The Photocycloaddition of Benzophenone to Ketenimines

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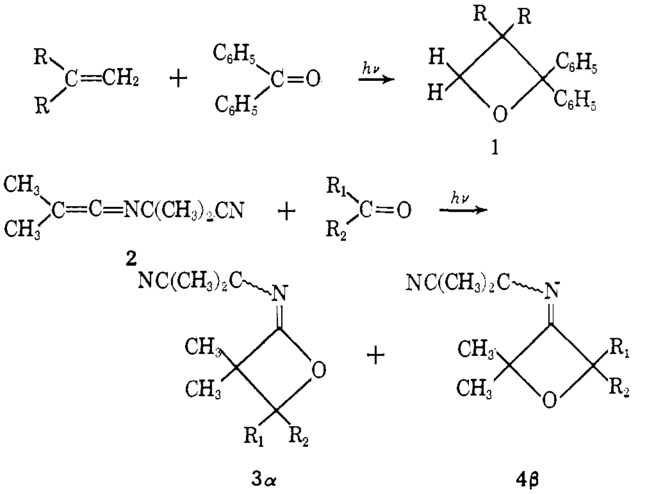
Abstract: The photocycloaddition of benzophenone across the carbon–carbon double bond of ketenimines to give iminooxetanes of α or β structure (structure type **3** and **4**) has been studied with dimethyl-N-(cyclohexyl)- (**5**), dimethyl-N-(phenyl)- (**6**), ethylphenyl-N-(*sec*-butyl)- (**7**), ethylphenyl-N-(phenyl)- (**8**), diphenyl-N-(*sec*-butyl)- (**9**), and diphenyl-N-(phenyl)ketenimine (**10**). The α- and β-structural assignments of the photoadducts were made on the basis of thermal stability differences and mass spectral cleavage patterns. The trialkylketenimine (**5**) reacts 110 times faster with benzophenone than does the triarylketenimine (**10**) and, in general, the replacement of an alkyl group by an aryl group in the ketenimine structure decreases the reactivity. These results are interpreted as a competition between cycloaddition with and energy transfer to the ketenimine by triplet benzophenone. Diphenyl-N-(phenyl)- and ethylphenyl-N-(phenyl)ketenimine quench the benzophenone photoreduction as efficiently as ferric dipivaloylmethide, indicating that energy transfer can occur from benzophenone triplet to the aryl-substituted ketenimines. Diphenyl-N-(*sec*-butyl)ketenimine displays no quenching ability. The benzophenone–dimethyl-N-(cyclohexyl)ketenimine reaction is not retarded by quenchers in low concentration (atmospheric oxygen, ferric dipivaloylmethide 10^{-4} M, naphthalene 10^{-4} M); however, quenching is observed with naphthalene at concentrations $>10^{-3}$ M (quenching constant 33.6 l./mole). The quantum yield for the benzophenone–dimethyl-N-(cyclohexyl)ketenimine reaction (0.71) is independent of ketenimine concentration in the range 0.013–0.204 M, but in the presence of 10^{-2} M naphthalene, the quantum yield is dependent on the ketenimine concentration. The simplest possible reaction scheme necessary to accommodate these results leads to a k_r for the cycloaddition of benzophenone triplet to ketenimine **5** of $\sim 4 \times 10^8$ l. mole^{-1} sec^{-1}. An alternative scheme involving complex formation between benzophenone triplet and ketenimine **5** is proposed and the derived rate law for the quantum yield results in a k_c (rate of complexation) of $\sim 5 \times 10^8$ l. mole^{-1} sec^{-1}.

In recent years,[1-4] there has been considerable attention directed toward the photoinduced cycloaddition of aldehydes and ketones to olefins[5] to give oxetanes (**1**). The extension of this reaction to ketenimines was previously demonstrated.[6] Adducts occur which result from both possible directions of addition of aromatic aldehydes and ketones to dimethyl-N-(2-cyanopropyl)ketenimine (**2**) (adducts **3** and **4** referred to as α and β, respectively).

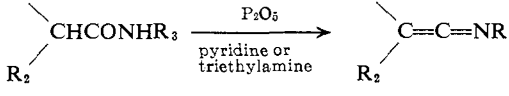


It was qualitatively observed that reactivity increased with decreasing triplet energy of the carbonyl compound and that there was a correlation with the photoreduction reaction[7] to the extent that 2-acetonaphthone and 1-naphthaldehyde did not react with **2**. It was concluded that carbonyl compounds with n–π^* triplet states are reactive while those with π–π^* are not[7,8] and that triplet energy transfer to ground-state ketenimine competes with cycloaddition.

We now wish to report some recent studies on the photocycloaddition of benzophenone to six aryl- and alkyl-substituted ketenimines which supports this mechanistic interpretation.

Results

Ketenimines. Diphenyl-N-(phenyl)- (**10**) and diphenyl-N-(*sec*-butyl)ketenimine (**9**) were prepared in moderate yields (25–30%) by dehydration of the corresponding amides with phosphorus pentoxide in pyridine.[9] Ethylphenyl-N-(phenyl)- (**8**), ethylphenyl-N-(*sec*-butyl)- (**7**), dimethyl-N-(phenyl)- (**6**), and dimethyl-N-(cyclohexyl)ketenimine (**5**) were obtained in yields of *ca.* 20% by the same procedure except that the more basic triethylamine was the solvent.



$$\mathrm{R_1R_2CHCONHR_3} \xrightarrow[\text{pyridine or triethylamine}]{\mathrm{P_2O_5}} \mathrm{R_1R_2C{=}C{=}NR_3}$$

Compd	R_1	R_2	R_3
5	CH_3	CH_3	C_6H_{11}
6	CH_3	CH_3	C_6H_5
7	C_2H_5	C_6H_5	*sec*-C_4H_9
8	C_2H_5	C_6H_5	C_6H_5
9	C_6H_5	C_6H_5	*sec*-C_4H_9
10	C_6H_5	C_6H_5	C_6H_5

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[1] G. Büchi, C. G. Inman, and E. S. Lipinsky, *J. Am. Chem. Soc.*, 78, 876 (1956).

[2] J. F. Harris, Jr., and D. D. Coffman, *ibid.*, **84**, 1153 (1962).

[3] D. R. Arnold, R. L. Hinman, and A. H. Glick, *Tetrahedron Letters*, 1425 (1964).

[4] (a) N. C. Yang, M. Nussim, M. J. Jorgenson, and S. Murov, *ibid.*, 3657 (1964); (b) N. C. Yang, *Pure Appl. Chem.*, 9, 591.

[5] E. Paterno and G. Chieffi, *Gazz. Chim. Ital.*, 39, 341 (1909).

[6] L. A. Singer and P. D. Bartlett, *Tetrahedron Letters*, 1887 (1964).

[7] G. S. Hammond and P. A. Leermakers, *J. Am. Chem. Soc.*, **84**, 207 (1962).

