viously.[4] All decarbonylations were carried out at 129.6 ± 0.1° using chlorobenzene as the solvent. The relative amounts of *trans*-2-hexene, *cis*-2-hexene, and the sum of 4-methyl-*trans*-2-pentene and 4-methyl-*cis*-2-pentene could be conveniently determined employing the TCEP column (30°). The *trans*- to *cis*-4-methyl-2-pentene ratio was determined separately on the PGSN column (26°). Alternatively, the two columns could be connected in series to resolve all four components (47°). The detector responses of the four olefins were the same within experimental error, so that the integrated peak areas could be compared directly. All the necessary precautions[4] were taken in order to obtain reproducible data. The aldehyde solutions were heated for varying lengths of time, depending upon their concentrations. The reaction periods used were: 6–4.0 *M*, 20 min; 3.0 *M*, 25 min; 2.0 *M*, 30 min; 1.5 *M*, 35 min; 1.0 *M*, 45 min; 0.75 *M*, 60 min; 0.50–0.38 *M*, 90 min; 0.25–0.094 *M*, 120 min. The products from 3-methyl- and 2-methyl-*trans*-4-hexenal (Tables II and IV) show that less than 10% decarbonylation occurred in the 4.0 and 0.50 *M* solutions. Additionally, it was shown that aldehyde solutions could be heated twice as long as the reaction periods listed above without significantly changing the olefin ratios obtained.

Product Studies. The decarbonylation reaction products of 3-methyl- and 2-methyl-*trans*-4-hexenal were investigated employing the reaction conditions used in the study of the relationship between olefin ratios and initial aldehyde concentrations. Solutions (4.0 and 5.0 *M*) of both aldehydes were prepared and decarbonylated following the procedure outlined under Olefin Ratios. So little products were formed that it was necessary to characterize the various products by their retention times alone. Trace components were identified by peak augmentation with presumed products. A precisely weighed quantity of methylcyclohexane was added as an internal standard to each of the product solutions in order to determine the yield of products. The results of the analyses are reported in Tables II and IV. Acetone, *t*-butyl alcohol, di-*t*-butyl peroxide, and unreacted aldehyde were present in substantial quantities, but were not included in the tables.

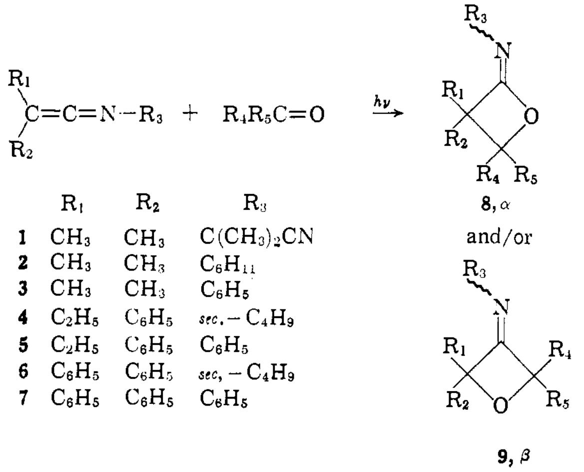
The Photocycloaddition of Fluorenone to Ketenimines

Lawrence A. Singer and Gene A. Davis

Contribution from the Department of Chemistry, The University of Chicago, Chicago, Illinois 60637. *Received October 12, 1966*

Abstract: The facile photocycloaddition of fluorenone across the carbon–carbon double bond of six ketenimines to give α-iminooxetanes (**8**) is described. Isomerization of the α adducts to β lactams has been observed. The use of mass spectroscopy in structural elucidation of the α adducts and β lactams and previously reported β adducts (**9**) is described in some detail. The relative rates of photocycloaddition of fluorenone to dimethyl-N-(cyclohexyl)- (**2**), dimethyl-N-(phenyl)- (**3**), ethylphenyl-N-(*sec*-butyl)- (**4**), ethylphenyl-N-(phenyl)- (**5**), diphenyl-N-(*sec*-butyl)- (**6**), and diphenyl-N-(phenyl)ketenimine (**7**) are within a factor of 4 of each other. The absence of a reactivity spread throughout this series suggests that energy transfer from triplet fluorenone to ground-state ketenimine is not competitive with photocycloaddition as was the case with the previously studied benzophenone–ketenimine system. The possible importance of dipole–dipole interactions between ground-state ketenimine and the electronically excited carbonyl compound in influencing the direction of cycloaddition is considered.

