dure described in the reaction between **1d** and **2a** with **1d** (4.28, 0.02 mol), α-chlorophenylacetyl chloride (9.45 g, 0.05 mol), and triethylamine (10.1 g, 0.1 mol). After similar treatment **6d** and **1,3,4-triphenyl-3,4-dichloropyrrolidine (16d)** were obtained in 5 (0.33 g) and 22% (1.70 g) yields.

16d had mp 197–199°; ir (Nujol) 1790 and 1735 cm^{-1} (C=O); nmr ($CDCl_3$) δ 7.20–7.50 (d, phenyl protons); mass spectrum (70 eV) m/e 395 and 397 (M^+) and 325 and 327 ($M^+ - 2\ Cl$).

Anal. Calcd for $C_{22}H_{15}NO_2Cl_2$: C, 66.68; H, 3.82; N, 3.53. Found: C, 66.71; H, 3.91; N, 3.81.

Registry No.—**1a**, 2056-74-8; **1b**, 23386-62-1; **1c**, 28924-14-3; **1d**, 3839-89-2; **2a**, 3496-32-0; **2b**, 29804-92-0; **6a**, 51003-31-7; **6b**, 51003-32-8; **6c**, 51003-33-9; **7a**, 51003-34-0; **7b**, 51003-35-1; **7c**, 51021-64-8; **7d**, 51003-36-2; **8a**, 51003-02-2; **9b**, 51003-37-3; **10c**, 51003-38-4; **11a**, 51003-39-5; **11b**, 51003-40-8; **11c**, 51003-41-9; **12b**, 51003-42-0; **12c**, 51003-43-1; **13a**, 51003-44-2; **13b**, 51003-45-3; **13c**, 51003-46-4; **13d**, 51003-47-5; **15b**, 51003-48-6; **16b**, 51003-49-7; **16d**, 51003-50-0; **18c**, 51003-51-1; phenylacetyl chloride, 103-80-0; α-chlorophenylacetyl chloride, 2912-62-1.

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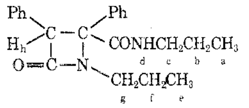

The Mechanism of Cycloaddition of Diphenylketene with Azo Compounds[1]

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Cycloadditions of diphenylketene with cis azo compounds, PhN=NY [Y = CO_2Et, $CH(CH_3)_2$, and $N(CH_3)_2$], with *cis*-azobenzenes, $PhN{=}NC_6H_4X$ [X = CH_3O, CH_3, H, Cl, CN, NO_2] and with *trans*-$PhN{=}NCO_2Et$ have been studied. 1,2-Diazetidin-3-one products form cleanly in most cases, by a near-concerted mechanism, as shown by small effects of solvents and substituents on rates, small regioselectivity among the azobenzenes, and absence of trappable intermediates. In contrast to diphenylketene, isocyanates give no evidence of reaction with azo compounds.

Since Staudinger first reported the cycloaddition of ketenes with azo compounds in 1912,[2] the reaction has been used many times for the synthesis of 1,2-diazetidinones.[3] However, little effort has been directed toward study of the mechanism of this cycloaddition. In contrast, extensive studies of the cycloaddition reactions of ketenes with alkenes[4] and with enol ethers[5] have shown that these reactions are essentially concerted, as shown by stereospecificity, isotope effects, and small solvent effects on rates. Cycloadditions of ketenes with enamines[6] and imines[7] have been found to be at least partly ionic processes, based upon trapping of dipolar intermediates and large solvent effects on rates. Cycloadditions of ketenes with nitroso compounds have been alleged to occur in part by concerted and in part by dipolar mechanisms.[8,9] Barker[10] has studied the cycloaddition of ketenimines with azo compounds and found it to be nearly concerted.

In order to observe cycloaddition between *trans*-azobenzene and diphenylketene (**1**), the neat reactants had to be heated at 130°.[2] However, it was subsequently found that *cis*-azobenzene, unlike *trans*-azobenzene, reacted rapidly with diphenylketene at room temperature.[11] The reaction is often run, therefore, by *in situ* generation of cis azo compound by irradiation of the trans azo compound in the presence of the ketene.[12] We have usually followed this same procedure.

Two of the most important tools of mechanistic exploration, stereochemistry and hydrogen isotope effects, are rendered unusable by the nature of the products and reactants, respectively, in the ketene + azo cycloaddition. Therefore, the mechanistic criteria employed in this study include the regioselectivity of the reaction; kinetic criteria, including effects of substituents and solvents on reaction rates; and attempts to intercept intermediates. Direct substitution on the azo group was employed in order to effect maximum regioselectivities, as well as traditional benzene-ring substitution to provide isolable cis isomers for kinetic studies.

Results and Discussion

Azobenzene. Solutions of *trans*-azobenzene (**2a**) and diphenylketene (**1**) at room temperature are indefinitely stable; no reaction can be detected. In contrast, *cis*-azobenzene reacts rapidly with the ketene,[11] whether isolated chromatographically from irradiated azobenzene solutions or generated *in situ* by irradiation.[12] After 5-hr irradiation through a 5% cupric sulfate–6.5% cobaltous sulfate filter solution,[13] the cycloaddition is complete, as judged by absence of infrared absorption of the ketene at 2130 cm^{-1}. 1,2,4,4-Tetraphenyldiazetidin-3-one was isolated in 76% yield from a carbon tetrachloride solution; comparable yields (64–75%, correcting for recovered azobenzene) were obtained from the reaction in ethyl ether, benzene, or cumene solution. The reaction was also run in benzene and methylene chloride, using a fivefold excess of **1**; again, only the diazetidinone could be isolated. The infrared spectra of the reaction mixtures gave no evidence of 2:1 adducts arising from reaction of **1** with dipolar intermediates,[6,7] such as unaccountable carbonyl peaks.