[8] L. H. Piette, J. H. Sharp, T. Kuwana, and J. N. Pitts, Jr., *J. Chem. Phys.*, **36**, 3094 (1962).

[9] C. L. Stevens and G. H. Singhal, *J. Org. Chem.*, **29**, 34 (1964).

Ketenimines **9** and **10** are solids at room temperature (mp 39–40 and 56–57°, respectively) and are conveniently purified by crystallization from petroleum ether while ketenimines **5–8** were purified by vacuum distillation (see Experimental Section for boiling points). Ketenimines **9** and **10** are reasonably stable and can be kept for extended periods of time at 0°. Ketenimines **5–8** appear to be oxygen sensitive but can be adequately stored in degassed and sealed ampoules for several months at 0°. Satisfactory combustion analyses were obtained on all the ketenimines. Compounds **5–10** all show the characteristic ketenimine band in the infrared at about 2000 cm^{-1}.[10] These values along with the nmr data are shown in Table I. The ultraviolet absorption spectra of ketenimines **5–10** are given in Figure 1.

Table I. Properties of the Ketenimines

Ketenimine	Characteristic infrared band,[a] cm^{-1}	Nmr data[b] Aromatic δ (no. of H)	Nmr data[b] Aliphatic δ (no. of H)
Dimethyl-N-(cyclohexyl)-	2022		1.1–2.1 m } (16) 1.57 s } 2.9–3.3 m (1)
Dimethyl-N-(phenyl)-	2016	7.3 s (5)	1.75 s (6)
Ethylphenyl-N-(*sec*-butyl)-	2011	7.1–7.3 m (5)	3.6 m (1) 2.4 q (2) 0.9–1.8 m (11)
Ethylphenyl-N-(phenyl)-	2002	7.1 s } (10) 7.4 s }	2.6 q (2) 1.2 t (3)
Diphenyl-N-(*sec*-butyl)-	2014	7.2–7.3 s (10)	3.6 m (1) 0.9–1.8 m (8)
Diphenyl-N-(phenyl)-	2003	7.2–7.5 m	

[a] In carbon tetrachloride. [b] In carbon tetrachloride with tetramethylsilane as internal standard. The abbreviations used are: m, multiplet; s, singlet; q, quartet; t, triplet.

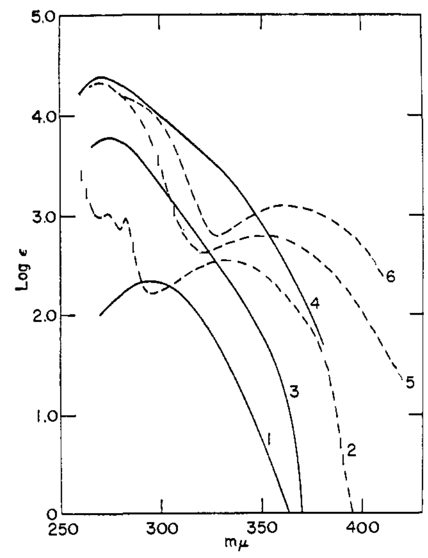
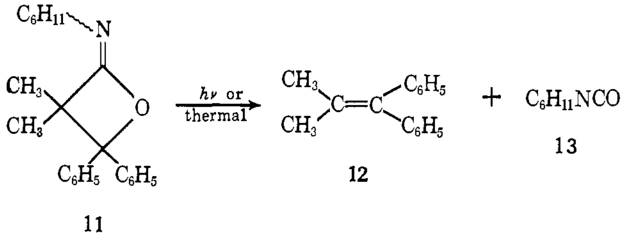


Figure 1. Ultraviolet absorption spectra of ketenimines in cyclohexane. Curve 1, dimethyl-N-(cyclohexyl)ketenimine; 2, dimethyl-N-(phenyl)ketenimine; 3, ethylphenyl-N-(*sec*-butyl)ketenimine; 4, diphenyl-N-(*sec*-butyl)ketenimine; 5, ethylphenyl-N-(phenyl)ketenimine; 6, diphenyl-N-(phenyl)ketenimine.

Benzophenone Adducts. The benzophenone adducts of ketenimines **5** and **6** were prepared by irradiating degassed benzene solution, *ca.* 0.2 *M* in each reactant, in sealed Pyrex ampoules with a 450-w Hanovia lamp, for the times given in Table II. Infrared analyses of the crude products indicated 95 and 70% consumption of starting materials. Attempts at direct crystallization failed and the reaction mixtures were chromatographed on Florisil.

Chromatography of the benzophenone–**5** reaction mixture yielded a solid (50%), mp 104–107°, which displayed the adduct band in the infrared[6] and readily formed isocyanate on xylene pyrolysis (150°, 24 hr) and irradiation through Vycor. The product showed only one spot in thin layer chromatography. The mass spectrum of the material contained the base peak at *m/e* 208 (olefin **12**), and a peak assigned to dimethyl-N-(cyclohexyl)ketenimine at *m/e* 151 was observed at 41% relative abundance. The intense olefin fragment precludes a β-adduct structure while a β-lactam formulation[11] is dismissed since the expected dominant imine fragment for that structure, *m/e* 263 for diphenyl-N-(cyclohexyl)ketimine, was present in only 2% relative abundance.[12] The product is assigned α-adduct structure **11**. Although the isolated yield of this adduct is only 50%, infrared analysis of the crude reaction mixture with an adduct calibration curve indicates a 92% yield of adduct. This high conversion to adduct is important for the kinetic work presented below where the quantum yield for adduct formation is determined by following the ketenimine disappearance.



11 **12** **13**

Chromatography of the benzophenone–dimethyl-N-(phenyl)ketenimine system gives a solid (mp 87–88°, 27%) which has the characteristic adduct band in the infrared but does not give isocyanate on xylene pyrolysis or irradiation through Vycor. A second isolated solid (mp 126–129°, 22%) also contains the adduct band in its infrared spectrum but readily yields isocyanate on xylene pyrolysis and on irradiation through Vycor. Figure 2 shows the mass spectra of the two products which are assigned α- (mp 126–129°) and β-adduct (mp 87–88°) structures. The β-adduct displays a base peak owing to a ketenimine fragment (*m/e* 145) with only a very small possible olefin peak (*m/e* 208, 2% relative abundance) while the α-adduct has an olefin base peak and no ketenimine peak. A β-lactam structure is precluded for the higher melting product since independent synthesis of the expected lactam by the addition of benzophenone anil to dimethylketene gives a compound, mp 122–124°, with a different infrared

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[10] C. L. Stevens and J. C. French, *J. Am. Chem. Soc.*, 75, 657 (1953).

[11] It was necessary to exclude a β-lactam structure for the isolated material because of an α-adduct–β-lactam isomerization that was encountered in studies in the fluorenone–ketenimine system. This isomerization was found to occur during Florisil chromatography and, to a lesser extent, during mass spectral analysis.

