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PHOTOUREIDOMETHYLATION OF CYANOBENZENES WITH TETRAMETHYLUREA

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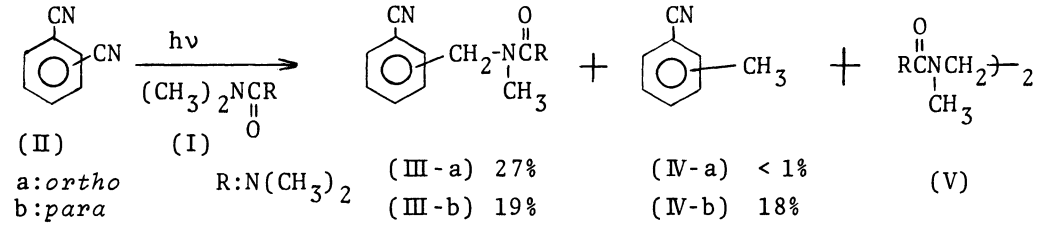
Novel ureidomethylation to an aromatic ring occurred easily, when a mixture of tetramethylurea and cyanobenzenes in acetonitrile was irradiated.

While many studies have been carried out on the photochemistry of amides,[1] little is known of the photoreaction of ureas. Recently, we have investigated photoreaction of N,N-dimethylcarbamoyl compounds in the presence of photo-excited species,[2,3] and we reported in a previous paper[3] that a new ureidomethylation took place efficiently in the photoreaction of *n*-π* photo-excited carbonyl compounds with tetramethylurea (I). We now wish to report the reaction of photo-excited cyanobenzenes with (I).

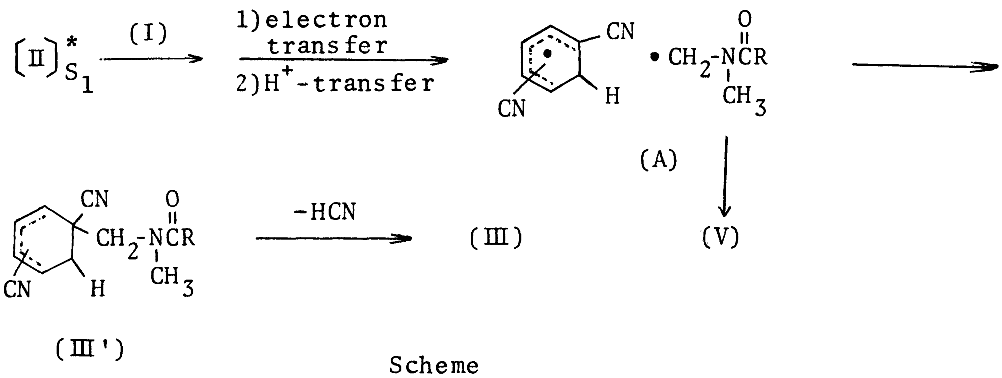
On irradiation of acetonitrile solutions of (I) and an equimolar amount of dicyanobenzenes (II-a,b) with a 500-W high pressure mercury lamp for 10h, the ureidomethylated products (III-a,b) were obtained in considerable yields, together with tolunitriles (IV-a,b) and a dimer (V), as shown hereunder.



In order to obtain significant information regarding the reaction path, following experiments were carried out. In the reaction of (I) and (II-b) in non-polar solvent such as benzene, ureidomethylation was suppressed perfectly. Furthermore, fluorescence of (II) in acetonitrile was quenched by added (I).[4]

Based on the above results, the present ureidomethylation is supposed to proceed via electron transfer from (I) to (II) excited in π-π* singlet state as shown in the Scheme.

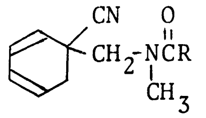
Namely, in acetonitrile, electron transfer from (I) to (II) excited in π-π* singlet state occurs followed by proton transfer to yield a pair of cage radicals (A). While coupling of (A) in a cage leads to the formation of unstable (III'), which changes to (III) accompanied by the elimination of hydrogen cyanide, homocoupling of free ureidomethyl radicals escaped out of a cage gives rise to (V).



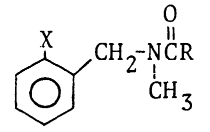
Scheme

Concerning the formation of (IV) from (III), it was confirmed by the photolytic experiment of (III) itself.

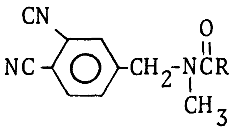
Moreover, the validity of (III') as an intermediate in this ureidomethylation might be supported by the fact that the coupling product (VI) obtained from the reaction of benzonitrile with (I) was thermally transformed into (VII) easily.



(VI) R:N$(CH_3)_2$



(VII) X:H, R:N$(CH_3)_2$
(VIII) X:CN, R:CH_3



(IX) R:CH_3

It is of very interest that in the similar reaction of N,N-dimethylacetamide with (II-a), a new amidomethylation occurred to give an amidomethylated products (VIII) and (IX) in 23% and 3.5% yields, respectively. The detailed study on the above reaction is now in progress and reported shortly.

References and Footnotes

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2. Y.Katsuhara, R.Tsujii, K.Hara, Y.Shigemitsu, and Y.Odaira, *Tetrahedron Lett.*, 1974, 453.
3. Y.Tsujimoto, A.Nakahara, Y.Nishimura, T.Miyamoto, and Y.Odaira, *Bull.Chem.Soc.Jpn.*, 49, 3705(1976).
4. The slopes of the Stern-Volmer plots were 78.5 M^{-1} and 87.5 M^{-1} for (II-a) and (II-b), respectively.

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