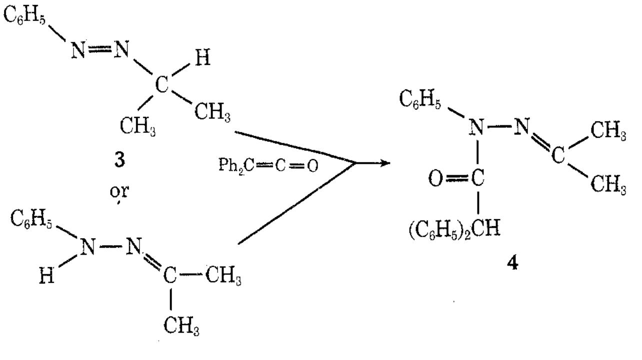
The rate of cycloaddition of *cis*-azobenzene (**2a**) with **1** was studied by irradiating a solution of *trans*-azobenzene of known concentration and absorbance so as to partially convert it to cis, adding a small excess of **1**, and following the rapid decrease of absorbance at 475 nm. After at least 10 half-lives the final absorbance gave the amount of unreacted *trans*-azobenzene left and, by subtraction, the amount of *cis*-azobenzene present before adding the ketene. Good second-order kinetics were observed, based on this initial concentration and the known concentration of ketene added. Rate coefficients found follow: cyclohexane (E_T 31.2),[14] $2.1 \pm 0.4 \times 10^2\ M^{-1}\ sec^{-1}$; benzene ($E_T$ 34.5),[14] $5.4 \pm 1.0 \times 10^2\ M^{-1}\ sec^{-1}$; methylene chloride

(E_T 41.4),[14] 6.9 ± 0.4 × 10^2 M^{-1} $\sec^{-1}$; acetonitrile (E_T 46.0),[14] 20 ± 2 × 10^2 M^{-1} $\sec^{-1}$. These remarkably fast rates provide a vivid contrast with the completely unreactive *trans*-azobenzene.

2-(Phenylazo)propane.[15] The visible spectrum of 2-(phenylazo)propane (**3**) in cyclohexane shows an $n \rightarrow \pi^*$ transition at 403 nm (ϵ 137), indicating a trans geometry. After 20-min irradiation with a mercury lamp through a 5% cupric sulfate filter solution,[16] the absorbance at *ca.* 400 nm had increased by 12%, and the maximum had shifted to slightly shorter wavelength. No significant change in the spectrum occurred when the irradiated solution was allowed to stand in the open for 45 min, but, upon addition of a small quantity of **1**, there was an immediate decrease in absorbance, which leveled off within 1 min and remained unchanged thereafter, despite the presence of excess ketene. The wavelength of maximum absorbance appeared at 405 nm.

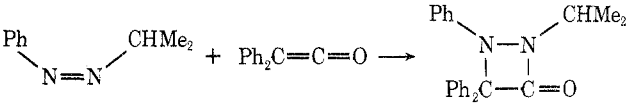
These observations suggest that *trans*-**3**, like *trans*-**1a**, is relatively unreactive toward diphenylketene, but is converted by irradiation to a reactive cis isomer.

When *trans*-**3** and **1** were stirred together in carbon tetrachloride solution, a slow reaction did occur, the ketene being consumed after 15 hr. The ir spectrum of the mixture did not, however, indicate any cycloadduct. The product was an air- and moisture-sensitive solid which could not be purified owing to decomposition during chromatography or crystallization. Its ir spectrum showed important bands at 1675 (amide) and 1610 cm^{-1} (>C=N-), and its nmr spectrum showed a complex multiplet around τ 2.7 (aromatic protons), a weak singlet at τ 5.0 (CH), and two singlets at τ 2.05 and 2.30 (CH_3). These data suggested that the material might be acetone *N*-(diphenylacetyl)-*N*-phenylhydrazone (**4**). In confirmation of this hypothesis, the same material was formed quantitatively by reaction of acetone phenylhydrazone with diphenylketene.



The product **4** apparently arises from an "ene" reaction[17] involving the α hydrogen of the isopropyl group of **3**. An analogous reaction was also observed in the only previous study of the reaction of a ketene and an aliphatic azo compound (α-azotoluene).[18] Thus *trans*-**3** and **1** do react thermally, but not by cycloaddition.

However, if a solution of **3** and diphenylketene in carbon tetrachloride was irradiated through a 5% cupric sulfate filter solution[16] in order to produce *cis*-**3**, all the ketene disappeared within 5 hr, and the ir spectrum did show a sharp diazetidinone carbonyl absorption at 1778 cm^{-1}, in addition to the bands of **4**. Chromatography of the reaction mixture on alumina gave, in 12% yield, a white solid, mp 117-118.5°, which gave a correct analysis for a 1:1 cycloadduct. The nmr spectrum of this material showed a multiplet at τ 2.4-3.3 (*ca.* 15 H), a septet at τ 6.28 (1 H), and a doublet at τ 8.63 (6 H). The low-field resonance of the α H of the isopropyl group suggested that the isopropyl was in the 2 position of the diazetidinone ring (*i.e.*, the amide nitrogen) rather than the 1 position; *cf.* *N*-isopropylacetamide, τ 6.00,[19] and *N*-isopropyl-*N'*-phenylhydrazine, τ 7.11. That the cycloadduct was 1,4,4-triphenyl-2-isopropyldiazetidin-3-one was proven by its mass spectrum, in particular by the presence of peaks at *m/e* 257 ($Ph_2C{=}NPh^+$) and 180 ($PhC{\equiv}NPh^+$). Thus, *cis*-**3**, unlike *trans*-**3**, reacts with **1** by cycloaddition (at least in part).



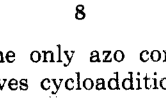
1-Phenyl-3,3-dimethyltriazene. This triazene, **5**, apparently has the trans configuration, based on its dipole moment of 2.28 D[20] (*cf.* *trans*-*p*-dimethylaminoazobenzene, 2.48 D).[21] When **5** was stirred with **1** in carbon tetrachloride for 4 days, no reaction occurred. However, irradiation of such a solution through a 5% $CuSO_4$ filter solution[16] resulted in consumption of all the ketene within 4 hr, as indicated by infrared, which also showed two new bands, at 4.4 (isocyanate) and 5.62 μ (carbonyl). The isocyanate band was due to phenyl isocyanate, as shown by isolation of 25% 1,3-diphenylurea upon addition of aniline to the reaction mixture. Chromatography then yielded unreacted **5** (56%) and a thermally sensitive white solid, which proved to be 3,3,4,4-tetraphenyl-1-dimethylamino-2-azetidinone (**6**, 35% yield) based on spectra, analysis, and synthesis of an authentic sample from **1** and benzophenone dimethylhydrazone.[22] We conclude that the reaction occurred by the sequence outlined in Scheme I.