[12] Mass spectral studies in our laboratories indicate that the base peak of β-lactams is usually an imine fragment.

Table II. Preparation and Characterization of Benzophenone–Ketenimine Adducts

Ketenimine	Irradiation time and filter,[a] hr	Yield, % Adduct structure Mp, °C	Characteristic infrared band,[b] cm^{-1}	Nmr data[c] δ (no. of H)	Mol wt by mass spectroscopy,[d] exptl (theor)[e]
5	6.5 Pyrex	50.0 α 104–107	1745	7.1–7.5 m (10) 3.4–3.9 m (1) 1.1–2.0 m (16) 1.12 s	333.206723 (333.209254)
6	22.5 Pyrex	22.0 α 126–129	1739	6.7–7.8 m (15) 1.29 s (6)	327.161176 (327.162306)
		27.0 β 87–88	1738	7.1–7.6 m (15) 1.27 s (6)	327.16180 (327.162306)
7	64.0 Vycor	40.0 α Oil	1736	6.8–7.6 m (15) 3.8–4.2 m (0.5) 3.2–3.6 m (0.5) 0.7–2.0 m (13)	383.225848 (383.224903)
9	26.0 Vycor	32.0 α 167–169	1737	7.52 s (20) 4.1–4.5 m (1) 0.9–2.0 m (8)	431.223422 (431.224903)

[a] Irradiation of benzene solutions, *ca.* 0.2 *M* in each reactant, with a 450-w Hanovia lamp No. 679A-36. [b] In dichloromethane solution on a Beckman IR-7 spectrometer. [c] In carbon tetrachloride solution with tetramethylsilane as an internal standard. The abbreviations used are: m, multiplet; s, singlet. [d] Measured on an AEI-MS-9 spectrometer at a resolving power of 13,000. [e] J. H. Beynon and A. E. Williams, "Mass and Abundance Tables for Use in Mass Spectrometry," Elsevier, Amsterdam, 1963.

spectrum and a mass spectrum that has a larger imine (*m/e* 257) than olefin (*m/e* 208) peak. The imine fragment in the mass spectrum of the α-adduct results from α-adduct to β-lactam isomerization in the probe prior to cleavage.

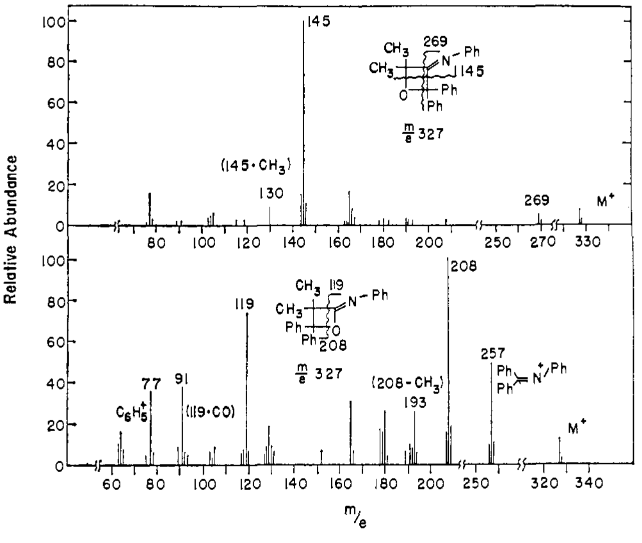


Figure 2. The upper half shows the mass spectrum of β-adduct of benzophenone and dimethyl-N-(phenyl)ketenimine. The lower half shows the mass spectrum of α-adduct of benzophenone and dimethyl-N-(phenyl)ketenimine.

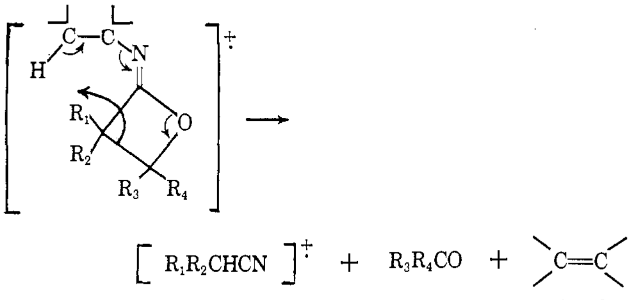
The benzophenone adducts with ketenimines **7** and **9** were prepared by irradiating argon-flushed, benzene solutions, *ca.* 0.2 *M* in each reactant, through Vycor, with a 450-w Hanovia lamp, for the times given in Table II. Infrared analyses of the crude reaction mixture of **7** revealed about 30% remaining starting material, 30% isocyanate, and 40% adduct, while **9** showed 45% starting material, 25% isocyanate, and 40% adduct. Both product mixtures were chromatographed on Florisil.

From the benzophenone–ethylphenyl-N-(*sec*-butyl)-ketenimine (**7**) reaction was obtained a 40% yield of a viscous oil which gave only one spot to thin layer chromatography and displayed the adduct band in the infrared. The material yielded isocyanate on xylene pyrolysis and irradiation through Vycor. The mass spectrum of the adduct showed strong fragment peaks at *m/e* 201, ethylphenyl-N-(*sec*-butyl)ketenimine, and *m/e* 284, 1,1,2-triphenyl-1-butene, but no imine fragment at *m/e* 237, diphenyl-N-(*sec*-butyl)ketimine. Accordingly, an α-adduct structure is assigned to this adduct.

The reaction mixture from the benzophenone–diphenyl-N-(*sec*-butyl)ketenimine (**9**) reaction yielded 32% of a solid (mp 167–169°) by chromatography. The product displayed the characteristic adduct band in the infrared. The mass spectrum of the product contained the base peak at *m/e* 193 (diphenylacetonitrile)[13] and showed an olefin fragment, *m/e* 332, for tetraphenylethylene, of 42% relative abundance and a ketenimine fragment, *m/e* 249, for diphenyl-N-(*sec*-butyl)ketenimine, of 10% relative abundance. No imine fragment, *m/e* 237, for diphenyl-N-(*sec*-butyl)ketimine, was observed. This cleavage pattern is consistent with α-adduct **14**.

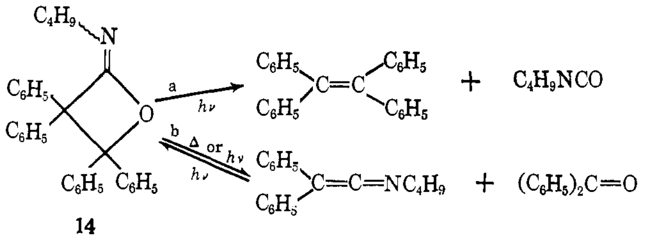
Xylene pyrolysis of **14** (150°, 24 hr) leads only to ketenimine and benzophenone (path b cleavage) while

(13) In these structures that have a β-hydrogen on the N substituent,



the base peak very often is a nitrile fragment and presumably arises from a fragmentation as shown.

photochemical cleavage through Vycor results in considerable isocyanate formation (path a cleavage). However, since path b cleavage is reversible under photochemical conditions, the observed path a photochemical cleavage products are not necessarily kinetically determined, and any apparent inconsistencies between the thermal and photochemical cleavage may not be real.



