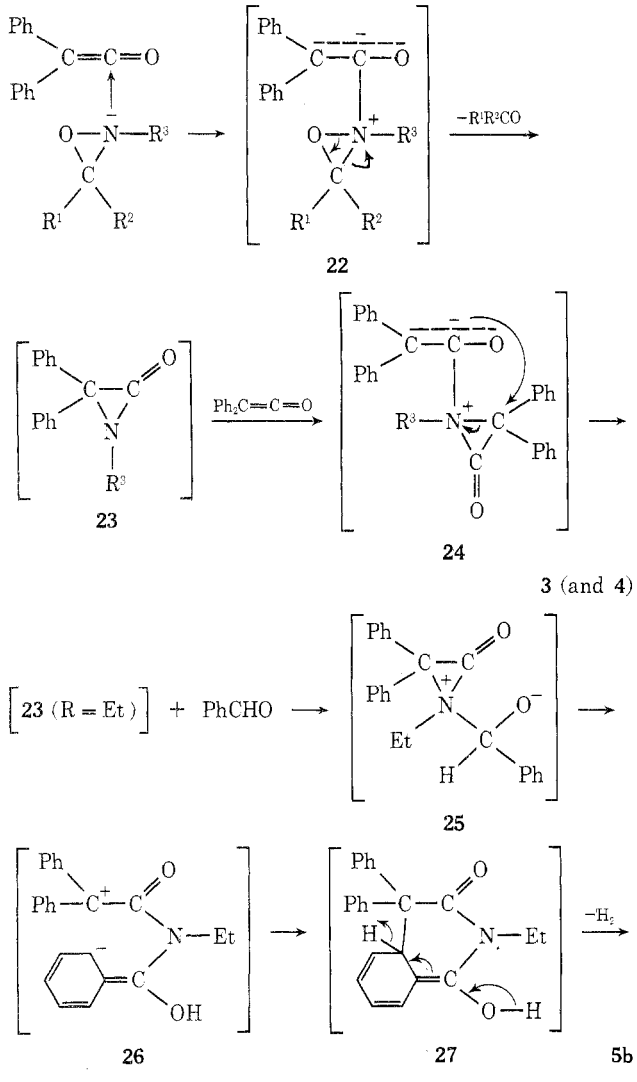
These reactions are classified into two types, the one initiated by the nucleophilic attack of a nitrogen atom of an oxaziridine to a center carbon atom of a heterocumulene and the other initiated by that of an oxygen atom. The reaction with the ketene belongs to the former and the reaction with isocyanates to the latter, and the both types were observed in the reactions with the carbodiimide.

In the reaction with the ketene **2**, the formation of the cycloadduct **3** is assumed to proceed *via* an α-lactam intermediate **22** as shown in Scheme I. The reaction is initiated by a nucleophilic attack of a nitrogen atom of an oxaziridine followed by the release of a carbonyl compound to give a highly strained intermediate **23**, which immediately reacts with an additional ketene molecule to afford an intermediate **24**. Ring closure of the intermediate **24** gives an oxazolidinone **3** and a succinimide **4**, but the former is predominant because of steric hindrance of phenyl groups against ring closure. The observed influence

of C substituents on the yield of oxazolidinones 3 correlates with carbonyl character of the leaving molecule.

The formation of a small amount of the isoquinolinedione **5b** in the reaction of **1b** is perhaps caused by the recombination of the intermediate **23** and the released

Scheme I



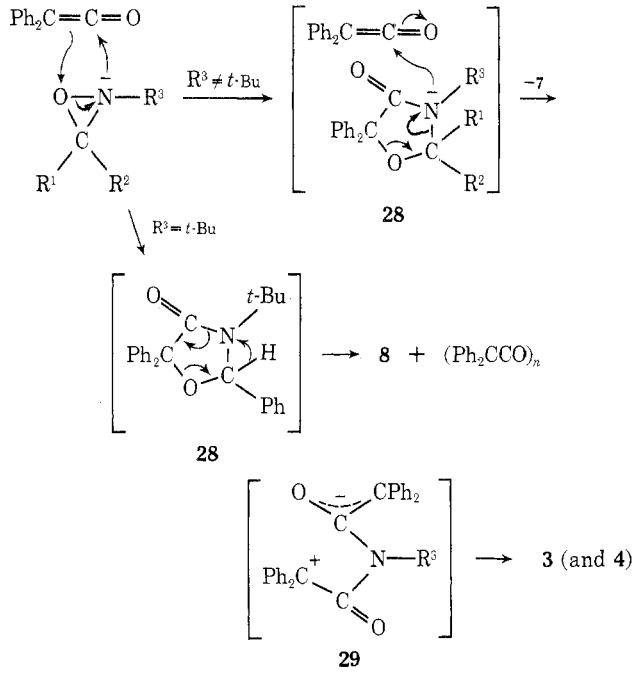
benzaldehyde. The dehydrogenation from **27** giving **5b** may be promoted by the oxaziridine, as it is an oxidizing agent.

Though generation of a nitrene in photolysis of some oxaziridines is reported,[14] the initial step of the reaction is not the formation of nitrenes because the reactions with isocyanates under similar conditions can never be understood by the formation of nitrenes.

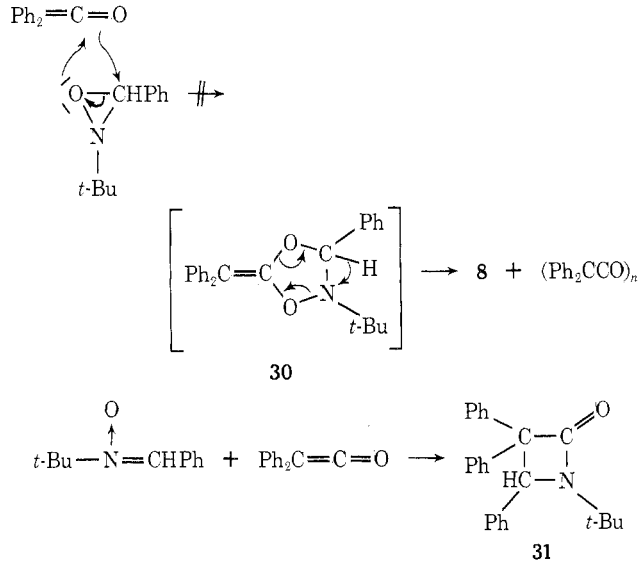
The oxaziridine **1f** rearranges to the isomeric nitrone on heating.[15] Therefore rearrangement to the amide **8** suggests participation of the ketene in this isomerization. To explain the whole reaction including this isomerization, an alternative mechanism *via* an intermediate **28**, a 1:1 cycloadduct of an oxaziridine and the ketene, can also be assumed (Scheme II). It seems that the bulky substituent inhibits the nucleophilic attack to an additional ketene by the nitrogen atom of the intermediate **28**, which in turn decomposes thermally into the amide and the ketene. Nevertheless, it is less likely that the intermediate **28** further reacts with the ketene to form betaine intermediate **29** with the release of a carbonyl compound **7**.

