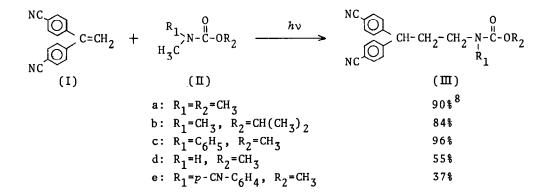
PHOTOCHEMICAL CARBAMOYLATION OF 1,1-BIS(*P*-CYANOPHENYL)ETHYLENE WITH SOME CARBAMATES

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As a variety of carbamates have been found to have physiological properties, they have been widely utilized as antileukemic agents, tranquilizers, herbicides etc.¹ Much attention has been paid on the chemical behavior of them, but their photochemical reaction is limited to photo-Fries rearrangement² and oxetan formation with 1,1-diphenylethylene.³ Recently, we have investigated photochemical behavior of N, N-dimethylcarbamoyl compounds,⁴⁻⁷ and demonstrated in a previous paper⁷ that novel photoureidomethylation takes place very smoothly in the photoreaction of 1,1-bis(p-cyanophenyl)ethylene (I) with tetramethylurea via electron transfer from the urea to triplet state of the olefin.

We wish to report in this communication that photoreaction of I with some carbamates affords carbamoylated compounds in high yield, which is contrasted to the results of photoreaction of 1,1-diphenylethylene with ethyl carbamates.³



On irradiation of an acetonitrile solution of I and five molar excess of carbamates (IIa,b) with a 500W high pressure mercury arc for 20-30 hr, carbamoylated products (IIIa,b) were obtained in good yields. Similar

irradiation of I and IIc for 45 hr was followed by the formation of IIIc almost quantitatively. In these reactions, aminooxetan derivatives (N) could not be detected at all, which was reported in the photoreaction of 1,1-diphenylethylene with ethyl carbamate or ethyl carbanilate.³

On the contrary to this, in the cases with IId,e, which is supposed to have higher ionization potential compared with IIa-c, the yield of III was reduced markedly, though N was not given also in this case. In addition, photoreaction of 1,1-diphenylethylene or 1,1-bis(p-anisy1)ethylene with IIa under similar conditions resulted in the formation of complex mixtures and the corresponding adducts could not be obtained.

$$\begin{bmatrix} I \end{bmatrix}_{T_{1}}^{*} \xrightarrow{(II)}_{R_{1} \cup R_{2}} H_{3}C - N - C \bullet \bullet C(Ar)_{2} \xrightarrow{(II)}_{R_{1} \cup R_{2}} H_{3}C - N - C \bullet - C(Ar)_{2} \xrightarrow{(IV)}_{R_{1} \cup R_{2}} H_{3}C - N - C - C(Ar)_{2} \xrightarrow{(IV)}_{R_{1} \cup R_{2}} H_{3}C - N - C - C(Ar)_{2} \xrightarrow{(IV)}_{R_{1} \cup R_{2}} \xrightarrow{(II)}_{R_{1} \cup R_{2}} H_{3}C - N - C - C(Ar)_{2} \xrightarrow{(IV)}_{R_{1} \cup R_{2}} \xrightarrow{(II)}_{R_{1} \cup R_{2}} \xrightarrow{(II)}_{R_{1} \cup R_{2}} \xrightarrow{(II)}_{R_{1} \cup R_{2}} \xrightarrow{(III)}_{R_{1} \cup R_{2} \cup R_{2} \cup R_{2}} \xrightarrow{(III)}_{R_{1} \cup R_{2} \cup R_{2} \cup R_{2}} \xrightarrow{(III)}_{R_{1} \cup R_{2} \cup R_{2} \cup R_{2} \cup R_{2}} \xrightarrow{(III)}_{R_{1} \cup R_{2} \cup R$$

Based on the above facts as well as the results of a previous report,⁷ the reaction pathway is best explained in terms of quick electron transfer from I to the triplet state of I in an initial step followed by subsequent processes as shown in scheme.

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- (8) Yield is based on unrecovered I.

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