Recently, we described the photoinduced cycloaddition of aldehydes and ketones to ketenimines **1–7** to give iminooxetanes of α (**8**) or β (**9**) structure.[1,2] This reaction is an extension of the well-known Paterno–Büchi reaction in which aldehydes and ketones undergo photocycloaddition with simple olefins to give oxetanes.[3–7]



	R₁	R₂	R₃
1	CH_3	CH_3	$C(CH_3)_2CN$
2	CH_3	CH_3	C_6H_{11}
3	CH_3	CH_3	C_6H_5
4	C_2H_5	C_6H_5	*sec*,−C_4H_9
5	C_2H_5	C_6H_5	C_6H_5
6	C_6H_5	C_6H_5	*sec*,−C_4H_9
7	C_6H_5	C_6H_5	C_6H_5

We[1] and others[6,7] have pointed out two important reactivity features of the Paterno–Büchi reaction involving olefins and ketenimines: (i) that there is correlation with the photoreduction reaction[8] to the extent that carbonyl compounds with n–π* triplet states are more reactive than those with π–π* triplet states[8,9] and (ii) that energy transfer from the triplet carbonyl compound to ground-state olefin or ketenimine is competitive with cycloaddition when the triplet level of the carbonyl compound is higher than that of the olefin or ketenimine. The first condition is demonstrated by the decreased reactivity of 2-acetonaphthone and 1-naphthaldehyde (π–π* triplet states[8]) toward olefins[6,7] and ketenimines[1a] and the second by the absence of oxetane formation when benzophenone is irradiated in the presence of dienes ($E_t \sim 60$ kcal/

---

[1] (a) L. A. Singer and P. D. Bartlett, *Tetrahedron Letters*, 1887 (1964); (b) L. A. Singer and G. A. Davis, *J. Am. Chem. Soc.*, **89**, 598 (1967).

[2] The question of *syn-anti* isomers in these adducts is not yet resolved.

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

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

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

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

[7] N. C. Yang, M. Nussim, M. J. Jorgenson, and S. Murov, *ibid.*, 3657 (1964).

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

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

Table I. Preparation and Characterization of the Fluorenone–Ketenimine Adducts

Ketenimine	Irradiation time,[a] hr	Method of isolation and mp, °C (yield, %)	Characteristic[b] infrared band, cm^{-1}	Nmr[c] data, δ (no. of H)	Mol wt by mass spec,[d] exptl (theor)[e]
2	3.0	Direct cryst 124–126 (74)	1744	7.2–7.7 m (8) 3.5–3.9 m (1) 1.2–2.1 1.33 s (16)	331.193775 (331.193604)
3	23.0	Direct cryst 133–135 (22)	1739	7.0–7.7 m (13) 1.40 s (6)	325.144457 (325.146656)
4	5.5	Direct cryst 109–110 (78)	1737	6.5–7.9 m (13) 3.8–4.1 m (1) 2.6 q (10) 0.7–2.0 m (12)	381.211152 (381.209254)
5	30.0	Chrom[f] 174–176 (30)	1743[f]	6.5–7.9 m (13)[f] 2.6 q (1) 1.6 q (1) 0.8 t (3)	401.179657[f] (401.177955)
6	3.0	Direct cryst 176–177 (64)	1737	6.5–7.7 m (18) 3.8–4.2 m (1) 0.9–1.9 m (8)	429.208544 (429.209254)
7	15.0	Direct cryst 186–188 (50)	1728	7.0–8.0 m	449.176595 (449.177955)

[a] Degassed benzene solutions *ca.* 0.1–0.3 *M* in each reactant were irradiated with a 450-w Hanovia lamp, No. 679-36. [b] In carbon tetrachloride on a Beckman IR-7 spectrometer. [c] In chloroform-*d* with tetramethylsilane as an internal standard. Abbreviations used are: m, multiplet; s, singlet; q, quartet; t, triplet. [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 Publishing Co., Amsterdam, 1963. [f] This product is a β lactam.