As another possibility, the steric hindrance of the *N*-*tert*-butyl group can be assumed in the initial cyclization.

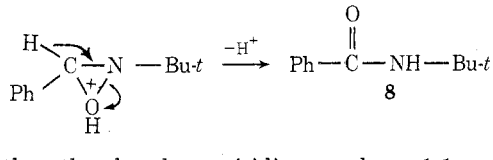
Scheme II



In this case, a nucleophilic attack by an oxygen atom results exclusively in an acetal-type intermediate **30**, which is expected to be formed from its isomeric nitrone and the ketene. This mechanism, however, is excluded by the reaction of α-phenyl-*N*-*tert*-butylnitrone with the ketene under the same conditions, giving no rearranged amide but the β-lactam **31**.

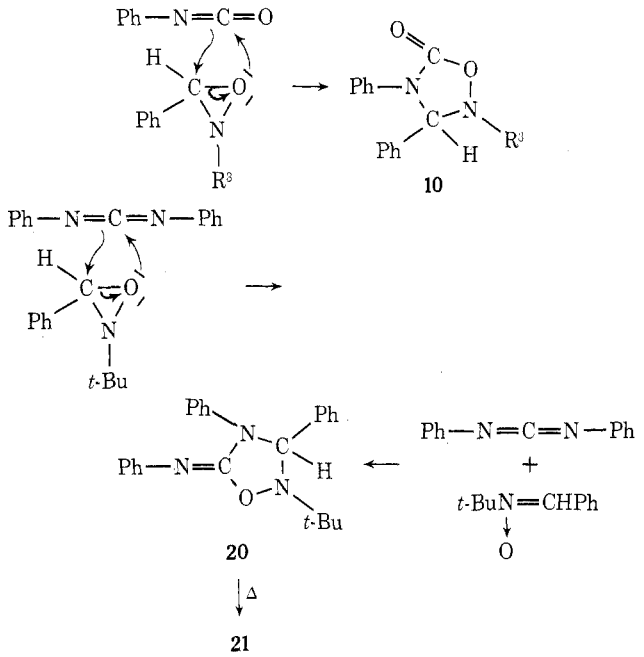


The rearrangement of the oxaziridine **1f**, whose nucleophilic attack to the ketene is sterically restricted, is thus considered to be promoted by trace amounts of diphenylacetic acid derived from the ketene.

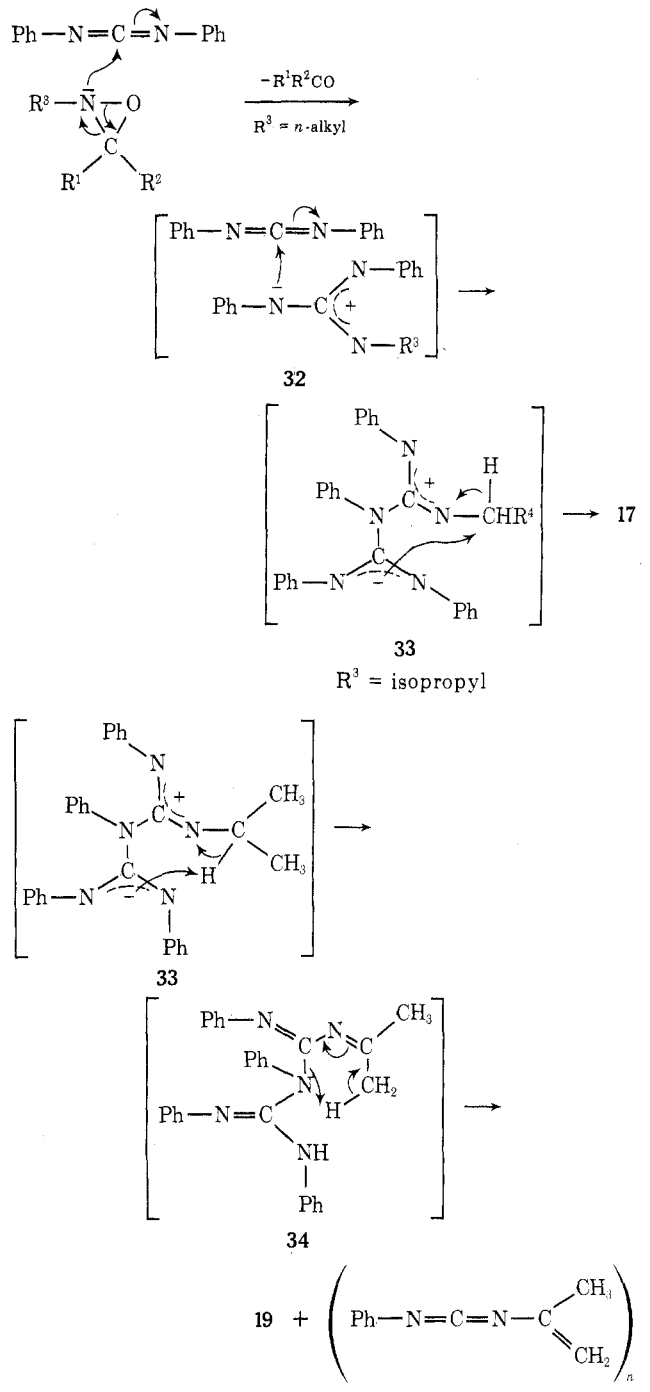


On the other hand, oxaziridines undergo 1:1 cycloadditions with isocyanates which are similar in nature to reactions of other three-membered heterocycles with heterocumulenes. The adducts, oxadiazolidinone derivatives, have been reported in the reaction of a nitrone with an isocyan-

Scheme III



Scheme IV



ate,[11] but there was no evidence for isomerization of oxaziridines to nitrones in the course of the reactions. If this isomerization would occur under the employed conditions, the reaction of the oxaziridine **1f** with the ketene **2** or the reaction of the oxaziridine **1a** with the carbodiimide **16** should have given such products as obtained in the reaction of the corresponding isomeric nitrone.[13] Thus the reaction may proceed as shown in Scheme III.

The nucleophilic attack by an oxygen atom, which is quite different from the reaction with the ketene **2**, was also observed to take place in the reaction of **1f** with diphenylcarbodiimide (**16**) and was evidenced to cause the nitrone-type 1,3 cycloaddition. The adduct **20** readily rearranges to the triazolidinone **21** upon heating. Similar rearrangement of an acetal-type intermediate, which is reported in the reactions of oxiranes with isocyanates,[3] formed by cycloaddition of an oxaziridine across the C=O bond of an isocyanate might have given the oxadiazolidinone **10**. In contrast to the reaction with the ketene, the nucleophilic attack by the nitrogen atom of an oxaziridine cannot lead to the product in these reactions.

