Mechanistic Aspects of the Photochemistry of Unsaturated Nitriles

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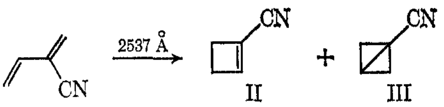
Simple unsaturated nitriles [acrylonitrile, crotononitrile, and 2-cyanobutadiene (I)] were shown to undergo well-defined photochemical reactions. Mechanistic aspects of these reactions were studied with the aid of quantitative measurements. The isolation of 1-cyanobicyclobutane (III) as the major product from the photolysis of I suggests a diradical intermediate (IV).

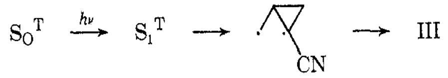
This investigation was initiated to determine the effect of the nitrile function on the solution photochemistry of simple olefins and dienes.[1] At the start of our study, only scattered accounts[2,3] of photochemistry which might involve nitrile participation had appeared. Recently, examples of triplet-state α,β-unsaturated nitriles have been reported.[4-6]

Photoisomerization of 2-Cyanobutadiene.—The solution photochemistry of acyclic 1,3-dienes has been studied in detail.[7] In general, singlet dienes tend to undergo photocyclization, while triplet dienes tend to dimerize. 2-Cyano-1,3-butadiene (I) was irradiated in dilute ether solution with 2537-Å light. The products, 1-cyanocyclobutene (II) and 1-cyanobicyclobutane (III), were isolated by gas chromatography and compared with authentic samples prepared by standard methods.[8-10] The bicyclobutane was also indentified *via* a crystalline diiodide. Quantum yields for the formation of II and III (in ether) were determined by crystal violet leucocyanide actinometry at 30°. Measurements in other solvents were hampered by the tendency of I to undergo photopolymerization. Repeated large-scale photolysis in ether consistently allowed isolation III as the major product (usually the ratio of III/II was 1.5). Similar large-scale results were obtained in 1,2-dichloroethane and carbon tetrachloride. Attempts to sensitize the photoisomerization of I with acetone ($E_T \approx 80$, 3000 Å), triphenylene ($E_T = 67$, 3500 Å), benzophenone ($E_T = 69$, 3500 Å), acetophenone ($E_T = 74$, 3500 Å), and 9,10-dibromoanthracene ($E_{T_1} = 42$, $E_{T_2} \approx 75$; 3500 Å) gave essentially no reaction. The inability of triplet sensitizers to cause photoisomerization tends to exclude the triplet of I as the precursor of II and III; the absence of substantial dimerization suggests that the triplet of I is nonreactive.[11] No fluorescence or phosphorescence was observed for I in dilute ethanol solution at −190°. These data exclude luminescence as a major path for energy loss.



I II III
($\phi = 0.009$) ($\phi = 0.029$)

The mechanism of diene photoisomerization is of current theoretical interest,[12] as is the mechanism of bicyclobutane[13] and cyclobutene[14] ring opening. Quantum mechanical considerations have amply demonstrated their usefulness in this problem,[12,13,15] but, thus far, these deal only with concerted processes. Even so, it is not clear from these treatments whether the formation of a bicyclobutane from a transoid diene (S_1^T) is a concertedly allowed process. Moreover, the vast majority[7,16] of acyclic dienes photoisomerize to cyclobutenes as their sole product; this presents a paradox when it is recalled that simple acyclic dienes are largely transoid.[7] Although bicyclobutanes may have been recently[17] implicated in acyclic diene photolysis, the isolation of III as the major product from reaction of I is surprising. A reasonable mechanism for its formation is shown. The formation of III *via* intermediate



IV

IV supports Srinivasan's generalization.[12] In comparing the reaction of I with that of the parent butadiene in which bicyclobutane was only a minor product, we see no reason why concerted ring closure to III should be favored by substitution of a nitrile group. A number of paths exist for the conversion of I into II. The disrotatory closure[12,15] of S_1^C is appealing, but it may not be correct. Particular care must be taken in assigning mechanism since stereochemical arguments are not available, and an independent criterion of concertedness is lacking.

