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Photochemical Reactions of 1,1-Diphenylpolycyanocyclopropanes in the Presence of Amines. Formal Extrusion of Dicyanomethylene

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Irradiation of 1,1,2,2-tetracyano-3,3-diphenylcyclopropane in the presence of triethylamine results in the formation of 1,1-dicyano-2,2-diphenylethylene, which is suggested to be formed as a result of spontaneous 1,2 elimination of stabilized ion pairs in the initially formed amine-cyclopropane adducts.

It is now well documented that photochemical reactions of cyclopropanes$^{1)}$ are greatly improved by use of electron acceptors and many useful electron-transfer-mediated photoreactions have been reported.$^{2)}$ However, in most of these reactions, cyclopropanes are used as electron donors which donate a single electron to give a cyclopropane cation radical. Recently, we reported$^{3,4)}$ that cyclopropanes bearing electron-withdrawing groups can act as electron acceptors when irradiated in the presence of amines to give cyclopropane anion radicals, which give rise to formation of new C-C bonds as a result of cross combination. As an extension of the new type of reaction, we examined the effect of substituents on the photo-reactivities of cyclopropane in the presence of amine and found that some cyclopropanes bearing polycyano groups underwent elimination of stabilized ion pairs in the initially formed amine-cyclopropane adducts to give alkenes under these conditions.

Irradiation of 1-cyano-2,2-diphenylcyclopropane (**1a**) in the presence of a five-molar excess of triethylamine produced$^{3)}$ an amine-adduct (**2a**) along with the reductively cleaved product (**3a**). In a marked contrast, similar irradiation of 1,1,2,2-tetracyano-3,3-diphenylcyclopropane (**1e**) resulted in the formation of 1,1-dicyano-2,2-diphenylethylene (**4**) at the complete expense of **2e** as well as **3e**. Other diphenylcyclopropanes bearing different number of cyano groups at different positions also underwent smooth photoreaction with the amine to form either **3** or **4** or both depending on the pattern of substitution. Thus, the results

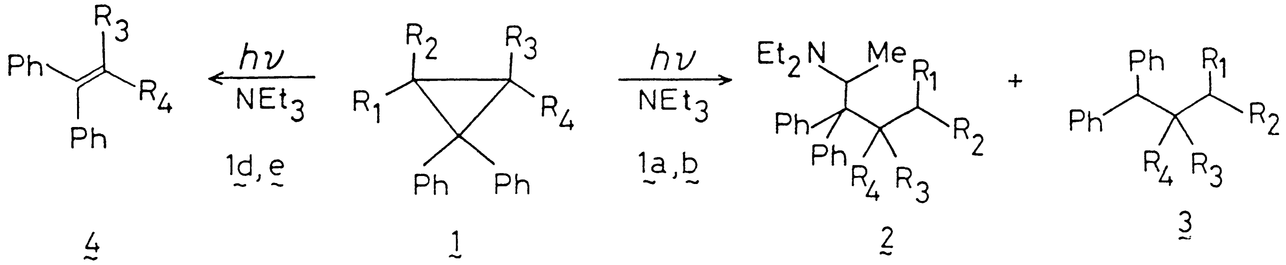


Table 1. Photoreaction of Polycyanocyclopropanes (**1**) with Triethylamine[a)]

1	R_1	R_2	R_3	R_4	Conv./%	Yield/%[b)] **2**	**3**	**4**
a	CN	H	H	H	39.8	39.6	60.3	0
b	CN	H	CN	H	35.0	0	54.0	0
c	CN	CN	H	H	31.1	0	17.7	29.5
d	CN	CN	CN	H	35.2	0	0	11.9
e	CN	CN	CN	CN	75.0	0	0	57.3

