Photocycloaddition of Acetone to Ketenimines. Syn–Anti Exchange Barriers in β-Iminooxetanes

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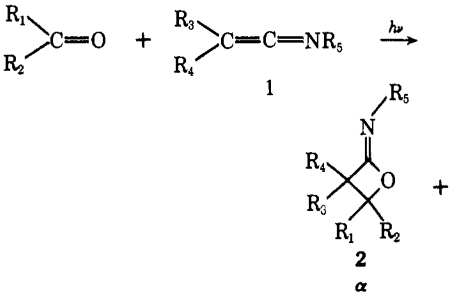
Abstract: The photolysis of acetone solutions containing dimethyl-*N*-(cyclohexyl)- (**4**) or dimethyl-*N*-(phenyl)-ketenimine (**5**) leads to photoadducts of the iminooxetane type. Energy transfer from electronically excited acetone to ground-state ketenimine appears to compete with the cycloaddition. The acetone-**4** α adduct rearranges readily to unsaturated amide **8**. The barriers to syn–anti exchange in the β adducts of acetone-**4** and acetone-**5** were calculated to be $\Delta G_c^{\ddagger}$ = 21.8 and 18.7 ± 0.3 kcal/mol, respectively.

Previous publications in this series describe the photocycloaddition of aryl ketones to ketenimines (**1**) which leads to adducts of the general structures **2** (termed α) and **3** (termed β).[2] This reaction is a special case of the widely studied Paterno–Büchi photocycloaddition of aldehydes and ketones to olefins.[3]



Mechanistic studies with benzophenone and fluorenone indicate that (a) the ketone triplet adds to the ground-state ketenimine with a bimolecular rate constant very close to the diffusion limit ($k_r \approx 10^9$ l. mol^{-1} sec^{-1}) and that (b) energy transfer (k_t) from the triplet ketone to the ground-state ketenimine can compete with the cycloaddition. This competition is illustrated in the benzophenone–ketenimine system where a decrease in reaction efficiency is observed as alkyl groups are replaced by aryl groups in the ketenimine structure.[4]

Fluorenone reacts with diethyl-*N*-(cyclohexyl)-ketenimine *via* the singlet as well as the triplet state as the transient fluorenone singlet is sufficiently long-lived for bimolecular interactions in fluid media ($\tau \approx 10^{-8}$ sec[2b]).

In the present study, we describe the acetone–ketenimine photocycloaddition reaction and some of the properties of the photoadducts. In particular, we have determined the barriers to syn–anti exchange in two adducts having the β-type structure which helps to explain our failure to isolate syn–anti isomers with previously described iminooxetanes.[2]

Results

Photocycloaddition Reactions. Acetone solutions containing either dimethyl-*N*-(cyclohexyl)ketenimine (**4**) or dimethyl-*N*-(phenyl)ketenimine (**5**) at ~0.07 *M* were photolyzed for 10 and 30 hr, respectively, with a 450-W Hanovia lamp through Vycor (cutoff, ~2500 A). Table I lists the products isolated by chromatography on Florisil and Table II summarizes the important spectral data used in structure elucidation.

Table I. Products from the Photolyses of Acetone-**4** and Acetone-**5** Solutions at Room Temperature

Product	Mmol of product/mmol of starting ketenimine Acetone-4	 Acetone-5
Ketenimine trimer	0.0	trace
β adduct	0.29	0.41
α adduct (amide)[a]	0.28	0.0
Recovered ketenimine[b] (amide)	0.33	0.15
Total	0.90	0.56

[a] α adduct rearranges to unsaturated amide during chromatography. [b] Remaining ketenimine is hydrolyzed to amide during chromatography.

The chromatography of the acetone-**4** reaction mixture yielded a solid, mp 54–56°, which displayed an imine band in the infrared (1728 cm^{-1}) but which was stable to pyrolysis in xylene (156°/18 hr) and further photolysis (Vycor/17 hr). Previous work indicates that α-adduct structures fragment under these conditions while β-adduct structures are stable.[2] The accurate mass (209.1797) corresponds to an elemental composition of $C_{13}H_{23}NO$ (acetone-**4** adduct formulation). The mass spectral fragmentation pattern supports the β-structural assignment since there is no major fragment corresponding to 2,3-dimethylbutene (*m*/*e* 84) which would be expected from the α adduct based on earlier work.[2c] Lastly, the two singlets in the nmr

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[1] (a) Alfred P. Sloan Fellow, 1970–1972; to whom all correspondence should be addressed at the Department of Chemistry, University of Southern California; (b) NSF Trainee, 1968–1970.