mole) or low triplet energy olefins.[6] Further, it is observed that the rate of photocycloaddition of benzophenone to ketenimines decreases with aryl substitution in the ketenimine structure owing to energy transfer becoming more important as aryl substituents lower the triplet energy of the ketenimine.[1b]

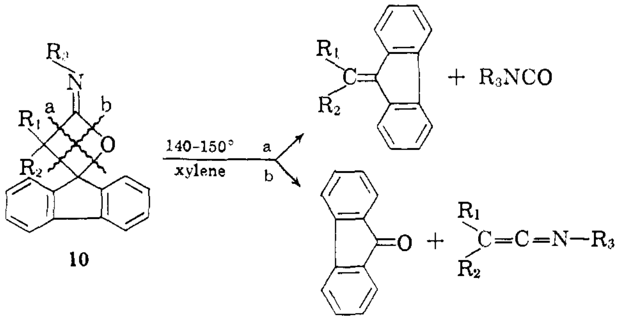
We now wish to report on the facile photocycloaddition of fluorenone to ketenimines **2**–**7** which leads exclusively to α adducts (**8**).

Results

Fluorenone α-Adducts. Ketenimines **2**–**7** were prepared as previously described.[1b] The adducts were prepared by irradiating degassed and sealed Pyrex ampoules containing benzene solutions 0.1–0.3 *M* in each reactant for the times given in Table I with a 450-w Hanovia lamp. Infrared analyses of the crude reaction mixtures indicated 80–100% consumption of the ketenimines and fluorenone and the formation of a strong adduct band[1] at *ca.* 1720–1750 cm^{-1}. In addition, a band due to isocyanate (from 5 to 30% of product) was observed due to photocleavage of the α adducts (see below). The fluorenone adducts of **2**, **3**, **4**, **6**, and **7** could be isolated by direct crystallization of the reaction mixture from petroleum ether–ether after removal of the benzene under reduced pressure. Table I summarizes the important information for the preparation and characterization of these adducts.

The α-adduct structure (**8**) is assigned to these adducts on the basis of thermal and mass spectral cleavage patterns. All (fluorenone–**2**, –**3**, –**4**, –**6**, and –**7**) cleave to isocyanate and olefin (Chart I, path a) and ketenimine and fluorenone (path b) in xylene at 140–150°. Photochemical cleavage by path a also can occur since irradiation of these adducts in benzene under the conditions of their preparation leads to extensive isocyanate formation. Therefore, the isolated adduct yields reported in Table I are lower limits of the extent of cycloaddition.

Chart I



Additional structural information is available from the mass spectral cleavage patterns of these adducts. They all show olefin and ketenimine fragments from path a and path b cleavages which can only arise from an α formulation. The β adducts would be expected to show only ketenimine fragments. This contrast in cleavage patterns is illustrated in Figure 1 in the mass spectra of the α- and β-benzophenone–**1** adducts.[1,10] While the α adduct shows very strong olefin (*m/e* 208) and ketenimine (*m/e* 136) fragments, the β adduct shows only the two possible ketenimine fragments at *m/e* 136 and *m/e* 260. Another very good example of this contrast in cleavage patterns can be found in the previously reported mass spectra of the α and β adducts of benzophenone–**3**.[1b]

It will be noted that, in the mass spectra shown in Figure 1, the base peak for both adducts is at *m/e* 69. It has been observed that in structures where the

(10) Previously,[1a] it was reported that only the β adduct of benzophenone–**1** could be isolated by Florisil chromatography because of hydrolysis of the α adduct to amide on the column. However, we find that by drying the Florisil at 130° before use, the α adduct is also isolable.

