Reaction of Diaziridines with Diphenylketene and Isocyanates

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The reactions of 1,2,3-trialkyldiaziridines **1** with diphenylketene, phenyl isocyanate, and benzoyl isocyanate were studied. The products of **1** with diphenylketene were acyclic 1:2 adducts, *N*-alkyl-*N*-(1-alkylamino-2-alkyl-3-oxo-4,4-diphenylbut-1-en-1-yl)diphenylacetamides **3**. The products of **1** with benzoyl isocyanate were triazolidinones **15**. With phenyl isocyanate, reactions of **1** were complicated. Mechanisms for these reactions were suggested.

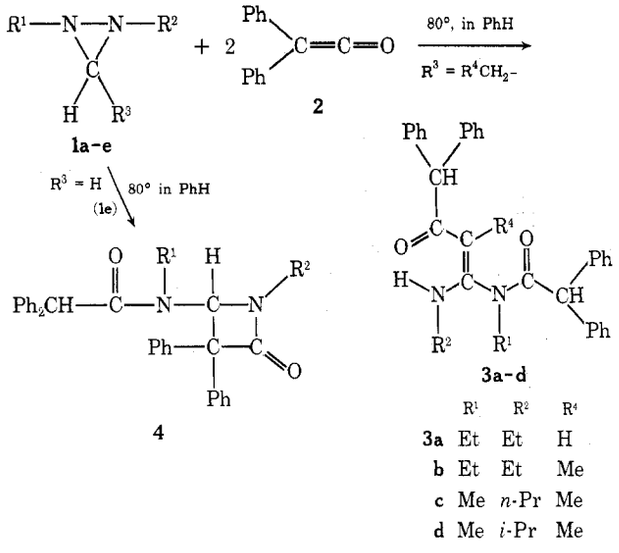
In contrast to the widely investigated chemistry of three-membered heterocycles such as oxiranes and aziridines, chemical properties of three-membered rings containing two heteroatoms such as diaziridines and oxaziridines have been less known. Their preparation and behaviors in some typical reactions (hydrolysis, reduction, acylation, rearrangement, etc.) have been reported by Schmitz and his coworkers, but there are few reports on their synthetic applications.[1]

We previously reported that the reactions of oxaziridines with heterocumulenes result in five- or six-membered heterocyclic compounds. In the reactions, oxaziridines undergo 1,3-cycloaddition in some cases and, in other cases, form unstable three-membered intermediates, which in turn decompose or react with additional cumulenes, followed by elimination of carbonyl compounds. Thus a new aspect of the chemistry of oxaziridines has been established.[2,3]

We have now compared the behavior of diaziridines with that of oxaziridines[2] or aziridines[4] toward heterocumulenes. As we have stated in a preliminary report,[5] diaziridines react with diphenylketene in a completely different manner from those of other three-membered heterocycles. In this paper, reactions with heterocumulenes as well as mechanistic discussion are described.

Results

Reaction with Diphenylketene. 1,2,3-Trialkyldiaziridines **1a–d** reacted with diphenylketene (**2**) in refluxing benzene to give the acyclic 1:2 adducts, *N*-alkyl-*N*-(1-alkylamino-2-alkyl-3-oxo-4,4-diphenylbut-1-en-1-yl)diphenylacetamides **3a–d**, while the 1,2-dialkyldiaziridine **1e** gave the azetidinone derivative **4**. These products would not be anticipated from the known reactions of oxiranes,[6,7] thiiranes,[8] or oxaziridines[2,3] with diphenylketene.



	R¹	R²	R⁴
3a	Et	Et	H
b	Et	Et	Me
c	Me	*n*-Pr	Me
d	Me	*i*-Pr	Me

Table I
Reaction of Diaziridines with Diphenylketene

	Diaziridine (1) R¹	R²	R³	Mole ratio 1:2[a]	Reaction[b] Temp, °C	Time, min	Product[c]	Yield, %
1a	Et	Et	Me	0.5	80	5	**3a**	6
1b	Et	Et	Et	0.5	80	5	**3b**	53
1b	Et	Et	Et	0.5	70	5	**3b**	32
1b	Et	Et	Et	1.0	80	5	**3b**	17
1c	Me	*n*-Pr	Et	0.5	80	5	**3c**	15
1c	Me	*n*-Pr	Et	0.5	45	5		
1d	Me	*i*-Pr	Et	0.5	80	5	**3d**	31
1e	Et	Et	H	0.5	80	5	**4**	26

[a] **2**: diphenylketene. [b] Benzene was employed as a solvent. [c] Considerable amounts of *N*-ethyldiphenylacetamide (**5**) and polymeric substances were also obtained and the latter remarkably increased in low-yield runs.

The results listed in Table I show that the reaction temperature should not be lower than 70°, since polymerization of the ketene is rather faster at such temperatures in the presence of the diaziridines. This was probably due to the action of the diaziridines as a basic catalyst. Even when equimolar quantities of diphenylketene and diaziridines were employed, only the 1:2 adduct **3** was isolated.

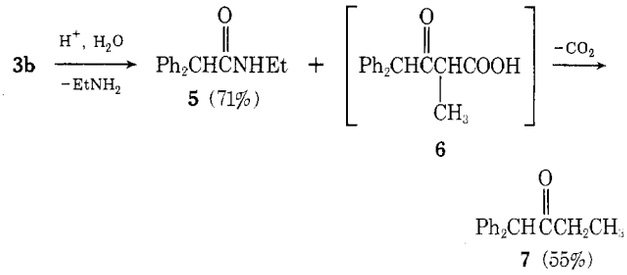
Mass spectra and analytical data show that the amide **3** is a 1:2 adduct of the diaziridine and the ketene, and the structure was confirmed satisfactorily by the spectral data (see Experimental Section and the preliminary report[5]). In the nmr spectra of the amides **3**, the signals due to the alkyl substituent R^3 in the starting materials **1a–d** could not be found but a singlet at δ 4.93 assignable to an olefinic proton (**3a**) or a singlet around δ 1.6 assignable to methyl protons adjacent to a vinyl group (**3b–d**) were found, indicating the migration of the two α-methylene protons of the 3-alkyl substituent. An exchangeable NH peak at δ 10–11 is consistent with that observed in other enamino ketones.[9] The amino function was inert to such acylating agents as acetyl chloride, acetic anhydride, diphenylketene, or phenyl isocyanate.

It should be also noted that highly complex multiplets were observed for the signals of *N*-methylene protons of the substituents R^1 and R^2 of **3a** and **3b**. The complexity derives from nonequivalence of the geminal protons of the methylene moiety adjacent to the nitrogens and is ascribable mainly to the sterically restricted free rotation of the carbon–nitrogen bonds. Similar nonequivalence is also found for the methylene group of **3c** or the two methyl groups of the isopropyl function of **3d**. These multiplets were successfully assigned with the aid of spin decoupling by double resonance.

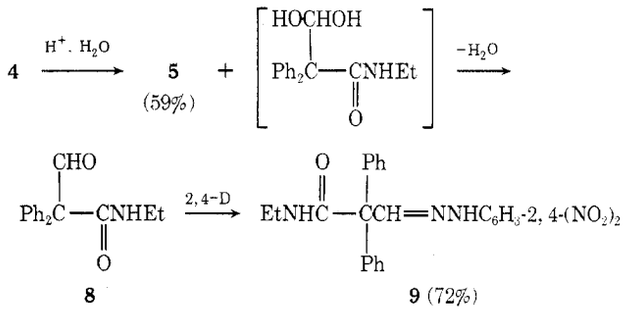
The two alkyl substituents R^1 and R^2 are easily distinguishable by observing the coupling with the amino pro-

tons. The substituent R^1 proved to be the less bulky one. It was also found that difference between the chemical shifts of the geminal methylene protons of R^1 is greater than that of R^2. The nmr spectrum of **3a** observed at higher temperature indicates reduction of rotational restriction; the two complex multiplets at δ 2.5–3.2 (three protons) and at δ 3.3–4.2 (one proton) observed at 23° in benzonitrile altered into a clear quartet at δ 2.96 (two protons) and a complex multiplet at δ 3.4–3.8 (two protons) at 120°.