The difference of the initial nucleophilic attacks among these reactions should be attributed to the balance of steric hindrance of N substituents and electrophilicity of heterocumulenes. Thus it may well be concluded that sufficient electrophilicity of a center carbon atom of a cumulative bond can cause a nucleophilic attack by the oxygen atom which is less nucleophilic but also less hindered. This is consistent with the fact that an attack by a nitrogen atom was observed in the reaction of the oxaziridine **1′** whose nitrogen atom is not sterically hindered and in the reaction with the ketene whose center carbon is considered to be less electrophilic.

In this regard, a nucleophilic attack by a nitrogen atom of an oxaziridine to the carbodiimide **16**, whose center carbon has poor electrophilicity compared with the isocyanate **9**, is expected. The results are consistent with this prediction. As for the low reactivity of dicyclohexylcarbodiimide **16′**, a cyclohexyl group cannot delocalize the negative charges on the nitrogen atoms and rather inhibits such polarization with their electron donation.

In the reaction of 2-*n*-alkyl- or *sec*-alkyloxaziridine with the carbodiimide **16**, the initial step is similar to that of the reaction with the ketene. A betaine intermediate **32** (Scheme IV) is expected instead of an iminodiaziridine intermediate, which corresponds to the α-lactam intermediate **23**, because of the smaller N-N bond energy. This is compatible with the reversible isomerization of such iminodiaziridines.[16] The intermediate **32** attacks an additional corbodiimide to give an intermediate **33**, whose negatively charged nitrogen atom is located rather nearer to the carbon atom than to the positive nitrogen atom because of the repulsion between the two nitrogens. 1,2-Hydride shift therefore occurs to give the hexahydrotriazine **17**. An alternative mechanism *via* an oxadiazolidinimine, a 1:1 cycloadduct of an oxaziridine and the carbodiimide, is also possible. In the case of the isopropyl-substituted oxaziridine **1d**, approach of the negative nitrogen atom of the intermediate **33** to the carbon atom is sterically hindered and the proton abstraction occurs. The resultant intermediate **34** is thermally decomposed to the guanidine **19** and polymer of vinylcarbodiimide.

Another possible mechanism for these reactions may involve the intermediacy of diradicals. This mechanism is based on the stimulating concept of diradical intermediates in 1,3-dipolar cycloadditions suggested by Firestone,[18] applying Linnet electron theory.[19] The concept aroused much interest but has not been well established yet.[20] Furthermore, the reaction of the oxaziridine **1b** with the ketene in the presence of chloranil showed no essential difference from that without chloranil.

Experimental Section

All melting points were determined on a Yanagimoto micro melting point apparatus and are uncorrected. Ir, nmr, and mass spectra were obtained on a JASCO IR-E spectrophotometer, JEOL LNM-3H-60 and JEOL JNM-PS-100 spectrometers, and a Hitachi RMU-6E spectrometer, respectively. Carbonyl compounds contained in the distillates of the reaction mixtures were identified and determined by glpc using a 10% Apiezon L on Diasolid L (60–80 mesh, 4 mm × 2 m) column.

All reactions were carried out under nitrogen stream in a 50-ml four-necked flask equipped with a stirrer, a reflux condenser, a dropping funnel, and a thermometer, and products were isolated by column chromatography (basic aluminum oxide–benzene).

Materials. Diphenylketene (**2**) and diphenylcarbodiimide (**16**) were prepared according to known methods.[21,22] Phenyl isocyanate and *n*-butyl isocyanate were purchased from a commercial source.

Preparations of 2-alkyloxaziridines **1a–h** were done with perbenzoic acid according to Pews' method.[23] 2-Benzoyl-3,3-pentamethyleneoxaziridine (**1i**) was prepared by the benzoylation of 3,3-pentamethyleneoxaziridine.[12,24] Boiling points or melting point and yields are as follows: 2-methyl-3-phenyloxaziridine (**1a**), 67° (5 mm), 70%; 2-ethyl-3-phenyloxaziridine (**1b**), 74–75° (0.2 mm), 66%; 2-*n*-butyl-3-phenyloxaziridine (**1c**), 74–75° (0.5 mm), 75%; 2-isopropyl-3-phenyloxaziridine (**1d**), 73–74° (1.5 mm), 60%; 2-cyclohexyl-3-phenyloxaziridine (**1e**), 90° (0.2 mm), 50%; 2-*tert*-butyl-3-phenyloxaziridine (**1f**), 78–79° (1.5 mm), 75%; 2-*n*-butyl-3-methyl-3-phenyloxaziridine (**1g**), 60° (0.35 mm), 61%; 2-*n*-butyl-3-methyl-3-ethyloxaziridine (**1h**), 76° (13 mm), 46%; 2-benzoyl-3,3-pentamethyleneoxaziridine (**1i**), mp 68°, 28%.

The purities [active oxygen content (AO)] were determined by iodometry.

A. Reaction with Diphenylketene. All reactions were carried out by the same procedure as the reaction of the oxaziridine **1b**.

Reaction of the Oxaziridine 1b. To a solution of the ketene **2** (9.7 g, 50 mmol) in benzene (10 ml), a solution of the oxaziridine **1b** (4.2 g, 25 mmol, AO 90%) in benzene (5 ml) was added dropwise with stirring at such a rate as the temperature did not rise above 60°. Half an hour later, the characteristic ir absorption of the ketene disappeared. The reaction mixture was distilled and 1.58 g (59%) of benzaldehyde was obtained. The residue was chromatographed to give 4.12 g (38%) of 3-ethyl-5,5-diphenyl-2-diphenylmethylidene-1,3-oxazolidin-4-one (**3b**), 0.46 g (4%) of *N*-ethyltetraphenylsuccinimide (**4b**), and 0.31 g (4%) of 2-ethyl-4,4-diphenyl-1,3-(2*H*,4*H*)-isoquinolinedione (**5b**). The major product **3b** was recrystallized (benzene–hexane) to afford colorless granules: mp 144–144.5°; ir (Nujol) 1726 (C=O) and 1630 cm^{-1} (C=C); nmr ($CDCl_3$) δ 0.83 (t, 3, J = 6.9 Hz, CH_3), 3.14 (q, 2, J = 6.9 Hz, CH_2), 7.0–7.7 (m, 20, 4 Ph); mass spectrum (70 eV) m/e 431 (M^+, calcd 431), 332 ($Ph_2C{=}CPh_2^+$), 221 ($Ph_2C{=}C{=}NEt^+$), 194 (Ph_2CCO^+).

Anal. Calcd for $C_{30}H_{25}NO_2$: C, 83.50; H, 5.84; N, 3.25. Found: C, 83.39; H, 5.83; N, 3.13.