[2] (a) L. A. Singer and G. A. Davis, *J. Amer. Chem. Soc.*, **89**, 158, 941 (1967); (b) L. A. Singer, G. A. Davis, and V. P. Muralidharan, *ibid.*, **91**, 897 (1969); (c) L. A. Singer and G. A. Davis, *ibid.*, **89**, 598 (1967).

[3] D. R. Arnold, *Advan. Photochem.*, **6**, 301 (1968), and references therein.

[4] In both the benzophenone–dimethyl-*N*-(cyclohexyl)ketenimine and benzophenone–dimethyl-*N*-(phenyl)ketenimine reactions, $k_r \approx 10^9$ l. mol^{-1} sec^{-1} but k_t/k_r = 0.0 and 1.5, respectively. Presumably, substitution of phenyl for cyclohexyl lowers the triplet energy of the ketenimine close to the value of benzophenone ($E_T \approx$ 69 kcal/mol), thus facilitating energy transfer from benzophenone triplet to ground-state ketenimine;[5] G. A. Davis, Ph.D. Thesis, University of Chicago, 1968.

[5] W. G. Herkstroeter and G. S. Hammond, *J. Amer. Chem. Soc.*, **88**, 4769 (1966).

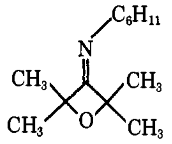
Table II. Spectral and Physical Data on Products from the Acetone–**4** and Acetone–**5** Photolyses

Product (mp, °C)	Ir,[a] cm^{-1}	Nmr,[b] δ	Accurate mass (theoretical)[c]
Trimer of **5** (163–165)	1675 (s)	1.44 (s) (CH_3) 6.7–7.2 (m) (aromatic)	435[d]
Acetone–**4** (54–56) β adduct	1728 (s)	1.35 (s) 1.42 (s) } (CH_3) 0.7–2.0 (m) (C_6H_{11})	209.1797 (209.1779)
Acetone–**5** (oil) β adduct	1740 (s)	1.24 (s) 1.49 (s) } (CH_3) 6.5–7.3 (m) (Aromatic)	203.1294 (203.1310)
Acetone–**4** (71–76) α adduct Rearrangement product Characteristic band	1672 (s)	1.20 (s) (*gem*-CH_3) 1.70 (s) (CH_3) 0.75–1.93 (m) (C_6H_{11}) 4.8 (m) (vinyl H)	 209.1760 (209.1779)

[a] In carbon tetrachloride, s = strong. [b] In carbon tetrachloride, s = singlet, m = multiplet. [c] Based on theoretical elemental composition. Accurate mass measured on AEI MS-9 spectrometer. [d] Nominal mass measured on Varian M-66 spectrometer.

(δ 1.35 and 1.42) assigned to the syn and anti methyl group protons coalesce at elevated temperatures (see later discussion). These properties indicate the β-adduct (**6**) structure for this compound rather than the α-adduct structure (**7**).

A second solid was isolated from chromatography of the acetone–**4** reaction (mp 71–76°) which shows an accurate mass of 209.1760 indicating the same elemental composition as the β adduct. This product has a strong band in the infrared at 1672 cm^{-1} (CONHR). The nmr spectrum reveals the presence of vinyl H (δ 4.8) and two different methyl groups (δ 1.20 and 1.70) in the ratio of 2:1, respectively. The mass spectral fragmentation pattern contains a base peak at *m/e* 84 (2,3-dimethylbutene). We assign the unsaturated amide structure **8** to this compound and formulate the dominant mass spectral fragmentation as involving a transfer of hydrogen from nitrogen to carbon.