Chemical evidence for the structure of **3** was obtained by the acidic hydrolysis of **3b,** which gave *N*-ethyldiphenylacetamide (**5**) and 1,1-diphenylbutan-2-one (**7**). The latter product is considered to be formed by decarboxylation of the initially produced β-ketocarboxylic acid **6.**



The β-lactam **4,** the main product of the reaction of 1,2-diethyldiaziridine (**1e**) which has no 3-alkyl substituent to participate in the reaction, is also a 1:2 adduct. The adduct shows strong ir absorptions at 1755 (lactam CO) and 1633 cm^{-1} (amide CO). The mass and nmr spectra are wholly compatible with the structure. Hydrolysis of the lactam **4** in refluxing aqueous ethanol in the presence of sulfuric acid gave the amide **5** and 2-ethylcarbamoyl-2,2-diphenylethanal (**8**), which was isolated as its 2,4-dinitrophenylhydrazone **9.** The hydrolysis probably occurs on the aminal-like linkage and is comparable to the hydrolysis of a β-amino-β-lactam which forms an α-carbamoylaldehyde.[10]



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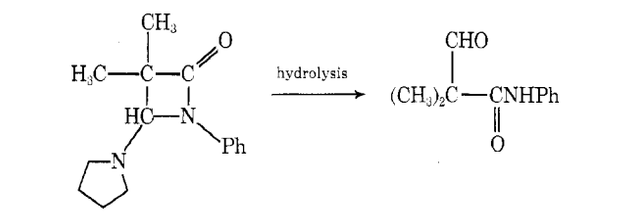
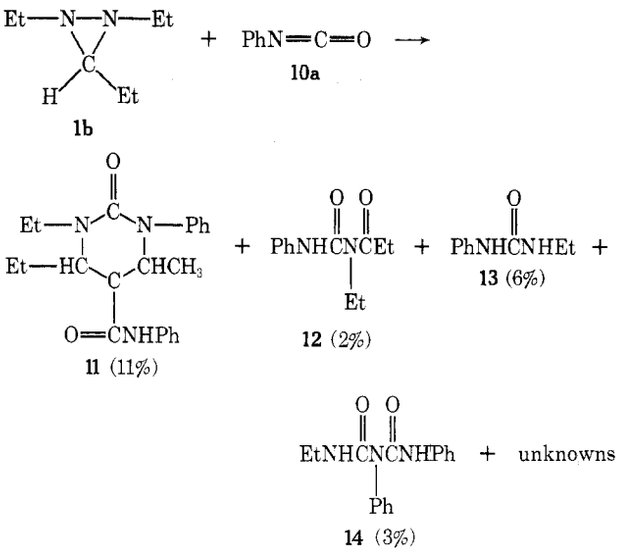
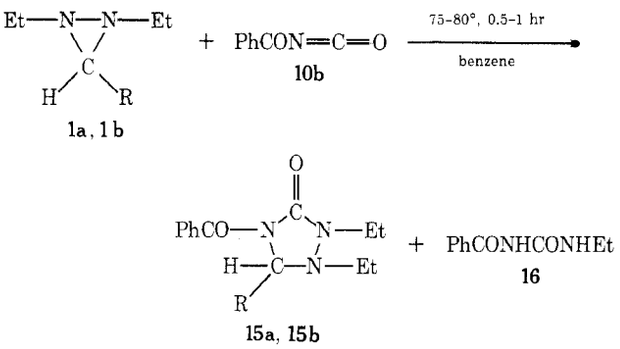


Reaction with Isocyanates. The reaction of 1,2,3-triethyldiaziridine (**1b**) with phenyl isocyanate (**10a**) in refluxing benzene or acetonitrile gave 2-methyl-5,6-diethyl-3-phenyl-1-phenylcarbamoylhexahydro-1,3,5-triazin-4-one (**11**), *N*-ethyl-*N*-propionyl-*N'*-phenylurea (**12**), *N*-ethyl-*N'*-phenylurea (**13**), and 1-ethyl-3,5-diphenylbiuret (**14**). The first compound **11** was proved to consist of 1 mol of the diaziridine **1b** and 2 mol of the isocyanate **10a** by elemental analysis and its molecular weight determined by mass spectroscopy. In the infrared spectrum, two strong absorption bands at 1685 and 1622 cm^{-1} (C=O) and an absorption at



3200 cm^{-1} (NH) were observed. In the nmr spectrum, the signals due to the EtCH moiety were found at δ 1.02 (triplet, 3, J = 7.5 Hz), 2.03 (pentuplet, 2, J = 7.5 Hz), and 5.44 (triplet, 1, J = 7.5 Hz). Nevertheless, only one of the *N*-ethyl functions was found as signals at δ 1.16 (triplet, 3, J = 7.1 Hz), 3.20 and 3.64 (double quartet, 1, J_{vic} = 7.1, J_{gem} = 14.2 Hz, NCH**H**– and NC**H**H–, respectively). A doublet at δ 1.35 (3, J = 6.0 Hz) and a quartet at δ 5.78 (1, J = 6.0 Hz) indicated that the other *N*-ethyl group in the starting diaziridine had been converted to a $-NCHCH_3$ moiety. The proton of the original *N*-ethyl group appeared as an NH proton whose signal was included in those of aromatic protons at δ 6.9–7.5. These spectral and mass spectral data (see Experimental Section) support the structure of **11,** and the other products were identified with authentic samples or confirmed by spectral and analytical data.

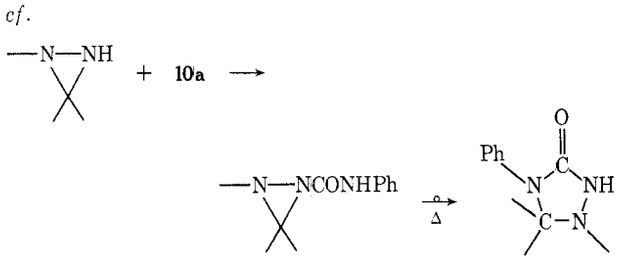
Because of the complexity of this reaction which might have been caused by the low reactivity of the isocyanate **10a** (reaction time 8–16 hr compared to 5 min for the ketene **2**), it was decided to employ benzoyl isocyanate (**10b**) in place of **10a.** The isocyanate **10b,** however, reacted with 1,2,3-trialkyldiaziridines **1a** and **1b** to give the 1:1 cycloadducts **15** and *N*-ethyl-*N'*-benzoylurea (**16**). This seems to be the first example of a cycloaddition reaction of a diaziridine.



	Yield, %	
	15	16
a, R = Me	30	18
b, R = Et	44	39

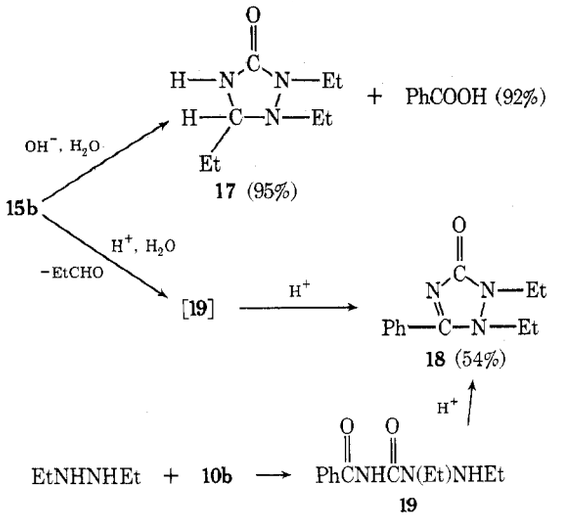
Though 1:1 cycloaddition of *N*-alkyloxaziridines to phenyl isocyanate[2] and addition reactions of N-substituted aziridines to the isocyanate under catalysis of lithium halide have been known, N,N'-dialkylated diaziridines do not undergo 1:1 cycloaddition with phenyl isocyanate or with diphenylketene. Nabeya and her coworkers recently reported

the anilinoformylation of 1,3-dialkyl-3-aryl- or 1-alkyl-3-aryldiaziridines with phenyl isocyanate and the rearrangement of the resulting 1-anilinoformyl-2-alkyl-3-aryldiaziridines to the isomeric triazolidinones.[12] Schmitz has also reported the formation of an anilinoformyl derivative of 1,3-dialkyldiaziridine and a triazolidinone from 1,3,3-trialkyldiaziridine,[13] showing subtle effects of the substituents. In view of Nabeya's results, the latter product is considered to be given not by a 1:1 cycloaddition but by a rearrangement of a labile anilinoformyldiaziridine.