Recrystallization of one of the minor products **4b** yielded colorless plates: mp 216–218°; ir (Nujol) 1765 (C=O, weak) and 1700 cm^{-1} (C=O); nmr ($CDCl_3$) δ 1.09 (t, 3, J = 7.0 Hz, CH_3), 3.81 (q, 2, J = 7.0 Hz, CH_2), 6.9–7.2 (m, 20, 4 Ph); mass spectrum (70 eV) m/e 431 (M^+, calcd 431), 332 ($Ph_2C{=}CPh_2^+$), 221 ($Ph_2C{=}C{=}NEt^+$), 194 (Ph_2CCO^+).

Anal. Calcd for $C_{30}H_{25}NO_2$: C, 83.50; H, 5.84; N, 3.25. Found: C, 83.50; H, 5.66; N, 3.40.

The last compound **5b** was recrystallized from benzene–hexane to give colorless granules: mp 230–231°; ir (Nujol) 1706 and 1658 cm^{-1} (C=O); nmr ($CDCl_3$, 100 MHz) δ 1.11 (t, 3, J = 7.1 Hz, CH_3), 4.03 (q, 2, J = 7.1 Hz, CH_2), 6.7–7.6 (m, 13, aromatic protons), 8.2–8.3 (m, 1, H-8); the last signal of a complex multiplet well agreed with the computed pattern for the proton of the 6 position of benzocyclobuten-1-ol[7]; mass spectrum (70 eV) m/e 341 (M^+, calcd 341), 312 (M^+ − Et), 270 (M^+ − EtNCO), 241 (270 − COH), 239 ($Ph_2CHCONHEt^+$), 119 (M^+ − Ph_2CCO − $CH_2{=}CH_2$).

Anal. Calcd for $C_{23}H_{19}NO_2$: C, 80.92; H, 5.61; N, 4.10. Found: C, 80.98; H, 5.50; N, 4.19.

Reaction of the Oxaziridine 1a. The same treatment of the ketene **2** (9.5 g, 50 mmol) and the oxaziridine **1a** (9.5 g, 49 mmol, AO 70%) as the above reaction gave 2.6 g (26%) of 3-methyl-5,5-diphenyl-2-diphenylmethylidene-1,3-oxazolidin-4-one (**3a**) and 0.69 g (27%) of benzaldehyde. Recrystallization (benzene–hexane) of the compound **3a** gave colorless granules: mp 131–131.5°; ir (Nujol) 1730 (C=O) and 1660 cm^{-1} (C=C).

Anal. Calcd for $C_{29}H_{23}NO_2$: C, 83.43; H, 5.55; N, 3.36. Found: C, 83.39; H, 5.31; N, 3.33.

Reaction of the Oxaziridine 1c. From 12.7 g (67 mmol, AO 94%) of the oxaziridine **1c** and 11.8 g (61 mmol) of the ketene **2**, 5.5 g (40%) of 3-*n*-butyl-5,5-diphenyl-2-diphenylmethylidene-1,3-oxazolidin-4-one (**3c**) and 2.0 g (62%) of benzaldehyde were obtained, and 3.3 g of the oxaziridine **1c** was recovered. The product **3c** was recrystallized from benzene–hexane to give colorless granules: mp 125–126°; ir (Nujol) 1732 (C=O) and 1660 cm^{-1} (C=C); nmr (CCl_4) δ 0.68 (t, 3, CH_3), 0.8–1.5 (m, 4, 2 CH_2), 3.12 (t, 2, NCH_2), 6.8–7.7 (m, 20, 4 Ph); the triplets are considerably deformed; mass spectrum (70 eV) m/e 459 (M^+, calcd 459), 402 (M^+ − Bu), 332 ($Ph_2CCPh_2^+$).

Anal. Calcd for $C_{32}H_{29}NO_2$: C, 83.63; H, 6.36; N, 3.05. Found: C, 83.63; H, 6.38; N, 3.04.

Reaction of the Oxaziridine 1d. The reaction between the oxaziridine **1d** (4.6 g, 27 mmol, AO 95%) gave 3.8 g (64%) of 3-isopropyl-5,5-diphenyl-2-diphenylmethylidene-1,3-oxazolidin-4-one (**3d**), 0.61 g (43%) of benzaldehyde, and 1.05 g (23%) of *N*-isopropylbenzamide. The oxazolidinone **3d** was recrystallized from benzene–hexane to afford colorless granules: mp 163–164.5°; ir (Nujol) 1726 (C=O) and 1642 cm^{-1} (C=C); mass spectrum (70 eV) m/e 445 (M^+, calcd 445), 403 (M^+ − $CH_3CH{=}CH_2$), 375 (403 − CO), 332 ($Ph_2CCPh_2^+$).

Anal. Calcd for $C_{31}H_{27}NO_2$: C, 83.57; H, 6.14; N, 3.14. Found: C, 83.71; H, 5.94; N, 3.31.

Reaction of the Oxaziridine 1e. After the treatment as above, the oxaziridine **1e** (10.2 g, 45 mmol, AO 90%) and the ketene **2** (10.0 g, 52 mmol) gave 2.0 g (75%) of benzaldehyde and 3.5 g (28%) of 3-cyclohexyl-5,5-diphenyl-2-diphenylmethylidene-1,3-oxazolidin-4-one (**5e**). Recrystallization of the latter from benzene–hexane gave colorless granules: mp 208°; ir (Nujol) 1726 (C=O) and 1640 cm^{-1} (C=C); mass spectrum (70 eV) m/e 485 (M^+, calcd 485), 402 (M^+ − C_6H_{11}), 374 (402 − CO), 332 ($Ph_2CCPh_2^+$).

Anal. Calcd for $C_{34}H_{31}NO_2$: C, 84.09; H, 6.43; N, 2.88. Found: C, 84.58; H, 6.29; N, 2.85.

Reaction of the Oxaziridine 1f. After the reaction of the oxaziridine **1f** (3.0 g, 17 mmol, AO 98%) with the ketene **2** (3.3 g, 17 mmol), 2.7 g (92%) of *N*-*tert*-butylbenzamide (**8**) was obtained. The amide **8** was identical with the authentic sample from benzoyl chloride and *tert*-butylamine, mmp 140–141.5°.

Reactions of the Oxaziridines 1g and 1h. From 10.1 g (43 mmol, AO 81%) of the oxaziridine **1g** and 10.3 g (53 mmol) of the ketene **2**, 9.7 g (80%) of the oxazolidinone **3c** was obtained. The compound **3c** was also yielded in the reaction of the oxaziridine **1h** (10.0 g, 52 mmol, AO 74%) with the ketene **2** (10.0 g, 52 mmol) in 32% yield (3.8 g).