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The benzophenone adducts with ketenimines **8** and **10** could not be prepared in sufficient quantity for characterization even by irradiating dilute benzene solutions (0.02 *M*) for extended periods of time through Vycor.

There is no evidence for any thermal or photoinitiated dimerization of any of the ketenimines. Also, adduct formation does not occur in the dark at room temperature, or at 125° after several days. The additional structural question regarding *syn-anti* isomerization around the imine bond is unsettled at this time. Variable-temperature, nmr studies are now in progress, and hopefully will resolve this problem.

Relative Rates of Photocycloaddition. The relative rates of photocycloaddition of benzophenone with ketenimines **5**–**10** were determined by irradiating at room temperature a series of degassed and sealed Pyrex ampoules containing 0.05 *M* ketenimine and 1.0 *M* ketone in benzene on a rotating photochemical assembly. The light from a 450-w Hanovia lamp mounted in a water-cooled, Pyrex immersion well was passed through Corning 7-39 filters (transmission 320–400 mμ). Tubes were periodically removed and analyzed on a Beckman IR-7 spectrometer for disappearance of ketenimine. A minimum of four points from 0 to 25% reaction was used to determine the rates of ketenimine disappearance. Under the filtering and concentration conditions of the experiment, the amount of light absorbed by benzophenone varied from 100% with ketenimine **5** to 55% with ketenimine **10** because of light absorption by the ketenimines. However, filtering by the adduct products under the conditions of the experiment is unimportant. The corrected relative rates of photocycloaddition appear in Table III. The over-all rate spread in the benzophenone series is 110.

Table III. Relative Rates of Photocycloaddition of Benzophenone to Ketenimines[a]

Ketenimine	ϕ/ϕ_0[b]	Ketenimine	ϕ/ϕ_0[b]
5	1.00	**8**	0.056
6	0.46	**9**	0.097
7	0.37	**10**	0.0089

[a] Degassed and sealed Pyrex ampoules containing a benzene solution of 0.05 *M* ketenimine and 1.0 *M* benzophenone were irradiated on a rotating photochemical assembly with a 450-w Hanovia lamp through Corning 7-39 filters. [b] Rates relative to ketenimine **5** were corrected for light filtering by the ketenimines as follows: **5**, 0%; **6**, 9%; **7**, 5%; **8**, 30%; **9**, 17%; **10**, 45%.

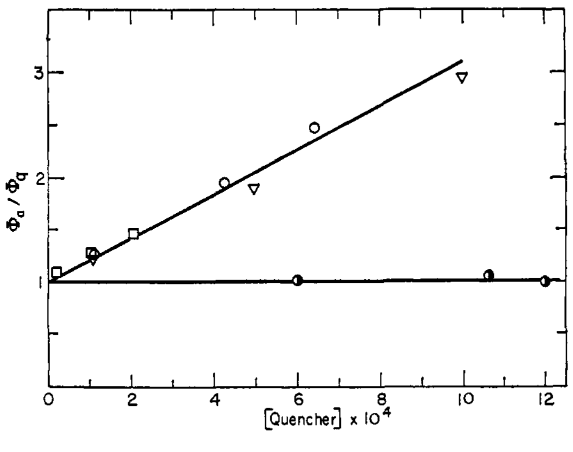

Figure 3. Ketenimine quenching of benzophenone photoreduction: ▽, ketenimine **8**; ◑, ketenimine **9**; ○, ketenimine **10**; □, ferric dipivaloylmethide.

The conditions and results of the rate studies clearly show that the primary light absorption process is excitation of the carbonyl compound.

Ketenimines as Quenchers of the Benzophenone Photoreduction. Since it was thought that the inefficiency of the photocycloaddition of benzophenone to the aryl-substituted ketenimines was due to a competing triplet, energy-transfer step, the effect of ketenimines on the benzophenone photoreduction (a well-defined reaction involving the benzophenone n–π* triplet state[14,15]) was investigated.

The method of Moore and Keetchum[15] was used to determine quenching curves for ketenimines **8**, **9**, and **10** and, for comparison, the quenching curve for ferric dipivaloylmethide[16] was run. Degassed and sealed Pyrex ampoules containing benzophenone, 0.12 or 0.20 *M*, and benzhydrol, 0.082 or 0.20 *M*, with and without added quencher, *ca.* 10^{-4} *M*, were irradiated to 25–30% consumption of benzophenone on a rotating photochemical assembly with a 450-w Hanovia lamp. The light was filtered through Corning 7-51 filters (transmissions 320–410 mμ). The maximum amount of light taken up by the added quencher in each case was as follows: ketenimine **8**, 6.6%; **9**, 1.2%; **10**, 5.4%; and ferric dipivaloylmethide, 5.2%. The disappearance of benzophenone in the presence and absence of quencher was followed either by ultraviolet or infrared (with use of a benzophenone calibration curve) techniques. The Stern–Volmer plots of ϕ_a/ϕ_q (the relative amount of benzophenone reacted in the absence and presence of quencher) against quencher concentration are shown in Figure 3. While ketenimines **8** and **10** show about the same quenching constant as ferric dipivaloylmethide (*ca.* 2300 l./mole), ketenimine **9** shows no quenching efficiency.

Quantum Yield Determinations. The quantum yields for the benzophenone–ketenimine **5**, **6**, and **9** reactions at different ketenimine concentrations were determined by using benzophenone–benzhydrol actinometry.[14a] Degassed and sealed Pyrex tubes containing benzene solu-

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(14) (a) W. M. Moore, G. S. Hammond, and R. P. Foss, *J. Am. Chem. Soc.*, **83**, 2789 (1961); (b) G. S. Hammond, W. P. Baker, and W. M. Moore, *ibid.*, **83**, 2795 (1961).

(15) W. M. Moore and M. Keetchum, *ibid.*, **84**, 1368 (1962).

(16) We wish to thank Dr. Steve Nelsen, University of Wisconsin, for a sample of this compound.

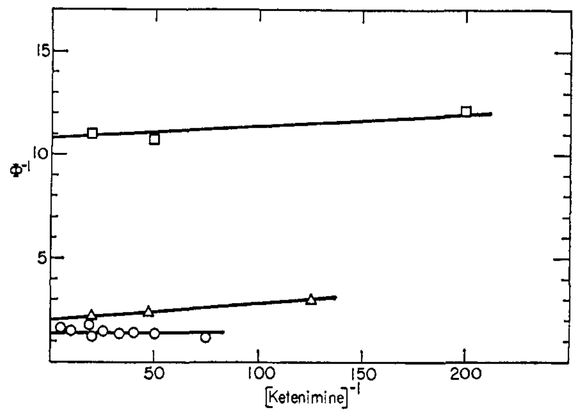

Figure 4. Dependency of the reciprocal of the quantum yield for ketenimine disappearance on the reciprocal of ketenimine concentration: O, ketenimine 5; △, ketenimine 6; □, ketenimine 9.