The triazolidinones **15** show two strong carbonyl stretching vibrations at 1720 and 1650 cm^{-1} in their ir spectra. Fragmentations in the mass spectra and the nmr signals are also in good agreement with the structure of **15.** In the nmr spectra, the methylene protons of the ethyl group of the 2 position are nonequivalent (J_{gem} = 7.0 Hz), as is observed for the *N*-alkyl groups of the amides **3.**

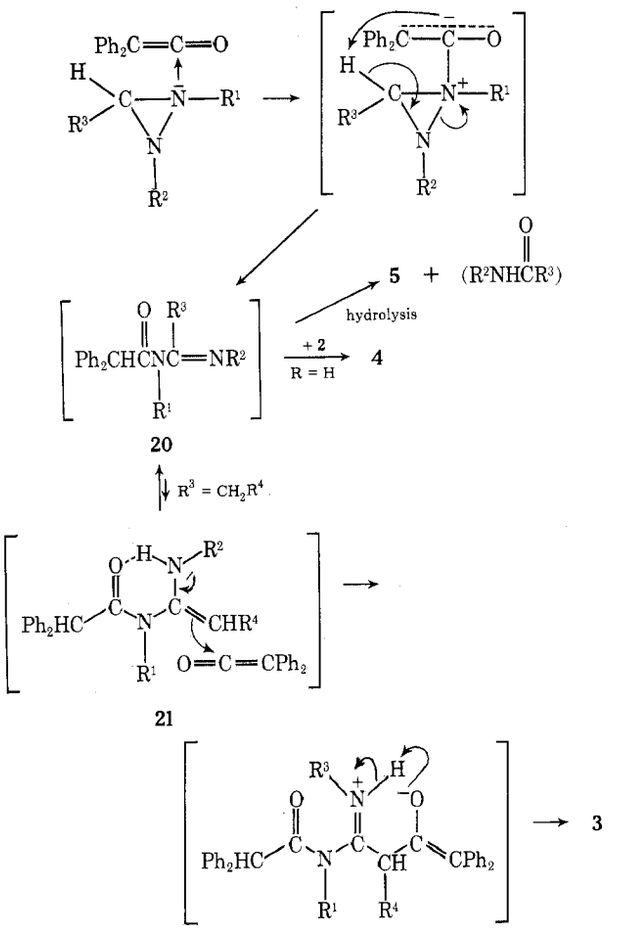
Hydrolysis of the 1:1 adduct **15b** gave further chemical evidence for the structure; alkaline hydrolysis gave 1,2,5-triethyl-1,2,4-triazolidin-3-one (**17**) and benzoic acid quantitatively, while acidic hydrolysis afforded 1,2-diethyl-5-phenyl-1,2,4-triazolin-3-one (**18**). The latter compound **18** is formed *via* the 4-acylsemicarbazide intermediate **19,** which was verified by the acidic treatment of the acylsemicarbazide **19** prepared from *N,N'*-diethylhydrazine and the isocyanate **10b.**[14]



Discussion

A possible mechanism for the reaction of 1,2-dialkyldiaziridines with diphenylketene involves a nucleophilic attack of the nitrogen atom of a diaziridine to a central carbon atom of a cumulative bond of the ketene **2** followed by ring opening and transfer of the hydrogen on the ring carbon, leading to an amidine-type intermediate **20**[30] (Scheme I). The intermediate **20** probably tautomerizes into a ketene aminal-type intermediate **21** if the substituent R^3 is a primary alkyl group and the latter intermediate **21** in turn attacks the ketene, affording the amide **3.** When the substituent R^3 is a hydrogen (*i.e.,* **1e**), the intermediate **20** cannot convert into the aminal-type intermediate **21.** In this case, **20** reacts with diphenylketene to give the β-lactam **4.** Similar cycloadditions of ketenes to azomethines, including benzamidine derivatives,[15] are known to give β-lactams, 1,3-oxazin-6-ones, or piperidine-2,4-diones.[16]

Scheme I



In the reactions of **1a–e** with **2,** a considerable amount of *N*-ethyldiphenylacetamide (**5**) was produced. The formation of **5** is ascribed to the hydrolysis of the intermediate **20.** The other reason for the low yields of the amides **3** is polymerization of the ketene catalyzed by the basic species in the system, *e.g.,* starting diaziridines.

Steric factors apparently are important in the addition of the diaziridine to the ketene, since it is the nitrogen bearing the least bulky substituent that adds to the carbonyl carbon of the ketene.

Our attempts to isolate the intermediate **20** from a reaction mixture containing equimolar quantities of the diaziridine and the ketene were in vain. As an alternative path to the intermediate **20,** the reaction of amidines **22,** isomers of the diaziridines **1,** with the ketene **2** was studied, since it is reasonable to expect the formation of **20** in this system.

The reactions of amidines instead of diaziridines under the same conditions resulted in the same products in better yields and the results (listed in Table II) apparently indi-

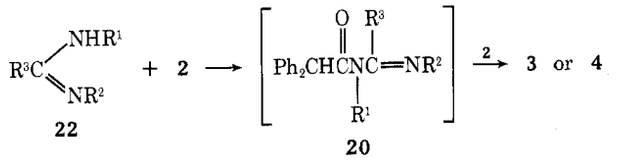
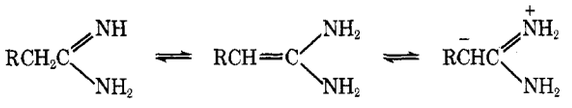


Table II
Reaction of Amidines with Diphenylketene

Amidine (22)				Reaction conditions[a]			
	R^1	R^2	R^3	Temp, °C	Time, min	Product	Yield, %
22a	Et	Et	Me	80	10	**3a**	12
22b	Et	Et	Et	80	10	**3b**	51
22e	Et	Et	H	70	10	**4**	63

[a] Benzene was employed as a solvent. Mole ratio of the amidine 22 to diphenylketene (2) was 0.5.

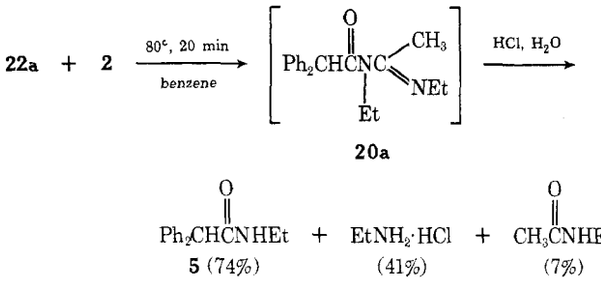
cate the intermediacy of **20.** The nucleophilicity of α carbons of amidines having α-methylene groups as is present in **20** has been reported by Schaefer and his coworkers in the reactions of amidines with *s*-triazines; the ketene aminal form of the amidine is postulated to be the reactive



species as our assumption in Scheme I.[17] In addition, ketene aminals have been reported to form linear 1:1 or 1:2 adducts when treated with ketenes[18] or isocyanates[19] in accord with the assumed mechanism. Similar equilibria between azomethines and enamines have been proved[20] and enamines having a hydrogen on their β carbons also give linear 1:1 adducts with heterocumulenes.[21]

Since attempts to isolate the amidine-type intermediate **20** by chromatography or vacuum distillation from the reaction mixtures were unsuccessful, the nature of these reaction mixtures was studied.

The infrared spectrum of the mixture obtained by treating the ketene **2** with an excess of *N,N'*-diethylacetamidine (**22a**) followed by removal of the excess **22a** showed an intense absorption at 1640 cm^{-1} and no absorption due to the 1:2 adduct. This mixture was hydrolyzed in the presence of hydrochloric acid and the resultant products imply that the main component of the mixture was the amidine **20a.**

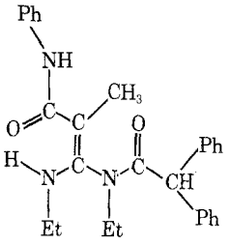


20a

5 (74%) (41%) (7%)

An equimolar mixture of *N,N'*-diethylpropioamidine (**22b**), the isomer of the diaziridine **1b,** and the ketene **2** in benzene was warmed to 80° for 1 min. The ir spectrum of the mixture showed a deep and broad absorption band at 1640 cm^{-1} and none of the bands due to the amide **3b.** The nmr spectrum of the mixture exhibited a sharp singlet at δ 5.6 assignable to the amino proton of the unreacted amidine **22b** and a singlet at δ 4.89 assignable to the methine proton of the diphenylacetyl moiety of the 1:1 adduct **20.** The reaction did not proceed so far in the state of this mixture. The spectrum was then taken soon after an additional 1 mol of the ketene had been added to this mixture. At this stage, the signal of the amino proton of the unreacted amidine diminished and the signals which coincided well with those of the 1:2 adduct **3b** increased in intensity. Though a considerable amount of the 1:1 adduct **20** was detected, none of the signals due to the aminal structure **21** (*e.g.*, a doublet of methyl protons of $C{=}CHCH_3$) was observed in the spectra. Thus the equilibrium between the intermediattattates is completely in favor of the amidine form **20.**

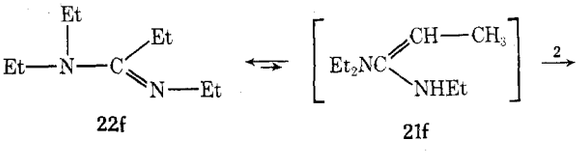
When the equimolar mixture of **22b** and **2** was treated with phenyl isocyanate instead of the ketene, the reaction was very slow and gave but a trace amount of the adduct **23,** corresponding to the amide **3.** This is consistent with



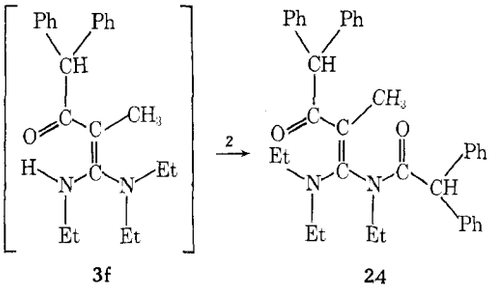
23

the result that the reaction of phenyl isocyanate (**10a**) with a diaziridine gave no 1:2 adduct corresponding to the amide **3** (or **23**).