Ozonolysis of the Oxazolidinone 3b. A mixture of ozone–air (generated by a Nippon Ozone Model 0-1-2 ozone generator operated at 60 V at a flow rate of 150 ml/min) was passed through a solution of the compound **3b** (440 mg, 1.0 mmol) in 15 ml of methanol–carbon tetrachloride (2:1 mixture) cooled in an ice bath for 30 min. Then the mixture was refluxed for 3 hr. The ir spectrum of the mixture showed the formation of benzophenone and the yield was determined by glpc, 157 mg, 85%. The mixture was chromatographed to afford 114 mg (40%) of 3-ethyl-5,5-diphenyl-1,3-oxazolidine-2,4-dione (**6b**) as colorless granules (from benzene–hexane): mp 93.5–94.5°; ir (Nujol) 1818 and 1730 cm^{-1} (C=O); nmr ($CDCl_3$) δ 1.26 (t, 3, J = 7.2 Hz, CH_3), 3.65 (q, 2, J = 7.2 Hz, CH_2), 7.2–7.6 (m, 10, 2 Ph); mass spectrum (70 eV) m/e 281 (M^+, calcd 281), 210 (M^+ − EtNCO), 182 (Ph_2CO^+).

Anal. Calcd for $C_{17}H_{15}NO_3$: C, 72.58; H, 5.37; N, 4.98. Found: C, 72.75; H, 5.28; N, 5.07.

Acidic Hydrolysis of the Oxazolidinone 3b. To a solution of 880 mg (2.0 mmol) of the compound **3b** in 30 ml of ethanol, 3 ml of concentrated hydrochloric acid and 1 ml of water were added. The mixture was refluxed for 20 hr, extracted (benzene), dried (Na_2SO_4), concentrated *in vacuo*, and chromatographed to give

355 mg (69%) of 2-hydroxy-2,2-diphenylethanamide, 133 mg (23%) of 2-ethoxy-2,2-diphenylethanamide, 90 mg (21%) of diphenylacetic acid, and 200 mg (41%) of ethyl diphenylacetate.

2-Hydroxy-2,2-diphenylethanamide was obtained as colorless needles (from benzene–hexane): mp 105–106°; ir (Nujol) 3340, 3200 (OH and NH), 1650 (C=O), and 1055 cm^{-1} (CO); nmr ($CDCl_3$) δ 1.06 (t, 3, J = 7.5 Hz, CH_3), 3.23 (double q, 2, $J(CH_3)$ = 7.5 Hz, J(NH) = 6.0 Hz, CH_2), 6.4 (broad, 1, OH), 7.0–7.6 (m, 11, Ph and NH); the signal assigned to the hydroxy proton appeared very near that of 2-hydroxy-2-phenylacetic acid and was not completely removed by addition of deuterium oxide, showing the existence of strong hydrogen bonding; mass spectrum (70 eV) m/e 255 (M^+, calcd 255), 183 (Ph_2COH^+), 105 ($PhCO^+$).

Anal. Calcd for $C_{16}H_{17}NO_2$: C, 75.27; H, 6.71; N, 5.49. Found: C, 75.46; H, 6.73; N, 5.57.

2-Ethoxy-2,2-diphenylethanamide was obtained as colorless needles (from benzene–hexane): mp 86.5–87.5°; ir (Nujol) 3300 (NH), 1648 (C=O), and 1068 cm^{-1} (CO); nmr ($CDCl_3$) δ 1.15 (t, 3, J = 7.1 Hz, CH_3), 1.19 (t, 3, J = 6.8 Hz, CH_3), 3.09 (q, 2, J = 7.1 Hz, OCH_2), 3.32 (double q, 2, $J(CH_3)$ = 6.8 Hz, J(NH) = 7.8 Hz, NCH_2), 7.0–7.7 (m, 11, Ph and NH); mass spectrum (70 eV) m/e 283 (M^+, calcd 283), 211 (Ph_2COEt^+), 183 (Ph_2COH^+), 105 ($PhCO^+$).

Anal. Calcd for $C_{18}H_{21}NO_2$: C, 76.29; H, 7.47; N, 4.94. Found: C, 76.28; H, 7.52; N, 5.01.

Diphenylacetic acid and ethyl diphenylacetate were identified with authentic samples.

Reaction of α-Phenyl-*N*-*tert*-butylnitrone. To a solution of the ketene **2** (3.0 g, 15 mmol) in benzene (5 ml), a solution of the nitrone (2.7 g, 15 mmol) in benzene (10 ml) was added dropwise over 20 min at 80°. The mixture was maintained at 80° for another 5 hr, just as the conditions in the reaction of the oxaziridine **1f**. An ir spectrum of the mixture did not show the formation of *N*-*tert*-butylbenzamide. Then the mixture was concentrated and chromatographed to give 2.1 g (43%) of 1-*tert*-butyl-3,3,4-triphenylazetidin-2-one (**31**) as colorless plates (from benzene–ethanol): mp 131–132°; ir (Nujol) 1730 cm^{-1} (C=O); nmr ($CDCl_3$) δ 1.33 (s, 9, *t*-Bu), 5.34 (s, 1, CH), 6.8–7.7 (m, 15, 3 Ph); mass spectrum (70 eV) m/e 355 (M^+, calcd 355), 298 (M^+ − Bu), 256 (M^+ − BuNCO), 194 (Ph_2CCO^+), 178 ($PhCCPh^+$).

Anal. Calcd for $C_{25}H_{25}NO$: C, 84.47; H, 7.09; N, 3.94. Found: C, 84.60; H, 7.09; N, 3.89.

The azetidinone was also given by the reaction of the ketene with an excess amount of *N*-*tert*-butylbenzylidenamine under similar conditions.

B. Reaction with Isocyanate. Reaction of the Oxaziridine 1c. A mixture of the oxaziridine **1c** (6.2 g, 38 mmol, AO 92%), phenyl isocyanate (**9**, 4.5 g, 38 mmol), and 8 ml of benzene was sealed in a 50-ml glass tube and allowed to stand for 25 hr at 85°. The reaction mixture was concentrated *in vacuo* and chromatographed to give 3.8 g (36%) of 2-*n*-butyl-3,4-diphenyl-1,2,4-oxadiazolidin-5-one (**10c**). When the reaction was carried out according to the same procedure as the following runs, the yield of **10c** was slightly low. The oxadiazolidinone **10c** was recrystallized from benzene–hexane to give colorless needles: mp 114–115°; ir (Nujol) 1738 cm^{-1} (C=O); mass spectrum (70 eV) m/e 296 (M^+, calcd 296), 252 ($M^+ - CO_2$ or $CH_3CH{=}CH_2$), 180 ($PhN{=}CPh^+$).

Anal. Calcd for $C_{18}H_{20}N_2O_2$: C, 72.94; H, 6.80; N, 9.45. Found: C, 72.65; H, 6.72; N, 9.47.