We interpret the effect of light on this reaction, by analogy with the reactions of **2a** and **3**, as due to formation of *cis*-**5**, which reacts rapidly with **1**. Attempts to detect *cis*-**5** directly by irradiation of solutions of *trans*-**5** [λ_{max} 285, 308 nm (sh)][20] in carbon tetrachloride, cyclohexane, or benzene failed; rapid loss of all ultraviolet absorption above 250 nm occurred. We infer that *cis*-**5** is thermally unstable and decomposes rapidly[23] or, if **1** is present, undergoes rapid cycloaddition.

The apparent instability of the diazetidinone formed from **1** and **5** is consistent with previous observations that electron-donating groups cause lowered thermal stability in diazetidinones,[2,12] and with our own observations (*vide infra*) to the same effect.

Again, reaction of **5** with excess **1** gave the same products. The infrared spectrum of the product mixture gave no evidence of 2:1 adducts, and none was isolated.

Ethyl Phenylazoformate. The product of thermal reaction of ethyl phenylazoformate (**7**) with **1**, originally assigned the structure **8** by Ingold and Weaver,[24] was more recently found to be **9**.[25]



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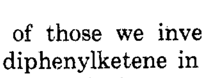
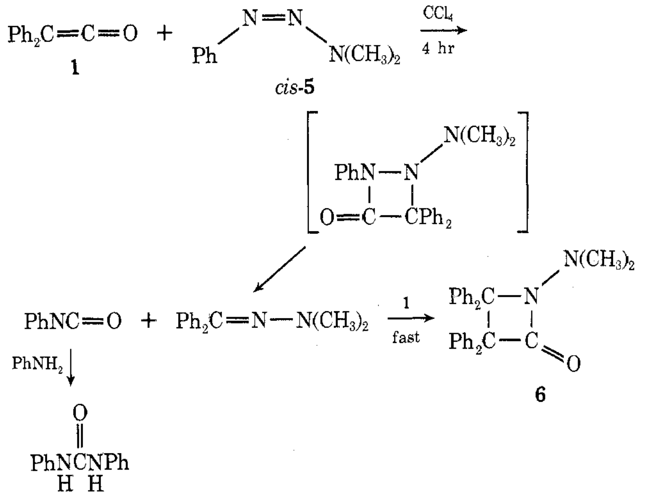


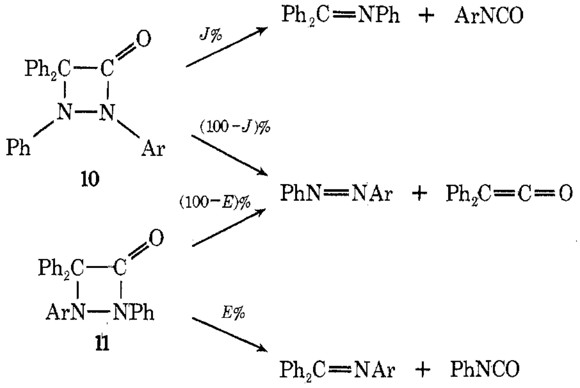
9

7 is the only azo compound of those we investigated which gives cycloaddition with diphenylketene in the absence of irradiation.[26] This is not due to its possessing a cis structure; the intensity of the $n \rightarrow \pi^*$ transition at 418 nm (ϵ 146, dioxane solution)[27] indicates that **7** has the trans structure. However, the relatively slow reaction of **7** with diphenylketene in cyclohexane was found to be accelerated by irradiation with a mercury lamp through a 5% cupric sulfate filter solution.[16] The product was **9**, the same as from the unirradiated reaction,[25] isolated in 69% yield. An infrared spectrum of the mixture immediately

Scheme I
Reaction of Diphenylketene with 1-Phenyl-3,3-dimethyltriazene

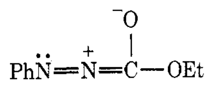


Scheme II
Thermolysis of Diazetidinone Mixtures



after reaction showed only the two peaks belonging to **9** at 1788 and 1742 cm^{-1} in the carbonyl region, and a small shoulder at *ca.* 1820 cm^{-1} possibly due to **8**. Again reaction with excess **1** gave the same results, with no evidence of any 2:1 adduct.

The acceleration upon irradiation is again thought to be due to formation of transient *cis*-**7**. Irradiation of a cyclohexane solution of *trans*-**7** at room temperature resulted in no change in either the wavelength or intensity of the $n \rightarrow \pi^*$ band at 425 nm. Apparently the cis isomer formed reverts to *trans*-**7** very rapidly, perhaps *via* a linear transition state involving carbonyl-group stabilization.[28]


$Ph\ddot{N}=\overset{+}{N}=\overset{^{-}O}{C}-OEt$

The reaction of **7** with diphenylketene in cyclohexane at 25.00° was followed by monitoring the absorbance at 475 nm. The reaction was first order in each reactant, and proceeded with a second-order rate coefficient of $3.9 \pm 0.4 \times 10^{-3}\ M^{-1}\ sec^{-1}$. In acetonitrile at the same temperature, the rate coefficient was $11.7 \pm 0.6 \times 10^{-3}\ M^{-1}\ sec^{-1}$, only three times faster than in cyclohexane. Clearly *trans*-**7** is much less reactive (*ca.* 10^5) than the cis azo compounds discussed herein, but much more reactive than other trans azo compounds. The reason for the latter remains obscure.

Substituted Azobenzenes $PhN{=}NC_6H_4X$. Reaction of **1** with unsymmetrically substituted azobenzenes leads to two isomeric diazetidinones. The analysis of the product mixtures was performed by a gas chromatographic method in which the mixture was injected into a vaporizer block at a temperature sufficiently high as to pyrolyze the diazetidinones. The main products of such pyrolysis (Scheme II) were an isocyanate and a Schiff base; to some degree the azo compound **2** and ketene **1** were also produced. The analysis was based on determination of the amounts of the two Schiff bases. In order to correct for the different branching ratios for decomposition of the isomers **10** and **11** in the two possible directions, one (or both) of the diazetidinones was isolated from each reaction by extensive column chromatography and/or recrystallization, and its (their) branching ratio was determined directly and used in correcting the observed Schiff base ratio, so as to yield an accurate diazetidinone ratio. Three to six determinations were made in all cases. The data obtained for reaction of azo compounds **2b–f** with **1** are given in Table I; the uncertainties shown are maximum deviations observed among the various determinations.