The entire spectral and chemical evidence on the mixtures is a satisfactory rationale for the postulated mechanism. Furthermore, *N,N,N'*-triethylpropioamidine (**22f**), a model compound for the intermediate **20,** was allowed to react with the ketene **2** to give the amide **24** (12% yield), which is considered to be formed *via* the amide **3f** corresponding to the amide **3.** The low reactivity of the model compound **22f** compared with the intermediate **20** may be attributed to the lack of contribution of the hydrogen bonding in the form of the aminal-type intermediate **21f** in contrast to **21.** Though the amide **3f** further reacts with the ketene to give the amide **24,** the amino function of



22f **21f**

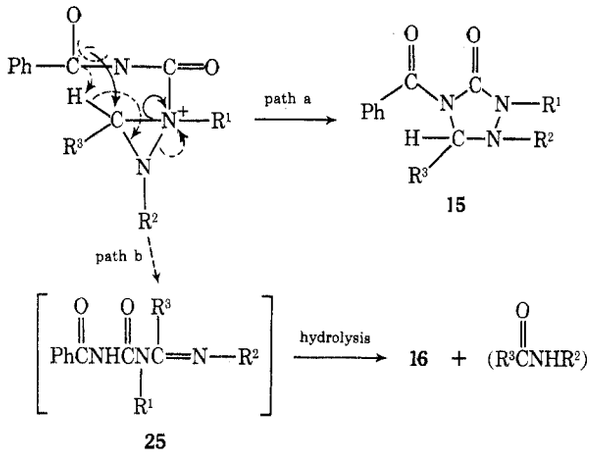


3f **24**

the amide **3** was not susceptible to the ketene or other acylating agents. This is because of replacement of an ethyl group by diphenylacetyl moiety that reduces the nucleophilicity of the amino nitrogen with its electron-withdrawing and steric hindrance.

In contrast to the reaction of diaziridines with diphenylketene, whereby the nitrogen–nitrogen bond of the ring is cleaved, diaziridines react with benzoyl isocyanate by rupture of the carbon–nitrogen bond of the ring (path a in Scheme II). The formation of the urea **16,** however, suggests hydrolysis of an amidine-type 1:1 adduct **25,**[30] which corresponds to the intermediate **20.** Hence, both fissions of the carbon–nitrogen and the nitrogen–nitrogen bonds were observed in this reaction. The difference from the reaction with the ketene **2** would be attributable to the higher basicity of the anion developed on the ketene upon nucleophilic attack of a diaziridine compared with the de-

Scheme II



localized one on the isocyanate **10b.** The more basic anion on the ketene will cause the exclusive hydrogen abstraction from the diaziridine which leads to the intermediate **20.**

In the case of phenyl isocyanate (**10a**), the situation is expected to be intermediate between the above two cumulenes. The products identified in the reaction with **10a** can be interpreted as depicted in Scheme III. Path b is similar to that for the other cumulenes and further reaction of the intermediate **25'** [30] to the hexahydrotriazinedione **27** is deducible from the reported reaction of formamidine and isocyanates.[22] The formation of the urea **12,** the urea **13,** and the biuret **14** is ascribable to hydrolysis of **25'** and **27,** respectively. Path c does not lead to a 1:1 cycloadduct but instead to the hexahydrotriazinone **28** as a result of a hydride shift. Such hydride shifts giving a hexahydrotriazine structure have been observed in the reaction of oxaziridines with diphenylcarbodiimide.[2] These hexahydrotriazine derivatives, including the intermediates, are generally unstable and their decomposition and further reactions with **10a** are also possible. For example, the intermediate **26** may be in equilibrium with ethyl isocyanate and *N*-ethyl-*N*-anilinoformyl-*N'*-propioamidine through a diazetidinone.[22] Hence, these complicated systems will make the reaction complex. The behavior of diaziridines, however, is similar to that in the reaction with the ketene showing the nitrogen–nitrogen bond cleavage.

Experimental Section

All melting points were determined on a Yanagimito micro melting point apparatus and are uncorrected. Infrared, nuclear magnetic resonance, and mass spectra were taken on a Jasco IR-E spectrophotometer, JEOL LNM-PS-100 and JEOL LNM-3H-60 spectrometers, and a Hitachi RMU-6E spectrometer, respectively.

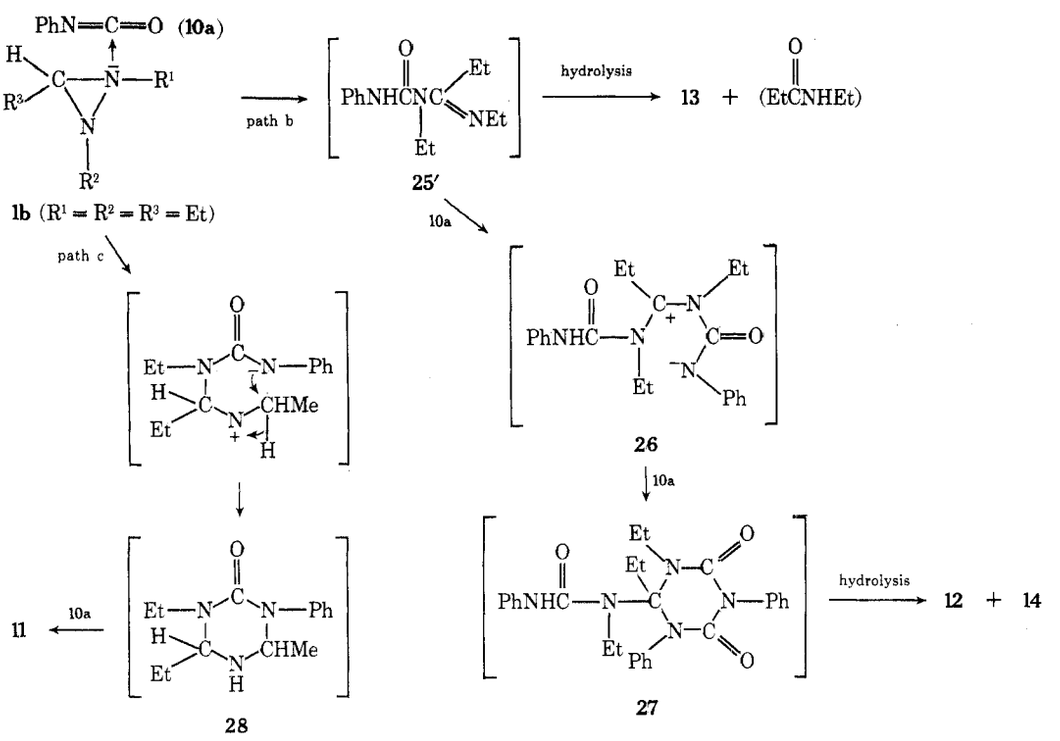
All reactions were carried out under a nitrogen stream in a 50-ml four-necked flask equipped with a stirrer, a reflux condenser, a dropping funnel, and a thermometer. Products were isolated by column chromatography (basic aluminum oxide–benzene).

Materials. Diphenylketene (**2**) and benzoyl isocyanate (**10b**) were prepared by known methods.[23,24] Commercially available phenyl isocyanate (**10a**) was used after distillation. Diaziridines **1a–e** were prepared according to Schmitz's procedures.[25] Boiling points, purities determined by iodometry[25] and glpc, and yields are as follows: 1,2-diethyl-3-methyldiaziridine (**1a**), 53–55° (70 mm), 90%, 14%; 1,2,3-triethyldiaziridine (**1b**), 56° (40 mm), 93%, 35%; 1-methyl-2-*n*-propyl-3-ethyldiaziridine (**1c**), 63° (60 mm), 93%, 16%; 1-methyl-2-isopropyl-3-ethyldiaziridine (**1d**), 74–77° (62 mm), 84%, 4%; 1,2-diethyldiaziridine (**1e**), 95°, 91%, 5%.