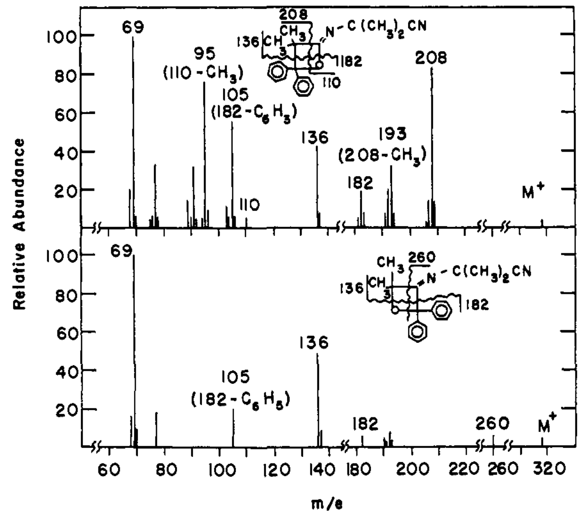
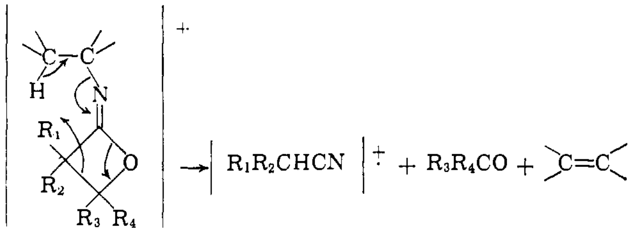


Figure 1. Upper, mass spectrum of α adduct of benzophenone–**1**; lower, mass spectrum of β adduct of benzophenone–**1**.

N substituent has an abstractable β hydrogen (**11**), the base peak is due to nitrile and presumably arises from a fragmentation as shown in Chart II. Thus, the base peak at *m/e* 69 is due to 2-cyanopropane.

Chart II

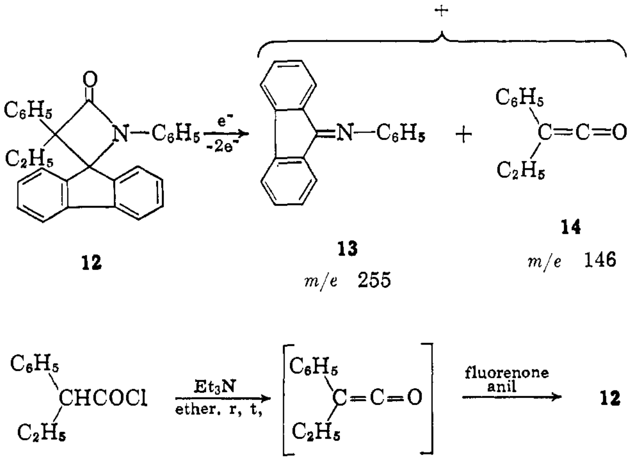


11

The mass spectrum of the fluorenone-**2** adduct is shown in Figure 2 (upper) for illustration. Also the mass spectra of the fluorenone adducts of **3**, **4**, **6**, and **7** are consistent with the α formulation.

β-Lactams. The fluorene–**5** product which was isolated after Florisil chromatography is assigned a β-lactam rather than α-adduct structure.[11] Attempts at direct crystallization of the reaction mixture were unsuccessful. No isocyanate was found on xylene pyrolysis of the isolated material but irradiation of a benzene solution did result in isocyanate formation. The mass spectrum (Figure 2, lower) shows a base peak at *m/e* 255 which is assigned to the fluorenone anil ion molecule (**13**). The ketene ion molecule (**14**) is also formed at a relative abundance of 4%. There are no peaks due to ketenimine or olefin. The β lactam was independently synthesized by the ketenimine route shown in Chart III and was found to be identical in all respects with the isolated material.