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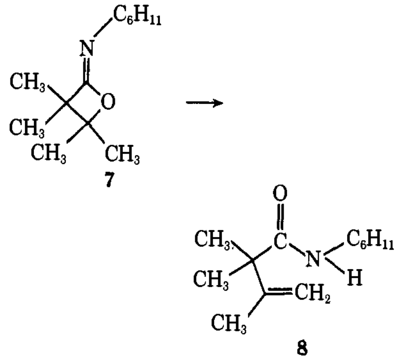

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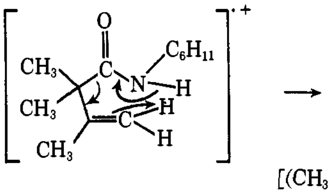
8



$[(CH_3)_2C{=}C(CH_3)_2]^{+\cdot}$ + $C_6H_{11}NCO$

m/e 84

Amide **8** arises from the photochemical and chromatographic rearrangements of the α-adduct **7**. Photolyses of acetone–**4** mixtures through Pyrex (22 hr), followed by nmr analysis, revealed four singlets of which two correspond to the β adduct. The other two (δ 1.45 and 1.27) decrease in intensity upon further photolysis through Vycor or pyrolysis in xylene (150°/20 hr) while peaks assignable to the unsaturated amide **8** appear. We believe the two additional singlets in the nmr of the crude mixture are due to the labile α adduct. Our several attempts at isolating **7** by chromatography were unsuccessful leading only to the amide. Apparently the rearrangement of **7** → **8** is facile.

Later fractions of the chromatography of the acetone–**4** photolysis mixture yielded **4** recovered as the corresponding amide which arises from hydrolysis of the ketenimine on the Florisil column. From these later fractions also was recovered a complex mixture of carbonyl-containing compounds which are attributable to photodegradation of acetone. Photolysis of acetone alone under our reaction conditions yielded a mixture showing 11 peaks by vpc analysis. Others have identified biacetyl, 2,4-pentadiene, 2,5-hexadiene, 2-propanol, and pinacol among the photolysis products of acetone.[6]

The major product isolated by Florisil chromatography of the acetone–**5** photolysis mixture was a colorless liquid (41%) which displays a strong band in the infrared at 1740 cm^{-1} (characteristic imine adduct band). The nmr spectrum shows two singlets at δ 1.24 and 1.49 of equal intensity, and a multiplet between 6.5 and 7.3. The two singlets coalesce above 94°. This product is stable to pyrolysis in chlorobenzene (140°/18 hr) and photolysis (Vycor/36 hr). Mass spectroscopic analysis reveals an accurate mass of 203.1294 which indicates an empirical formula of $C_{13}H_{17}NO$. The base peak at *m/e* 145 corresponds to fragmentation to **5** but there is no observed fragment at *m/e* 84 (2,3-dimethylbutane). This product is assigned the β-adduct structure **9**.

In addition to **9**, a white solid (mp 163–164°) was isolated in 10–20-mg quantity from the chromatography of the acetone–**5** photolysis mixture. This material does not display an imine adduct band in the infrared (1725–1740 cm^{-1}) but does show a strong band at 1675 cm^{-1}. The nmr spectrum reveals only two types of hydrogen: a singlet at δ 1.44 and a multiplet between 6.7 and 7.2. The mass spectrum indicates a nominal mass of 435 with the only other important peak being that at *m/e* 145. The latter corresponds to fragmentation to **5**. This compound is believed to be the trimer of **5** and either **10** or **11** is compatible with the spectral data. Attempts to prepare the trimer by photolysis

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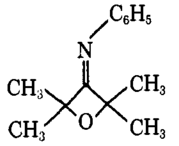
[6] (a) K. Pfordte and G. Leuschner, *Justus Liebigs Ann. Chem.*, 646, 23 (1961); (b) K. Shima and S. Tsutumi, *Kogyo Kagaku Zasshi*, 64, 460 (1961), as reported in *Chem. Abstr.*, 57, 2088*d* (1962).

Table III. Comparison of Experimental and Simulated Nmr Peak Shapes for **9**

Temp, °C	Exptl peak:valley	Exptl half-width	Simulated peak:valley	Simulated half-width	Lifetime, sec
60	81.5		81.499		0.232
80	4.40		4.408		0.0481
85	2.43		2.432		0.0344
87	1.93		1.925		0.0299
89	1.63		1.634		0.9269
90	1.22		1.231		0.0219
91	1.19		1.188		0.0212
92	1.10		1.095		0.0196
93	1.08		1.080		0.0193
95		25.7		25.72	0.0153
97		23.2		23.24	0.0141
100		15.0		15.02	0.0102
105		9.82		9.81	0.00732
115		5.26		5.25	0.00414

and thermolysis of **5** were unsuccessful. It is possible that the trimer is formed during the preparation of **5** (dehydration of the corresponding amide with phosphorus pentoxide–alumina in triethylamine).