Preparations of the amidines **22a** and **22b** were done by a modified procedure of Brown[26] and the amidines **22e** and **22f** were prepared by known methods.[27,28] Boiling points, purities checked by glpc and nmr spectra, and yields are as follows: *N,N'*-diethylacetamidine (**22a**), 80° (30 mm), 98%, 61%; *N,N'*-diethylpropioamidine (**22b**), 88° (28 mm), 92%, 31%; *N,N'*-diethylformamidine (**22e**), 69° (20 mm), 92%, 24%; *N,N,N'*-triethylacetamidine (**22f**), 87° (27 mm), 96%, 33%.

Reaction with Diphenylketene (2). Reaction of the Diaziridine 1a. A solution of the ketene **2** (5.8 g, 30 mmol) in benzene (10 ml) was heated to 75° under a nitrogen atmosphere. Then 1,2-diethyl-3-methyldiaziridine (**1a,** 1.7 g, 15 mmol) was added dropwise with stirring at such a rate that the reaction temperature did not rise above 80°. The ir spectrum of the mixture showed disappearance of **2** in 5 min. The reaction mixture was concentrated and chromatographed to give 421 mg (6%) of *N*-ethyl-*N*-(1-ethylamino-3-oxo-4,4-diphenylbut-1-en-1-yl)diphenylacetamide (**3a**), a small amount of *N*-ethyldiphenylacetamide (**5**), and a large amount of viscous oil. The amide **3a** was recrystallized from benzene–ethanol to give colorless granules: mp 175–176°; ir (Nujol) 3350 (broad and weak, NH), 1655 (amide C=O), 1615 (C=O),

Scheme III



1582 (sh) and 1568 cm^{-1} (C=C or C=N); nmr ($CDCl_3$) δ 0.93 (t, J = 7.2 Hz, 3, CH_3), 1.10 (t, J = 7.0 Hz, 3, CH_3), 2.65 (ddq, J (*gem*) = 13.1, J (CH_3) = 7.2, J (NH) = 5.8 Hz, 1, HNCHH–), 2.97 (ddq, J (*gem*) = 13.1, J (CH_3) = 7.2, J (NH) = 5.8 Hz, 1, HNCHH–), 3.02 (dq, J (*gem*) = 14.0, J (CH_3) = 7.0 Hz, 1, NCHH–), 3.92 (dq, J (*gem*) = 14.0, J (CH_3) = 7.0 Hz, 1, NCHH–), 4.89 (s, 1, Ph_2CH), 4.96 (s, 1, C=CCH), 5.13 (s, 1, Ph_2CH), 6.9–7.5 (m, 20, 4 Ph), 10.3 (t, J = 5.8 Hz, 1, NH); mass spectrum (70 eV) *m/e* 502 (M^+, calcd 502), 335 ($M^+ - Ph_2CH$), 307 ($M^+ - Ph_2CHCO$), 264 ($M^+ -$ PhCHCONEt), 222 (Ph_2CCNEt^+), 194 (Ph_2CCO^+).

Anal. Calcd for $C_{34}H_{34}N_2O_2$: C, 81.24; H, 6.82; N, 5.57. Found: C, 81.00; H, 6.86; N, 5.81.

Reactions of the Diaziridine 1b. The diaziridine **1b** (0.93 g, 7.3 mmol) was treated with the ketene **2** (2.9 g, 15 mmol) in refluxing benzene for 5 min by the same procedure as above. The reaction mixture was concentrated to precipitate 1.99 g (53%) of crystalline *N*-ethyl-*N*-(1-ethylamino-2-methyl-3-oxo-4,4-diphenylbut-1-en-1-yl)diphenylacetamide (**3b**) and the residue was viscous oily materials. Recrystallization of the amide **3b** from benzene–hexane afforded colorless granules: mp 153–154°; ir (Nujol) 3400 (broad and weak, NH), 1668 (amide C=O), 1610 (C=O), 1580 (sh) and 1560 cm^{-1} (C=C or C=N); nmr ($CDCl_3$) δ 0.85 (t, J = 6.9 Hz, 3, CH_3), 1.11 (t, J = 7.1 Hz, 3, CH_3), 1.51 (s, 3, C=CCH_3), 2.60 (ddq, J (*gem*) = 13.2, J (CH_3) = 6.9, J (NH) = 5.5 Hz, 1, NHCHH–), 2.96 (ddq, J (*gem*) = 13.2, J (CH_3) = 6.9 Hz, 1, NHCHH–), 3.41 (dq, J (*gem*) = 14.3, J (CH_3) = 7.1 Hz, 1, NCHH–), 3.68 (dq, J (*gem*) = 14.3, J (CH_3) = 7.1 Hz, 1, NCHH–), 4.86 (s, 1, Ph_2CH), 5.38 (s, 1, Ph_2CH), 6.9–7.6 (m, 20, 4 Ph), 11.3 (t, J = 5.5 Hz, 1, NH); mass spectrum (70 eV) *m/e* 516 (M^+, calcd 516), 349 ($M^+ - Ph_2CH$), 321 ($M^+ - Ph_2CHCO$), 278 ($M^+ - Ph_2 -$ CHCONEt), 221 (Ph_2CCNEt^+), 194 (Ph_2CCO^+).

Anal. Calcd for $C_{35}H_{36}N_2O_2$: C, 81.36; H, 7.02; N, 5.42. Found: C, 81.59; H, 7.11; N, 5.49.

When the reaction temperature was a little lower (70°), the yield of the amide **3b** decreased; from 2.1 g (16 mmol) of **1b** and 6.1 g (31 mmol) of **2**, 2.56 g (32%) of the amide **3b** was obtained. An equimolar reaction also gave the amide in a low yield: 1.25 g (17%) of **3b** was obtained from the reaction mixture of 5.7 g (29 mmol) of **2** and 3.9 g (30 mmol) of **1b** treated at 80° for 5 min. The amide **3b** was isolated by column chromatography in the latter two reactions and 50–100 mg of the amide **5** and large amount of polymeric substances were obtained.

Reactions of the Diaziridine 1c. The same treatment (80°, 5 min) of the diaziridine **1c** (1.9 g, 15 mmol) and the ketene **2** (5.2 g, 27 mmol) as in the above reactions gave 1.02 g (15%) of *N*-methyl-*N*-(1-*n*-propylamino-2-methyl-3-oxo-4,4-diphenylbut-1-en-1-yl)-diphenylacetamide (**3c**) and polymeric materials with a small amount of the amide **5**.

When the reaction was carried out at 45°, the infrared spectrum of the reaction mixture showed the rapid consumption of **2** and the formation of a large amount of poymers of **2**.

The amide **3c** was recrystallized from benzene–hexane to give colorless granules: mp 110–111°; ir (Nujol) 3350 (broad and weak, NH), 1665 (amide C=O), 1612 (C=O), 1580 (sh) and 1562 cm^{-1} (C=C or C=N); nmr ($CDCl_3$) δ 0.71 (t, J = 7.4 Hz, CH_3), 1.52 (s, 3, C=CCH_3), 1.57 (dq, J (CH_2) = 6.6, J (CH_3) = 7.4 Hz, 2, CH_2CH_3), 2.58 (ddt, J (*gem*) = 13.3, J (CH_2) = 6.6, J (NH) = 5.8 Hz, 1, NHCHH–), 2.87 (ddt, J (*gem*) = 13.3, J (CH_2) = 6.6, J (NH) = 5.8 Hz, 1, NHCHH–), 3.01 (s, 3, NCH_3), 4.86 (s, 1, Ph_2CH), 5.36 (s, 1, Ph_2CH), 7.0–7.6 (m, 20, 4 Ph), 11.2 (t, J = 5.8 Hz, 1, NH); mass spectrum (70 eV) *m/e* 516 (M^+, calcd 516), 349 ($M^+ - Ph_2CH$), 321 ($M^+ - Ph_2CHCO$), 292 ($M^+ - Ph_2CHCONMe$), 207 (Ph_2CCNMe^+), 194 (Ph_2CCO^+).

Anal. Calcd for $C_{35}H_{36}N_2O_2$: C, 81.36; H, 7.02; N, 5.42. Found: C, 81.21; H, 7.03; N, 5.70.