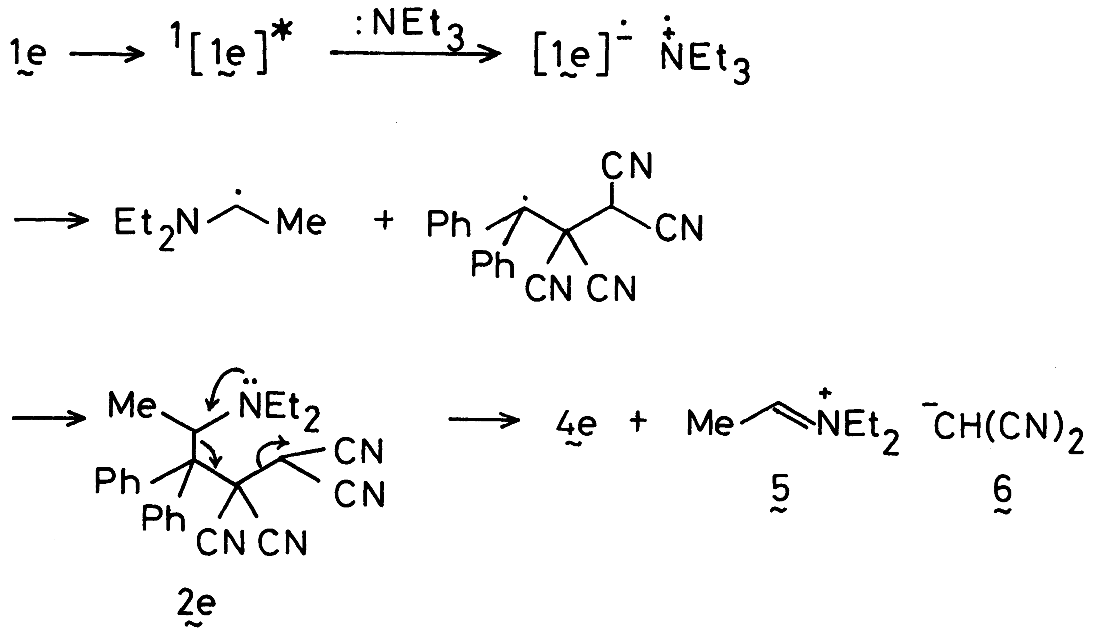
a) Irradiations were carried out on 10 mM degassed solution of **1** in MeCN in the presence of 5 molar excess of trietylamine for 1 h through quartz with a 300 W high-pressure Hg lamp. b) Determined by GC.

summarized in Table 1 suggest that the demethylation reaction took place only when one introduced two cyano groups at the geminal position of **1**.

In order to obtain insight into the mechanism concerning this puzzling dedicyanomethylation reaction, the following control experiments were done. First, no reactions were observed in the absence of the amine nor without light. Second, the reactions were found to be sensitive to the nature of solvent employed. Thus, the reaction proceeded quite smoothly in acetonitrile, while **1** was essentially unreactive in other less polar solvents (e.g., tetrahydrofuran) even in the presence of a large excess of the amine. Third, no new absorption was observed in the mixture of **1a** and the amine, suggesting change-transfer interaction in the ground state is not feasible. Finally, fluorescence of **1e** was quenched by the amine. Stern-Volmer plots of fluorescence quenching are linear for amine concentration giving $k_q\tau$ of 15.7 M^{-1}. However, no new emission ascribable to exciplex fluorescence was observed in the quenching experiments.

The foregoing findings are strongly reminiscent of the related photochemical reaction of stilbene[5,6] or **1a**[3] with amines, which has been explained in terms of electron transfer-proton transfer leading to amine adducts. Apparently it is not easy to find some routes which circumvent the formation of the amine adduct. Thus, presumable possibility is that **1e** follows exactly the same reaction pathway with that of **1a** to give the adduct (**2e**) but that **2e** is simply unstable due to its inherent structure and generates **4** upon its formation. Inspection of the structure of **2** immediately suggests that it has favorable structure for generating **4** by 1,2 elimination probably via an intramolecular push-pull mechanism. The reaction is similar to that[7] of arylazo-tert-cumylmalononitriles which undergo the heterolysis of a carbon-carbon bond to generate tert-cumyl cation and the conjugate base of hydrazomalononitrile. Supporting evidence was obtained by the findings of malononitrile in the photolysates of **1e**. All attempts to isolate the amine adduct (e.g., **2e**) were, however, unsuccessful at present, showing highly unstable nature of the amine adducts. The high instability of **2e** is expected when one considers that both ions **5** and **6** generated from **2e** are highly stabilized by delocalization through the electron-donating amino group and two electron-withdrawing cyano groups, respectively, and is in agreement with the observation[8] that 1-(4-aminophenyl)-2-phenylazotetracyanoethane formed by the reaction of 1,3-diphenyltriazene with (4-aminophenyl)-tetracyanoethane is also not isolated due to the generation of highly stabilized ions.

Finally, in order to know the scope and limitation of the present photodemethylation reaction, the effects of the structure of amines and cyclopropane substituents were investigated. Thus, irradiation of **1e** with a secondary amine (e.g., diethylamine) similarly produced the alkene **4** although the efficiency of the reaction was appareciably decreased. Similar irradiation in the presence of a primary amine (e.g., n-propylamine), however, afforded benzophenone imine (e.g., $Ph_2C=NPr^i$) at the complete expense of **4e**. The formation of the imine was demonstrated, however, to be resulting from the secondary reaction of the initially photogenerated **4e** with the amine by control experiments. The triethylamine-sensitized irradiation of 1,1-bis(methoxycarbonyl)-2,2-diphenylcyclopropane, on the other hand, gave the amine adduct (**2**, $R_1=R_2=CO_2Me$, $R_3=R_4=H$) and the reductively cleaved product (**3**), no **4** ($R_3=R_4=H$) being detected. This is interpreted as simply suggesting that the bis-(methoxycarbonyl)methanide has not enough ability as a leaving group in spite of the pushing group at β position at least under these conditions.



In conclusion, the present findings provide a formally new type of photochemical reaction of cyclopropanes mediated by amines and suggest a new set of eliminating groups.

References

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