

RADICAL IONS IN PHOTOCHEMISTRY. 12. THE PHOTOADDITION OF OLEFINS TO  
CYANO AROMATIC COMPOUNDS IN POLAR SOLVENTS.

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**Abstract** - The photochemical reactions of 1,4-dicyanobenzene (1) and 1,4-dicyanonaphthalene (2) with 2,3-dimethyl-2-butene (4) in acetonitrile solution have been studied. Irradiation of 1 and 4 gives the photosubstitution products, 2,3-dimethyl-1-(4-cyanophenyl)-2-butene (14) and 2,3-dimethyl-3-(4-cyanophenyl)-1-butene (15). Irradiation of 2 and 4, on the other hand, gives 1,4-dicyano-5,6,6-trimethyl-2,3-benzotricyclo[3.3.1.0-4,7]nonane (16), 1,4-dicyano-5,9,9-trimethyl-2,3-benzotricyclo-[3.3.1.0-4,7]nonane (17), and 1,5-dicyano-2,2,3-trimethyl-6,7-benzotricyclo[3.2.-2,0<sup>3,8</sup>]nonane (18). The structures of 16, 17 and 18 have been established by X-ray crystallographic analysis. It is proposed that both reactions initially involve radical ion intermediates. Generalizations, useful for predicting the result of irradiating cyano aromatic compounds in the presence of olefins are formulated.

#### INTRODUCTION

We have frequently used cyano aromatic compounds, particularly 1,4-dicyanobenzene (1) and 1,4-dicyanonaphthalene (2) as photosensitizers (electron acceptors) for the formation of olefin radical cations (Ref. 1). Usually the photosensitizer was largely recovered after the olefin was consumed, which indicates that the sensitizer radical anion was stable under the reaction conditions and was ultimately oxidized, by electron transfer, back to the neutral cyano aromatic compound. This experience is in contrast with the known photocycloaddition reaction of olefins to cyanobenzene (3) reported many years ago by G. Buchi and coworkers (Ref. 2) and more recently reinvestigated by T. S. Cantrell (Ref. 3). Products resulting from photocycloaddition to both the cyano group and to the aromatic ring were found by these and other workers (Reactions 1 and 2) (Ref. 2-4). Also at variance with these results is the report by J.J. McCullough and his coworkers of the formation of 1:1:1 addition products upon irradiation of 2-cyanonaphthalene (10) in the presence of 2,3-dimethyl-2-butene (4) and methanol (Reaction 3) (Ref. 5).

We first noticed product formation between the cyano aromatic compound and the olefin during our studies of the photosensitized (electron transfer) cross cycloaddition of olefins. Irradiation of 1,1-diphenylethylene and 4 using 1 as the photosensitizer (electron acceptor) in acetonitrile solution, led to the cross cycloaddition products; however, 1 was partially consumed. The photosubstitution products 14 and 15 were identified (Reaction 4) (Ref. 1a).

In this paper we report the results of a more thorough study of the photochemical reactions of 1,4-dicyanobenzene (1) and 1,4-dicyanonaphthalene (2) with 2,3-dimethyl-2-butene (4) in acetonitrile solution. We will discuss the mechanism of these reactions which we believe involves the initial formation of the radical ion intermediates. Our conclusions are pertinent not only to the problem of identifying the pathways leading to destruction of the sensitizers in photosensitized (electron transfer) reactions, but also serve as a basis for formulating generalizations concerning the potentially useful photocycloaddition and photosubstitution reactions of cyano aromatic compounds with olefins.

#### RESULTS

Ultraviolet irradiation of an acetonitrile solution of 1,4-dicyanobenzene (1) and 2,3-dimethyl-2-butene (4) through a Pyrex vessel gave the three dimers of 4-H plus two other volatile products 14 (10%) and 15 (18%) (Reaction 4) (Note a). Both 14 and 15 were isolated by

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Note a. The yields of 14 and 15 reported in our previous communication (Ref. 1a) were inadvertently reversed.

preparative vapor phase chromatography (vpc). They both have a parent peak of 185 m/e in their mass spectra (ms) which indicates that they are substitution products; i.e. 1:1 adducts -HCN. The  $^1\text{Hmr}$  spectrum of 14 showed three methyl groups, a methylene group and a *para*-substituted phenyl ring, which is consistent with the structure of 2,3-dimethyl-1-(4-cyanophenyl)-2-butene. The  $^1\text{Hmr}$  spectrum of 15 showed two terminal vinylic protons one of which is coupled to an allylic methyl group, two weakly coupled methyl groups and a *para*-substituted phenyl ring, which is consistent with the structural assignment, 2,3-dimethyl-3-(4-cyanophenyl)-1-butene.

Ultraviolet irradiation of 1,4-dicyanonaphthalene (2) and 2,3-dimethyl-2-butene (4) in acetonitrile solution gave again the three dimers of 4-H plus three major products which, according to their ms, are 1:1 adducts (Reaction 5). The combined yield of these three products accounts for ca. 60% of 2 so this reaction is useful for the preparation of these complex molecules. The  $^{13}\text{Cmr}$  and  $^1\text{Hmr}$  spectra reveal that all three adducts consist of a benzo group, two cyano groups, three methyl groups, two methylene groups, one methine group and four quaternary substituted carbons. There are several possible structures which can accommodate these features. Deuterium was not incorporated upon refluxing any of the adducts in methanol-0d-sodium methoxide. This rules out those possible structures which have the methine proton adjacent to the cyano group which would exchange under these conditions.