Reaction of the Diaziridine 1d. From the reaction of 0.80 g (6.2 mmol) of the diaziridine **1d** and 2.46 g (13 mmol) of the ketene **2**, 0.98 g (31%) of *N*-methyl-*N*-(1-isopropylamino-2-methyl-3-oxo-4,4-diphenylbut-1-en-1-yl)diphenylacetamide (**3d**) and 0.1 g of the amide **5** were obtained after the same treatment as above. Recrystallization of **3d** from benzene–ether gave colorless granules: mp 149–151°; ir (Nujol) 3350 (broad and weak, NH), 1657 (amide C=O), 1615 (C=O), 1580 (sh) and 1562 cm^{-1} (C=C or C=N); nmr ($CDCl_3$) δ 0.68 and 1.08 (d, J (CH) = 6.6 Hz, 3, CH_3, respectively), 1.45 (s, 3, C=CCH_3), 3.04 (s, 3, NCH_3), 3.40 (d-septet, J (CH_3) = 6.6, J (NH) = 9.6 Hz, 1, NHCH–), 4.90 (s, 1, Ph_2CH), 5.36 (s, 1, Ph_2CH), 6.9–7.7 (m, 20, 4 Ph), 11.3 (d, J = 9.6 Hz, 1, NH); mass spectrum (70 eV) *m/e* 516 (M^+, calcd 516), 349 ($M^+ - Ph_2CH$), 322 ($M^+ - Ph_2CCO$), 207 (Ph_2CCNMe^+), 194 (Ph_2CCO^+).

Anal. Calcd for $C_{35}H_{36}N_2O_2$: C, 81.36; H, 7.03; N, 5.42. Found: C, 81.50; H, 6.96; N, 5.58.

Reaction of the Diaziridine 1e. The treatment of the diaziridine **1e** (1.53 g, 15 mmol) with the ketene **2** (5.82 g, 30 mmol) at 80° for 5 min resulted in 1.90 g (26%) of 1-ethyl-3,3-diphenyl-4-(*N*-ethyldiphenylacetamido)azetidin-2-one (**4**) and the amide **5** (380 mg).

The azetidinone **4** for analysis was obtained by recrystallization from benzene–ethanol as colorless granules: mp 154°; ir (KBr disk) 1755 and 1633 cm^{-1} (C=O); nmr ($CDCl_3$) δ 0.99 (t, J = 7.2 Hz, 3, CH_3), 1.15 (t, J = 7.2 Hz, 3, CH_3), 2.63 (dq, J (*gem*) = 14.4, J (CH_3) = 7.2 Hz, 1, –CHH– on the ring nitrogen), 2.70 (dq, J (*gem*) = 14.4, J (CH_3) = 7.2 Hz, 1, –CHH– on the ring nitrogen), 2.89 (dq, J (*gem*) = 14.2, J (CH_3) = 7.2 Hz, 1, NCHH–), 3.59 (dq, J (*gem*) = 14.2, J (CH_3) = 7.2 Hz, 1, NCHH–), 5.12 (s, 1, Ph_2CH), 6.80 (s, 1, NCHN), 6.9–7.9 (m, 20, 4 Ph); mass spectrum (70 eV) *m/e* 488 (M^+, calcd 488), 294 ($M^+ - Ph_2CCO$), 222 ($M^+ - Ph_2CHCO - EtNCO$), 71 ($EtNCO^+$).

Anal. Calcd for $C_{33}H_{32}N_2O_2$: C, 81.12; H, 6.60; N, 5.73. Found: C, 81.39; H, 6.71; N, 5.62.

Hydrolysis of the Amide 3b. To a solution of the amide **3b** (3.0 g, 5.8 mmol) in tetrahydrofuran (30 ml), 5 ml of 47% hydrobromic acid was added and the mixture was refluxed for 36 hr. Then the solvent was removed and extracted (ether). The aqueous layer was made alkaline and extracted (ether). The combined ethereal extract was dried (Na_2SO_4), concentrated, and chromatographed to give 992 mg (71%) of *N*-ethydiphenylacetamide (**5**) and 710 mg (55%) of 1,1-diphenylbutan-2-one (**7**). The amide **5** was identical with an authentic sample and the latter compound **7** was purified by pot distillation (110°, 20 mm): ir (neat) 1720 cm^{-1} (C=O); nmr (CCl_4) δ 1.02 (t, 3, J = 7.2 Hz, CH_3), 2.49 (q, 2, J = 7.2 Hz, CH_2), 5.01 (s, 1, CH), 7.0–7.3 (10, 2 Ph); mass spectrum (70 eV) *m/e* 224 (M^+, calcd 224), 167 (Ph_2CH^+).

Hydrolysis of the Azetidinone 4. A solution of the azetidinone **4** (845 mg) in ethanol (50 ml) containing 2.5 ml of 50% sulfuric acid was refluxed for 20 hr. Then 300 mg of 2,4-dinitrophenylhydrazine and 2 ml of dilute sulfuric acid were added and the solution was refluxed for an additional 1 hr. The solution was concentrated, extracted (benzene), and dried (Na_2SO_4). From the organic layer, 165 mg (72%) of *N*-ethyl-2,2-diphenyl-3-(2,4-dinitrophenylhydrazono)propanamide (**9**), 72 mg (59%) of the amide **5**, and 595 mg of the unreacted **4** were obtained. The yields are calculated on the hydrolyzed **4**.

The hydrazone **9** was recrystallized from benzene–ethanol to give a yellow powder: mp 238–240°; ir (Nujol) 3400 and 3220 (NH), 1650 (C=O), 1610 (C=N), 1580 (NH), and 1500 cm^{-1} (NO_2); nmr ($CDCl_3$) δ 1.17 (t, 3, CH_3), 3.45 (q, 2, CH_2), 5.60 (s, 1, CONH), 7.1–7.5 (m, 10, 2 Ph), 7.58 (d, 1), 8.27 (dd, 1), 8.47 (s, 1, N=CH), 9.14 (d, 1), 11.23 (s, 1, NHN) (the unassigned three signals are due to the protons of the 6, 5, and 3 position of the dinitrophenyl group, respectively; the singlet in the lowest field disappeared upon addition of deuterium oxide); mass spectrum (70 eV) *m/e* 447 (M^+, calcd 447), 375 ($M^+ - EtNHCO$), 341 ($M^+ - Ph - Et$), 239 ($EtNHCOCHPh_2^+$).

Anal. Calcd for $C_{23}H_{21}N_5O_5$: C, 61.74; H, 4.73; N, 15.65. Found: C, 61.74; H, 4.53; N, 15.61.

Reactions of the Amidines 22a, 22b, and 22e. Reactions of these amidines with the ketene **2** were carried out under such conditions as those in the reactions of the corresponding diaziridines **1a, 1b,** and **1e.** The results are listed in Table II.

Acidic Hydrolysis of the Reaction Mixture of the Amidine 22a and the Ketene 2. To a solution of 5.70 g (50 mmol) of the amidine **22a** in 10 ml of benzene, 5.20 g (27 mmol) of the ketene **2** was added dropwise with stirring at 80° over 5 min and the mixture was stirred and refluxed for another 20 min. The ir spectrum of the reaction mixture showed a strong absorption band at 1640 cm^{-1} and none of those corresponding to the 1:2 adduct **3a.** Then the mixture was distilled to remove the solvent and the excess amidine, which amounted to 1.95 g (74% yield calculated on the basis of the equimolar reaction). The residue indicated no essential changes in the infrared spectrum and 4.05 g of the residue was hydrolyzed in refluxing ethanol containing 1 ml of concentrated hydrochloric acid for 12 hr. Concentration and cooling of the mixture gave 1.27 g of the amide **5** and 0.42 g (41%) of ethylamine hydrochloride. The filtrate was alkalified and extracted ($CHCl_3$), dried (Na_2SO_4), concentrated, and distilled under reduced pressure up to 70° (1 mm). The distillate was proved to contain 77 mg (7%) of *N*-ethylacetamide. The residue was chromatographed to give 1.04 g of the amide **5** whose total yield was 74%.

Treatment of an Equimolar Reaction Mixture of the Ami-

dine 22b and the Ketene 2 with Phenyl Isocyanate (10a). Only a trace amount of 1:1:1 adduct, *N*-ethyl-*N*-(1-ethylamino-2-phenylcarbamoyl-1-propen-1-yl)diphenylacetamide (**23**), was obtained. The ir and mass spectra showed replacement of one of the diphenylacetyl groups of **3b** with a phenylcarbamoyl group: ir (Nujol) 3300 (NH), 1650 (C=O), 1600, and 1545 cm^{-1}; mass spectrum (70 eV) *m/e* 441 (M^+).

