

THE PHOTOCYCLOADDITION OF AROMATIC ALDEHYDES AND  
KETONES TO DIMETHYL-N-(2-CYANO-2-PROPYL)KETENIMINE

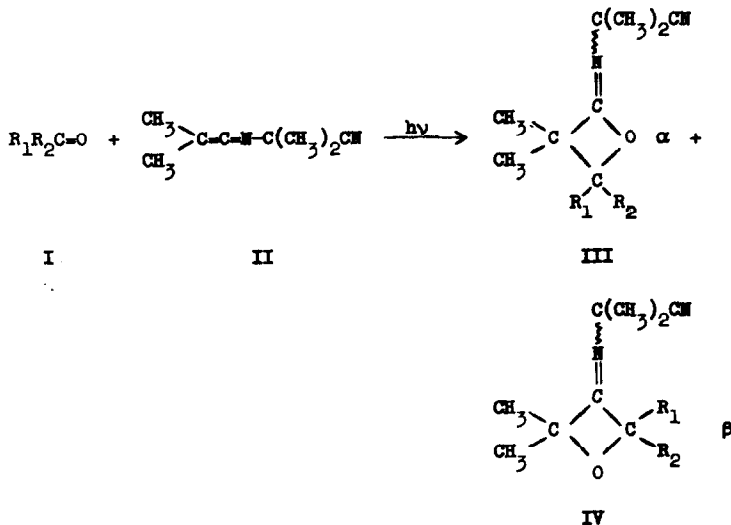
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We have observed photocycloaddition of 6 aromatic aldehydes and ketones across the carbon-carbon double bond of dimethyl-N-(2-cyano-2-propyl)-ketenimine (II) to give iminoketanes (III and IV). This reaction is an extension to a cumulative double bond system of the previously well-known light-induced additions of aldehydes and ketones to simple olefins.<sup>1-4</sup>



The photoreactions were run in sealed Pyrex test tubes containing degassed

benzene solutions of the carbonyl compound and II<sup>5</sup> (ca. .3 M in each). The reaction mixtures were irradiated with a 550-watt, medium pressure, Hanovia lamp, at 7-12°C., for periods of 10 to 40 hours. The ketenimine (II) is reasonably stable under these conditions<sup>5</sup> with only 8.4% decomposition to tetramethylsuccinonitrile being observed after 20.0 hours of direct photolysis. There was no adduct formation in the dark in any of the systems that were studied.

The product compositions were determined by n.m.r. analyses of the crude reaction mixtures. The singlet methyl patterns of the ketenimine,<sup>6</sup> tetramethylsuccinonitrile,<sup>6</sup> and the adducts lend themselves to fairly easy interpretation. The peaks due to the  $\beta$ -adducts were identified after isolation of these adducts by Florisil chromatography. The  $\alpha$ -adducts are not isolable in this manner since they readily hydrolyze to their corresponding amides on Florisil. The  $\alpha$ -adduct of fluorenone and II was isolated by direct crystallization of the reaction mixture and its n.m.r. spectrum was used in determining the product composition of the crude reaction mixture.

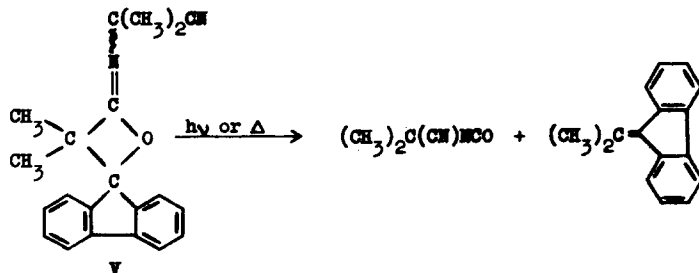
The assigned adduct structures are supported by the analyses<sup>7</sup> of the isolated photoproducts of II with p-chlorobenzaldehyde (m.p. 119.5-120.5°C. Calcd. for C<sub>15</sub>H<sub>17</sub>N<sub>2</sub>OCl: C, 65.09; H, 6.19; N, 10.12; Cl, 12.81. Found: C, 65.19; H, 6.22; N, 10.27; Cl, 12.84.), benzaldehyde (m.p. 141.2-142.5°C. Calcd. for C<sub>7</sub>H<sub>6</sub>N<sub>2</sub>O: C, 74.35; H, 7.49; N, 11.56. Found: C, 74.22; H, 7.68; N, 11.40.), benzophenone (m.p. 103.0-104.0°C. Calcd. for C<sub>21</sub>H<sub>22</sub>N<sub>2</sub>O: C, 79.21; H, 6.97; N, 8.80. Found: C, 79.31; H, 6.99; N, 8.51.), and fluorenone (m.p. 134-7°C. Calcd. for C<sub>21</sub>H<sub>20</sub>N<sub>2</sub>O: C, 79.72; H, 6.37; N, 8.85. Found: C, 79.58; H, 6.42; N, 8.98.). All of these adducts display a strong band in the infrared between 5.76 and 5.80 $\mu$  which is ascribed to the imine band shifted down from its normal position around 6.0 $\mu$ <sup>5</sup> because of ring strain.