While the spectra of the three adducts is consistent with structures 16-19, the data did not allow us to distinguish from among these four possibilities. We could tentatively single out adduct 16 since the  $^1\text{Hmr}$  resonance for the protons of all the methyl groups are of normal chemical shifts (i.e.  $\sim 1$  ppm). With the other three structures there would be one high field methyl group which would be that which is situated in the shielding region of the phenyl ring. It was also possible to tentatively distinguish adduct 17 from the other two adducts since the methylene and methine protons are all coupled.

The structures of 16, 17 and 18 were determined by X-ray crystallographic analysis. Stereoscopic views of the molecules in the final structure are given in Fig. 1, 2, and 3.

There were at least three volatile minor products (total  $\sim 7\%$ ) detected by vpc, which we have not identified. One of these products was observed to build up to a small constant amount during the irradiation and became scarcely detectable after 2 was completely consumed. This may correspond to one of the proposed monophotonic reaction intermediates which will be discussed later; however, we were never able to isolate a sufficient quantity of this product to allow identification.

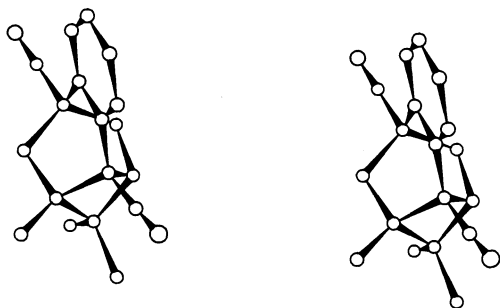


Fig. 1. Stereoscopic view of 16 (mp 101-102°)

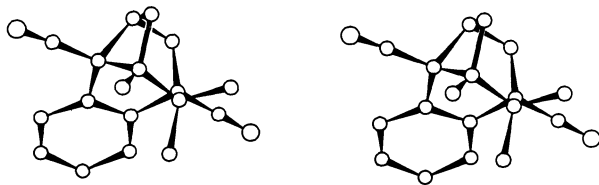


Fig. 2. Stereoscopic view of 17 (mp 156-157°)

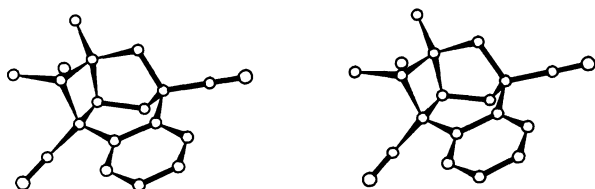


Fig. 3. Stereoscopic view of 18 (mp 173-174°)

#### DISCUSSION

A remarkable feature of the photochemical reactivity of cyano aromatic compounds with olefins is the dramatic dependence of the type of reaction upon both the nature of the reactants and the solvent. Seven (at least) distinct types of reactivity have now been observed:

- 1) substitution of the aromatic ring by the olefin at the ambident sites of the allylic radical with loss of the cyano group, (Reaction 4 provides the first example of this type (Ref. 1a));
- 2) addition of the olefin, at the ambident sites of the allylic radical, to the aromatic ring, (Reaction 5 provides the first example of this type, which, in this case, is followed by further photochemical reaction of the primary photoaddition product);
- 3) cycloaddition of the olefin to the cyano substituted aromatic ring (Reaction 2);
- 4) cycloaddition of the olefin to the cyano group (Reaction 1);
- 5) formation of 1:1:1 adducts incorporating alcohol solvent (Reaction 3);
- 6) the ring of the cyano aromatic is sometimes reduced upon irradiation in the presence of olefins (e.g. formation of 13 in Reaction 3); and finally,
- 7) the photosensitized (electron transfer) reaction (Ref. 1).

This plethora of reactivity is illustrated (Reactions 1-5) with the common olefin 2,3-dimethyl-2-butene (4) and different cyano aromatic compounds and conditions.

In the discussion that follows, we will propose mechanisms (Schemes 1 and 2) for the new reactions (4 and 5). It is then possible, by applying this mechanistic reasoning, to explain why these reactions are observed instead of other possibilities. While much remains to be learned, a pattern of reactivity is beginning to emerge which will be useful in predicting the type of reactivity observed upon irradiation of a given system.

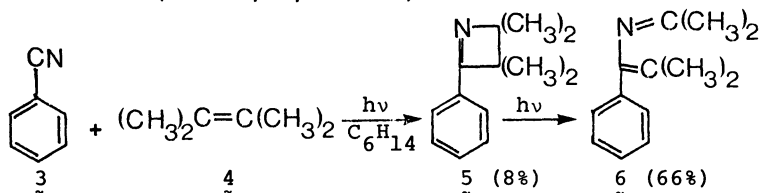
The first few steps in Schemes 1 and 2 are the same. The ultraviolet absorption spectra of mixtures of 1 and 2 with 4, at the concentration of the irradiation mixtures, show enhanced absorption relative to the spectra of the individual components. This long wavelength tail (there is no detectable shoulder or maximum) is indicative of the formation of a weak charge-transfer complex and this charge-transfer transition is in the actinic region (i.e.  $\lambda > 290$  nm). Nevertheless, most of the light must be absorbed directly by 1 and 2.

That the singlet states of 1 and 2 are reactive species follows from the rapid fluorescence quenching of 1<sup>\*</sup> and 2<sup>\*</sup> by 4. The quenching rate constants, obtained from the slopes of the Stern-Volmer plots and the measured singlet lifetimes of 1<sup>\*</sup> and 2<sup>\*</sup>, are essentially diffusion controlled.

