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Elimination Reactions. 3. Light-Assisted HCN Elimination from 2-[*p*-(*N*,*N*-Dimethylamino)phenyl]-2,3,3-tricyanopropionamide

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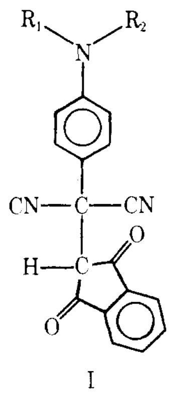
The introduction of a new single bond between two carbon atoms via a photochemically induced elimination of a small, stable molecule (e.g., N_2, CO_2, SO_2, and CO) is a well-known reaction.[1] There are also examples of both intra- and intermolecular photoinduced eliminations of hydrogen halides which lead to new single-bond formation,[1,2] but relatively few reports of the analogous introduction of a double (or multiple) bond, although these include isolated examples of HCl, HBr, and HI photoeliminations.[3] Similarly, a few examples of the photoinduced elimination of H_2O,[4] NH_3,[5] and C_2H_4[6] are known, together with a possible example of HCN photoelimination.[7]

In the course of some earlier work, we noted that some poly(cyano)ethanes eliminate HCN under photochemical conditions in addition to the expected base-catalyzed (thermal) HCN-elimination reaction.[8] (Other workers have employed base-catalyzed HCN elimination from both cyclic and acyclic compounds to obtain the corresponding olefins.[9]) The C–CN bond is a fairly stable one under the usual photochemical conditions, except for that in compounds such as crystal violet or malachite green, leucocyanides, and there are few reports of its photochemical cleavage. Both homolytic and heterolytic cleavage of the C–CN bond is known for the leucocyanides, depending upon the nature of the solvent,[10] while short-wavelength irradiation of nitriles usually leads to homolytic bond cleavage (e.g., acetonitrile[11]). A recent reference[12] to "an unusual photoelimination of HCN" from I to yield the corresponding olefin[13] prompts us to report further on the similar HCN elimination from II. Unlike other poly(cyano)ethanes studied, II does not yield significant amounts of olefin under thermal, base-catalyzed reaction conditions, even after extended reaction times.



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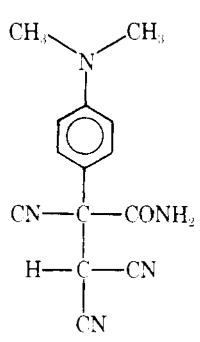

II

Experimental Section

Materials. Organic solvents were Fisher spectrograde, dried and redistilled twice before use. Doubly distilled water was deionized before use. 2-[4-(*N*,*N*-Dimethylamino)phenyl]-2,3,3-tricyanopropionamide (II) was prepared according to the literature procedure:[8] decomposition above 190 °C; λ_{max} 262 nm (ϵ 18 000), λ_{sh} 295 nm (ϵ 7100) in methanol.

Method. Photolyses (3500 Å) were carried out in silica tubes in a Rayonet reactor, equipped with a merry-go-round unit. The temperature was maintained at 25 ± 1 °C. Five-milliliter portions of a 10^{-4} M solution of II in a given solvent were introduced into the silica tubes and each tube was flushed with oxygen-free nitrogen, saturated with the vapor of the solvent. The tubes were then closed, placed in the reactor, and irradiated. The reactions were analyzed spectroscopically by measuring the product development as a function of time (30-s or 1-min time intervals). Blank experiments confirmed that no reaction took place in the absence of irradiation, that reaction ceased on removal of the irradiation, and that 93–97% yields of product were obtained under the photochemical conditions employed. The intensity of the incident radiation was 6×10^{16} quanta/s, as determined by a potassium ferrioxalate actinometer.

In the presence of acid, solutions of the product are blue (λ_{max} 620 nm), whereas they are pink in methanol–water solutions (λ_{max} 426 nm). To confirm that rate determinations in the presence of acid were valid, runs in neutral media (90% MeOH–10% H_2O) were analyzed spectroscopically at both 620 and 426 nm (after addition of excess HCl). The data were identical within experimental error.

HCN elimination was followed to 65 ± 5% reaction in all cases and the data obtained were extrapolated to zero time. Good linear plots for first- or second-order kinetics were obtained with very little deviation over the range of reaction studied.