Chart III



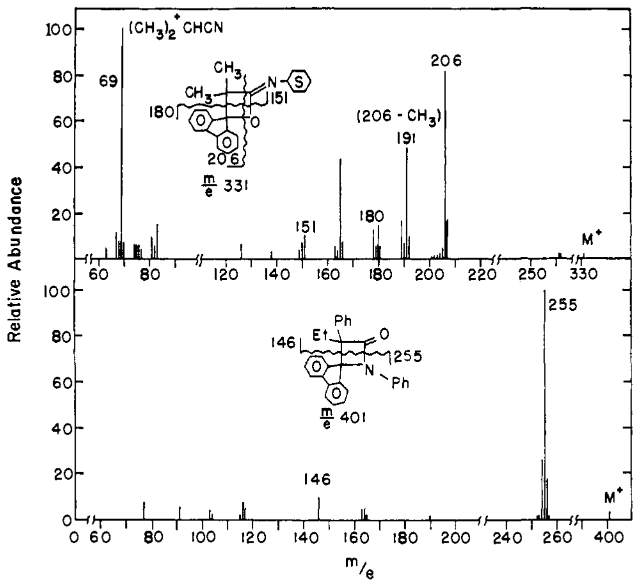
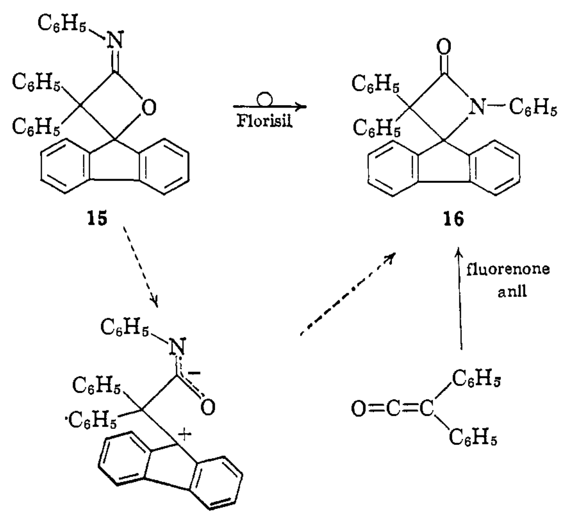


Figure 2. Upper, mass spectrum of α adduct of fluorenone-**2**; lower, mass spectrum of β lactam from ethylphenylketene and fluorenone anil. Isomerization product of α adduct of fluorenone-**5**.

Apparently the initial photoproduct from the fluorenone–**5** reaction is an α adduct and **12** is an isomerization product. Isomerization may have occurred during Florisil chromatography since when α adduct **15** is passed down a Florisil column with ether–petroleum ether, β-lactam **16** is formed. β-Lactam **16** was identified by comparison with an authentic sample prepared by the addition of diphenylketene to fluorenone anil (Chart IV). These rearrangements may pro-

Chart IV



---

[11] Unfortunately, infrared analysis is not helpful in distinguishing between α-adduct and β-lactam structures since the imino group of the former and the carbonyl group of the latter have almost identical stretching frequencies.

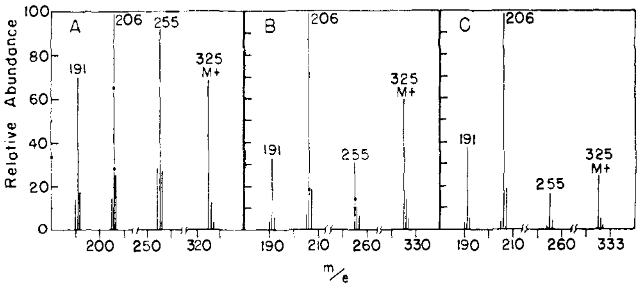
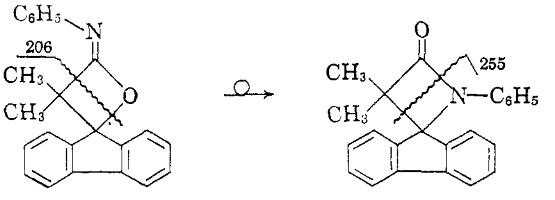


Figure 3. Effect of ionizing voltage and probe temperature on mass spectrum of α adduct of fluorenone–**3**: A, 70 ev, 190°; B, 20 ev, 190°; C, 16 ev, 140°.

ceed by way of a zwitterionic intermediate such as is shown in **17**.

This isomerization also occurs to a lesser extent during mass spectrometric analysis since imine peaks are observed in the mass spectra of some of the α adducts. However, while the imine fragments are the base peaks in β-lactam spectra[12] with the olefin fragments being present in 10% or less relative abundance (Figure 2), in the spectra of the α adducts the ketenimine and/or olefin fragments are more intense. Further, the intensity of the imine fragment relative to the olefin fragment decreases as the ionizing voltage and probe temperature are lowered because of a corresponding decreases in the extent of isomerization. Figure 3 shows this effect for the fluorenone–**3** α adduct (**18**). At 70 ev and a probe temperature of 190° (Figure 3A), the imine peak (*m/e* 255) is almost as intense as the olefin peak (*m/e* 206). The peak at 191 is 206 – CH_3. At 20 ev and 190° (Figure 3B), the imine peak is considerably reduced in intensity, and at 16 ev and 140° (Figure 3C), this trend continues.