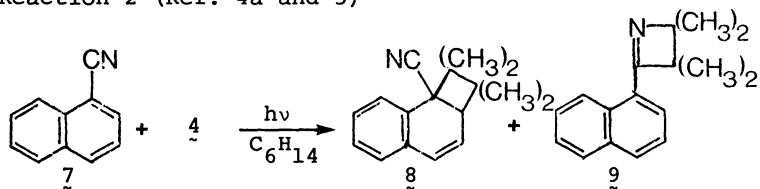
Quenching by electron transfer is energetically feasible. The free-energy change ( $\Delta G$ ) for this process, estimated using the now familiar semi-empirical approach developed by A. Weller and his coworkers (Ref. 6), are listed in Table 1. It seems likely, in view of the high dielectric of the solvent (acetonitrile,  $\epsilon = 35.6$ ) and the large difference in electronegativity between 1 (and 2) and 4, that the excited state of the charge-transfer complex, if formed, would rapidly dissociate. There was no evidence for emission from an excited state of the charge-transfer complex, even in solutions containing high concentrations of 4, so that the fluorescence from 1 and 2 was strongly quenched.

Also listed in Table 1 is an estimate of the free-energy change upon formation of radical ions between the excited state of benzene and 4. In contrast, the electron transfer process is not favored in this case. Irradiation of benzene in the presence of 4 is reported (Ref. 7) to give three 1:1 adducts (Reaction 6). This reaction is apparently not affected by change in solvent dielectric; the product ratio is similar in hexane and in acetonitrile solution. This, and other evidence, suggests that the product ratio is determined by competitive reactions of the exciplex which, in this case, would not be very polar and would therefore be less likely to form radical ions.

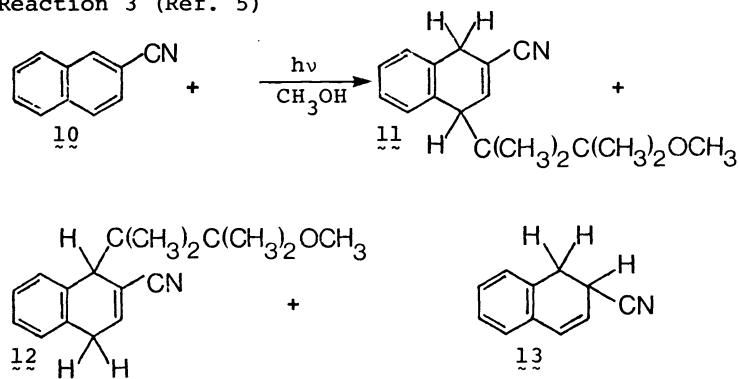
## Reaction 1 (Ref. 2, 3, and 4a)



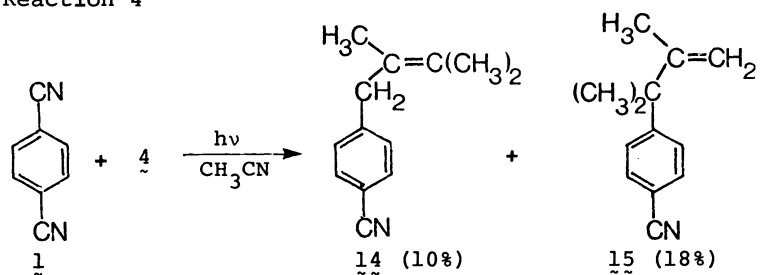
## Reaction 2 (Ref. 4a and 5)



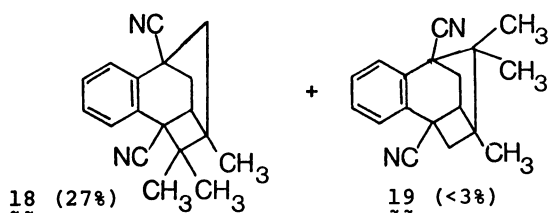
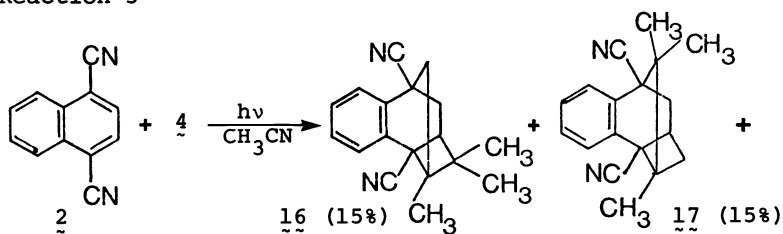
## Reaction 3 (Ref. 5)



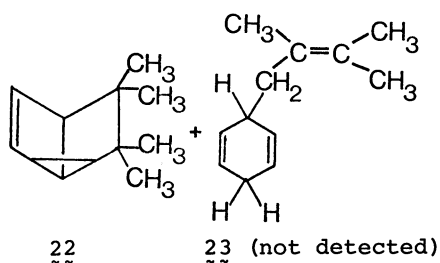
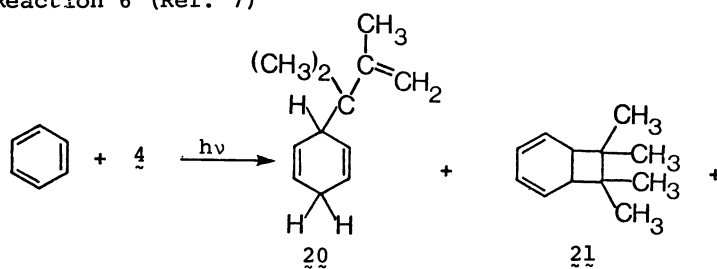
## Reaction 4



## Reaction 5



## Reaction 6 (Ref. 7)



When radical ions are involved and if proton transfer (Scheme 1 and 2, 3a) occurs, then products which would result from coupling of the allylic radical at both ambient sites should be observed. Particularly diagnostic, therefore, is the absence of this product (23) from reaction 6 in comparison to 14 from reaction 4.