The data indicate that reaction time at 80° and the lamp used (runs 3 and 12) have essentially no effect on the ratio of **11** to **10**. However, the temperature of the reaction does slightly affect the product distribution (runs 1, 6, 10): the amount of **11** decreases from 70% at 30° to 64% at 80° and remains about the same at 120°. Moreover, prolonged refluxing at 120° does produce some change, presumably the consequence of partial reversibility of the initial cycloaddition, leading to incipient thermodynamic control.

The most striking fact about the product ratios is the *very low regioselectivity* observed in all cases. The ratio of **11**/**10** in no case exceeds 4, indicating a very slight rela-

Table I
Results from Reactions of 1 with Azobenzenes 2a–f

Run	Compd	X	Solvent	Lamp[a]	Temp, °C	Time, hr	Injector temp, °C	% E (from **11**)	% J (from **10**)	Produced in reaction % **11**	Produced in reaction % **10**
1	**2b**	OCH_3	C_6H_6	uv	80	15	202	91.8 ± 0.6	95.4 ± 0.6	64 ± 2	36 ± 2
2	**2c**	CH_3	C_6H_6	uv	80	39	235	79 ± 4	78 ± 2	54 ± 3	46 ± 3
3	**2d**	Cl	C_6H_6	uv	80	8	238	85 ± 2	77 ± 2	59 ± 2	41 ± 2
4	**2e**	NO_2	C_6H_6	ir	80	1	270	52 ± 3	68 ± 2	61 ± 2	39 ± 2
5	**2f**	CN	C_6H_6	ir	80	42	290	58 ± 3	54 ± 3	64 ± 3	36 ± 3
6	**2b**	OCH_3	C_6H_6	R	30	15	210	94.6 ± 0.1	94.6 ± 0.4	70 ± 1	30 ± 1
7	**2b**	OCH_3	CH_2Cl_2	R	30	15	210	94.6 ± 0.1	94.6 ± 0.4	79 ± 1	21 ± 1
8	**2b**	OCH_3	CH_3CN	R	30	15	210	94.6 ± 0.1	94.6 ± 0.4	77 ± 1	23 ± 1
9	**2b**	OCH_3	$PhCH_3$	uv	120	24	225	94.6 ± 0.1	94.6 ± 0.4	58 ± 1	42 ± 1
10	**2b**	OCH_3	$PhCH_3$	uv	120	0.5	225	94.6 ± 0.1	94.6 ± 0.4	66 ± 1	34 ± 1
11	**2b**	OCH_3	$PhCH_3$	uv	120	1	225	94.6 ± 0.1	94.6 ± 0.4	65 ± 1	35 ± 1
12	**2d**	Cl	C_6H_6	ir	80	22	280	75 ± 3	74 ± 2	58 ± 1	42 ± 1

[a] Lamps used for *in situ* generation of *cis*-**2** from *trans*-**2**: uv indicates a Gates 420-U1 360-W equipped with a G. E. UA-3 lamp; ir indicates a Fisher Infrarediator equipped with G. E. 250-W infrared lamps; R indicates a Rayonet Photochemical Reactor equipped with RPR-3500 A lamps.

Table II
Rates of Cycloaddition in Benzene at 25°

Compd	X	k_T[a]	k of **11**[a,c]	k of **10**[a,c]
2b	OCH_3	20 ± 5[b]	13 ± 4[b]	7 ± 2
2c	CH_3[d]	7.8 ± 0.2	4.2 ± 0.1	3.6 ± 0.1
2a	H	5.4 ± 1.0	2.7 ± 0.5	2.7 ± 0.5
2d	Cl	2.5 ± 0.2	1.5 ± 0.1	1.0 ± 0.1
2f	CN[d]	21 ± 10	13 ± 7	8 ± 5

[a] Rates are in units of $10^2\ M^{-1}\ sec^{-1}$. [b] Standard deviations, based on 4–12 runs. [c] Obtained by multiplying overall rate, k_T, by the fractions of **11** or **10** from Table I. [d] At 21.8°.

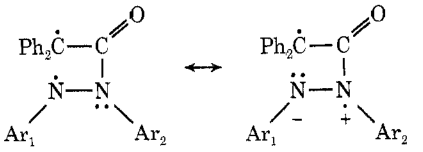
tive effect of substituents on the two transition states. The second important observation is that *the same isomer,* **11**, *predominates whether the substituent X is electron withdrawing or electron donating.* Under the same conditions (runs 1–5), somewhat greater regioselectivity is obtained with strongly interacting substituents (X = OCH_3, **11**/**10** = 1.8; CN, 1.8; NO_2, 1.6) than with weaker ones (Cl, 1.4; CH_3, 1.2). The regioselectivity is higher in more polar solvents than in less polar ones, but again the effect is small (runs 6–8).

In order further to assess substituent effects, the rates of reaction of *cis*-**2b–f** with **1** were studied. The cis isomers were prepared by photolysis of *trans*-**2b–f**, isolated by column chromatography at 0°, and used directly. The reactions were followed by monitoring the decrease in the long-wavelength n → π^* bands of *cis*-**2b–f** at *ca.* 440 nm. Second-order kinetics (first order in each reactant) were observed. The results are given in Table II.

Again, the striking fact is the *very small effect of substituents on rates,* all falling within a power of 10. There is no overall trend relating rate to electronic effect of substituent; the fastest rates are observed with both the best electron-withdrawing and the best electron-donating group. The rate of formation of **11** appears to be slightly more affected by substituents than that of **10**, but the difference is modest. The rate of cycloaddition of **2a** with **1** is only modestly dependent on solvent (*vide supra*).

Discussion of Mechanism. Like any cycloaddition, that of **1** and **2** may in principle proceed by a dipolar, diradical, or concerted mechanism. The results obtained (low regioselectivity, the preferred direction of regioselectivity, low solvent effect on rates and regioselectivity, no evidence of trappable intermediates) seem wholly inconsistent with a dipolar mechanism.