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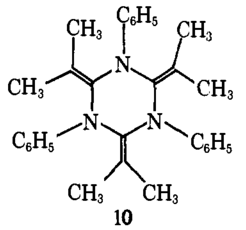

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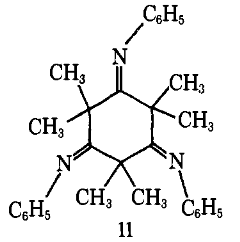

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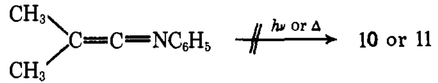

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Also isolated by chromatography of the acetone–**5** photolysis mixture was 15% of **5** recovered as the amide and the same mixture of acetone photodegradation products as recovered from the acetone–**4** reaction.

Variable-Temperature Nmr Study of the β Adducts. Variable-temperature nmr spectra were recorded of the β adducts **6** and **9** in *p*-dichlorobenzene in degassed and sealed tubes on a Varian Associates HA-100 nmr spectrometer. Coalescence of the singlets due to the syn and anti geminal methyl groups was observed in both cases at elevated temperature as seen in Figures 1 and 2. The data collected with **9** were sufficiently good to allow matching of the experimental nmr spectra at various temperatures with computer-simulated spectra (Figure 2).[7] A series of simulated spectra were generated at each temperature for different mean configurational lifetimes. These spectra were compared with the experimental spectra on the basis of peak:valley ratios below the coalescence temperature; *i.e.*, the ratio of the maximum curve height to the height of the minimum between the peaks. Above the coalescence temperature, the peak half-widths were compared. In this way, the mean configurational lifetimes shown in Table III were obtained. These data are plotted in Figure 3.

Discussion

Photocycloaddition Reactions. The acetone singlet state has been shown by others to react with 1,2-dicyanoethylene,[8] 1-methoxy-1-butene,[9] and methacrylonitrile.[10] This result is not surprising in view of the lifetime of the transient singlet state of 2.1 × 10^{-9} sec.[8a] This lifetime is sufficiently long for bimolecular interactions of the acetone singlet with potential reactants to occur at concentrations of the latter approaching *ca.* 0.1 *M*. Accordingly, we suspect that the photocycloaddition of acetone to the ketenimines under our conditions is a mixed reaction involving both the singlet and triplet states of acetone and, in this respect, resembles the previously studied fluorenone–dimethyl-*N*-(cyclohexyl)ketenimine photocycloaddition.[2a,b]

We believe the longer reaction time required for the acetone–**5** reaction (30 hr *vs.* 10 hr) is significant and reflects the greater relative importance of an energy-transfer step involving electronically excited acetone and ground-state **5**. A generalized reaction scheme is shown in Scheme I.

Scheme I

$$A \longrightarrow A^* \qquad \text{excitation} \qquad (1)$$

$$A^* \xrightarrow{k_d} A \qquad \text{all deactivation processes} \qquad (2)$$

$$A^* + K \xrightarrow{k_r} \text{adduct} \qquad \text{cycloaddition} \qquad (3)$$

$$A^* + K \xrightarrow{k_t} A + K^* \qquad \text{energy transfer} \qquad (4)$$

The replacement of a cyclohexyl group by a phenyl group in the ketenimine structure lowers the energy of the singlet and triplet states of **5** relative to **4** so that energy transfer from the electronically excited acetone (singlet or triplet) to **5** may be expected to be faster than to **4**. Apparently the energy-transfer

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(7) H. S. Gutowsky, R. L. Vold, and E. J. Wells, *J. Chem. Phys.*, **43** 4107 (1967). This program was modified at the Computer Sciences Laboratory at the University of Southern California.

(8) (a) J. C. Dalton, P. A. Wriede, and N. J. Turro, *J. Amer. Chem. Soc.*, **92**, 1318 (1970); (b) N. J. Turro, P. A. Wriede, and J. C. Dalton, *ibid.*, **90**, 3274 (1968).

(9) (a) N. J. Turro and P. A. Wriede, *ibid.*, **92**, 320 (1970); (b) *ibid.*, **90**, 6863 (1968).

(10) J. A. Barltrop and H. A. J. Carless, *Tetrahedron Lett.*, 3901 (1968).