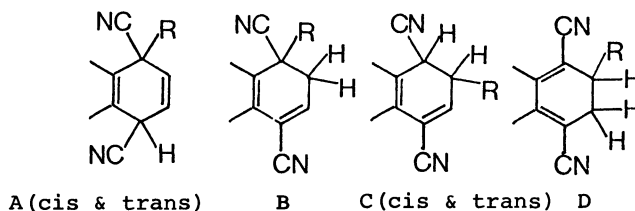
TABLE 1. The calculated free-energy change ( $\Delta G$ ) for formation of the radical ion pair resulting from electron transfer within the encounter complex<sup>a</sup>

Acceptor (A)	$E_{\frac{1}{2}}^{\text{red}}(\text{A})$ (V) <sup>b</sup>	${}^1\Delta E_{\text{O}_2}(\text{A})$ (kcal mol <sup>-1</sup> )	$\Delta G$ (kcal mol <sup>-1</sup> )
Benzene	-3.60 <sup>c</sup>	109.8 <sup>f</sup>	+ 2.6
Benzonitrile	-2.74 <sup>d</sup>	104.0 <sup>g</sup>	-11.4
1-Cyanonaphthalene	-2.33 <sup>e</sup>	89.4 <sup>e</sup>	- 6.3
1,4-Dicyanobenzene (1)	-2.00 <sup>e</sup>	97.6 <sup>e</sup>	-22.1
1,4-Dicyanonaphthalene (2)	-1.67 <sup>e</sup>	86.4 <sup>e</sup>	-18.5

- a With 2,3-dimethyl-2-butene (4) as the donor in acetonitrile. The oxidation potential of 4 is 1.3 vs. Ag/AgNO<sub>3</sub> (0.1 M) in acetonitrile (this work).  
 b The reference electrode is Ag/AgNO<sub>3</sub> (0.1 M) in acetonitrile.  
 c F. Gerson, H. Ohya-Nishiguchi, and C. Wydler, *Angew. Chem. Int. Ed. Eng.*, **15**, 552 (1976).  
 d P.H. Rieger, I. Bernal, W.H. Reinmuth, and G. Fraenkel, *J. Am. Chem. Soc.*, **85**, 683 (1963).  
 e A.J. Maroulis, Y. Shigemitsu, and D.R. Arnold, *J. Am. Chem. Soc.*, **100**, 535 (1978).  
 f Value taken from J.B. Birks, "Photophysics of Aromatic Molecules", p. 74, Wiley-Interscience (1970).  
 g K. Takei and Y. Kanda, *Spect. Acta*, **18**, 201 (1962).

The radical coupling process (Scheme 1 and 2, 3b) should favor attachment of the allylic fragment so as to form the more heavily substituted olefin. That is, products derived from 24 should be favored over those from 25 in reaction 4 and products from 26 should dominate those from 27 during reaction 5. The ratio of products from reaction 5 indicates that this is the case, 16+18:17, ca. 3:1. In reaction 4, however, the opposite is true, 14:15, ca. 0.5. These results suggest that the product ratio will in general depend upon the relative rates of proton transfer (step 3a) and radical ion coupling (step 4a). Note that the alternative allylic radical coupling products were not observed from reaction 3. J.J. McCullough and his co-workers suggest a mechanism analogous to step 4a and they show, by isotopic labeling studies, that a step analogous to 3a is not involved. The factors influencing these rates have not yet been defined. It is clear, however, that the presence of alcohol tends to favor products formally derived from the radical ion coupling pathway (Ref. 4b and 5).

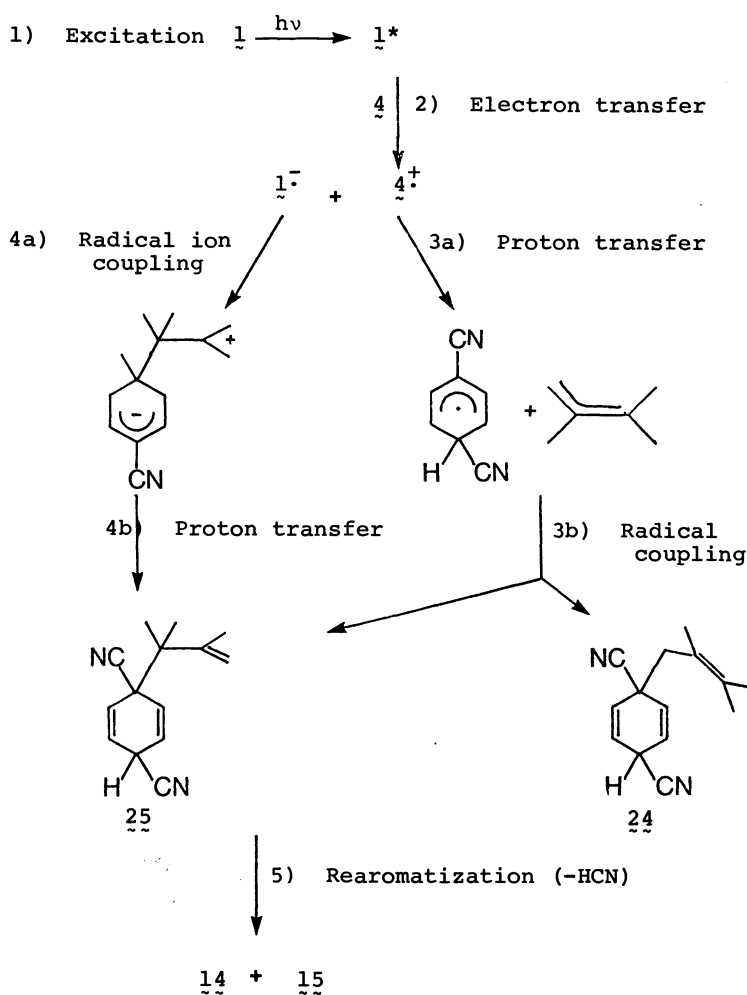
It is interesting to consider the factors which influence the sites of addition to the cyano aromatic, i.e. 1,2- vs. 1,4-addition, and carbon or proton bonded to cyano-bearing or unsubstituted position. In the case of 1 and 2 there are at least six possible primary products.