A diradical mechanism for reaction of **1** and **2** would appear, *a priori*, to be relatively favorable, involving the intermediacy of the stable diradical **12**. Qualitative studies of hydrazyl radical–tetrazane equilibria indicate that hydrazyl radicals like **12** are stabilized by electron-donating groups on either nitrogen and by electron-withdrawing groups on the divalent nitrogen, but destabilized by electron-withdrawing groups on the trivalent nitrogen.[29] This is qualitatively consistent with the observed preference for formation of isomer **11** rather than **10** in all cases. The products observed in the reactions of azo compounds PhN=NY [Y = CO_2Et, $CH(CH_3)_2$, and $N(CH_3)_2$] are likewise qualitatively consistent with a diradical mechanism, the following diradicals evidently being preferred over the isomeric ones.



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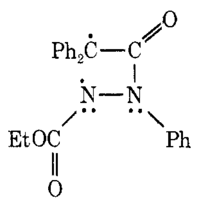
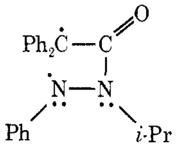
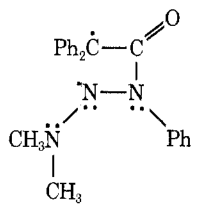
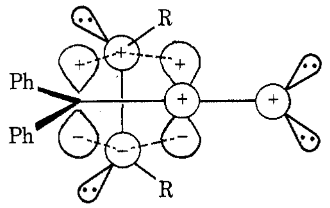






However, for a diradical intermediate, one would have expected greater regioselectivity with electron-withdrawing X groups than with electron-donating X groups, which is not found to be the case. Moreover, the small size of the effects of substituents on rates and on product distribution does not seem to support a true diradical intermediate.

The relative insensitivity of the reaction to substituents X is most easily explained in terms of a nearly concerted reaction mechanism. A reagent as unsymmetrical as diphenylketene would be unlikely to react by a perfectly synchronous process, but a practically concerted process similar to that proposed by Woodward and Hoffmann[30,31] for the reaction of ketenes with alkenes appears quite feasible. In this $[_\pi2_s + {}_\pi2_a]$ process, the cis azo compound and the ketene approach orthogonally, an arrangement which is made favorable by (a) a donor–acceptor interaction between the π_{CC} orbital of the ketene and the π^*_{NN} orbital of the azo compound; (b) most important, a donor–acceptor interaction between the π_{NN} orbital of the azo compound and the unusually low-lying[32] π^*_{CO} orbital of the ketene; (c) favorable alignment of dipoles of cis azo compound and ketene; and (d) absence of steric repulsions among the substituent groups.



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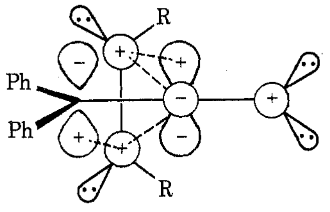

b

In contrast, one R group of a trans azo compound must project to the left in the above diagrams, and may be expected to seriously interfere with one phenyl group of the diphenylketene. This, in addition to the intrinsically lower ground-state energy of trans azo compounds (*trans*-**2a** is 10 kcal lower in energy than *cis*-**2a**),[33] accounts for the generally low reactivity of trans azo compounds in these cycloadditions. In summary, we feel that the evidence is most consistent with a concerted but not synchronous mechanism, with lack of perfect concert reflected in a small amount of diradical character in the transition state.

The notion of partial diradical character has been repeatedly invoked to explain regioselectivity and substituent effects on concerted reactions, particularly the Diels–Alder[34] and 1,3-dipolar addition[35] reactions. Mild rate accelerations by both electron-donating and -withdrawing groups have been reported for these reactions, analogous to those reported here.[36]

The Woodward–Hoffmann concept of concerted ketene cycloadditions involving the low-lying π^*_{CO} orbital of the ketene[30] is also supported by the unreactivity of isocyanates, which lack a sufficiently low-lying π^* orbital (PhNCO, for example, has its longest wavelength $n \rightarrow \pi^*$ absorption at 278 nm,[37] compared to Ph_2CCO at 407 nm). Attempts to force reaction of aryl isocyanates or sulfonyl isocyanates with *cis*-**2a** or with **7** at temperatures up to 200° were uniformly unsuccessful, only starting materials being recovered.[47]

Experimental Section[38]

Diphenylketene (**1**) was prepared by the method of Martin.[39] Ethyl phenylazoformate (**7**)[40] and 1-phenyl-3,3-dimethyltriazene (**5**)[41] were prepared by literature methods. *p*-Methoxyazobenzene (**2b**) was prepared by methylation of *p*-phenylazophenol by a literature procedure.[42] Azobenzenes **2c–e** were prepared by condensation of the appropriate aniline with nitrosobenzene, and purified by column chromatography and recrystallization. *p*-Cyanoazobenzene (**2f**) was prepared by nitrosation of *p*-phenylazoaniline, followed by treatment with cupric sulfate–potassium cyanide.[43] All had melting points in agreement with literature values.

***N*-Benzhydrylidene-*p*-cyanoaniline.** Benzophenone (10.0 g, 55 mmol), *p*-cyanoaniline (6.05 g, 52 mmol), and 3 drops of concentrated HCl were heated together under nitrogen at 200° for 30 min, and then the mixture was distilled at 170° (2 mm) to remove excess reactants. The undistilled residue was chromatographed on a silica gel column, from which eluted first benzophenone, then the Schiff base (solvent 60% benzene–40% pentane). The latter was recrystallized four times from ethanol: mp 126–128°; ir (KBr) 4.53 (m, $-C{\equiv}N$), 6.18 (s, $>C{=}N-$), 6.28 (s), 11.8 (s), 13.6 (m), 14.2μ (s).

Anal. Calcd for $C_{20}H_{14}N_2$: C, 85.11; H, 4.97; N, 9.93; mol wt, 282. Found: C, 84.66; H, 5.25; N, 9.86; mol wt, 284.

The other Schiff bases, $Ph_2C{=}N\text{-}p\text{-}C_6H_4X$ (X = H, OCH_3, Cl, CH_3, NO_2), were prepared similarly, and gave melting points in agreement with literature values.