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[1] A preliminary account of the photodimerization of acrylonitrile has appeared: R. S. H. Liu and D. M. Gale, *J. Amer. Chem. Soc.*, **90**, 1897 (1968).

[2] J. G. Atkinson, D. E. Ayer, G. Buchi, and E. W. Robb, *ibid.*, **85**, 2257 (1963).

[3] J. A. Barltrop and R. Robson, *Tetrahedron Lett.*, 597 (1963); P. DeMayo, R. W. Yip, and S. T. Reid, *Proc. Chem. Soc.*, 54 (1963).

[4] J. Runge and R. Kache, *Zeit. Chem.*, **8**, 382 (1968); S. Hosaka and S. Wakamatsu, *Tetrahedron Lett.*, 219 (1968).

[5] W. L. Dilling and R. D. Kroening, *ibid.*, 5101 (1968).

[6] J. A. Barltrop and H. A. J. Carless, *ibid.*, 3901 (1968).

[7] R. Srinivasan, *Advan. Photochem.*, **4**, 113 (1966).

[8] I am indebted to Dr. H. K. Hall, Jr., for the sample of III[9] and to Dr. W. G. Kenyon for the sample of II[10] used in this study.

[9] H. K. Hall, Jr., U. S. Patent 3,457,194 (1969).

[10] R. Tietz and W. G. Kenyon, U. S. Patent 3,468,861 (1969).

[11] One may argue here that the triplet was never formed under the reaction conditions.

[12] R. Srinivasan, *J. Amer. Chem. Soc.*, **90**, 4498 (1968), and references cited therein.

[13] G. L. Closs and P. E. Pfeffer, *ibid.*, **90**, 2452 (1968), and references cited therein.

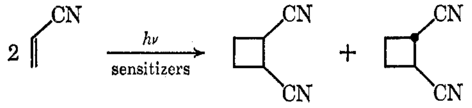
[14] H. M. Frey, B. M. Pope, and R. F. Skinner, *Trans. Faraday Soc.*, **63**, 1166 (1967); H. M. Frey and R. Walsh, *Chem. Rev.*, **69**, 103 (1969).

[15] H. C. Longuet-Higgins and E. W. Abrahamson, *J. Amer. Chem. Soc.*, **87**, 2045 (1965). R. B. Woodward and R. Hoffmann, *ibid.*, **87**, 395 (1965); *Accounts Chem. Res.*, **1**, 17 (1968). K. B. Wiberg, *Tetrahedron*, **24**, 1083 (1968). R. Hoffmann, Abstracts, 21st National Organic Symposium of the American Chemical Society, Salt Lake City, Utah, June 1969, p 116; R. B. Woodward and R. Hoffmann, *Angew. Chem., Int. Ed. Engl.*, **8**, 781 (1969).

[16] K. J. Crowley, *Tetrahedron Lett.*, **21**, 1001 (1965); *Proc. Chem. Soc.*, 245, 334 (1962); 17 (1964).

[17] (a) R. E. K. Winter and P. Kalicky, Abstracts of the 156th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept 1968, ORGN 36. (b) J. A. Barltrop and H. E. Browning, *Chem. Comm.*, 1481 (1968).

Photodimerization of Acrylonitrile.—Acrylonitrile photocyclodimerizes[1,4,6] to a mixture of *cis-* and *trans-*1,2-dicyanocyclobutane[18] (V and VI, respectively) in the presence of triplet sensitizers. Less than 2% 1,3-dicyanocyclobutanes[19] were detected; these isomers were shown to be stable to the reaction conditions. Table I summarizes the 1,2-dicyanocyclobutane product ratios and quantum yields as a function of sensitizer and solvent. The product ratio varies with the medium but not with sensitizer, suggesting the intermediacy of triplet acrylonitrile. The almost exclusive head-to-head dimerization argues against the Schenk[20] scheme for "chemical relay" of energy; a complex of a sensitizer, such as benzophenone, and acrylonitrile would likely give rise to 1,3-dinitrile on reaction with another molecule of acrylonitrile. The Schenk mechanism does not explain why 1- and 2-acetonaphthone are ineffective sensitizers or why benzophenone and 9,10-dibromoanthracene give essentially identical results. The preference for head-to-head dimerization is indicative of a diradical intermediate. Successful dimer formation in ethanol and furan as solvents tends to exclude a strained isomer of acrylonitrile as the reactive species. Attempts to observe direct singlet–triplet absorption for acrylonitrile in ethyl iodide solution (10-cm cell) were unsuccessful. Sensitization by the anthracenes probably occurs *via* their T_2 states.[1,21] An interesting aspect of this study is the unequivocal demonstration of nitrile participation in the excited state. The quantum yield measurements require that acrylonitrile (≈65 kcal/mol) have a lower triplet energy than that expected for ethylene (>80 kcal/mol).