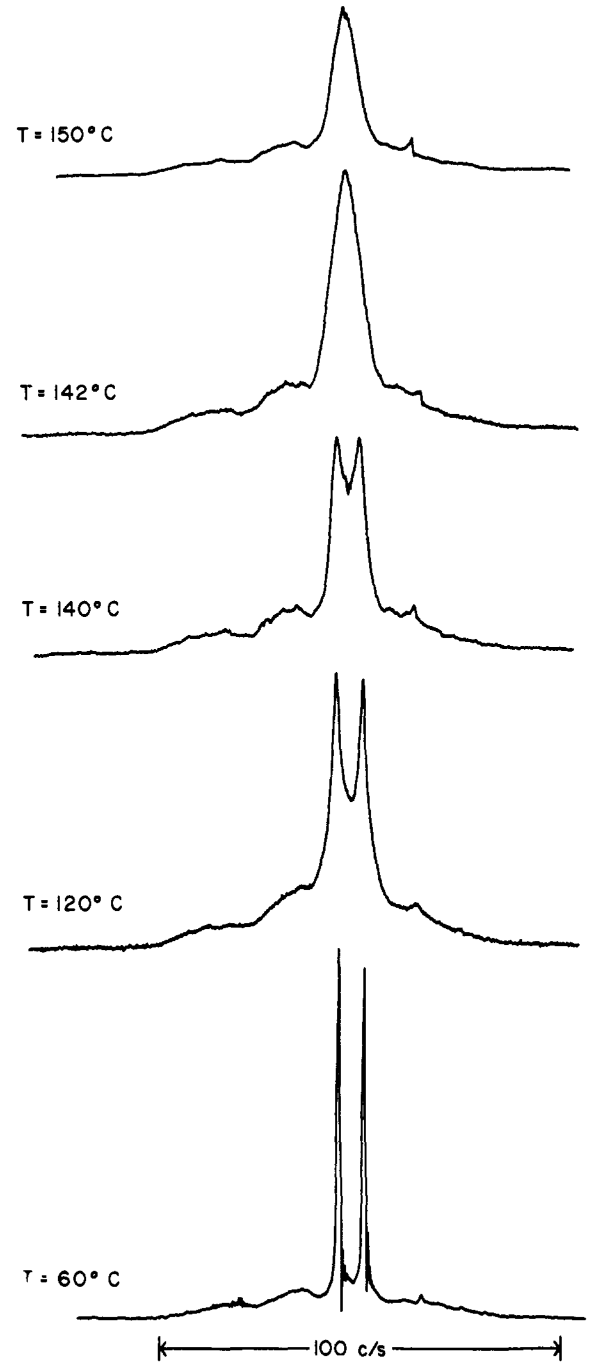

Figure 1. Variable-temperature nmr spectra for β-adduct **6**.

processes operate to the exclusion of cycloaddition with the more heavily arylated ketenimines than **5** since no cycloaddition was observed to ethylphenyl-*N*-(phenyl)- or triphenylketenimine.[11]

The lability of acetone–**4** α adduct follows a pattern established earlier with the fluorenone and benzophenone α adducts.[2] These adducts fragment readily to alkenes and isocyanates and also ketones and ketenimines above 100°. In addition, several of the fluorenone adducts having *N*-phenyl substituents rearrange to β-lactams during chromatography on Florisil. Subsequent work revealed that adduct **12** rearranges to β-lactam **14** in less than several minutes at room temperature in acetonitrile in the presence of lithium per-