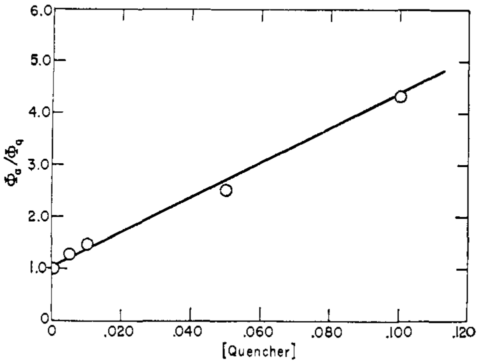

Figure 5. Stern–Volmer plot of naphthalene quenching for benzophenone–dimethyl-N-(cyclohexyl)ketenimine reaction. Quenching constant is 33.6 l./mole.

tions of 0.10 or 1.0 *M* benzophenone and various ketenimine concentrations were irradiated along with actinometer tubes in the rotating photochemical assembly. The light from a 450-w Hanovia lamp was filtered through Corning 7-39 filters (transmission 320–400 $\mathrm{m}\mu$). The rate of disappearance of ketenimine was followed to 25–35% reaction by infrared techniques. Good straight lines were obtained in all cases with a minimum of four points. The rates of ketenimine disappearance at the different ketenimine concentrations were adjusted to molar conversion rates by multiplying by the ketenimine concentration. The quantum yield was calculated by reference to the rate of benzophenone disappearance in the actinometer samples. The dependency of the reciprocal of the quantum yield for ketenimine disappearance on the reciprocal of the ketenimine concentration is shown in Figure 4 for ketenimines **5**, **6**, and **9**.[17] The limiting quantum yields for these three ketenimines are $\phi = 0.71$, 0.50, and 0.092.

Effect of Triplet Quenchers on the Benzophenone–Ketenimine 5 Reaction. The effect of added quenchers on the benzophenone–**5** reaction was investigated by following the rates of disappearance of ketenimine in the presence and absence of added quenchers. Degassed benzene solutions, 0.05 *M* in ketenimine and 1.0 *M* in benzophenone, were irradiated and analyzed as described above. No rate decrease was observed with added triplet quenchers in low concentrations, ferric dipivaloylmethide at 3×10^{-4} *M*, and atmospheric oxygen. However, naphthalene in concentrations greater than 10^{-2} *M* showed a quenching effect.

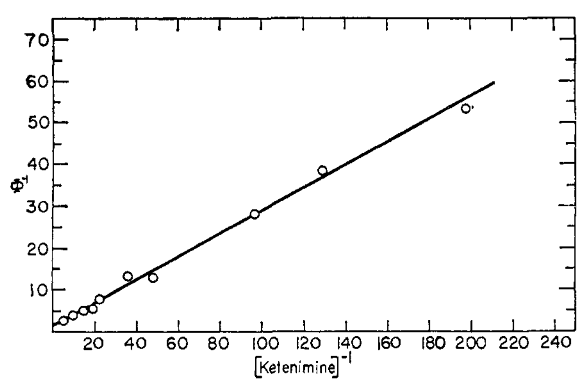

Figure 6. Reciprocal of quantum yield against reciprocal of ketenimine concentration for benzophenone–dimethyl-N-(cyclohexyl)ketenimine reaction in the presence of 0.10 *M* naphthalene.

To eliminate the problem of light filtering by naphthalene at high quencher concentrations, solutions of 1.0 *M* naphthalene in cyclohexane were used as additional filters for both the quenched and unquenched runs. A Stern–Volmer plot of naphthalene quenching of the benzophenone–ketenimine **5** reaction (1.0 *M* benzophenone, 0.05 *M* ketenimine in benzene) is shown in Figure 5. The calculated quenching constant is 33.6 l./mole.

The effect of varying ketenimine concentration on the quantum yield in the presence of 0.10 *M* naphthalene was determined for the benzophenone–ketenimine **5** reaction. The same techniques as described above for the naphthalene quenching experiment were employed. The rates of ketenimine disappearance were compared to the rate of benzophenone disappearance in benzophenone–benzhydrol actinometer tubes, and quantum yields were accordingly determined. The plot of the reciprocal of the quantum yield for ketenimine disappearance against the reciprocal of the ketenimine concentration (Figure 6) gives a straight line from 0.005 to 0.20 *M* ketenimine with a slope of 0.28 mole/l. and with an intercept that indicates a limiting quantum yield of 0.77.

Discussion

The scope of the photocycloaddition reaction of benzophenone to ketenimines seems fairly well defined. The reaction is only of preparative value with the more highly alkylated ketenimines, and both α- and β-adducts can result.

There appears to be a trend toward β-adduct with higher triplet energy carbonyl compounds. In the dimethyl-N-(2-cyanopropyl)ketenimine system,[6] *p*-chloro-, *p*-methoxy-, and unsubstituted benzaldehyde gave exclusively β-adducts, benzophenone gave mixtures of α- and β-adducts, and fluorenone yielded only α-adduct. Studies are underway to elucidate the factors controlling the direction of addition.

The relative rates of cycloaddition (Table III), the observed quenching of the benzophenone photoreduction by ketenimines **8** and **10**, and the naphthalene quenching of the benzophenone–**5** reaction suggest a

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[17] The data for ketenimines **6** and **9** were corrected for light absorption by ketenimine as follows: ketenimine **6**, 0.050 *M*, 9%, 0.022 *M*, 3.8%; ketenimine **9**, 0.050 *M*, 17%, 0.020 *M*, 6.8%, 0.005 *M*, 1.7%.

triplet mechanism. The simplest possible scheme (Scheme I) that fits these results involves excitation of

Scheme I

$$\mathrm{B} \xrightarrow{h\nu} {}^1\mathrm{B}^* \tag{1}$$

$$ {}^1\mathrm{B}^* \longrightarrow {}^3\mathrm{B}^* \tag{2}$$

$$ {}^3\mathrm{B}^* \xrightarrow{k_d} \mathrm{B} + \text{energy} \tag{3}$$

$$ {}^3\mathrm{B}^* + \mathrm{K} \xrightarrow{k_r} \mathrm{B{-}K} \tag{4}$$

$$ {}^3\mathrm{B}^* + \mathrm{K} \xrightarrow{k_t} \mathrm{B} + {}^3\mathrm{K}^* \tag{5}$$

$$ {}^3\mathrm{K}^* \longrightarrow \mathrm{K} \tag{6a}$$

benzophenone to its n–π^* singlet (1), crossover of the singlet to the triplet state (2), deactivation of the excited state by a first-order mechanism (3), and competing reactions of cycloaddition with (4), and energy transfer (5) to ground-state ketenimine. The excited ketenimine resulting from energy transfer returns to the ground state by some process that does not lead to a product (6a). This scheme is of the type presented for simple oxetane formation.[4,5]

The reactivity spread in the benzophenone series is due to step 4 becoming more important relative to step 3 as the triplet energy of the ketenimine is decreased with aryl substitution.