Considering first reaction 4, we cannot, with the existing data, choose between A and B (or both); A is shown by analogy with reaction 6 and some other related results (Ref. 8). We find no evidence for *meta*-substituted derivatives so apparently C is not produced. The products from reaction 5 are indicative of formation of B.

It is perhaps speculative to attach much significance to the absence of possible products from reaction 4 and 5, particularly in view of the rather low yields and the possibility that rearrangements or secondary reactions of initially formed products may have occurred. Nevertheless, it may be useful to point out that molecular orbital calculations (MNDO) indicate that the 1-position of the anion radicals of both 1 and 2 bears the largest charge and spin density (Table 2). Electron spin resonance studies provide direct evidence for this point (Ref. 9). The calculated localization energy also supports the view that initial reaction at the 1-position of both 1 and 2 is favored. It may be that the initial adducts from reaction 5 do in fact have structure A and that isomerization of the double bond into conjugation (structure B) precedes intramolecular cyclization.

## Scheme 1



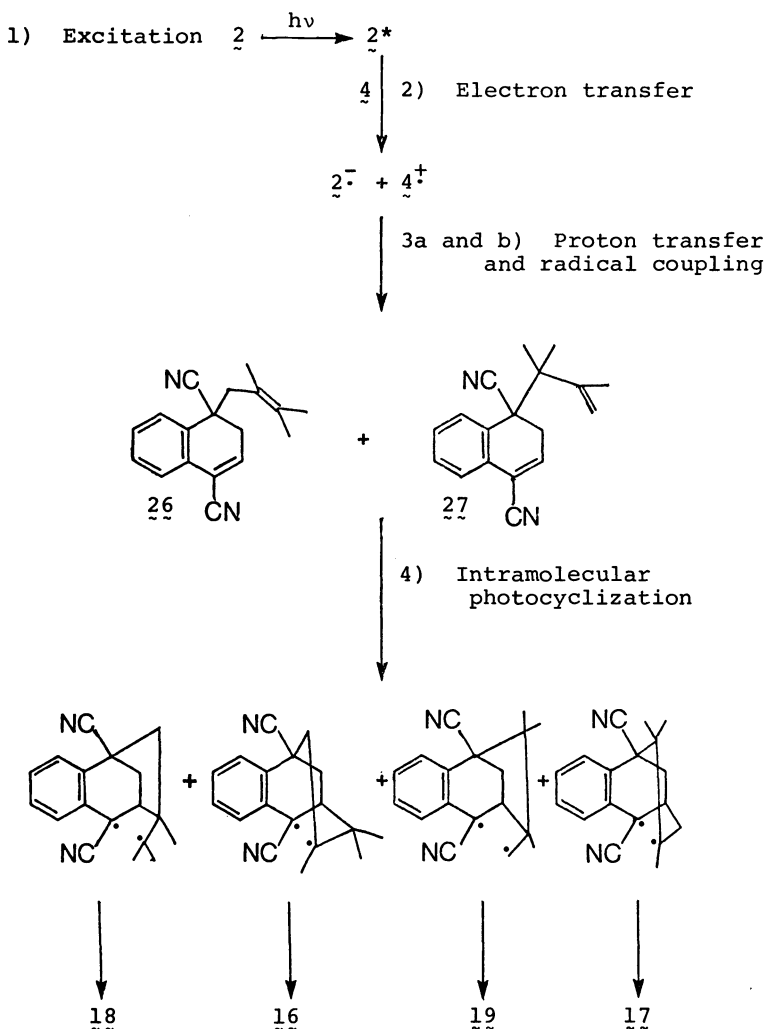
The mechanistic schemes for reactions 4 and 5 diverge after step 3. It is reasonable to assume that the intermediate in reaction 4, i.e.  $\underline{24}$  and  $\underline{25}$  will more rapidly lose HCN to rearomatize the phenyl ring, than would the analogous compounds in reaction 5, where the driving force is rearomatization of the naphthalene ring system. We found no evidence for the analogous naphthalene substitution products in reaction 5.

The formation of  $\underline{16}$ ,  $\underline{17}$  and  $\underline{18}$  was not anticipated. We believe that the intermediates  $\underline{26}$  and  $\underline{27}$ , which were not identified, undergo an efficient intramolecular cycloaddition to give the observed products. The regioselectivity of the cyclization of  $\underline{26}$  and  $\underline{27}$  is explicable in terms of the involvement of 1,4-diradical intermediates. If we make the reasonable assumption that one of the radical sites will be at the tertiary benzylic-, cyano-position, then the 1,4-diradical precursors of  $\underline{16}$ ,  $\underline{17}$ , and  $\underline{18}$  also have a tertiary position for the other radical site. The other possible product,  $\underline{19}$ , which was not observed, would require formation of a less stable primary radical site. It seems likely that the intramolecular photocyclization is a triplet sensitized reaction with the triplet of  $\underline{2}$  serving as the sensitizer. This would account for the fact that  $\underline{26}$  and  $\underline{27}$  never attain a high concentration.