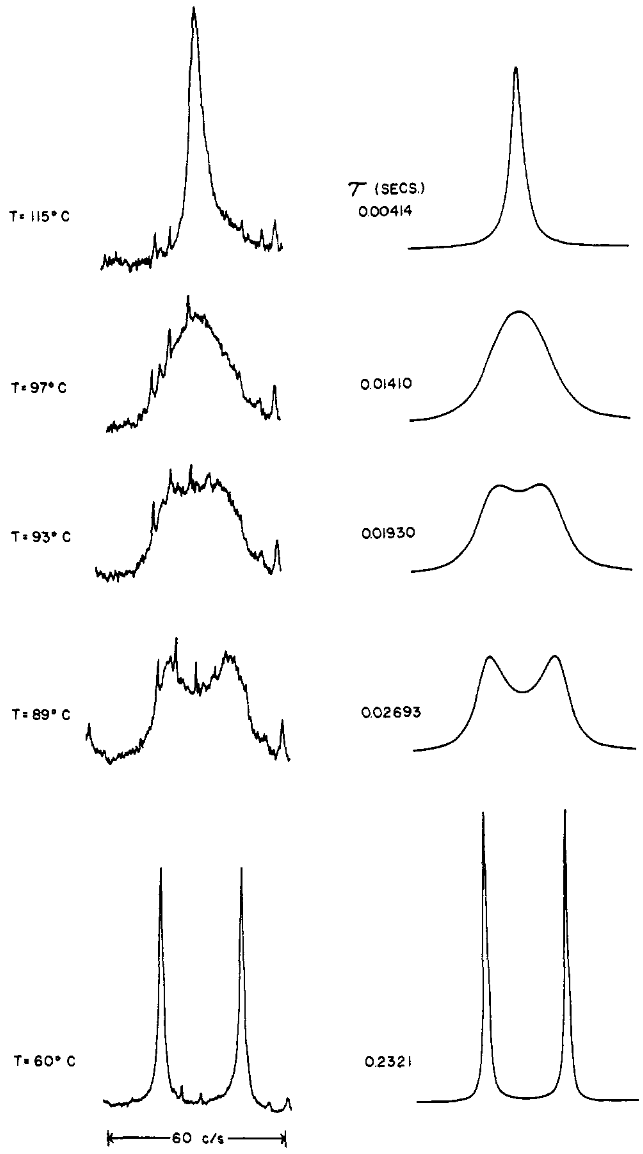

Figure 2. Comparison of experimental and simulated nmr spectra for β-adduct **9**.

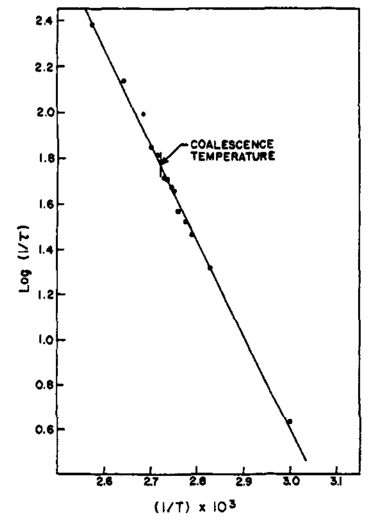

Figure 3. Dependence of the log of the reciprocal mean configurational lifetime of β-adduct **9** on the reciprocal of the absolute temperature.

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(11) G. A. Davis, unpublished results.

Table IV. Activation Parameters for Syn–Anti Exchange in β-Iminooxetanes

System	T_c,[a] °C	E_a, kcal/mol	Log A, sec^{-1}	$\Delta G_c^{\ddagger}$, kcal/mol
9	94	19.0 ± 0.3	13.1 ± 0.2	18.7 ± 0.3
6	141			21.8

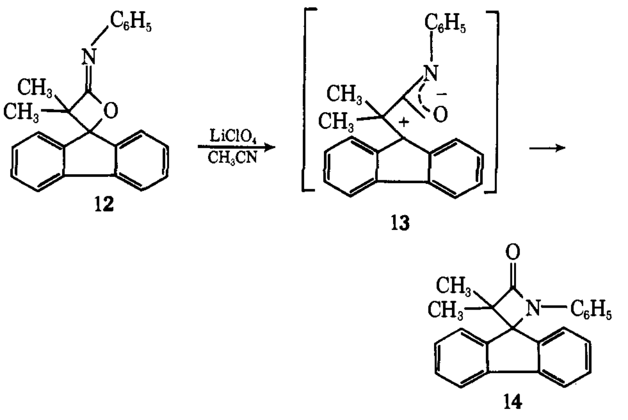
[a] Coalescence temperature in *p*-dichlorobenzene.

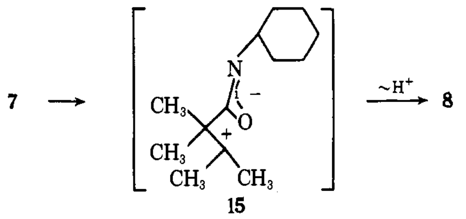
Table V. Selected Examples of Barriers for Syn–Anti Isomerization in Open-Chain Imines

System	Solvent	T_c, °C	$\Delta G_c^{\ddagger}$, kcal/mol	Ref
$(CH_3)_2C{=}NCH_2C_6H_5$ (**16**)	Quinoline	*a*	≫23	*c*
$(CH_3)_2C{=}NC_6H_5$ (**17**)	Quinoline	140	21	*c*
p-$ClC_6H_4(C_6H_5)C{=}NCH_3$ (**18**)	Cyclohexane	*b*	26.1 ± 0.3	*d*
(*p*-$CH_3OC_6H_4)_2C{=}NC_6H_5$ (**19**)	Carbon tetrachloride	62.2	18	*e*

[a] No coalescence observed up to 170°. [b] Ultraviolet spectroscopy experiment. [c] Reference 18. [d] Reference 17. [e] Reference 15.

chlorate.[12] This rearrangement is formulated as involving zwitterion **14** as an intermediate. A similar zwitterionic species **15** may be involved in the rearrangement of the acetone–**4** α adduct to the unsaturated amide (**7** → **8**).