Reaction of 1 with 2a. Solutions of **1** (4.03 g, 0.02 mol) and **2a** (3.69 g, 0.020 mol) each in 25 ml of carbon tetrachloride were combined in a 125-ml erlenmeyer flask fitted with a reflux condenser and drying tube and having a syringe-stoppered side arm for removal of samples. The solution was stirred magnetically and irradiated with an external mercury lamp for 5.5 hr, after which no ketene peak at 4.8 μ remained in the ir. The solvent was stripped and the residue was washed with methanol and recrystallized from ethyl acetate, giving 5.09 g (68%) of 1,2,4,4-tetraphenyl-1,2-diazetidin-3-one, mp 175–178° (lit.[12] mp 175–176°). Crude **2a** (*ca.* 11%) was recovered from the mother liquor by ethanol recrystallization.

Reaction in cumene gave 66% of diazetidinone and 31% of recovered azobenzene (by alumina chromatography); similar results were also obtained in ethyl ether and benzene. Reaction with a fivefold excess of **1** gave a product mixture whose ir spectrum showed no extraneous $>C{=}O$ absorptions due to 2:1 adducts; the diazetidinone was isolated in 50% yield despite difficulties due to hydrolysis and oxidation products from the excess **1**.

Reaction of 1 with 3. A. With Photolysis. **1** (2.69 g, 0.014 mol) and **3** (2.04 g, 0.014 mol) in 50 ml of carbon tetrachloride were irradiated as above, but through a 5% cupric sulfate filter solution.[16] After 5 hr, the ir showed no remaining ketene, but did show two $>C{=}O$ absorptions, at 5.61 and 5.97 μ. The solvent was stripped and the residue was chromatographed on neutral alumina. Elution with 15% ether in benzene gave 0.512 g (12%) of white solid: mp 117–118.5° after crystallization from pentane; ir (Nujol mull) 5.66 (s), 6.25 (m), 6.31 (m), 7.79 (m), 9.83 (m), 12.73 (m), 13.21 (m), 13.56 (m), and 14.35 μ (m); nmr ($CDCl_3$) see text; mass spectrum (direct inlet, 40°) *m/e* (rel intensity, interpretation) 342 (3.5, P), 313 (1.8, P − C_2H_5), 299 (2.3, P − C_3H_7), 271 (2.3, P − C_3H_7 − CO), 257 (4.4, Ph_2CNPh), 194 (85.4, Ph_2CCO), 180 (16.7, PhCNPh), 166 (36.4, Ph_2C), 165 (42.4, fluorenyl), 105 (47, PhN_2), 77 (100, Ph), 43 (29.2, C_3H_7), 41 (30.0, C_3H_5). These data show this product to be 2-isopropyl-1,4,4-triphenyl-1,2-diazetidin-3-one.

Anal. Calcd for $C_{23}H_{22}N_2O$: C, 80.70; H, 6.43; N, 8.19. Found: C, 80.77; H, 6.53; N, 8.08.

Prior elution of the column with benzene yielded a small amount (*ca.* 5%) of benzophenone. The major product produced in the reaction was **4**, judging by ir, but **4** was destroyed on chromatography, allowing isolation of the diazetidinone.

B. Without Photolysis. **1** (1.94 g, 0.010 mol) and **3** (1.49 g, 0.010 mol) were stirred together in 50 ml of carbon tetrachloride for 15 hr. The ir spectrum showed a large $>C{=}O$ peak at 5.97 μ, with at most a trace at 5.61 μ. Evaporation of the solvent left a solid product which could not be purified due to air and moisture sensitivity, but which was identical (ir, nmr) with the product **4** formed by reaction of **1** with acetone phenylhydrazone.

Reaction of 1 with Acetone Phenylhydrazone. **1** (1.94 g, 0.010 mol) and acetone phenylhydrazone (1.52 g, 0.010 mol) were allowed to react in 50 ml of carbon tetrachloride for 18 hr. Partial evaporation of the solvent followed by addition of pentane precipitated an air- and moisture-sensitive yellow solid, **4**: ir (CCl_4) 5.97 (s, amide $>C{=}O$), 6.25 (s), 6.70 (s), 6.90 (m), 7.35 (m), 9.69 (m) 14.29 μ (s); nmr (CCl_4) see text.

Reaction of 1 with 5. **1** (1.94 g, 0.010 mol) and **5** (1.49 g, 0.010 mol) in 50 ml of carbon tetrachloride were irradiated through a 5% copper sulfate solution[16] as above for 4 hr. The ir showed a peak at 4.4 (-NCO) and 5.62 μ ($>C{=}O$). Aniline (0.936 g, 0.010 mol) was added to react with the isocyanate; filtration after 2.5 days gave a solid, which was recrystallized from ethanol to give 0.532 g (25%) of 1,3-diphenylurea, mp 242–244°, mmp 242–244° (authentic mp 244–245°). The filtrate was evaporated, and the residue was chromatographed on neutral alumina, which yielded a mixture of a solid and an oil. The pentane-soluble oil was recovered **5** (ir, nmr), 0.84 g (56%). The pentane-insoluble white solid, mp 145–148°, 0.724 g (35%), was 1-(dimethylamino)-3,3,4,4-tetraphenylazetidin-2-one.

Anal. Calcd for $C_{29}H_{26}N_2O$: C, 83.25; H, 6.22; N, 6.70. Found: C, 83.13; H, 6.35; N, 6.64.

The infrared of a reaction mixture using five times as much **1** showed only peaks attributable to the ketene, phenyl isocyanate, and the azetidinone.

Reaction of 1 with Benzophenone Dimethylhydrazone.[44] **1** (1.95 g, 0.010 mol) and the hydrazone (2.35 g, 0.010 mol) were stirred for 10.5 hr in 75 ml of carbon tetrachloride, after which the solvent was stripped, and pentane was added to precipitate the product: mp 145–148°; ir (Nujol mull) 5.62 (s $>C{=}O$), 6.05 (m), 6.26 (m), 6.62 (m), 13.25 (m), 13.42 (m), 13.75 (m), 14.20 μ (m); nmr ($CDCl_3$) τ 2.92 (m, 20 H), 6.92 (s, 6 H). The mixture melting point with the azetidinone from above was 145–148°.