That energy transfer can occur from triplet benzophenone to ground-state ketenimine (step 3 in Scheme I) is clearly demonstrated by the quenching of the benzophenone photoreduction by ketenimines **8** and **10**. The lack of quenching by ketenimine **9** (which reacts faster with benzophenone than ketenimines **8** and **10**) can be attributed to less efficient energy transfer and/or more facile adduct formation that rapidly destroys the potential quencher.

Emission studies on the ketenimines are planned to directly determine their triplet energies. Also, we intend to investigate the effect of the ketenimines on the efficiency of benzophenone phosphorescence.

Kinetic Analysis

Kinetic analysis of Scheme I leads to the following rate law

$$1/\phi = 1 + [k_d + k_t(\mathrm{K})]/k_r(\mathrm{K}) = 1 + k_t/k_r + k_d/k_r(\mathrm{K})$$

where (K) is the concentration of ketenimines. This rate law explains the decrease in quantum yield with aryl substitution in the ketenimine structure for the benzophenone reaction as an increase in the k_t/k_r term. However, the slope of zero obtained in the plot of $1/\phi$ against 1/(K) (Figure 4) for the benzophenone–dimethyl-N-(cyclohexyl)ketenimine reaction is not adequately explained.

A slope of this magnitude means that k_r is *at least* 10^3 times greater than k_d. The very elegant discussion by Moore, Hammond, and Foss on the meaning of the k_d/k_r ratio in the benzophenone photoreduction[14a] can be applied here. A singlet mechanism is precluded by the greater than diffusion-controlled rate constant for photocycloaddition that results from a singlet k_d of $\sim 5 \times 10^9$ sec^{-1}. Using a k_d of 1×10^5 sec^{-1} for deactivation of the benzophenone triplet[18] leads to a k_r of, at least, 10^8 l. mole^{-1} sec^{-1}. Similarly, for the Stern–Volmer plot of naphthalene quenching of the 1.0 *M* benzophenone–0.05 *M* ketenimine **5** solutions (Figure 5) the following relationship holds

$$\phi_a/\phi_q = 1 + k_q(\mathrm{Q})/[k_d + k_r(\mathrm{K}) + k_t(\mathrm{K})] = 1 + k_q(\mathrm{Q})/\{k_d + [k_r + k_t](\mathrm{K})\} \approx 1 + k_q(\mathrm{Q})/[k_r + k_t](\mathrm{K})$$

where (Q) is the concentration of quencher. From the intercept in the case of the unquenched runs in Figure 4, $k_t/k_r = 0.4$; therefore

$$\phi_a/\phi_q = 1 + k_q(\mathrm{Q})/1.4k_r(\mathrm{K})$$

Since the slope is 33.6 l./mole at 0.05 *M* ketenimine, $k_q/k_r = 2.3$. Using a k_q for naphthalene in benzene of 1.0×10^9 l. mole^{-1} sec^{-1} [19] leads to a k_r of $\sim 4 \times 10^8$ l. mole^{-1} sec^{-1}, which agrees well with the previous estimate. The k_r for hydrogen atom abstraction by benzophenone triplet from benzhydrol is 5.0×10^6 l. mole^{-1} sec^{-1}.[14a] Thus the photocycloaddition reaction is *considerably faster* than the photoreduction reaction by this scheme.

Careful ultraviolet spectral analysis of benzophenone and dimethyl-N-(cyclohexyl)ketenimine solutions revealed no evidence for a ground-state complex that help explain this fast reaction rate.[20]

A second scheme, which we find more satisfying, involves irreversible[21] complex formation between benzophenone triplet and ground-state ketenimine (see Scheme II). Steps 1–5 are also found in Scheme I.

Scheme II

$$\mathrm{B} \xrightarrow{h\nu} {}^1\mathrm{B}^* \tag{1}$$

$$ {}^1\mathrm{B}^* \longrightarrow {}^3\mathrm{B}^* \tag{2}$$

$$ {}^3\mathrm{B}^* \xrightarrow{k_d} \mathrm{B} \tag{3}$$

$$ {}^3\mathrm{B}^* + \mathrm{K} \xrightarrow{k_t} \mathrm{B} + {}^3\mathrm{K}^* \tag{4}$$

$$ {}^3\mathrm{K}^* \longrightarrow \mathrm{K} \tag{5}$$

$$ {}^3\mathrm{B}^* + \mathrm{K} \xrightarrow{k_c} ({}^3\mathrm{B}^*, \mathrm{K}) \tag{6b}$$

$$ ({}^3\mathrm{B}^*, \mathrm{K}) \xrightarrow{k_{d'}} \mathrm{B} + \mathrm{K} \tag{7}$$

$$ ({}^3\mathrm{B}^*, \mathrm{K}) \xrightarrow{k_r} \mathrm{B{-}K} \tag{8}$$

Step 6b describes complex formation between benzophenone triplet and ground-state ketenimine. The complex can either deactivate (7) or proceed to adduct (8). The rate law that results from this scheme is

$$1/\phi = 1 + k_{d'}/k_r + [k_d + k_t(\mathrm{K})](k_{d'} + k_r)/k_r k_c(\mathrm{K})$$

Separating terms gives

$$1/\phi = 1 + k_{d'}/k_r + k_t(k_{d'} + k_r)/k_r k_c + k_d(k_{d'} + k_r)/k_r k_c(\mathrm{K})$$

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[18] J. A. Bell and H. Linschitz, *J. Am. Chem. Soc.*, **85**, 528 (1963).

[19] By using a k_q/k_r of 435 for naphthalene quenching of the benzophenone photoreduction[15] and a k_q/k_r of 400 for quenching by ferric dipivaloylmethide[14a] and a k_q for the latter of 0.9×10^6 l. mole^{-1} sec^{-1}.[18]

[20] Rate constants of this magnitude have been reported for reactions involving the n–π^* triplet state of ketones. P. J. Wagner and G. S. Hammond, *J. Am. Chem. Soc.*, **87**, 4009 (1965); **88**, 1245 (1966), report k_r's for intramolecular hydrogen atom abstraction in 2-hexanone and 2-pentanone of 1×10^9 and 2.0×10^8 sec^{-1}, respectively. The extent of reaction from the triplet state in these compounds is estimated as 60 and 95%, respectively.

[21] A very similar conclusion can be reached by employing reversible complex formation.