## CONCLUSIONS

We are now in a position to give a preliminary summary of some generalizations regarding the type of reactivity to be expected upon irradiation of a cyano aromatic compound in the presence of an olefin. Reactions 1 and 2 require the exciplex intermediate (Ref. 3-5). Polar solvents, which deactivate polar exciplexes through formation of the component radical ions, will inhibit these reactions. It is therefore not surprising that irradiation of neither  $\underline{1}$  nor  $\underline{2}$  in the presence of  $\underline{4}$  yields the 1-azetine or cyclobutane when acetonitrile is the solvent.

## Scheme 2



From the limited number of examples studied, the competition between reactions 1 and 2 shows an interesting pattern. Formation of the 1-azetine (and 2-azabutadiene formed as a secondary photolysis product) is favored with electron-rich olefins, while the cyclobutane products are favored with less electron-rich olefins. Cyano aromatic compounds larger than naphthalene form cyclobutanes as the exclusive cycloaddition products, even with electron-rich olefins. This preference between reactions 1 and 2 has been attributed to variation in the structure of the exciplex (Ref. 36 and 4d).

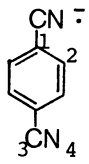
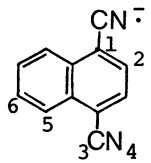
In polar solvents the photochemical reaction between cyano aromatic compounds and olefins takes an entirely different course; consistent with the involvement of radical ion intermediates. Reactions 3-5 illustrate reactions of the radical ion pair involving alcohol solvent, proton transfer between the radical ions, and coupling of the radical cation and anion. The factors which influence the competition between these various possibilities have yet to be determined.

When the radical anion of the cyano aromatic is protonated during the reaction pathway, the eventual formation of the reduction product (i.e. 13 in Reaction 3), formed for example by disproportionation, is likely. Similarly, the dimer(s) resulting from coupling to the allylic radicals is to be expected as a competing reaction when proton transfer from the radical cation occurs. These types of reactions will depend upon the kinetic acidity of the radical ions and the stability of the intermediate radicals.

We offer the prediction that the synthetic utility of any particular type of photochemical reaction between a cyano aromatic compound and an olefin will be limited to special cases. This is in view of the many diverse types of reactions which are possible and the complexity of the reaction mechanisms which in most cases involve a number of reactive (unselective) intermediates. The challenge for the organic photochemist is to discover ways to influence reactivity in the desired way with any combination of reactants.



TABLE 2. Molecular orbital (MNDO) calculations on the radical ions of 1 and 2

	Position	Charge Density	Spin Density	Localization Energy
	1	-0.19	0.27	1.81
	2	-0.05	0.08	2.08
	3	+0.01	0.02	
	4	-0.27	0.05	
	1	-0.15	0.21	1.53
	2	-0.05	0.07	1.87
	3	+0.01	0.01	
	4	-0.23	0.03	
	5	-0.13	0.10	
	6	-0.09	0.04	

## EXPERIMENTAL

Acetonitrile (Aldrich Gold Label) was refluxed over calcium hydride under a dry nitrogen atmosphere and distilled. 1,4-Dicyanobenzene (Aldrich) was recrystallized from ethanol four times. 1,4-Dicyanonaphthalene was prepared by the reaction of 1,4-dibromonaphthalene with cuprous cyanide and was purified by sublimation under vacuum, column chromatography (neutral alumina, Fisher) and recrystallization from benzene/hexanes. 2,3-Dimethyl-2-butene (Aldrich) was fractionally distilled before use.

Mass spectra were recorded from a Varian Mat 311A mass spectrometer. The infrared spectra were recorded on a PE-621 or a PE-180 infrared spectrometer calibrated with the 1602  $\text{cm}^{-1}$  absorption of polystyrene. The  $^1\text{Hmr}$  spectra were obtained either on a Varian T-60, a Varian CFT-20 or a Varian XL-100 spectrometer. The  $^{13}\text{Cmr}$  spectra were recorded on either a Varian CFT-20 or a Varian XL-100-15 spectrometer. Cyclic voltammetric measurements were performed as previously described (Ref. 1).

Fluorescence quenching experiments were performed using an Aminco-Bowman spectrophotofluorometer. Stern-Volmer plots were obtained from the fluorescence at the maximum. The samples were degassed on a mercury-free vacuum line using three freeze-pump-thaw cycles. From the measured singlet lifetimes of 1 (9.7 nsec.) and 2 (10.1 nsec.), quenching rate constant of  $8.4 \pm 0.1 \times 10^9$  and  $10.2 \pm 0.1 \times 10^9 \text{ M}^{-1} \text{ sec}^{-1}$  respectively were obtained for 4 in acetonitrile at room temperature.

Irradiations were performed using a General Electric Co. 1-kW medium pressure mercury vapour arc lamp with a quartz cooling jacket (Photochemical Research Associates) at 10°C. All solutions were placed in Pyrex vessels flushed with dry nitrogen and sealed with rubber septa.

X-ray crystallographic analysis

The crystals of all three compounds were of an adequate size and were apparently well formed. They did not diffract well. The reflection data were all collected on a CAD4 automatic diffractometer and the structures were solved by routine applications of the Tangent formula using the Sheldrick SHELX 76 system. The trial structures were refined by full matrix least-squares with isotropic temperature factors on the heavy atoms of compound 17 and anisotropic temperature factors on the heavy atoms of the other two compounds. The refinements converged with  $R = .048$ ,  $.104$ , and  $.071$  on the three compounds respectively.