V VI

TABLE I

PHOTOSENSITIZED DIMERIZATION OF ACRYLONITRILE (AN)[a]

Sensitizer (E_T)	[AN], *M* (solvent)[a]	Ratio of VI/V[b]	$\Sigma\phi$[c]
Xanthone (74)	10 (B)	0.8	*d*
Acetophenone (74)	Neat	0.82[e]	*d*
	1.8 (F)[f]	1.7[e]	
Triphenylene (67)	Neat	0.82[e]	*d*
Benzophenone (69)	Neat	0.84[e]	0.062
	10 (B)	0.8	
	1.0 (B)	1.3	
	0.3 (B)	2.33[e]	
	10 (A)	0.8	
	1.0 (A)	0.8	
	0.9 (P)	1.08[e]	
2-Acetonaphthone (59)	Neat	None	<0.002[g]
1-Acetonaphthone (56)	Neat	None	<0.002[g]
9-Fluorenone (51)	Neat	None[e]	<0.002[g]
9,10-Dibromoanthracene (DBA)	Neat	0.82[e]	0.078
	10 (B)	0.7	
	1.0 (B)	1.2	
	0.3 (B)	2.33[e]	
	10 (A)	0.7	
	1.0 (A)	0.7	
	0.2 (EA)[f]	0.82[e]	
	2.7 (T)[f]	1.8[e]	
Cu^+, Cu^{2+} possible[h]	0.4 (E)	1.6[e]	
(9-Fluorenone + DBA)[i]	Neat	0.01	
9-Bromoanthracene	Neat	0.9	0.067

[a] Irradiated in Pyrex tubes in a "merry-go-round" apparatus with Dow-Corning 0-52 and 7-60 filters. Solvent: benzene (B), acetonitrile (A), ether (E), pyridine (P), furan (F), ethanol (EA), or trichloroethylene (T). [b] ~10% error, unless specified. [c] Benzophenone–benzhydrol actinometry. Analysis by gc on a silicone gum nitrile column at 175 or 200°. Values are not corrected for intersystem-crossing efficiency. [d] Qualitatively similar to benzophenone. [e] Large-scale experiment with ir and nmr identification. [f] Other products noted. [g] Limit of detection. [h] Saturated with "CuCl;" quartz apparatus and 2537-Å light used. [i] 1.67 × 10^{-2} 9-fluorenone, 6.67 × 10^{-4} *M* DBA; *ca.* 80% of the light absorbed by 9-fluorenone.

***cis–trans* Isomerization in Crotononitrile.**—Crotononitrile undergoes facile photosensitized *cis–trans* isomerization. Stationary states were determined for high energy sensitizers by approach from both directions (Table II). With lower energy sensitizers, such as 1-acetonaphthone, Michler's ketone (E_T = 61), the rate of isomerization was much diminished, suggesting triplet energies for these isomers in the sixties, in good agreement with the value obtained for acrylonitrile. Among the lower energy sensitizers, several anomalous results were obtained. Rapid equilibration was observed with 2-acetonaphthone (*cis/trans* ratio, 1.6), 9,10-dibromoanthracene, and 9-methyl-10-bromoanthracene. The ketone may be catalyzing the isomerization *via* a radical addition mechanism.[20] The brominated anthracenes appear to be photoprecursors of atomic bromine (see Table III) which, in turn, catalyzes the isomerization.[22] This result is in sharp contrast to the need to invoke T_2 states of brominated anthracenes[21] to explain the rapid dimerization of acrylonitrile.