18 **19**

Relative Rates of Photocycloaddition. The relative rates of photocycloaddition of fluorenone to ketenimines **2–7** were determined by irradiating a series of degassed and sealed Pyrex ampoules containing benzene solutions of 0.05 *M* ketenimine and 1.0 *M* fluorenone on a rotating photochemical assembly. The light from a 450-w Hanovia lamp was filtered through Corning 7–39 filters (transmission 320–400 mμ). The rates were determined by following the disappearance of the ketenimines by infrared techniques. A minimum of four points from 0 to 25% consumption of ketenimine gave good straight-line plots. The relative rates are given in Table II. The quantum yield for the fluorenone–**2** reaction under these conditions was determined with benzophenone–benzhydrol actinometry[13] and is 0.33.

Table II. Relative Rates of Photocycloaddition of Fluorenone to Ketenimines[a]

Ketenimine	ϕ/ϕ_0[b]	Ketenimine	ϕ/ϕ_0[b]
2	1.00 (ϕ = 0.33)[c]	**5**	0.32
3	0.27	**6**	0.80
4	0.54	**7**	0.32

[a] Degassed and sealed Pyrex ampoules containing benzene solutions of 0.05 *M* ketenimine and 1.0 *M* fluorenone. [b] Rates relative to fluorenone–**2** reaction were corrected for light absorption by the ketenimines as follows: **2**, 0%; **3**, 2.3%; **4**, 2.2%; **5**, 9.5%; **6**, 3.5%; **7**, 19.8%. [c] The quantum yield for fluorenone–**2** reaction was measured with benzophenone–benzhydrol actinometry.[13]

Discussion

Relative Rates. Previously,[1b] we proposed a mechanism for the photocycloaddition of benzophenone to ketenimines which involves the n–π^* triplet state of the ketone in competing steps of cycloaddition and energy transfer to ground-state ketenimine. Such a scheme accommodates the reactivity spread of 110 found in the benzophenone–**2–7** series. Each introduction of an aryl group decreases the rate of cycloaddition because the triplet level of the ketenimine is accordingly decreased enhancing energy transfer relative to cycloaddition.

The lack of any significant reactivity spread in the fluorenone–**2–7** series suggests that energy transfer is not important anywhere in the series. This is not surprising in view of the 18-kcal/mole difference in triplet energies between the two ketones (benzophenone, E_t = 68.5;[14] fluorenone, E_t = 50[15]) and places a lower limit on the triplet levels of the ketenimines of about 50 kcal/mole. The upper limit is somewhat greater than the triplet level of benzophenone since energy transfer is not thought to occur in the benzophenone–**2** reaction (ϕ_{limiting} = 0.71).[1b]

Direction of Photocycloaddition. In this and other studies[1a] it is found that the photocycloaddition of fluorenone to seven ketenimines of alkyl and aryl substitution results in exclusive α-adduct formation. In contrast, benzophenone reacts with ketenimines **1** and **3** to give some β adduct,[1] and *p*-chloro-, *p*-methoxy-, and unsubstituted benzaldehyde add to **1** to give only β adduct.[1a]

At this time we can only speculate on this trend. While the observed pattern does indicate more β adduct with the higher triplet energy aldehydes and ketones (benzaldehyde, E_t = 71.9[14]), it is difficult to ascribe a role to this fact. More important may be the extent of dipole–dipole interactions between the carbonyl compound in its n–π^* excited state and the ground-state ketenimine.

Freeman and Klemperer[16] have shown that the dipole moment of formaldehyde is decreased in the n–π^* excited state (1.48 D.) relative to the ground state (2.34 D.[17]). This is an expected result for an excited electronic state where the electron density around oxygen is decreased and that around carbon is increased relative to the ground state. Unfortunately, the dipole moments of the excited states of benzaldehyde,

---

(12) In the mass spectrum of **16**, the base peak is also at *m/e* 255 as it is in **12**.

(13) (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); (c) W. M. Moore and M. Keetchum, *ibid.*, **84**, 1368 (1962).

(14) W. G. Herkstroeter, A. A. Lamola, and G. S. Hammond, *J. Am. Chem. Soc.*, **86**, 4537 (1964).