Reaction of the Oxaziridine 1d. To a solution of the oxaziridine **1d** (6.0 g, 30 mmol, AO 90%) in the same portion of benzene, the isocyanate **9** (3.1 g, 26 mmol) was added dropwise with stirring and the mixture was refluxed for 13 hr until the characteristic ir absorption of the isocyanate at about 2300 cm^{-1} disappeared. The mixture was cooled and the precipitate was recrystallized to give 7.05 g (95%) of 2-isopropyl-3,4-diphenyl-1,2,4-oxadiazolidin-5-one (**10d**) as colorless needles (from benzene–hexane): mp 140–141.5°; ir (Nujol) 1738 cm^{-1} (C=O); mass spectrum (70 eV) m/e 282 (M^+, calcd 282), 239 (M^+ − Pr), 238 ($M^+ - CO_2$ or $CH_3CH{=}CH_2$), 180 ($PhN{=}CPh^+$), 163 (M^+ − PhNCO).

Anal. Calcd for $C_{17}H_{18}N_2O_2$: C, 72.32; H, 6.43; N, 9.92. Found: C, 72.45; H, 6.39; N, 9.86.

The reaction between the oxaziridine **1d** (3.9 g, 22 mmol, AO 91%) and the isocyanate **9** (5.1 g, 43 mmol) in anisole for 25 hr gave 3.05 g (53%) of the oxadiazolidinone **10d** and considerable amounts of phenyl isocyanate trimer, *N*,*N*′-diphenylurea, and unreacted isocyanate **9**.

In acetonitrile, the oxaziridine **1d** (5.2 g, 30 mmol, AO 91%) and the isocyanate **9** (7.2 g, 30 mmol) gave 0.45 g (5%) of the oxadiazolidinone **10d**. Unreacted oxaziridine **1d** (4.15 g, 22 mmol, AO 88%) and the isocyanate **9** (1.20 g) were recovered by distillation and 4.12 g of isocyanate trimer and 1.20 g of the mixture of *N*,*N*′-diphenylurea and the trimer.

Reaction of the Oxaziridine 1d with *n*-Butyl Isocyanate (9′). After a solution of the oxaziridine **1d** (6.0 g, 36 mmol, AO 98%) and the isocyanate **9′** (2.5 g, 25 mmol) in benzene was refluxed for 17 hr, the mixture was distilled under reduced pressure to give 1.7 g of excess oxaziridine **1d** and a small amount of benzaldehyde. The residue was chromatographed to give 1.55 g (24%) of 2-isopropyl-4-*n*-butyl-3-phenyl-1,2,4-oxadiazolidin-5-one (**10′d**) as colorless needles (from benzene–hexane): mp 73–74°; ir (Nujol) 1742 cm^{-1} (C=O); mass spectrum (70 eV) m/e 262 (M^+, calcd 262), 218 ($M^+ - CO_2$ or $CH_3CH{=}CH_2$), 163 (M^+ − PhNCO).

Anal. Calcd for $C_{15}H_{22}N_2O_2$: C, 68.67; H, 8.45; N, 10.68. Found: C, 68.45; H, 8.46; N, 10.53.

Reaction of the Oxaziridine 1f. The reaction of 5.0 g (28.5 mmol, AO 99%) of the oxaziridine **1f** and 3.4 g (28.5 mmol) of the isocyanate **9** was carried out by the same procedure as above. Upon cooling, 7.95 g (94%) of 2-*tert*-butyl-3,4-diphenyl-1,2,4-oxadiazolidin-5-one (**10f**) was isolated. The oxadiazolidinone **10f** was identical with the adduct of α-phenyl-*N*-*tert*-butylnitrone and the isocyanate **9**.[11] The compound **10f** was recrystallized from benzene–hexane to afford colorless needles: mp 201–202°; ir (Nujol) 1738 cm^{-1} (C=O); nmr ($CDCl_3$) δ 1.28 (s, 9, *t*-Bu), 5.90 (s, 1, CH), 7.0–7.8 (m, 10, 2 Ph); mass spectrum (70 eV) m/e 296 (M^+, calcd 296), 252 ($M^+ - CO_2$), 240 ($M^+ - Me_2C{=}CH_2$), 180 ($PhN{=}CPh^+$), 177 (M^+ − PhNCO).

Anal. Calcd for $C_{18}H_{20}N_2O_2$: C, 72.94; H, 6.80; N, 9.45. Found: C, 72.69; H, 6.72; N, 9.40.

Reaction of the Oxaziridine 1i. To a solution of the oxaziridine **1i** (7.0 g, 30 mmol, AO 93%) in toluene (20 ml), the isocyanate **9** (3.57 g, 30 mmol) was added dropwise and the mixture was refluxed for 7 hr. The isocyanate **9** was recovered quantitatively. The residue was chromatographed to give 4.2 g (60%) of 2,2-pentamethylene-5-phenyl-1,3,4-dioxazoline (**15**): bp 95° (0.005 mm); ir (neat) 1618 (C=N), 1112 and 1072 cm^{-1} (CO); mass spectrum (70 eV) m/e 217 (M^+, calcd 217), 188 (M^+ − Et), 174 (M^+ − Pr), 119 ($M^+ - C_6H_{10}O$), 98 ($C_6H_{10}O^+$).

Hydrolysis and Pyrolysis of the Oxadiazolidinone 10f. To a solution of the oxadiazolidinone **10f** (1.0 g, 3.4 mmol) in ethanol (40 ml), aqueous potassium hydroxide solution was added. The mixture was refluxed for 5 hr, followed by extraction (benzene), drying (Na_2SO_4), and concentration, which gave 0.50 g (59%) of *N*-*tert*-butyl-*N*′-phenylbenzamidine (**14**). Recrystallization (benzene–hexane) gave colorless needles: mp 113.5–114°; ir (Nujol) 3520 (NH) and 1614 cm^{-1} (C=N); mass spectrum (70 eV) m/e 252 (M^+, calcd 252), 196 [$PhC(NH_2){=}NPh^+$], 180 ($PhN{=}CPh^+$); nmr ($CDCl_3$) δ 1.55 (s, 9, *t*-Bu), 4.0–4.6 (broad, 1, NH), 6.4–7.2 (m, 10, 2 Ph).

When the oxadiazolidinone **10f** was pyrolyzed under nitrogen stream, CO_2 evolved, which was detected with an aqueous solution of barium hydroxide, and the ir spectrum of the residue showed the formation of the amidine **14** with some other materials.

C. Reaction with Carbodiimide. All reactions were carried out by the same procedure as the reaction of the oxaziridine **1a**.