Reaction of the Amidine 22f. Treatment of the amidine **22f** (1.1 g, 7.0 mmol) and the ketene **2** (1.75 g, 9.0 mmol) in refluxing benzene for 1 hr yielded 0.29 g (12% of *N*-ethyl-*N*-(1-diethylamino-2-methyl-3-oxo-4,4-diphenylbut-1-en-1-yl)diphenylacetamide (**24**). The amide **24** was recrystallized from benzene to afford colorless granules: mp 136–138°; ir (Nujol) 1660 (amide C=O), 1625 (C=O), and 1580 cm^{-1} (C=C); nmr ($CDCl_3$) δ 0.88 (t, 6, 2 CH_3), 1.17 (t, 3, CH_3), 1.72 (s, 3, C=CCH_3), 2.5–3.4 (m, 5, 2 CH_2 and a proton of CH_2), 3.5–4.2 (m, 1, a proton of CH_2), 5.24 (s, 1, Ph_2CH), 5.46 (s, 1, Ph_2CH), 6.9–7.5 (m, 20, 4 Ph); nonequivalent *N*-methylene protons were similar to those of the amides **3**; mass spectrum (70 eV) *m/e* 377 (M^+ − Ph_2CH), 349 (M^+ − Ph_2CCO), 221 (Ph_2CCNEt^+).

Anal. Calcd for $C_{37}H_{40}N_2O_2$: C, 81.58; H, 7.40; N, 5.88. Found: C, 81.59; H, 7.51; N, 5.52.

Reaction with Isocyanates. Reaction of the Diaziridine 1b with the Isocyanate 10a. A mixture of 3.9 g (30 mmol) of the diaziridine **1b**, 4.8 g (40 mmol) of the isocyanate **10a** and 15 ml of acetonitrile was refluxed for 10 hr. The mixture was then concentrated and chromatographed to give 770 mg (11%) of 4-methyl-1,6-diethyl-3-phenyl-5-phenylcarbamoylhexahydro-1,3,5-triazin-2-one (**11**), 190 mg (2%) of *N*-ethyl-*N*-propionyl-*N'*-phenylurea (**12**), 405 mg (6%) of *N*-ethyl-*N'*-phenylurea (**13**), 155 mg (3%) of 1-ethyl-3,5-diphenylbiuret (**14**), small amounts of unidentified materials, and a large amount of viscous oil. The yields are calculated on the basis of **10a**.

Changes in the reaction temperature, the mole ratio of **1b** to **10a**, or solvents caused no essential changes in the products but slightly influenced on their yields.

The triazinone **11** was recrystallized from benzene–ethanol to afford colorless granules: mp 175–176°; ir (Nujol) 3200 (NH), 1685 (C=O), and 1622 cm^{-1} (C=O); nmr ($CDCl_3$) δ 1.02 (t, 3, J = 7.5 Hz, $CHCH_2CH_3$), 1.16 (t, 3, J = 7.1 Hz, NCH_2CH_3), 1.35 (d, 3, J = 6.0 Hz, $CHCH_3$), 2.03 (p, 2, J = 7.5 Hz, $CHCH_2$–), 3.20 and 3.64 (dq, 1, J (*vic*) = 7.1, J (*gem*) = 14.2 Hz, NCHH– and NCHH–, respectively), 5.44 (t, 1, J = 7.5 Hz, $CHCH_2$–), 5.78 (q, 1, J = 6.0 Hz, $CHCH_3$), 6.9–7.5 (m, 11, NH and aromatic protons); mass spectrum (70 eV) *m/e* 366 (M^+, calcd 366), 337 (M^+ − Et), 295 (M^+ − EtNCO), 274 (M^+ − PhNH), 247 (M^+ − PhNCO), 218 (337 − PhNCO), 204 (M^+ − EtNCONPh), 162 (247 − EtCHNEt), 134 ($PhNCONH^+$), 120 ($PhNHCO^+$), 119 ($PhNCOSUPN^+$), 85 ($EtCH{=}NEt^+$).

Anal. Calcd for $C_{21}H_{26}N_4O_2$: C, 68.83; H, 7.15; N, 15.29. Found: C, 69.13; H, 7.19; N, 14.97.

The urea **12** for analysis was obtained by recrystallization from benzene–hexane as colorless needles: mp 91–92°; ir (Nujol) 3380 (NH), 1700, 1648, 1592, and 1545 cm^{-1}; nmr ($CDCl_3$) δ 1.21 (t, 3, J = 7.1 Hz, CH_3), 1.29 (t, 3, J = 7.0 Hz, CH_3), 2.64 (q, 2, J = 7.1 Hz, CH_2), 3.87 (q, 2, J = 7.0 Hz, NCH_2), 6.9–7.6 (m, 5, Ph), 11.6 (broad, 1, NH); mass spectrum (70 eV) *m/e* 220 (M^+, calcd 220), 163 (M^+ − EtCO), 119 ($PhNCO^+$), 101 (M^+ − PhNCO).

Recrystallization of the biuret **14** from benzene–hexane gave colorless needles: mp 148–150°; ir (Nujol) 3280 and 3150 (NH), 1702, 1615, 1590, 1550 cm^{-1}; nmr ($CDCl_3$) δ 1.35 (t, 3, J = 7.0 Hz, CH_3), 3.93 (q, 2, J = 7.0 Hz, CH_2), 6.9–7.6 (m, 10, 2 Ph), 9.18 (s, 2, 2 NH); mass spectrum (70 eV) *m/e* 283 (M^+, calcd 283), 212 (M^+ − EtNCO), 164 (M^+ − PhNCO), 163 (M^+ − PhNHCO), 119 ($PhNCO^+$).

Reaction of the Diaziridine 1a with the Isocyanate 10b. A solution of 3.4 g (30 mmol) of the diaziridine **1a** in 10 ml of benzene was warmed to 80° and 3.8 g (26 mmol) of the isocyanate **10b** in 5 ml of benzene was added dropwise to the solution with stirring over 15 min. The mixture was stirred and refluxed for 20 min until ir absorption of the isocyanate disappeared. The mixture was concentrated and chromatographed to give 2.0 g (30%) of 5-methyl-1,2-diethyl-4-benzoyl-1,2,4-triazolidin-3-one (**15a**) and 0.87 g (18%) of *N*-ethyl-*N'*-benzoylurea (**16**). The former product was recrystallized from benzene–hexane to give colorless granules: mp 54–56°; ir (Nujol) 1720 and 1655 cm^{-1} (C=O); nmr ($CDCl_3$) δ 1.16 (t, 3, J = 7.0 Hz, CH_3), 1.19 (t, 3, J = 7.0 Hz, CH_3), 1.48 (d, 3, J = 6.0 Hz, $CHCH_3$), 2.88 (q, 2, J = 7.0 Hz, NCH_2), 3.16 and 3.63 (dq, 1, J (*vic*) = J (*gem*) = 7.0 Hz, NCHH– and NCHH–, respectively), 5.12 (q, 1, J = 6.0 Hz, CH), 7.2–7.7 (m, 5, Ph); mass spectrum (70 eV) *m/e* 261 (M^+, calcd 261), 246 (M^+ − Me), 156 (M^+ − PhCO), 87 ($EtNNHEt^+$).

Anal. Calcd for $C_{14}H_{19}N_3O_2$: C, 64.34; H, 7.33; N, 16.08. Found: C, 64.27; H, 7.35; N, 16.08.

The urea **16** was identified with an authentic sample.

Reaction of the Diaziridine 1b with the Isocyanate 10b. The same treatment of the diaziridine **1b** (6.4 g, 50 mmol) and the isocyanate **10b** (2.7 g, 18 mmol) in refluxing benzene as in the above reaction gave 2.20 g (44%) of 1,2,5-triethyl-4-benzoyl-1,2,4-triazolidin-3-one (**15b**) and 1.40 g (39%) of the urea **16**. The triazolidinone **15b** was recrystallized from benzene–hexane to give colorless prisms: mp 101–102°; ir (Nujol) 1720 and 1650 cm^{-1} (C=O); nmr ($CDCl_3$) δ 1.04 (t, 3, J = 6.4 Hz, $CHCH_2CH_3$), 1.17 (t, 3, J = 7.0 Hz, NCH_2CH_3), 1.19 (t, 3, J = 7.0 Hz, NCH_2CH_3), 1.5 (m, 1, $CHCHHCH_3$), 2.0 (m, 1, $CHCHHCH_3$), 2.88 (q, 2, NCH_2), 3.10 and 3.67 (dq, 1, J (*vic*) = 7.0, J (*gem*) = 14.0 Hz, NCHH– and NCHH–, respectively), 4.85 (dd, 1, $CHCH_2$), 7.3–7.7 (m, 5, Ph); mass spectrum (70 eV) *m/e* 275 (M^+, calcd 275), 246 (M^+ − Et), 170 (M^+ − PhCO), 141 (246 − PhCO).

Anal. Calcd for $C_{15}H_{21}N_3O_2$: C, 65.43; H, 7.67; N, 15.26. Found: C, 65.26; H, 7.85; N, 15.54.