Reaction of 1 with 7. **1** (1.94 g, 0.010 mol) and **7** (1.79 g, 0.010 mol) in 75 ml of cyclohexane were irradiated for 3 hr through a 5% $CuSO_4$ filter solution,[16] after which ir revealed only peaks at 5.59 and 5.73 μ in the carbonyl region, with a small shoulder at 5.50 μ. The residue from evaporation of the solvent was recrystallized from 95% ethanol, yielding 2.38 g (64%) of **9**: mp 128–130° (lit.[24] mp 132–133°); ir (Nujol mull) 5.59 (s, diazetidinone $C{=}O$), 5.73 (s, ester $C{=}O$), 6.25 (m), 7.91 (m), 8.91 (m), 9.88 (m), 13.30 (s), 13.69 (s), 14.50 μ (s); nmr ($CDCl_3$) δ 0.78 (t, 3 H), 3.80 (q, 2 H), 7.05–7.68 (m, 15 H). Chromatography of the mother liquor on silica gel gave a 7% recovery of **7**.

Attempted Reactions of Isocyanates with Azo Compounds. A. Azobenzene **2a** (2.31 g, 0.013 mol) and *p*-toluenesulfonyl isocyanate (**14**, 2.39 g, 0.012 mol) were refluxed in 75 ml of dioxane, while the solution was irradiated with an unfiltered mercury lamp. After 4 days, water was added to hydrolyze the isocyanate, and then the water and dioxane were removed at reduced pressure. The residue was dissolved in benzene and extracted with 2% aqueous NaOH. *p*-Toluenesulfonamide (0.91 g, 43%), mp 136–138.5°, was isolated by acidification of the aqueous layers. **2a** (2.34 g, 99%, mp 63–65°) was recovered by drying and evaporating the benzene layer.

B. Azobenzene **2a** (5.68 g, 0.031 mol) and **14** (6.41 g, 0.032 mol) were heated together neat for 2 hr, irradiated with a mercury lamp for 10 hr, and then stirred for an additional 48 hr, all at 100°. The mixture was added to water and worked up as above, giving 3.82 g (70%) of *p*-toluenesulfonamide and 4.84 g (85%) of **2a**.

C. Chlorosulfonyl isocyanate (*ca.* 1.4 g, 0.01 mol) and **2a** (1.697 g, 0.009 mol) in 25 ml of carbon tetrachloride were allowed to reflux for 13 hr and then irradiated for 2 hr at reflux. Water (2 ml) was then cautiously added. After 1 hr, the volatile materials were removed at reduced pressure and the residue was chromatographed on silica gel. Elution with pentane gave 1.58 g (93%) of **2a**; small amounts of unidentified polar materials were eluted with more polar solvents.

D. *p*-Nitrophenyl isocyanate (1.64 g, 0.010 mol) and **2a** (1.83 g, 0.010 mol) were heated together at 205° for 22 hr. After cooling,

Table III
Data on Products from Diphenylketene and Substituted Azobenzenes in Benzene at 80°

Substituent X	Time, hr	Lamp[a]	Yield, %[b]	Compd or mixture[c]	Mp, °C	λ_{CO}[d]
CH_3	42	uv	83	**10c** + **11c**	174–179[e]	5.66
CH_3	11	uv		**10c**	178–179	5.61
Cl	8	uv	78	**10d** + **11d**	133–135[e]	5.62
Cl	8	uv		**11d**	164	5.62
NO_2	1	ir	94	**10e** + **11e**	171–180[e]	5.58 5.60
NO_2	10.5	uv	18[f]	**11e**	167–168[e]	5.60
CN	12.2	ir		**11f**	188–190[e]	5.65
CN	12.2	ir		**10f**	219–221[e]	5.67

[a] See Table I, footnote *a*. [b] Total yield of diazetidinones **10** + **11** isolated. [c] Material to which data in remaining columns refer, as identified by pyrolytic vpc. [d] Diazetidinone carbonyl wavelength, in microns. [e] Satisfactory combustion data for C, H, N (±0.4%) were reported for these materials: Ed. [f] Compound **10e** decomposes on uv irradiation.

benzene was added and the solution was analyzed by vpc (5 ft × 0.25 in. 3% SE-30 column, 145°). Only starting materials were detected. Addition of 14 mg of phenyl isocyanate to the mixture (equivalent to a 1% yield) gave a readily detectable third peak in the vpc. A similar reaction with **2a** and *m*-chlorophenyl isocyanate at 36° gave similar negative results, with 1,3-bis(*m*-chlorophenyl)urea being obtained in 89% yield and **2a** recovered in 99% yield.

Reaction of 1 with 2b. A. A solution of **1** (1.005 g, 5,20 mmol) in 12 ml of benzene was added to a solution of **2b** (1.06 g, 5.00 mmol) in 25 ml of benzene in a 125-ml erlenmeyer flask having a syringe-stoppered side arm and a reflux condenser with Nujol bubbler gas-exit tube. The system was flushed with nitrogen and then irradiated with a mercury lamp for 5 hr with magnetic stirring. The benzene was stripped off, and the residue was chromatographed on neutral alumina. Pentane eluted 0.14 g (13% recovery) of **2b.** Benzene–pentane (1:1) eluted 0.13 g of material, mp 130–131°, which was found to be 1-(*p*-anisyl)-2,4,4-triphenyl-1,2-diazetidin-3-one (**11b,** 7%: ir (KBr) 5.61 (s, diazetidinone C═O), 6.59 (s), 6.64 (s), 7.34 (s), 8.00 (s), 8.46 (m), 9.61 (m), 11.96 (s), 13.22 (s), 14.16 (m), and 14.27 μ (s); nmr ($CDCl_3$) τ 2.5–2.9 (m, 15 H), 3.13 (d, $J = 9$ Hz, 2 H), 3.35 (d, $J = 9$ Hz, 2 H), 6.39 (s, 3 H).

Anal. Calcd for $C_{27}H_{22}N_2O_2$: C, 79.80; H, 5.42; N, 6.87. Found: C, 79.93; H, 5.54; N, 6.72.

Analysis by vpc (5 ft × 0.125 in. 3% QF-1 column, injector 202°, column 180°) showed only **1, 2b,** and *N*-benzhydrylidene-*p*-anisidine, from pyrolysis of **11b;** phenyl isocyanate could also be detected using a 130° column temperature. The ratio of Schiff base to azo compound, *J*, was 95.4/4.6 ± 0.6.