Variable-Temperature Nmr Studies. The slope of the plot in Figure 3 provides a measure of the activation energy for inversion of configuration at nitrogen[13] in β-adduct **9** *via* the Arrhenius equation (eq 5). A least-

$$\log \tau^{-1} = -[E_a/(2.3RT)] + \log A \qquad (5)$$

squares analysis of the mean lifetime data in Table III indicates $E_a = 19.0 \pm 0.3$ kcal/mol. The frequency factor is calculated to be $A = 1.26 \pm 1.6 \times 10^{13}$ sec^{-1}.

The variable-temperature data collected with β-adduct **6** could not be similarly handled because of the superposition of the resonances of the cyclohexyl and methyl protons. However, the coalescence temperature was readily determined to be 141° which leads to a mean configurational lifetime at the coalescence temperature of 0.056 sec using the simplified Gutowsky equation (eq 6),[16] where $\delta_{\nu\infty}$ is the chemical-shift differ-

$$\tau^{-1} = \sqrt{2}\pi\delta_{\nu\infty} \qquad (6)$$

ence between the methyl singlets at room temperature. The lifetime corresponds to a free energy of activation at the coalesence temperature of $\Delta G_{c\ddagger} = 21.8$ kcal/mol using the Eyring equation (eq 7).

$$\tau^{-1} = [(kT)/h]e^{-\Delta G^{\ddagger}/RT} \qquad (7)$$

The activation parameters in Table IV lead to a configurational lifetime at room temperature for **9** of $\tau = 60$ sec. If we assume similar preexponentials ($\log A = 13.1$ sec^{-1}) or entropies of activation ($\Delta S^{\ddagger} = -1.1$ eu) for **9** and **6**, we can estimate a configurational lifetime at room temperature for the latter of $\tau \approx 8$ min. These lifetimes indicate that facile syn–anti isomerization is to be expected in solution at room temperature for structures of the β-adduct type. With the other β-adduct structures that have been isolated up to now, such as the previously reported benzophenone–**5** β adduct,[2c] one isomer would be expected to be strongly preferred because of steric considerations, which could account for the lack of nmr evidence for more than one isomer in solution. However, it is important to point out that such detection methods could easily overlook several per cent or less of the less favored isomer.

The somewhat higher barrier calculated for **6** as compared with **9** follows the pattern of previously reported barriers in open-chain imines. A few selected examples appear in Table V from the work of Curtin[15,17] and Staab[18] which indicate that the barriers to syn–anti isomerization in *N*-alkylimines are larger than in *N*-arylimines.

The barriers observed with the iminooxetanes **6** and **9** are somewhat lower than those of the open-chain imines **16** and **17**. A possible explanation is steric acceleration of syn–anti isomerization in **6** and **9** due to relief of steric strain in going from the ground state to the transition state. This steric effect may also be responsible for the substantially lower coalescence tem-

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(12) J. A. Green, unpublished results.

(13) We do not wish to imply any specific description of the isomerization process by our choice of words. Our results cannot clearly distinguish between the two proposed mechanisms for isomerization around the carbon–nitrogen double bond which are (a) a rotational process similar to that in carbon–carbon double bonds[14] and (b) the process involving an sp-hybridized nitrogen at the barrier height, the so-called "lateral shift" process.[15]

(14) N. P. Marullo and E. H. Wagener, *J. Amer. Chem. Soc.*, **88**, 5034 (1966).

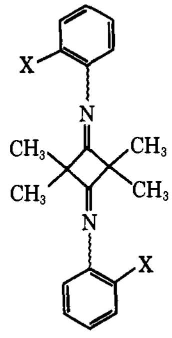
(15) D. Y. Curtin, E. J. Grubbs, and C. G. McCarty, *ibid.*, **88**, 2775 (1966).

(16) H. S. Gutowsky and C. H. Holm, *J. Chem. Phys.*, **25**, 1228 (1956).