Reaction of the Oxaziridine 1a. To a solution of diphenylcarbodiimide (**16**, 15.5 g, 80 mmol) in a small portion of benzene, the oxaziridine **1a** (5.4 g, 36 mmol, AO 90%) was added dropwise at 110° until ir absorption of N=C=N disappeared. After 1.5 hr, the reaction mixture was distilled to give 3.7 g (97%) of benzaldehyde. The residue was chromatographed to give 9.2 g (62%) of 1,3-diphenyl-2,4-bis(phenylimino)hexahydro-1,3,5-triazine (**17a**). The hexahydrotriazine **17a** was recrystallized from methanol to give colorless needles: mp 148°; ir (Nujol) 1640 and 1611 (C=N), 3340 and 1580 cm^{-1} (NH); nmr ($CDCl_3$) δ 4.93 (broad s, 2, CH_2), 5.3–5.8 (broad, 1, NH), 6.2–7.6 (m, 20, 4 Ph); the second signal disappeared upon addition of deuterium oxide: mass spectrum (70 eV) m/e 417 (M^+, calcd 417), 387 ($M^+ - NH_2CH_2$), 325 (M^+ − PhNH), 311 (M^+ − $PhNCH_2NH$), 297 [$PhN(C{=}NPh)_2^+$], 249 (M^+ − Ph − PhN), 223 (M^+ − PhNCNPh).

Elemental analysis of **17a** did not give a satisfactory result, as it was very hygroscopic.

Reaction of the Oxaziridine 1b. The reaction mixture of the oxaziridine **1b** (4.6 g, 29 mmol, AO 94%) and the carbodiimide **16** (7.5 g, 39 mmol) was poured into ether to separate 7.3 g (88%) of 6-methyl-1,3-diphenyl-2,4-bis(phenylimino)hexahydro-1,3,5-triazine (**17b**), which was recrystallized from benzene–ethanol to give colorless needles: mp 174–174.5°; ir (Nujol) 1660 and 1622 (C=N), 3440 and 1585 cm^{-1} (NH); nmr ($CDCl_3$) δ 1.84 (d, 3, J = 6.0 Hz, CH_3), 5.14 (q, 1, J = 6.0 Hz, CH), 4.8–5.3 (broad, 1, NH), 6.1–7.8 (m, 20, 4 Ph); the third signal disappeared upon addition of deu-

terium oxide; mass spectrum (70 eV) m/e 431 (M^+, calcd 431), 416 ($M^+ - CH_3$), 388 ($M^+ - NHCHCH_3$), 339 ($M^+ - PhNH$), 313 ($M^+ - PhNCNH$), 286 [PhNHC(NPh)=NPh$^+$], 237 ($M^+ - PhNCNPh$).

Anal. Calcd for $C_{28}H_{25}N_5$: C, 77.93; H, 5.84; N, 16.23. Found: C 78.20; H, 5.89; N, 16.10.

Reaction of the Oxaziridine 1c. From the oxaziridine **1c** (5.0 g, 24 mmol, AO 87%) and the carbodiimide **16** (4.8 g, 24 mmol), 1.0 g (76%) of benzaldehyde and 3.3 g (58%) of 6-*n*-propyl-1,3-diphenyl-2,4-bis(phenylimino)hexahydro-1,3,5-triazine (**17c**) were obtained. In the case of the mole ratio of the oxaziridine **1c** to the carbodiimide **16** of 0.5, the yield of the hexahydrotriazine **17c** increased. The reaction of **1c** (4.4 g, 22 mmol, AO 84%) with the carbodiimide **16** (9.7 g, 50 mmol) gave 8.1 g (85%) of the crude product **17c**. The filtrate was distilled to give 2.1 g (92%) of benzaldehyde. The compound **17c** was recrystallized from methanol to afford colorless needles: mp 154°; ir (Nujol) 1660 and 1616 (C=N), 3480 and 1580 cm^{-1} (NH); nmr ($CDCl_3$) δ 1.34 (t, 3, J = 6.0 Hz, CH_3), 1.5-2.4 (m, 4, 2 CH_2), 4.6-5.2 (broad, 2, CH and NH), 6.3-7.6 (m, 20, 4 Ph); mass spectrum (70 eV) m/e 459 (M^+, calcd 459), 416 ($M^+ - Pr$), 312 ($M^+ - PhNHCHPr$), 265 ($M^+ - PhNCNPh$).

Anal. Calcd for $C_{30}H_{29}N_5$: C, 78.40; H, 6.30; N, 15.24. Found: C, 78.30; H, 6.55; N, 15.27.

Reaction of the Oxaziridine 1d. By the same treatment of the oxaziridine **1d** (3.1 g, 19 mmol, AO 98%) and the carbodiimide **16** (3.7 g, 19 mmol), 1.53 g (56%) of *N,N',N''*-triphenylguanidine (**19**) was obtained. The guanidine was identical with an authentic sample prepared from the carbodiimide **16** and aniline, mmp 147.5-149°.

Reaction of the Oxaziridine 1f. A mixture of the oxaziridine **1f** (8.9 g, 50 mmol, AO 99%) and the carbodiimide **16** (9.8 g, 51 mmol) was allowed to react for 3 hr at 110°. The ir spectrum of the reaction mixture showed neither the absorption of N=C=N nor that of benzaldehyde. The mixture was then chromatographed to give 15.8 g (72%) of 2-*tert*-butyl-3,4-diphenyl-5-phenylimino-1,2,4-oxadiazolidine (**20**) and 0.25 g (2%) of the oxadiazolidinone **10f**. The former was identical with the adduct of α-phenyl-*N*-*tert*-butylnitrone and diphenylcarbodiimide.[13] The latter probably arose as a result of hydrolysis of the azomethine function during chromatography.

Reactions of the Oxaziridines 1g and 1h. The oxaziridine **1g** (7.4 g, 35 mmol, AO 90%) reacted with the carbodiimide **16** (15.0 g, 77 mmol) to give 17.4 g (100%) of the crude hexahydrotriazine **17c**. The filtrate was distilled to give 3.3 g (79%) of benzaldehyde. The same triazine was obtained in 52% yield (6.0 g) in the reaction of the oxaziridine **1h** (5.7 g, 25 mmol, AO 63%) with the carbodiimide **16** (9.7 g, 50 mmol). In this reaction, 1.4 g (78%) of methyl ethyl ketone was obtained by distillation.

Acidic Hydrolysis of the Hexahydrotriazine 17b. To a solution of 2.0 g (4.6 mmol) of the compound **17b** in 30 ml of ethanol, 6 ml of 6 *N* hydrochloric acid was added and the mixture was refluxed for 4.5 hr. The mixture was then allowed to stand overnight to precipitate colorless crystals. The solid was filtered off (0.78 g) and the filtrate was concentrated to give the same solid (0.90 g). The combined solid was recrystallized (ethanol-benzene) to give 1.19 g (58%) of 1,2,3,4-tetraphenylbiguanide hydrochloride and 0.16 g (8%) of *N,N'*-diphenylurea. The hydrochloride was treated with aqueous potassium hydroxide in refluxing ethanol to afford 1,2,3,4-tetraphenylbiguanide (**18**) and a small amount of *N,N'*-diphenylurea.