TABLE II

STATIONARY STATES FOR CROTONONITRILE

Sensitizer	*cis/trans* ratio at equilibrium[a]
Xanthone	1.05
Acetophenone	0.95
Benzophenone	0.87
Triphenylene	0.97

[a] Estimated error ±0.05.

TABLE III

CATALYZED ISOMERIZATION OF CROTONONITRILE

Catalyst	[Crotononitrile]	*cis/trans* ratio
9,10-Dibromoanthracene	0.6 *M* in benzene	1.49
9,10-Dibromoanthracene	50% in benzene	1.29
9,10-Dibromoanthracene	Neat	1.24
9-Methyl-10-bromoanthracene	0.6 *M* in benzene	1.49
Bromine	0.6 *M* in benzene	1.49
Bromine	50% in benzene	1.29
Bromine	Neat	1.25

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(18) E. C. Coyner and W. S. Hillman, *J. Amer. Chem. Soc.*, **71**, 324 (1949).

(19) K. C. Stueben, *J. Polym. Sci.*, **4**, 829 (1966).

(20) For a review of this point of view, see R. Steinmetz, *Fortsch. Chem. Forsch.*, **7**, No. 3, 445 (1967).

(21) R. S. H. Liu and J. R. Edman, *J. Amer. Chem. Soc.*, **91**, 1492 (1969).

(22) The uncatalyzed thermal equilibration of crotononitrile has been studied in the vapor phase: J. N. Butler and R. D. McAlpine, *Can. J. Chem.*, **41** (10), 2487 (1963).

Experimental Section

Photolysis of 2-Cyanobutadiene (I).—A 2% solution of I[23] in anhydrous ether, saturated with Cu_2Cl_2, was photolyzed for 5 days employing a quartz apparatus, cooled with tap water (*ca.* 15°) and equipped with 16 low-pressure mercury lamps.[24] The most intense wavelength produced by these lamps is 2537 Å. When the photolysis was completed, the reaction mixture was filtered and the ether was removed from the filtrate under reduced pressure (*ca.* 10–20 mm). A sample of the residue, stabilized with hydroquinone, was shown to contain III and II by nmr comparisons with authentic samples.

In another experiment, a 2.9-g sample of I dissolved in 350 ml of anhydrous ether saturated with Cu_2Cl_2 was photolyzed for 131.5 hr. The same work-up procedure led to 2 g of yellow liquid. Nmr analysis showed that III was formed in about 28.5% yield and II in about 15.5% yield. Short-path distillation of this residue led to mixtures of III and II, isolated in somewhat lower yields than determined by nmr. Similar results were obtained in ether without the Cu_2Cl_2, in 1,2-dichloroethane, and in CCl_4 (lower yield). Thus, the addition of Cu_2Cl_2 seems to have little effect on the process. Both II and III could also be isolated by gas chromatography (butanediol succinate column).

Quantum Yield Determinations.—A 2×10^{-4} *M* solution of crystal violet leucocyanide[25,26] in ethanol was used for a standard solution. The molar extinction coefficient of the dye at 5900 Å was taken as 1.1×10^5. A quartz cell (path length, 1 cm; volume, 3 ml) was separated (5.5 cm) from a low pressure mercury lamp ("pencil source") by a shutter assembly. The intensity of the light source was measured before and after each determination measuring the change in the absorbance at 5900 Å employing a Cary spectrophotometer (actually the intensity of this source was constant for long periods of time). The quantum yields for the formation of II and III were determined by exposing 0.13 *M* (~100% absorption of light) ether solutions (no Cu_2Cl_2; degassed with argon) of gc-pure I to the source for definite time intervals and analyzing for the concentration of products by gas chromatography (standard samples employed). Measurements were made at ambient temperature (~30°).