(17) D. Y. Curtin and J. W. Hausser, *J. Amer. Chem. Soc.*, **83**, 3474 (1961).

(18) H. A. Staab, F. Vögtle, and A. Mannsbreck, *Tetrahedron Lett.*, 697 (1965).

perature reported for the *o*-chlorobisimine **20**, compared with **21**.[19]



20, X = Cl; $T_c < 35°$
21, X = H; $T_c = 100°$

Experimental Section

Instrumentation. All nmr spectra, except for the variable-temperature spectra, were recorded on a Varian Associates A-60 analytical nmr spectrometer with tetramethylsilane as the internal standard. The variable-temperature nmr spectra were recorded on a Varian Associates Model HA-100 nmr spectrometer. Mass spectra were run either on an AEI MS-9 or Varian Associates M-66 mass spectrometer, as indicated.

Chemicals. Acetone, Mallinckrodt, analytical reagent, was distilled and stored over Linde Molecular Sieve, Type 4A. *p*-Dichlorobenzene, Mallinckrodt, was purified by fractional sublimation at 25 mm.

Photocycloadditions. General Procedure. A solution of *ca.* 2 g of the ketenimine[2a,b] in *ca.* 200 ml of dry acetone was distributed among several Vycor tubes which were capped with red, sleeve-type serum caps. The tubes were degassed (several freeze–thaw cycles on vacuum line) by means of syringe needles through the serum caps and taped to a Quartz well, fitted with a Vycor sleeve, containing a 450-W Hanovia lamp. The tubes were irradiated at 18–20° and the remaining acetone was removed *in vacuo*. The product mixtures were analyzed by ir and nmr and subjected to chromatography on Florisil with the results described in the main text.

Photolysis of Acetone. Distilled and dried acetone (150 ml) was photolyzed in Vycor tubes for 30 hr under the conditions described in the General Procedure. The remaining acetone and volatile materials were removed *in vacuo* to give a colorless liquid. Analysis of this product by vapor phase chromatography on a 20% SE-32 on Chromosorb P column showed 11 peaks of which two can be classified as strong, one as moderate, and the rest as weak. One of the strong peaks was identified as 2,5-hexadiene.

Variable-Temperature Nmr Spectra. Samples of freshly chromatographed β adducts in purified *p*-dichlorobenzene (**6**, 0.83 *M*; **9**, 0.46 *M*), sealed in degassed tubes, were analyzed at various temperatures between 35° and above the coalescence temperatures on a Varian Associates HA-100 nmr spectrometer. The temperature control dial on the instrument was calibrated using ethylene glycol over the temperature range 60–120° leading to an estimated accuracy of the temperature control in the probe of ±2°. Using the protons in *p*-dichlorobenzene as an internal lock for the magnetic field, expanded field spectra of the methyl group protons in **6** and **9** were recorded at various temperatures after waiting 20 min for thermal equilibration in the probe. The series of spectra shown in Figures 1 and 2 could be obtained either by going from low to high or high to low temperature. These data were handled as described in the Results.

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Irradiation of α,β-Unsaturated Ketones. Search for Intermediate Oxabicyclobutanes[1]

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Abstract: 3,4-Dimethyl-3-penten-2-one-*3-methyl-d_3*, 3-methyl-3-buten-2-one-*1,1,1-d_3*, and acrolein-*1-d_1* were irradiated through a Vycor filter in hydrocarbon solvents. Spectral analyses of recovered starting materials showed no intramolecular scrambling of deuterium. These results indicate that the respective oxabicyclobutanes are not photochemical intermediates that could have led to an energy-wasting step that regenerates starting materials.

Oxabicyclobutanes have been considered as unstable intermediates in the n,π* photochemistry of several cyclic α,β-unsaturated ketones.[2] In these cases[2] no specific evidence was presented for the formation of oxabicyclobutanes. Their formation was primarily considered for the sake of novelty or as a means of introducing an energy wasting step that would shorten the lifetime of intermediate excited states. The latter consideration was based on the premise that intermediate oxabicyclobutanes would rapidly fragment back to starting enone with no net observable chemistry. The only reaction which superficially indicates an oxabicyclobutane intermediate is the Pyrex photolysis of purpurogallin[3] to yield the rearranged product, 6,7,8-trimethoxynaphthoic acid methyl ester. Even here, however, the necessity of an aqueous solvent suggests that features other than oxabicyclobutane formation may control the course of the reaction. Oxabi-

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