Biguanide **18** was obtained as colorless needles (from benzene): mp 138.5-140°; ir (Nujol) 3380 (NH), 1605, 1575 (sh), and 1560 cm^{-1} (NH and C=N); mass spectrum (70 eV) m/e 405 (M^+, calcd 405), 313 ($M^+ - PhNH$), 287 ($M^+ - PhNCNH$), 211 [PhNHC(NH_2)NPh$^+$], 194 (PhNCNPh$^+$).

Anal. Calcd for $C_{26}H_{23}N_5$: C, 77.01; H, 5.72; N, 17.27. Found: C, 76.91; H, 5.68; N, 16.92.

Biguanide hydrochloride was obtained as colorless granules (from ethanol-benzene): mp 204-208°; ir (Nujol) 3600-3300 (broad), 3180, 1634, 1610, 1565 (strong), and 1530 cm^{-1}.

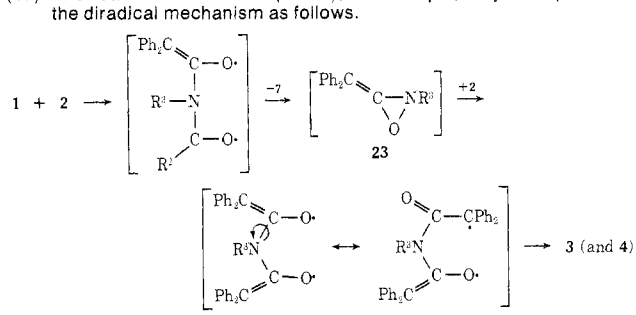
Anal. Calcd for $C_{26}H_{24}N_5Cl$: C, 70.67; H, 5.47; N, 15.91. Found: C, 70.34; H, 5.27; N, 15.81.

Acknowledgment. We gratefully acknowledge the valuable assistance of Messrs. Kiyoshi Yasuda and Kenji Mutoh in connection with this research.

Registry No.—**2,** 525-06-4; **4b,** 50484-22-5; **5b,** 50484-23-6; **5e,** 50484-12-3; **6b,** 50484-25-8; **14,** 50484-26-9; **15,** 2290-00-8; **16,** 622-16-2; **18,** 50484-28-1; **18** HCl, 50484-29-2; **31,** 50484-30-5; 2-hydroxy-2,2-diphenylethanamide, 10012-56-3; 2-ethoxy-2,2-diphenylethanamide, 50484-13-4; α-phenyl-*N*-*tert*-butylnitrone, 3376-24-7.

References and Notes

(1) K. Gulbins and K. Hamann, *Chem. Ber.*, **94,** 3287 (1961).
(2) R. Oda, S. Muneimiya, and M. Okano, *J. Org. Chem.*, **26,** 1341 (1961).
(3) K. Gulbins and K. Hamann, *Angew. Chem.*, **70,** 705 (1958); G. Speranza and W. Peppel, *J. Org. Chem.*, **23,** 1922 (1958); K. Gulbins, G. Benzing, R. Meisenhölder, and K. Hamann, *Chem. Ber.*, **93,** 1975 (1960); M. L. Weiner, *J. Org. Chem.*, **26,** 951 (1961).
(4) K. Gulbins and K. Hamann, *Justus Liebigs Ann. Chem.*, **698,** 180 (1966).
(5) Y. Ohshiro, T. Minami, K. Yasuda, and T. Agawa, *Tetrahedron Lett.*, 259 (1969).
(6) M. Komatsu, Y. Ohshiro, K. Yasuda, S. Ichijima, and T. Agawa, *J. Org. Chem.*, **39,** 957 (1974).
(7) T. B. Patrick and P. H. Patrick, *J. Amer. Chem. Soc.*, **95,** 5192 (1973).
(8) Y. Ohshiro, T. Minami, K. Yasuda, and T. Agawa, *Tetrahedron Lett.*, 263 (1969).
(9) (a) A. W. Dox, *J. Amer. Chem. Soc.*, **47,** 1471 (1925); (b) W. Rohr, R. Swoboda, and H. A. Staab, *Chem. Ber.*, **101,** 3491 (1968).
(10) E. Schmitz, S. Schramm, and R. Ohme, *J. Prakt. Chem.*, **36,** 86 (1967); *Chem. Abstr.*, **67,** 82137 (1967).
(11) S. Seidle, R. Huisgen, and R. Grashey, *Chem. Ber.*, **102,** 926 (1969); E. Beckmann, *ibid.*, **23,** 3332 (1890); **27,** 1957 (1894); H. Goldschmidt, *ibid.*, **23,** 2746 (1890).
(12) E. Schmitz and S. Schramm, *Chem. Ber.*, **100,** 2593 (1967).
(13) M. Komatsu, Y. Ohshiro, and T. Agawa, *J. Org. Chem.*, **37,** 3192 (1972).
(14) J. S. Splitter and M. Calvin, *Tetrahedron Lett.*, 1455 (1968).
(15) W. D. Emmons, *J. Amer. Chem. Soc.*, **79,** 5739 (1957).
(16) H. Quast and E. Schmidt, *Angew. Chem.*, **81,** 429 (1969).
(17) The reaction **1** + **2** → **3** (and **4**), for example, may be explained by the diradical mechanism as follows.



(18) R. A. Firestone, *J. Org. Chem.*, **37,** 2181 (1972); **33,** 2285 (1968); *J. Chem. Soc. A*, 1570 (1970).
(19) J. W. Linnet, "The Electronic Structure of Molecules," Metheun, London, 1964; *J. Amer. Chem. Soc.*, **83,** 2643 (1961); R. A. Firestone, *Tetrahedron Lett.*, 971 (1968); *J. Org. Chem.*, **34,** 2621 (1969); **36,** 702 (1971).
(20) R. Huisgen, *J. Org. Chem.*, **33,** 2291 (1968).
(21) H. Staudinger, *Chem. Ber.*, **44,** 1619 (1911).
(22) Y. Ohshiro, Y. Mori, T. Minami, and T. Agawa, *J. Org. Chem.*, **35,** 2076 (1970).
(23) R. G. Pews, *J. Org. Chem.*, **32,** 1628 (1967).
(24) E. Schmitz, R. Ohme, and S. Schramm, *Tetrahedron Lett.*, 1857 (1965).
(25) Recently, S. Toppet and his coworkers reported the same compound (**3c**): S. Toppet, G. L'abbe, and G. Smets, *Chem. Ind. (London)*, 1110 (1973).