Alkaline Hydrolysis of the Triazolidinone 15b. To a solution of 1.0 g (36 mmol) of the triazolidinone **15b** in 15 ml of ethanol, 2 ml of 6 *N* potassium hydroxide solution was added and the mixture was refluxed for 3 hr. The mixture was concentrated and extracted with chloroform and dilute aqueous potassium hydroxide. The organic layer was dried (Na_2SO_4) and concentrated to give 0.50 g (95%) of 1,2,5-triethyl-1,2,4-triazolidin-3-one (**17**). The aqueous layer was acidified with concentrated hydrochloric acid and extracted ($CHCl_3$), dried (Na_2SO_4), and concentrated to afford 0.44 g (92%) of benzoic acid. The triazolidinone **17** was purified by sublimation: colorless plates; mp 46–48°; ir (KBr disk) 3190 (NH) and 1680 cm^{-1} (C=O); nmr ($CDCl_3$) δ 0.92 (t, 3, J = 6.6 Hz, CH_3), 1.09 (t, 3, J = 6.9 Hz, CH_3), 1.15 (t, 3, J = 7.0 Hz, CH_3), 1.49 (dq, 2, J (CH_3) = 6.6, J (CH) = 6.0 Hz, $CHCH_2$), 2.84 (q, 2, J = 6.9 Hz, NCH_2), 2.9–3.9 (m, 2, NCH_2), 4.04 (t, 1, $CHCH_2$), 6.7 (broad s, 1, NH); the multiplet at 2.9–3.9 was similar to the pattern found for the *N*-methylene protons of the amide **3** and the last signal disappeared upon addition of deuterium oxide; mass spectrum (70 eV) *m/e* 171 (M^+, calcd 171).

Acidic Hydrolysis of the Triazolidinone 15b. To a solution of 600 mg (2.2 mmol) of the triazolidinone **15b** in 15 ml of ethanol, 1.5 ml of concentrated hydrochloric acid was added and the solution was refluxed for 9 hr. The solvent was removed *in vacuo* and extracted with ether and water. The ethereal layer was dried (Na_2SO_4) and concentrated to give 20 mg of 1,2-diethyl-5-phenyl-1,2,4-triazolin-3-one (**18**). The aqueous layer was made alkaline with aqueous sodium hydroxide and extracted (ether), dried (Na_2SO_4), and concentrated to afford 180 mg of **18**. The total yield was 43%. The triazolinone **18** was recrystallized from benzene to give colorless needles: mp 112–113°; ir (KBr disk) 1650 (C=O) and 1515 cm^{-1} (C=N); nmr ($CDCl_3$) δ 1.08 (t, 3, J = 7.2 Hz, CH_3), 1.28 (t, 3, J = 7.2 Hz, CH_3), 3.94 (q, 2, J = 7.2 Hz, CH_2), 3.97 (t, 2, J = 7.2 Hz, CH_2), 7.3–7.8 (m, 5, Ph); mass spectrum (70 eV) *m/e* 217 (M^+, calcd 217), 202 (M^+ − Me), 189 (M^+ − CO or $CH_2{=}CH_2$), 188 (M^+ − Et), 131 ($PhC{=}N{=}C{=}O^+$).

Anal. Calcd for $C_{12}H_{15}N_3O$: C, 66.34; H, 6.96; N, 19.34. Found: C, 66.41; H, 6.96; N, 19.20.

Preparation of the 4-Acylsemicarbazide 19. *N,N'*-Diethylhydrazine was prepared according to the procedure for the synthesis of *N,N'*-dimethylhydrazine using diethyl sulfate instead of dimethyl sulfate:[29] bp 82–87° (lit. bp 84–86°). To a solution of the hydrazine (1.5 g, 17 mmol) in 5 ml of ether, 1.9 g (13 mmol) of the isocyanate **10b** in 5 ml of ether was added dropwise over 20 min under a nitrogen atmosphere and the mixture was refluxed for 1 hr. After cooling, 550 mg (15%) of 1,2-diethyl-4-benzoylsemicarbazide (**19**) precipitated. Recrystallization of the precipitate from benzene–ethanol gave colorless needles: mp 171–172°; ir (Nujol) 3360 and 3180 (NH), 1683 and 1632 (C=O), and 1608 cm^{-1} (NH); nmr ($CDCl_3$) δ 0.93 (t, 3, J = 7.4 Hz, CH_3), 1.34 (t, 3, J = 7.3 Hz, CH_3), 3.35 (q, 2, J = 7.4 Hz, $NNCH_2$), 3.70 (q, 2, J = 7.3 Hz, $CONCH_2$), 5.6 (broad, 2, 2 NH), 7.1–7.7 (m, 5, Ph); the broad singlet at δ 5.6 disappeared upon addition of deuterium oxide; mass spectrum (70 eV) *m/e* 235 (M^+, calcd 235), 217 (M^+ − H_2O), 202 (217 − Me), 192 (M^+ − EtN), 105 ($PhCO^+$).

Anal. Calcd for $C_{12}H_{17}N_3O_2$: C, 61.25; H, 7.28; N, 17.86. Found: C, 61.42; H, 7.38; N, 17.74.

Cyclization of the 4-Acylsemicarbazide 19 to the Triazolinone 18. Acidic treatment of the acylsemicarbazide **19** was done under similar conditions to those for the hydrolysis of the triazoli-

dinone **15b**. A solution of 400 mg (1.7 mmol) of **19** in 15 ml of ethanol containing 2 ml of 6 *N* hydrochloric acid was refluxed for 4 hr. Then the solution was made alkaline (aqueous sodium hydroxide), extracted ($CHCl_3$), dried (Na_2SO_4), and concentrated to give 132 mg (36%) of the triazolinone **18** and 30 mg (14%) of 1,2-diethylsemicarbazide which was formed by hydrolysis of **19**.

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Registry No.—**1a,** 39169-68-1; **1b,** 39169-67-0; **1c,** 52225-94-2; **1d,** 52225-95-3; **1e,** 6794-94-1; **2,** 525-06-4; **3a,** 39169-70-5; **3b,** 39169-69-2; **3c,** 52225-96-4; **3d,** 52225-97-5; **4,** 52225-98-6; **7,** 6336-52-3; **9,** 52225-99-7; **10a,** 103-71-9; **10b,** 4461-33-0; **11,** 52225-74-8; **12,** 52225-75-9; **14,** 5040-62-0; **15a,** 52225-76-0; **15b,** 52225-77-1; **17,** 52225-78-2; **18,** 52225-79-3; **19,** 52225-80-6; **22a,** 44650-07-9; **22b,** 52225-81-7; **22e,** 2303-97-1; **22f,** 52225-82-8; **23,** 52225-83-9; **24,** 52225-84-0.

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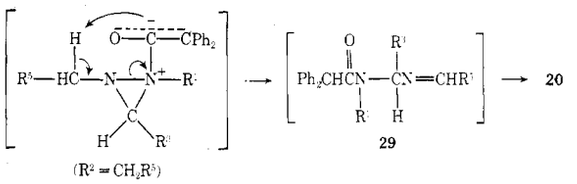
(30) The following mechanism leading to the intermediate **20** is also possible. This participation of an *N*-alkyl substituent in the reaction would be



compatible with the fact that the similarly acidic hydrogen on the ring carbon of an oxaziridine was not abstracted in the reaction with diphenylketene. The reactions with isocyanates can also be elucidated by the above mechanism including the abstraction of an α hydrogen on a N substituent. Thus further study of the mechanism is of future interest.

Studies on Ketene and Its Derivatives. LXIII.[1] Reaction of Diketene with Azobenzenes

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Irradiation of the solution of symmetric azobenzenes (**1a–k**) and diketene in chloroform resulted in the formation of 1:1 cycloadduct, 1,2-diarylhexahydropyridazine-3,5-dione (**2a–k**). Using asymmetric azobenzenes such as **1l–u**, the cycloaddition reaction occured stereoselectively to result in the formation of 1-(4-alkoxyphenyl)-2-arylhexahydropyridazine-3,5-dione (**2l–u**). The possible reaction mechanism is also discussed.

The cycloaddition of azo compounds with ketene is well known,[2] but reactions of azo compounds with diketene have not been reported. The present paper describes a study of reactions of diketene and azobenzenes to give 1,2-diarylpyridazinedione derivatives (**2**).

Refluxing of a solution of diketene and azobenzene (**1a**) in dry chloroform resulted in the recovery of starting materials; however, irradiation of the solution with stirring at room temperature gave rise to the 1:1 adduct (**2a**) in 62% yield. The ir spectrum of **2a** showed two carbonyl bands at 1746 and 1688 cm^{-1} ascribable to ketone and amide group, respectively. The nmr spectrum ($CDCl_3$) showed two singlet signals at 3.35 (2 H, $COCH_2CO$) and 4.34 ppm (2 H, NCH_2CO).