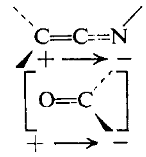
(15) N. C. Yang, *Pure Appl. Chem.*, **9**, 591 (1964).

(16) D. E. Freeman and W. Klemperer, *J. Chem. Phys.*, **40**, 604 (1964).

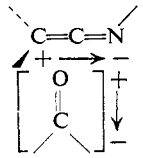
(17) J. N. Shoolery and A. H. Sharbaugh, *Phys. Rev.*, **82**, 95 (1951).

benzophenone, and fluorenone have not been measured. However, because of the extended nature of the molecular orbital into which the electron is promoted in the n–π* states of the aromatic carbonyl compounds, the reverse polarization should be considerably enhanced relative to formaldehyde. If the over-all dipole moment is actually *reversed*, dipole–dipole interactions would favor α-adduct formation.

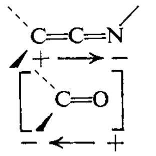
The calculated dipole moment of ketenimine **2** is ~1.2 D. by the bond-moment method.[18] A reverse dipole moment in the excited state of the carbonyl compound must be >1.5 D. at a distance of 3 A or less to influence the populations of the orientations shown in **20**, **21**, and **22**. For example, if the reverse dipole in the carbonyl compound is 2.0 D., at a distance of 3 A, the potential energy difference between **20** and **22** is about 18 × 10^{-14} erg/molecule (~2.6 kcal/mole), and that between **22** and **21** is about 9 × 10^{-14} erg/molecule. At 300°K, n_{22}/n_{20} = 79, and n_{22}/n_{21} = 9.[19]



20



21



22

In order for the product distribution to be determined by ground-state populations of **20**, **21**, and **22**, the activation energy for adduct formation must not be large relative to the barriers relating the ground-state orientation.[20] Kinetic studies[1b,20a] indicate that these photocycloadditions have rate constants >10^8 l. mole^{-1} sec^{-1} which means $\Delta F^{\ddagger} < 6.5$ kcal/mole. Therefore, the Curtin–Hammett principle may not apply to these fast photocycloadditions.[21]

Steric interactions would favor **20** relative to **22** and enhance β-adduct formation. To the extent that there is a balancing of dipolar and steric orienting effects, the tendency for α-adduct formation in fluorenone may be due to a minimal steric effect in this planar molecule as well as to a maximum polar effect. The degree to which each of these effects operates cannot be determined at this time. The over-all stereochemical results suggest that the relative magnitudes of the reverse dipole moments are fluorenone > benzophenone > benzaldehyde.

While this particular argument regarding the role of dipolar orienting forces in enhancing α-adduct formation is valid only *if the dipole moments of the excited states of the carbonyl compounds are* $\gtrsim$*1.5 D. in the reverse direction*, we suggest that, in general, consideration must be given to dipolar orienting influences in these *fast* photocycloadditions.

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 taken. **Benzophenone**, Matheson Coleman and Bell, **fluorenone**, Aldrich, and **benzhydrol**, Eastman, were all recrystallized from ether–petroleum ether prior to use. **Xylene**, Mallinckrodt analytical reagent, was dried over Linde Molecular Sieves prior to use. Ketenimines **2–7** were prepared as previously described.[1b]

Preparation of Photoadducts. Degassed and sealed Pyrex ampoules containing benzene solutions 0.1 to 0.3 *M* each in fluorenone and the ketenimine were taped to a quartz immersion well fitted with a Pyrex sleeve. The ampoules were irradiated with a 450-w Hanovia lamp, No. 679A-36, at room temperature for the times designated in Table I. The crude reaction mixtures were analyzed by infrared techniques for remaining starting material, extent of adduct formation, and degree of photocleavage of the α adducts to isocyanate and olefin. The benzene was removed *in vacuo;* the adducts were isolated by direct crystallization of the reaction mixture from ether–petroleum ether for the reactions of fluorenone with **2**, **3**, **4**, **6**, and **7**. The fluorenone-**5** reaction mixture could not be crystallized and was chromatographed on Florisil. Elution with 25% ether in petroleum ether produced the product reported in Table I. All the isolated adduct products gave excellent high-resolution mass spectrometric molecular weight analyses (Table I).