The amides resulting from Florisil chromatography hydrolyses of the

$\alpha$ -adducts of II and benzophenone (m.p. 170.0-171.0°C. Calcd. for  $C_{21}H_{24}N_2O_2$ : C, 74.97; H, 7.19; N, 8.33. Found: C, 74.78; H, 7.09; N, 8.13.) and II and fluorenone (m.p. 186.6-187.5°C. Calcd. for  $C_{21}H_{22}N_2O_2$ : C, 75.42; H, 6.63; N, 8.38. Found: C, 75.64; H, 6.67; N, 8.67.) were easily identified by their n.m.r. patterns and their characteristic infrared spectra.<sup>8</sup>

The  $\beta$ -adducts of II with *p*-methoxybenzaldehyde and acetophenone (the  $\beta$ -adduct structure is assigned because they were not hydrolyzed by Florisil chromatography) display this same band in the infrared, and their n.m.r. spectra were utilized in determining the product compositions of the crude reaction mixtures. These adducts were not analyzed nor characterized further. The  $\alpha$ -adduct of II with acetophenone was not isolated although the corresponding amide resulting from Florisil chromatography hydrolysis was obtained in impure form.

The  $\alpha$ -adduct from II and fluorenone (V) undergoes both photo (same conditions as above) and thermal (125°C., degassed xylene solution) decomposition to 2-cyano-2-propyl isocyanate (strong band in the infrared at 4.4 $\mu$ ) and 9-isopropylidene fluorene (isolated). All the  $\beta$ -adducts are thermal and photo-stable. Thus on the basis of the spectral evidence (n.m.r. and infrared) and



the reactivity differences,  $\alpha$  and  $\beta$  structures were assigned to the adducts.

These results are summarized in Table I. It is seen that neither 2-acetonaphthone nor 1-naphthaldehyde give photoadducts with II.<sup>9</sup> These two

compounds also do not readily undergo photoreduction. Hammond and Leermakers<sup>10</sup> relate the difficult photoreduction of these compounds to a  $\pi-\pi^*$  configuration for their lowest lying triplet states. Those compounds that readily undergo photoreduction have an  $n-\pi^*$  configuration for their lowest lying triplet state.<sup>10</sup> The similar patterns of photoadduct formation and photoreduction suggest that the  $n-\pi^*$  triplets of the carbonyl compounds are involved in the photocycloaddition reactions. Buchi and co-workers favor a similar mechanism for the photoadditions of aldehydes and ketones to simple olefins.<sup>2</sup>

The carbonyl compounds with higher triplet energies ( $E_{s-t}$ ) also tend to give more tetramethylsuccinonitrile formation. This observation can be explained by a competing triplet energy transfer reaction between excited carbonyl compounds and ground state ketenimine. A transfer of triplet energy to ketenimine to produce an excited ketenimine would result in dissociation of II into 2-cyano-2-propyl radicals which on symmetrical recombination produce tetramethylsuccinonitrile. The quenching of triplet states of aldehydes and ketones by  $\pi$  systems is well known<sup>11</sup> and others<sup>11c</sup> have pointed out that the quenching rate is related to the exo- or endothermicity of the energy transfer step.

We have extended this study to several other ketenimine systems and triplet quenching experiments are in progress to help elucidate the mechanism and explain the steric course of the addition. Studies on the photo and thermal cleavages of  $\alpha$ -adduct V and analogous ones from other ketenimine systems are also being pursued.

#### ACKNOWLEDGMENT

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TABLE I

Correlation of Photoreactions of Dimethyl-N-(2-cyano-2-propyl)ketenimine with the Photobehavior of Aromatic Aldehydes and Ketones.

$R_1R_2CO$	$E_{s-t}^a$	Photo reduction <sup>b</sup>	Products from II TDSM <sup>c</sup> Adducts		Adduct Structure
Cyclopropyl-phenyl Ketone	?	?	100	0	---
Acetophenone	74 <sup>d</sup>	Yes <sup>e</sup>	57	43	$\alpha, \beta$
p-Methoxy-benzaldehyde	?	?	66	34	$\beta$
p-Chloro-benzaldehyde	?	?	21 <sup>f</sup>	60 <sup>i</sup>	$\beta$
Benzaldehyde	72 <sup>d</sup>	Yes <sup>e</sup>	10 <sup>i</sup>	50 <sup>i</sup>	$\beta$
Benzophenone	70 <sup>d</sup>	Yes <sup>e</sup>	5	95	$\alpha, \beta$
2-Aceto-naphthone	59 <sup>d</sup>	No <sup>f</sup>	0	0	---
1-Naphth-aldehyde	57 <sup>d</sup>	No <sup>f</sup>	0	0	---
Fluorenone	53 <sup>g</sup>	? <sup>h</sup>	20	80	$\alpha$

(a) Ground state-triplet excitation energy in kcal.

(b) Whether or not compound undergoes photoreduction to pinacol.

(c) Per cent decomposition to tetramethylsuccinonitrile.

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(f) Ref. No. 10.

(g) G. S. Hammond and R. S. Liu, J. Am. Chem. Soc. 85, 477 (1963).

(h) No photoreduction in 1-propyl alcohol, W. E. Bachman, J. Am. Chem. Soc. 55, 394 (1933), however, fluorenopinacol photodecomposes to fluorenone, C. A. Schonberg and A. Mustafa, J. Chem. Soc. 1944, 67.

(i) Some unidentified products.

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- (9) No reaction was observed after irradiation of II and 2-acetonaphthone for 20.0 hours, and II and 1-naphthaldehyde for 40.0 hours.
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<sup>c</sup>G. S. Hammond, N. J. Turro, and P. A. Leermakers, *J. Phys. Chem.* 66, 1144 (1962).