Results and Discussion

Values of first- or second-order rate coefficients for photoinduced HCN elimination from II in various media are shown in Table I. Reactions in pure alcohols exhibit first-order dependence on the substrate, whereas those in the presence of bases or of carbonyl compounds exhibit second-order substrate dependence. Although no thermal base-catalyzed elimination of HCN occurs in the time required for the photoinduced reaction to go to completion, examination of the data shows that the photochemical reaction rate in methanol is enhanced by the presence of bases. This presumably reflects the increased acidity of the excited species although the rate enhancement by aromatic bases is only slight, relative to that calculated from the data in Table I for an uncatalyzed second-order reaction in methanol. The reaction is not particularly sensitive to the strength of the base (as measured by their values of pK_b in water) however, as rates in the presence of either of the three weaker bases are effectively the same. Similar behavior is found in the presence of the stronger bases,

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Table I. The Influence of Solvent, Added Base, and Added Acid upon the Rates of Photoinduced HCN Elimination from 2-[4-(*N,N*-Dimethylamino)phenyl]-2,3,3-tricyanopropionamide[a]

solvent	quantum yield
methanol	0.019
ethanol	0.017
tert-butyl alcohol	0.013

ϕ for the bases[b]

aniline	pyridine	2,3-lutidine	piperazine·$6H_2O$	diethylamine	piperidine	NaOH
0.022	0.024	0.024	0.060	0.061	0.060	0.057

ϕ for the amount of HCl (mol L^{-1}) equals

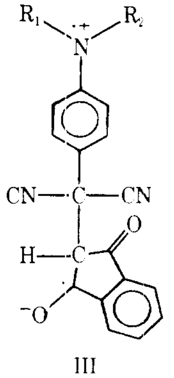
0	10^{-4}	10^{-3}	4×10^{-3}	8×10^{-3}	10^{-2}	4×10^{-2}	8×10^{-2}	10^{-1}
0.036 0.037[d]	0.032	0.032	0.022	0.016	0.013	0.0061	0.0033	0.0030

[a] A uniform light intensity was employed in all experiments; data quoted are averages of three or more runs and are reproducible to ±2%. [b] [Reactant] = 1.2×10^{-4} M; [base] = 2.0×10^{-3} M. [c] Values for 90% methanol–10% water solutions. [d] Measured at 620 nm.

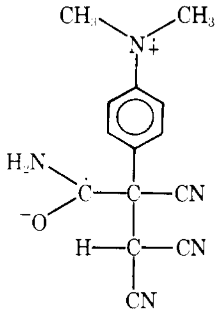
but with an approximately threefold rate enhancement. Although aniline has an absorption at 280 nm (ϵ 1430) and, as it is present in ca. 17-fold excess over the substrate, will absorb more incident radiation than the substrate below 350 nm, the other bases show no absorption in the 350-nm region. Similar rate coefficients in the presence of either aniline or pyridine suggest that light absorption by the added bases is not responsible for the varying rates observed. Reactions in ethanol containing radical trapping agents (e.g., 1,4-dinitrobenzene) show only slight rate enhancements (on comparison of derived first-order rate constants). The influence of the solvent upon the reaction rates is not great, but reaction rates are decreased in the presence of acid, showing inverse first-order dependence upon acid concentration.

An examination of I and II shows that, considering them as ethane derivatives, they both possess an acidic hydrogen atom, an electron-releasing, N-substituted, *p*-aminophenyl substituent on the adjacent carbon to that bearing the acidic hydrogen, and four electron-withdrawing groups. The leaving group is a poor one (CN^-) as evidenced by the lack of thermally induced elimination from II, and the relatively harsh conditions for thermal elimination from I (acetic acid, or butanol, at 100 °C).[13] Although facile HCN elimination from the enol form of I can be envisaged, this should be acid catalyzed, and the reaction in acetic acid does not suggest any significant rate enhancement. The behavior of II in the presence of acid implies that the neutral molecules, rather than the protonated species, are involved.

It is possible that the presence of the NR_2 group enhances the probability of elimination via excited species such as III or IV, formed on irradiation, as was proposed for elimination for aromatic esters of the type $ArCOOCH_2CH_2NR_2$.[14] Intramolecular proton transfer to oxygen followed by elimination of CN^-, subsequent proton loss, and regeneration of the electron pair on nitrogen would yield the observed products. Added base would facilitate proton removal both before and after loss of CN^-, although the latter would be a relatively fast step and hence give rise to only slight effects. Proton removal from the substrate would lead to intermolecular proton transfer, and hence second-order kinetics (as observed) if this is the slow step. A similar pathway can be envisaged for photoassisted elimination from the tetracyanoethane analogue of II.



III



IV

The reaction seems to provide an efficient method for HCN elimination in neutral media from suitably activated substrates and provides a further example of photoassisted formation of a double bond.

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Registry No.—II, 27781-30-2.

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