For the case of dimethyl-N-(cyclohexyl)ketenimine, energy transfer is assumed to be nonoperative ($k_t = 0$) and, therefore, the expression can be simplified.

$$1/\phi = 1 + k_{d'}/k_r + k_d(k_{d'} + k_r)/k_rk_c(\mathrm{K})$$

Since $(1 + k_{d'}/k_r)$ now determines the intercept in the plot of $1/\phi$ against the reciprocal of the ketenimine concentration, from Figure 4, $k_{d'}/k_r \approx 0.4$. Therefore, for this system

$$1/\phi = 1.4 + 1.4[k_rk_d/k_rk_c(\mathrm{K})] = 1.4 + 1.4k_d/k_c(\mathrm{K})]$$

In this scheme, by the argument given earlier, the rate constant for *complex formation* must have a minimum value of 10^8 l. mole^{-1} sec^{-1}. With the aryl-substituted ketenimines, as energy transfer becomes more important, the $k_t(k_{d'} + k_r)/k_rk_c$ term becomes large and the quantum yield decreases.

In the presence of 0.10 *M* naphthalene as quencher, additional steps are involved. Step 9 is energy

$$^3\mathrm{B}^* + \mathrm{Q} \xrightarrow{k_q} \mathrm{B} + {}^3\mathrm{Q}^* \qquad (9)$$

$$(^3\mathrm{B}^*, \mathrm{K}) + \mathrm{Q} \xrightarrow{k_{q'}} \mathrm{B} + \mathrm{K} + {}^3\mathrm{Q}^* \qquad (10)$$

transfer from noncomplexed benzophenone triplet to quencher and step 10 is quenching of the complex. The rate law in the presence of quencher follows.

$$1/\phi = 1 + \frac{k_{d'} + k_{q'}(\mathrm{Q})}{k_r} + \frac{[k_d + k_t(\mathrm{K}) + k_q(\mathrm{Q})][k_{d'} + k_{q'}(\mathrm{Q}) + k_r]}{k_rk_c(\mathrm{K})}$$

For the case of dimethyl-N-(cyclohexyl)ketenimine where $k_t = 0$, this simplifies to

$$1/\phi = 1 + [k_{d'} + k_{q'}(\mathrm{Q})]/k_r + [k_d + k_q(\mathrm{Q})][k_{d'} + k_r + k_{q'}(\mathrm{Q})]/k_rk_c(\mathrm{K})$$

The value of $[k_d' + k_q'(\mathrm{Q})]/k_r$ is available from the intercept of the plot of $1/\phi$ against the reciprocal of the ketenimine concentration in the quenching runs with 0.10 *M* naphthalene (Figure α) and is equal to 0.3. Therefore,

$$1/\phi = 1.3 + 1.3k_r[k_d + k_q(\mathrm{Q})]/k_rk_c(\mathrm{K}) = 1.3 + 1.3[k_d + k_q(\mathrm{Q})]/k_c(\mathrm{K})$$

From the runs in the absence of quencher, it is seen that $k_d/k_c(\mathrm{K}) \approx 0$ and therefore the slope in the presence of 0.10 *M* naphthalene is essentially determined by $1.3k_q(\mathrm{Q})/k_c$. Thus, at 0.10 *M* naphthalene, $k_q/k_c \approx 2.1$. Using a k_q for naphthalene of 1.0×10^9 l. mole^{-1} sec^{-1} [19] leads to a k_c of $\sim 5 \times 10^8$ l. mole^{-1} sec^{-1}. The difference between the two schemes then is that in the first the large rate constant in the denominator of the slope terms is k_r, and in the second it is k_c. We prefer the second interpretation because we find a rate constant of this magnitude more acceptable for *complex formation* than for a *bimolecular photocycloaddition.*

Conclusions

We conclude that for the benzophenone system (i) the primary photochemical process involves excitation of the carbonyl compound, (ii) that the reactive state of the carbonyl compound is its triplet state from which it can undergo cycloaddition with or energy transfer to ground-state ketenimine, and (iii) that reaction may proceed by way of complex formation between triplet benzophenone and ground-state ketenimine.

Experimental Section[22]

Materials. Benzene, Mallinckrodt, analytical reagent, was distilled through a 2-ft glass column packed with glass beads and a center cut was collected. **Benzophenone,** Matheson Coleman and Bell, and **benzhydrol,** Eastman, were recrystallized from ether–petroleum ether prior to use. **Xylene,** Mallinckrodt, analytical reagent, was dried over Linde Molecular Sieve prior to use.

Ketenimine Preparations. All the amides were prepared by conventional techniques from the appropriate acid chlorides and amines. Diphenyl-N-(*sec*-butyl)- (**9**) and diphenyl-N-(phenyl)-ketenimine (**10**) were prepared by dehydration of the corresponding amides by the procedure described by Stevens and Singhal.[9] Ketenimine **9** is a pale yellow solid, mp 39–40°, and ketenimine **10** is a bright yellow solid, mp 56–57°. Both can be obtained in yields of 25–30% by direct crystallization of the crude reaction mixture from ether–petroleum ether after the general work-up described by Stevens and Singhal.

Anal. Calcd for ketenimine **9**, $C_{18}H_{19}N$: C, 86.70; H, 7.68; N, 5.62. Found: C, 87.14; H, 7.82; N, 5.51.

Anal. Calcd for ketenimine **10**, $C_{20}H_{15}N$: C, 89.18; H, 5.61; N, 5.20. Found: C, 89.58; H, 5.81; N, 5.06.

Dimethyl-N-(cyclohexyl)- (**5**), dimethyl-N-(phenyl)- (**6**), ethylphenyl-N-(*sec*-butyl)- (**7**), and ethylphenyl-N-(phenyl)ketenimine (**8**) were prepared by the Stevens and Singhal dehydration procedure from the corresponding amides but using triethylamine as the solvent instead of pyridine. The above ketenimines could not be prepared in pyridine. A typical example is as follows for ketenimine **5**.

Into a 1 l., three-necked flask fitted with a condenser, an inlet tube for argon gas, and a good electric stirrer was added 20 g of dimethyl-N-(cyclohexyl)acetamide followed by 50 g each of phosphorus pentoxide and oven-dried (120°) Florisil and then 400 ml of triethylamine. The system was flushed with argon gas for 5 min and then vigorously stirred and refluxed under an argon atmosphere for 23 hr. The mixture was cooled to room temperature and the triethylamine solution was decanted from the solid residues. After the solvent was removed under reduced pressure, the oily residue was vacuum distilled to yield 3.2 g (17.7%) of a colorless liquid, bp 77° (9.0 mm). Ketenimines **6**, **7**, and **8** were similarly prepared and purified. Ketenimine **6**, pale yellow liquid, bp 81–83° (4.5 mm); **7**, pale yellow liquid, bp 91–93° (0.50 mm); **8**, deep yellow liquid, bp 130–135° (0.55 mm).

Anal. Calcd for ketenimine **5**, $C_{10}H_{17}N$: C, 79.40; H, 11.34; N, 9.26. Found: C, 79.04; H, 11.66; N, 9.83.