β Lactams. The β lactam of ethylphenylketene and fluorenone anil[23] was prepared in the following manner. To a solution of 1.0 g of triethylamine (0.010 mole) and 2.5 g of fluorenone anil[23] (0.010 mole) in 35 ml of ether was added dropwise at room temperature a solution of 1.82 g of 2-phenylbutyryl chloride (0.010 mole) in 15 ml of ether. A precipitate immediately formed. The mixture was stirred at room temperature for 0.5 hr and the solid was filtered off. The solvent was removed *in vacuo* and the oily residue was crystallized from dichloromethane–ether to give 0.60 g (15%) of white needles, mp 177–179°. The infrared and mass spectra of this material were identical with those of the product isolated from the fluorenone-**5** reaction after Florisil chromatography; characteristic infrared band at 1743 cm^{-1} (dichloromethane); mass spectrometric molecular weight, 401.179872; theoretical for $C_{29}H_{23}NO$, 401.177955.

The β lactam of diphenylketene[24] and fluorenone anil[23] was prepared as follows. To a solution of 2.0 g of fluorenone anil[23] (0.078 mole) in 50 ml of ether was added dropwise a solution of 1.5 g of diphenylketene[24] (0.078 mole) in 20 ml of ether. A slight exothermic reaction occurred and a precipitate immediately formed. The mixture was stirred for 0.5 hr and then filtered to give 2.9 g of a white solid. The product was recrystallized from dichloromethane–petroleum ether to give 2.4 g of a white solid, mp 279–284° dec (69%). The infrared spectrum of this compound was identical with the product isolated after Florisil chromatography of the α adduct of fluorenone-**7**; characteristic infrared band at 1744 cm^{-1} (dichloromethane); mass spectrometric molecular weight, 449.176594; theoretical for $C_{33}H_{23}NO$, 449.177955.

Kinetic Studies and Quantum Yield Determination. All relative rate measurements and quantum yield determinations were carried out on a rotating photochemical assembly as previously described.[1b]

Thermal and Photochemical Cleavages. Degassed and sealed Pyrex ampoules containing xylene solutions of adduct or β lactam (*ca.* 0.10 *M*) were heated at 140–150° or irradiated with a 450-w Hanovia lamp at room temperature through a Pyrex filter for *ca.* 24 hr. At the end of this time, the crude reaction mixture was analyzed by infrared techniques.

Mass Spectrometric Analyses.[25] All mass spectra were taken on an AEI-MS-9 spectrometer at an ionizing voltage of 70 ev and a probe temperature of *ca.* 170° unless otherwise specified.

Acknowledgment. We thank the Petroleum Research Fund, administered by the American Chemical Society, for a grant (197-G) in support of this work and the National Science Foundation for funds used in the purchase of the AEI-MS-9 spectrometer.

---

(18) C. P. Smyth, "Dielectric Behavior and Structure," McGraw-Hill Book Co., Inc., New York, N. Y., 1955, p 244.

(19) The potential energy (*V*) for **20** can be calculated in the usual manner from $\mu_1\mu_2/R^3$ where μ_1 and μ_2 are the interacting dipoles and *R* is the distance separating them. The potential energy for **22** is attractive rather than repulsive so that the difference between **22** and **20** is 2*V*. The dipole–dipole term for **21** is zero since the potential energy follows the cos θ where θ is the angle defined by the dipole moments. Thus, the difference between **22** and **21** is *V*. Since $\log n_1/n_2 = -\Delta E/2.3kt$, where Δ*E* is *V* or 2*V*, the relative populations of **20**, **21**, and **22** can be calculated for different values of μ and *R*.

(20) In the present situation the barriers are essentially the potential energy differences.

(20a) NOTE ADDED IN PROOF. See L. A. Singer and G. A. Davis, *J. Am. Chem. Soc.*, **89**, 158 (1967), for a kinetic study of the fluorenone-**2** system.

(21) See E. Eliel, "Stereochemistry of Carbon Compounds," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p 150, for a discussion of the Curtin–Hammett principle.

(22) All boiling points and melting points are uncorrected.

(23) G. Reddelien, *Ber.*, **43**, 2479 (1910).

(24) H. Staudinger, *ibid.*, **44**, 1619 (1911).

(25) We wish to thank Mr. Bill Klymus for technical assistance in running the mass spectra.