Elution of the alumina column with methanol then yielded 1.1 g (63%) of a mixture of **10b** and **11b**, mp 120–156° after rechromatographing and recrystallizing from methanol, ir (KBr) 5.61 μ (diazetidinone C═O, broad, s), nmr ($CDCl_3$) two CH_3 groups at τ 6.33 and 6.45. Vpc under the above conditions gave the same four peaks, plus those due to *N*-benzhydrylideneaniline and *p*-anisyl isocyanate, from **10b.** From data on pure **11b** and this pure binary mixture, the ratio of Schiff base to azo compound from pyrolysis of **10b** was 91.8/8.2, ± 0.6.

B. A solution of 0.500 g (2.36 mmol) of **2b** and 1.105 g (5.7 mmol) of **1** in 10 ml of benzene was irradiated with a mercury lamp for 15 hr, after which tlc showed no unreacted **2b.** Direct vpc analysis of this mixture under the conditions described above, using the data obtained above, indicated the products formed to be 64 ± 2% **11b** and 36 ± 2% **10b.**

The reactions of **2b** in the other solvents and of the remaining azo compounds **2c–f** were performed similarly to the above. Data obtained on the compounds **10** and **11** are given in Table III. These pure compounds were obtained by repeated chromatography and/or recrystallization until vpc indicated only one Schiff base upon pyrolysis in the injector block. The infrared lamp was used in the case of **2e** and **2f** because one or both diazetidinones was decomposed by ultraviolet light under the reaction conditions, as shown by the appearance of isocyanate bands in the infrared at *ca.* 4.4 μ. The infrared lamps used produce light down to *ca.* 400 nm, sufficient to excite the azo compounds with λ_{max} (n → π^*) at *ca.* 440 nm, but not to decompose the diazetidinones: **11e,** λ_{max} 342 nm (ϵ 10,200); mixture of **11e** (22%) and **10e** (78%), λ_{max} 344 nm (ϵ 9500). The uv-photostable mixture of **10d** and **11d,** in comparison, had λ_{max} 268 nm (ϵ 13,300).

Preparation of Cis Azo Compounds.[45] The cis azo compounds **2a–d** were prepared by irradiation of solutions of the trans isomers, preferably in 10% pentane–90% benzene, using Rayonet 3500-A lamps. A G. E. UA3 mercury lamp was used in the case of **2f.** It proved impossible to isolate *cis*-**2e** in sufficient quantity for use, owing to rapid thermal reversion.[45] All operations after the photoisomerization were performed in a darkened room, under a red safe-light, and the materials were kept at about 0° at all times. The isomers were separated by chromatography on neutral alumina in a jacketed (0°) column, the eluents being assayed by tlc on silica gel plates. The trans isomer always eluted first, using pentane or benzene; after its elution was complete the cis isomer was eluted, using methylene chloride or ether. The cis isomers were recrystallized from pentane at −78°. The following data were obtained for the n → π^* maxima of the cis isomers in benzene: **2a,** λ_{max} 440 nm (ϵ 1250); **2b,** 440 (1920); **2c,** 440 (1630); **2d,** 445 (1430); **2f,** 440 (1100).

Kinetic Studies. Solutions of **1** and **2a–f** in benzene, in the concentration range 5–50 × 10^{-5} *M*, were prepared by standard volumetric methods, and the rate of reaction was followed using a Cary 14 spectrophotometer at 440 nm, using the 0–0.1 A slide wire. The mixing time was kept as short as possible, *ca.* 7 sec, and the absorbance was monitored until no further change occurred. The data were plotted on the assumption of a second-order rate law, and gave reasonable straight lines in most cases. The data, given in Table II, are the averages of 4–12 runs each. Values more than three standard deviations from the average, if any, were rejected,[46] and new averages and standard deviations were determined and are reported in Table II. Some curvature was noted in the kinetic plots for **2f,** which reacted at about the limit of our ability to make measurements. The standard deviation is therefore quite high; however, **2f** unequivocally reacts faster than **2a, 2c,** or **2d.**

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Registry No.—**1,** 525-06-4; **2a,** 108-16-6; **2b,** 15516-72-0; **2c,** 6720-28-1; **2d,** 6530-97-8; **2e,** 15516-73-1; **2f,** 51003-24-8; **3,** 28053-14-7; **4,** 51002-91-6; **5,** 28053-15-8; **6,** 51002-90-5; **7,** 28052-13-6; **9,** 51002-89-2; **10b,** 51002-88-1; **10c,** 51003-22-6; **10d,** 51003-23-7; **10e,** 51002-87-0; **10f,** 51003-94-2; **11b,** 51003-95-3; **11c,** 51003-96-4; **11d,** 51003-97-5; **11e,** 51003-98-6; **11f,** 51003-99-7; **14,** 4083-64-1; *N*-benzhydrylidene-*p*-cyanoaniline, 51004-00-3; *p*-cyanoaniline, 873-74-5; benzophenone, 119-61-9; 2-isopropyl-1,4,4-triphenyl-1,2-diazetidin-3-one, 51004-01-4; acetone phenylhydrazone, 103-02-6; benzophenone dimethylhydrazone, 24398-55-8; *p*-toluenesulfonamide, 70-55-3; chlorosulfonyl isocyanate, 1189-71-5; *p*-nitrophenyl isocyanate, 100-28-7.

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1,3-Dipolar Cycloadditions of Nitrile Oxides with α- and β-Azidovinyl Ketones

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Three types of adducts (**2**, **3**, and **4**) were isolated from the reactions of α-azidovinyl ketones with nitrile oxides. They were characterized by ir, nmr, mass spectra, microanalyses, and chemical transformations. β-Azidovinyl ketones, on the contrary, reacted with benzonitrile oxides to give 4-acylisoxazoles (**14**) as the only products. In all the cases studied, the additions onto the C=C bonds were regiospecific and fully controlled by the azide function. The synthetic value of this observation is further demonstrated in this paper by the additions of benzonitrile oxide to α- and β-azidostyrene.

Several methods have been developed recently for the synthesis of α- and β-azidovinyl ketones in high yields.[1] This led us to explore their reactions with nitrile oxides. These 1,3-dipoles are known to add to C=C and C=O bonds, although the latter reactions are restricted to aldehydes and ketones activated by adjacent electron-withdrawing groups.[2] Cycloadditions of nitrile oxides with nonactivated carbonyl compounds such as acetaldehyde, acetone, etc., however, have been performed in the presence of boron trifluoride etherate as catalyst.[3] Starting with az-