Compound 16. Monoclinic;  $a = 7.872(4)$ ,  $b = 18.184(4)$ ,  $c = 10.456(2)$  Å;  $b = 100.76(3)^\circ$ .

Spacegroup  $P2_1/n$ ,  $Z = 4$ , 654 reflections with  $I > 3\sigma(I)$ .

Compound 17. Monoclinic;  $a = 9.163(3)$ ,  $b = 11.454(3)$ ,  $c = 13.639(4)$  Å;  $\gamma = 96.91(3)^\circ$ .

Spacegroup  $P2_1/n$ ,  $Z = 4$ , 408 reflections with  $I > 3\sigma(I)$ .

Compound 18. Triclinic;  $a = 7.291(2)$ ,  $b = 7.460(6)$ ,  $c = 13.992(3)$  Å;  $\alpha = 104.33(5)$ ,

$\beta = 93.82(2)$ ,  $\gamma = 93.02(5)$ . Spacegroup  $P\bar{1}$ ,  $Z = 2$ , 894 reflections with  $I > 3\sigma(I)$ .

Irradiation of 1,4-dicyanobenzene and 2,3-dimethyl-2-butene in acetonitrile

A solution of 1,4-dicyanobenzene (1, 100 mg, 0.8 mmol) and 2,3-dimethyl-2-butene (4, 420 mg, 5 mmol) in acetonitrile (6.25 ml) was irradiated for 42 h. The solvent was evaporated on a rotary evaporator and the oily residue obtained was divided into two parts; one part was used for the determination of the yields using vpc (10% DEGS, Chromosorb W, NAW, 60/80 mesh, internal standard triphenylmethane), and the other for the isolation of the products by semipreparative vpc. The crude reaction mixture was found to contain: recovered 1,4-dicyanobenzene (12 mg, 8% conversion), 2,3-dimethyl-1-(4-cyanophenyl)-2-butene (14, 14 mg, 10%), 2,3-dimethyl-3-(4-cyanophenyl)-1-butene (15, 24 mg, 18%), and three dimers of 2,3-dimethyl-2-butene (3% based on the amount of 2,3-dimethyl-2-butene). The spectroscopic properties of 14 and 15 described below were identical to our previous findings (Ref. 1a).

2,3-Dimethyl-1-(4-cyanophenyl)-2-butene (14): ir (neat)  $\nu$  2994, 2922, 2864, 2232, 1606, 1504, 884, 815  $\text{cm}^{-1}$ ;  $^1\text{Hmr}$   $\delta$   $\text{Me}_4\text{Si}$  ( $\text{CDCl}_3$ ) AB quartet, centered at 7.4 (ArH), 3.44 (broad s,  $\text{CH}_2$ ), 1.74 (broad s, gem  $\text{CH}_3$ 's), 1.56 (broad s, 2- $\text{CH}_3$ ); ms (70 eV) (rel.intensity): 185 (51,  $\text{M}^+$ ), 171 (13), 170 (100), 143 (16), 142 (34), 116 (17). Anal. calcd. for ( $\text{C}_{13}\text{H}_{15}\text{N}$ ): C 84.26, H 8.16; found: C 84.03, H 8.34.

2,3-Dimethyl-3-(4-cyanophenyl)-1-butene (15): ir (neat)  $\nu$  2977, 2233, 1640, 1607, 1502, 1095, 900, 843  $\text{cm}^{-1}$ ;  $^1\text{Hmr}$   $\delta$   $\text{Me}_4\text{Si}$  ( $\text{CDCl}_3$ ) AB quartet, centered at 7.49 (ArH), 4.95 (m, AB part of an ABX<sub>3</sub> system, which collapses to a pair of doublets, upon irradiation of the 2- $\text{CH}_3$ ;  $J_{\text{AB}} = 1.4$  Hz,  $J_{\text{AX}} = 0.7$  Hz,  $J_{\text{BX}} = 1.4$  Hz), 1.48 (doublet pair, 2- $\text{CH}_3$ ), 1.40 (s, gem  $\text{CH}_3$ 's); ms (70 eV) (rel.intensity): 185 (43,  $\text{M}^+$ ), 170 (100), 144 (22), 142 (33), 116 (40). Anal. calcd. for ( $\text{C}_{13}\text{H}_{15}\text{N}$ ): C 84.28, H 8.16; found: C 84.08, H 8.31.

Dimers of 2,3-dimethyl-2-butene (4-H): a 4:1:1 mixture of 2,3,6,7-tetramethylocta-2,6-diene-, 2,3,3,4,4,5-hexamethylhexa-1,5-diene and 2,3,3,5,6-pentamethylheptadiene based on the comparison of  $^1\text{Hmr}$  spectra reported for these compounds (Ref. 3b).

Irradiation of 1,4-dicyanonaphthalene and 2,3-dimethyl-2-butene in acetonitrile

A solution of 1,4-dicyanonaphthalene (2, 1.20 g, 6.74 mmol) and 2,3-dimethyl-2-butene (4, 3.00 g, 35.71 mmol) in acetonitrile (125 ml) was irradiated for 48 h. Vpc and the  $^1\text{Hmr}$  spectrum of the reaction mixture revealed that the 1,4-dicyanonaphthalene had been consumed. The solvent was evaporated and the residue, chromatographed on a silica gel (60/120 mesh) column using solvents of varying polarity, gave products in the following order of elution: a 4:1:1 mixture of 2,3,6,7-tetramethylocta-2,6-diene, 2,3,3,4,4,5-hexamethylhexa-1,5-diene and 2,3,3,5,6-pentamethylheptadiene (66 mg, 5.5% based on the amount of 2,3-dimethyl-2-butene); 16 (268 mg, 15% based on the amount of 1,4-dicyanonaphthalene); 17 (268 mg, 15%); 18 (480 mg, 27%); and at least three minor products (total ca. 7%) which were not further characterized.