Anal. Calcd for ketenimine **6**, $C_{10}H_{11}N$: C, 82.72; H, 7.64; N, 9.65. Found: C, 82.29; H, 7.78; N, 9.28.

Anal. Calcd for ketenimine **7**, $C_{14}H_{19}N$: C, 83.53; H, 9.51; N, 6.96. Found: C, 83.28; H, 9.75; N, 6.87.

Anal. Calcd for ketenimine **8**, $C_{16}H_{15}N$: C, 86.84; H, 6.83; N, 6.33. Found: C, 86.63; H, 7.10; N, 6.55.

Preparation of Photoadducts. The benzophenone–ketenimine **5** and **6** photoadducts were prepared in the following manner. Degassed (freeze–thaw cycle) and sealed Pyrex ampoules containing equimolar quantities of each reactant in benzene (*ca.* 0.1–0.3 *M*) were taped to a quartz immersion well fitted with a Pyrex sleeve and containing a 450-w Hanovia lamp, No. 679A-36, and were irradiated at room temperature for the times designated in Table II. The benzophenone–ketenimine **7** and **9** photoadducts were similarly prepared except that tightly stoppered Vycor ampoules containing argon-flushed benzene solutions were used and the quartz immersion well was fitted with a Vycor sleeve. The crude reactions were analyzed by infrared techniques for remaining starting materials, extent of adduct formation, and degree of photocleavage of the α-adducts to isocyanate and olefin. The benzene was removed *in vacuo*, and the adducts were isolated by column chromatography on Florisil. The yields reported in Table II are for *isolated* products. All the products gave excellent high resolution mass spectrometric molecular weight analyses (see Table II).

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(22) (a) Combustion analyses were performed by Micro-Tech Laboratories, Inc., Skokie, Ill., and Schwarzkopf Microanalytical Laboratory, Woodside 77, N. Y. (b) All boiling and melting points are uncorrected.

β-Lactam of Dimethylketene and Benzophenone Anil. To a solution of 0.90 g of triethylamine (0.089 mole) and 2.0 g of benzophenone anil[23] (0.078 mole) in 45 ml of benzene was added, at reflux temperature, and under an argon atmosphere, 0.85 g of isobutyryl chloride (0.080 mole) in 20 ml of benzene. The mixture was stirred and refluxed for an additional 4.0 hr and cooled to room temperature, and the precipitated triethylammonium chloride was filtered off. The filtrate was concentrated *in vacuo* to an oil which was crystallized from ether–petroleum ether to give 1.2 g of a solid, mp 91–104°. Several recrystallizations from ether–petroleum ether raised the melting point to 122–124°. The infrared spectrum of this material was different, in the same solvent, from that of the α-adduct of benzophenone and dimethyl-N-(phenyl)ketenimine: characteristic infraredb and at 1745 cm^{-1} (dichloromethane); mass spectrometric molecular weight: 327.164316; theoretical for $C_{23}H_{21}NO$: 327.162306.

Relative Rates, Quantum Yields, and Quenching Experiments. All quantitative measurements were made on a rotating assembly with a central light source. Samples in 13-mm Pyrex ampoules were placed in holders on the assembly 5.5 cm from a 450-w Hanovia lamp, No, 679A-36, maintained in a water-jacketed, Pyrex immersion well. Corning 2 × 2 in. filters of the types indicated in the text were mounted in four filter holders flush against the well. The rest of the well was taped to eliminate stray light. All studies were made at room temperature. Samples in 13-mm, Pyrex test tubes were degassed to 5×10^{-3} mm in two freeze–thaw cycles and then sealed. In experiments where naphthalene filters were used, the samples were prepared in 7-mm Pyrex test tubes which, after degassing and sealing, were positioned with a cork in 13-mm Pyrex test tubes partly filled with a 1.0 *M* naphthalene in cyclohexane solution. The "tube within a tube" arrangement was then placed in the rotating assembly. Benzophenone–benzhydrol actinometry[14a] was used for quantum yield determinations. In the quantum yield experiments for ketenimines **5**, **6**, and **9** (Figure 4) actinometry was accomplished with solutions of 0.10 *M* benzophenone and 0.10 *M* benzhydrol in benzene. An actinometer quantum yield of 0.66 was used.[14a] In the quantum yield determinations for the benzophenone–ketenimine **5** reaction in the presence of 0.10 *M* naphthalene, actinometer tubes containing 0.10 *M* benzophenone and 1.0 *M* benzhydrol in benzene were used with a quantum yield of 0.97[14a] (Figure 6).

Mass Spectrometric Analyses.[24] All mass spectra were taken on an AEI MS-9 spectrometer at an ionizing voltage of 70 ev and a probe temperature of *ca.* 150°.

Ultraviolet Spectral Analysis of Benzophenone–Ketenimine 5 Solution. The ultraviolet spectrum of a solution of 0.05 *M* benzophenone and 0.50 *M* dimethyl-N-(cyclohexyl)ketenimine in benzene was recorded on a Cary 14 spectrometer using 1-mm cells and was identical with the additive spectrum of the individual solutions from 340 to 400 mμ.

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[23] G. Reddelien, *Ber.*, 48, 1469 (1915).

[24] We wish to thank Mr. Bill Klymus for technical assistance in running the mass spectra.

The Valence Isomerization of 1,2-Divinylaziridines. Synthetic and Kinetic Studies[1,2]

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Abstract: The 1,2-divinylaziridine IV has been prepared by the low-temperature addition of hexafluoro-2-butyne to 2-vinylaziridine. Rate measurements of 1,2-divinylaziridine IV valence isomerization to the azepine V gives the kinetic expression $k_1 = 10^{12} \exp(-16{,}500/RT)$. It was established that the rate of the valence isomerization process is far less than that for inversion about the ring nitrogen. The low-temperature addition of hexafluoro-2-butyne to *trans*-2,3-divinylaziridine has yielded 1,2,3-trivinylaziridine VIII. The latter aziridine was shown to isomerize to the corresponding azepine IX at the same rate as the divinylaziridine IV.

Recent valence isomerization studies of *cis*-divinyl, three-membered rings have indicated that the thermal requirements for the transformation I → II is dependent upon the nature of the ring.

I II

X=C, N, O, S

The temperature necessary to induce ring expansion of I increases in the order: carbon,[3,4] nitrogen,[1] oxygen,[5] sulfur.[1] The fact that the above sequence also corresponds to increasing ring stability[6] suggests that the relief of ring strain plays an important role in the valence isomerization process. Consonant with this idea is the finding that *cis*-2,3-divinylaziridine requires a significantly lower isomerization temperature relative to the 60° reported[5] for *cis*-divinyloxirane and the 100° observed for *cis*-divinylthiirane.

The difficulty in assigning the isomerization temperature to the nitrogen analog lies in the limitations of the

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[1] Paper II in this series: E. L. Stogryn and S. J. Brois, *J. Org. Chem.*, 30, 88 (1965).

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