1,3-Diiodocyclobutanecarbonitrile.—To a 13-g sample of solid iodine (0.052 mol) mostly dissolved in 100 ml of CCl_4 was added 4.6 g (0.058 mol) of III dissolved in 25 ml of CCl_4. The purple mixture was stirred at room temperature for 16 hr and filtered to remove 1.7 g of a yellow solid. The filtrate was evaporated to dryness and the residue was crystallized from methanol. A total of 11.86 g (80%), mp 82–86° dec, of diiodonitrile was obtained. Recrystallization from methanol gave an analytical sample, mp 91–94° dec. The infrared spectrum showed saturated CH at 3.35 and $-C{\equiv}N$ at 4.51 μ and no $\equiv CCH_3$ absorption. The mass spectrum showed a parent ion at *m/e* 333 and the expected fragmentation. The nmr spectrum showed complex absorption at τ 5.3 (area 1) and 6.5 (area 4). *Anal.* Calcd for $C_5H_6NI_2$: C, 18.03; H, 1.51; N, 4.21; I, 76.25. Found: C, 18.15; H, 1.65; N, 4.30; I, 76.14.

A 200-mg sample of a mixture of III (three parts) and II (one part) obtained from the photolysis of I was dissolved in 25 ml of CCl_4 and stirred for 17 hr at room temperature with 610 mg of iodine (excess). The solvent and most of the unreacted iodine were removed leaving 0.6 g of crude diiodide, which was recrystallized from methanol (most soluble) to give 95% pure 1,3-diiodocyclobutanecarbonitrile (by nmr and ir comparisons with an authentic sample), mp 80–84° dec.

Photodimerization of Acrylonitrile.—In a typical experiment, 100 mg of recrystallized benzophenone (from ethanol) dissolved in 100 g of polymer-grade acrylonitrile (which had been further purified by washing with 5% sodium bicarbonate solution and three times with water, dried over magnesium sulfate, passed through Al_2O_3, and distilled under vacuum through a spinning-band column), in a glass vessel formed from 4-cm Pyrex tubing and cooled to 10° by internal coil, was degassed with Ar and irradiated with a bank of 16 germicidal uv lamps coated with a "black light" phosphor for 2 weeks (intensity of light estimated from lamp output was 0.2 einsteins/day absorbed). The solution remained clear except for the last few days when a small amount of polymer formed. The absorbance (1-cm cell) at 3500 Å changed from 0.7 to 0.6 (>99% absorption at end). The reaction mixture was concentrated to 6.7 g for gc analysis (butanediol succinate at 150°): 38% acrylonitrile, 28% VI (1.9% yield), 33% V (2.2% yield), and two peaks of less than 1% each with the retention times of *cis*- and *trans*-1,3-dicyanocyclobutanes. Attempts to collect the dinitrile products by gc were unsuccessful owing to decomposition. Further concentration for infrared and nmr analysis established the presence of the 1,2-dinitriles by comparison with spectra of authentic materials (see Table I).

Photoisomerization of Crotononitrile.—Stationary states were determined by dissolving sufficient sensitizer in near crotononitrile (both *cis* and *trans*) to make the solution "totally absorbing," and irradiating in Pyrex tubes in a "merry-go-round" apparatus with Dow-Corning 0-52 and 7-60 filters. All of the data in Tables II and III were obtained by starting with both pure isomers. Analyses were made by gc on a silicone gum nitrile column at 150°.

Registry No.—I, 5167-62-4; acrylonitrile, 107-13-1; *cis*-crotononitrile, 1190-76-7; *trans*-crotononitrile, 627-26-9; 1,3-diiodocyclobutanecarbonitrile, 23264-15-5.

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[23] C. S. Marvel and N. O. Brace, *J. Amer. Chem. Soc.*, **70**, 177 (1948).

[24] D. M. Gale, U. S. Patent 3,459,647 (1969).

[25] See J. G. Calvert and J. N. Pitts, Jr., "Photochemistry," John Wiley & Sons, Inc., New York, N. Y., 1966, p 788.

[26] I am indebted to Dr. A. MacLachlan for his assistance with these measurements.