Adduct 16: recrystallized from ether/pentanes (mp 101-103°); ir (KBr)  $\nu$  3015, 2950, 2885, 2250, 2235, 1480, 1450, 1395, 1380, 1310, 1192, 1135, 1095, 768, 745  $\text{cm}^{-1}$ ;  $^1\text{Hmr}$   $\delta$   $\text{Me}_4\text{Si}$  ( $\text{CDCl}_3$ ) 7.80-7.25 (m, 4H), 2.80-2.40 and 1.76-1.40 (m, ABC system,  $\text{CH}_2$  coupled with CH), AB quartet, centered at 2.00 ( $J_{\text{AB}} = 14$  Hz,  $\text{CH}_2$ ), 1.74 (s,  $\text{CH}_3$ ), 1.00 and 1.11 (5, gem  $\text{CH}_3$ 's);  $^{13}\text{Cmr}$   $\delta$   $\text{Me}_4\text{Si}$  ( $\text{CDCl}_3$ ) 140.3 (s), 128.7 (d), 128.4 (s), 128.1 (d), 126.1 (d), 122.0 (s), 120.0 (s), 119.6 (d), 48.4 (s), 44.7 (d), 44.1 (s), 41.0 (s), 40.6 (t), 35.1 (s), 32.7 (t), 24.2 (q), 19.8 (q), 17.1 (q); ms (70 eV) (relative intensity) 262 (15), 221 (6), 220 (19), 206 (10), 192 (21), 191 (16), 178 (100); ms (high resolution: m/e = 262.1470, calcd. 262.1466. Anal. calcd. for ( $\text{C}_{18}\text{H}_{18}\text{N}_2$ ): C 82.40, H 6.92; found: C 82.18, H 6.97.

Adduct 17: recrystallized from benzene/hexanes (mp 156-157°); ir (KBr)  $\nu$  2960, 2925, 2965, 2225, 1485, 1455, 1395, 1375, 1285, 1170, 1147, 1100, 772  $\text{cm}^{-1}$ ;  $^1\text{Hmr}$   $\delta$   $\text{Me}_4\text{Si}$  ( $\text{CDCl}_3$ ) 7.90-7.30 (m, 4H), 2.80-1.50 (m, similar to  $\text{AB}_2\text{C}_2$  system, two  $\text{CH}_2$  coupled to a centre CH), 1.43 (s,  $\text{CH}_3$ ), 1.20 and 0.38 (s, gem  $\text{CH}_3$ 's);  $^{13}\text{Cmr}$   $\delta$   $\text{Me}_4\text{Si}$  ( $\text{CDCl}_3$ ) 137.3 (s), 130.1 (s), 128.4 (d), 128.0 (d), 124.8 (d), 123.0 (d), 119.8 (s), 119.0 (s), 51.7 (s), 47.8 (s), 40.6 (s), 36.8 (t), 36.0 (d), 34.7 (t), 32.7 (s), 23.2 (q), 20.5 (q), 19.0 (q); ms (70 eV) (relative intensity) 262 (44), 247 (6), 221 (93), 206 (44), 191 (44), 178 (100). Anal. calcd. for ( $\text{C}_{18}\text{H}_{18}\text{N}_2$ ): C 82.40, H 6.92, N 10.68; found: C 82.21, H 6.77, N 10.68; found C 82.21, H 6.77, N 10.59.

Adduct 18: recrystallized from benzene/hexanes (mp 173-174°); ir (KBr)  $\nu$  3070, 2970, 2865, 2235, 2240 (shoulder), 1490, 1450, 1390, 1375, 1340, 1280, 1150, 1120, 1045, 760  $\text{cm}^{-1}$ ;  $^1\text{Hmr}$   $\delta$   $\text{Me}_4\text{Si}$  ( $\text{CDCl}_3$ ) 7.90-7.20 (m, 4H), AB quartet, centered at 2.30 ( $\text{CH}_2$ ,  $J_{\text{AB}} = 13$  Hz), 3.30-1.80 (m, ABC system,  $\text{CH}_2$  coupled with CH), 1.55 (s,  $\text{CH}_3$ ), 1.17 and 0.32 (s, gem  $\text{CH}_3$ 's);  $^{13}\text{Cmr}$   $\delta$   $\text{Me}_4\text{Si}$  ( $\text{CDCl}_3$ ) 136.7 (s), 130.4 (s), 128.7 (d), 128.2 (d, 2C), 124.4 (d), 120.7 (s), 119.8 (s), 49.6 (s), 47.8 (d+t, 2C), 46.6 (s), 45.3 (s), 44.6 (s), 37.6 (t), 25.9 (q), 21.1 (q), 19.8 (q); ms (70 eV) (relative intensity) 262 (30), 221 (29), 206 (21), 192 (24), 191 (34), 178 (100); ms (high resolution): m/e = 262.1468, found: 262.1470. Anal. calcd. for ( $\text{C}_{18}\text{H}_{18}\text{N}_2$ ): C 82.40, H 6.92; found: C 82.62, H 6.76.

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