(C-3), 51.5, 39.2, 27.4, 25.1, 24.3; C-4 was not observable; mass spectroscopic molecular weight, 141.0891 (calcd for $C_8H_{11}DO_2$, 141.0900). Ester 41 showed ^{13}C NMR ($CDCl_3$) δ 176.0, 126.4 (C-4), 124.9 (C-3), 51.5, 39.2, 27.4, 25.1, 24.3; IR (neat) $\nu_{C=O}$ 5.73 μm, $\nu_{C=C}$ 15.1 μm.

Acknowledgment. Financial support from the Research Corp. is gratefully acknowledged.

Registry No.—**1**-d_2, 63703-42-4; **4**-*d*, 63703-43-5; **6a**, 63703-44-6; **6b**, 63703-45-7; **7**, 63703-46-8; **9**, 7429-44-9; **11**, 63703-47-9; **12**, 63703-48-0; **12**-d_2, 63703-49-1; **17**, 63703-50-4; **18**, 63703-51-5; **22**, 63329-06-9; **28**-*d*, 63703-52-6; **36**, 63703-53-7; **37**, 63703-54-8; **38**, 61860-73-9; **41**, 6493-77-2; **41**-*3d*, 63703-55-9; **41**-*4d*, 63703-56-0; **42**, 63703-57-1; **45**, 63703-58-2; **56**, 6297-22-9; **57**, 63703-59-3; 1,2-bis(trimethylsiloxy)cyclobutene, 17082-61-0; 1,2-bis(trimethylsiloxy)cyclopentene, 6838-66-0; 2-hydroxycyclohexanone dimer, 30282-14-5; 2-hydroxycyclohexanone, 533-60-8; 2,3-bis(trimethylsiloxy)bicyclo[2.2.1]hept-2-ene, 63715-72-0; 3,3-dimethoxybicyclo[2.2.1]heptan-2-one, 35611-45-1; *p*-toluenesulfonyl chloride, 98-59-9; triflic anhydride, 358-23-6; 2,2,3-trimethoxybicyclo[2.2.1]heptane, 63703-60-6.

References and Notes

(1) (a) U. Schrapler and K. Ruhlmann, *Chem. Ber.*, **96**, 2780 (1963); (b) U. Schrapler and K. Ruhlmann, *ibid.*, **97**, 1383 (1964); (c) J. J. Bloomfield, *Tetrahedron Lett.*, 587 (1968); (d) J. J. Bloomfield, D. C. Owsley, and J. M. Nelke, *Org. React.*, **23**, 259 (1976).

(2) G. M. Rubottom, M. A. Vanzquez, and D. Pelegrina, *Tetrahedron Lett.*, 4319 (1974).

(3) X. Creary and A. J. Rollin, *J. Org. Chem.* **42**, preceding paper in this issue.

(4) (A(J. Salaun and J. M. Conia, *Chem. Commun.*, 1358 (1970); (b) J. M. Conia and J. R. Salaun, *Acc. Chem. Res.*, **5**, 33 (1972); (c) J. P. Barnier, J. M. Denis, J. Salaun, and J. M. Conia, *Tetrahedron*, 1405 (1974); (d) J. M. Conia and M. J. Robson, *Angew. Chem., Int. Ed. Engl.*, **14**, 473 (1975).

(5) (a) J. Omura, A. K. Sherma, and D. Swern, *J. Org. Chem.*, **41**, 957 (1976); (b) L. Huang, K. Omura, and D. Swern, *ibid.*, **41**, 3329 (1976).

(6) (a) J. C. Irvine and D. McNicoll, *J. Chem. Soc.*, **93**, 1601 (1908); (b) F. Chen, R. E. Robertson, and C. Ainsworth, *J. Chem. Eng. Data*, **16**, 121 (1971).

(7) (a) C. J. Collins, W. T. Rainey, W. B. Smith, and J. A. Kaye, *J. Am. Chem. Soc.*, **81**, 460 (1959); (b) W. B. Smith, R. E. Bowman, and T. J. Kmet, *ibid.*, **81**, 997 (1959).

(8) C. J. Collins, V. F. Raaen, B. M. Benjamin, and I. T. Glover, *J. Am. Chem. Soc.*, **89**, 3940 (1967).

(9) (a) G. D. Sargent in "Carbonium Ions", Vol III, G. A. Olah and P. v. R. Schleyer, Ed., Wiley, New York, N.Y., 1972, p 1110; (b) X. Creary, F. Hudock, M. Keller, J. F. Kerwin, and J. P. Dinnocenzo, *J. Org. Chem.*, **42**, 409 (1977).

(10) An analogous dimeric product has been observed in the acid-catalyzed treatment of α-hydroxycyclohexanone with alcohols. See: H. W. Dürbeck, C. G. B. Frischkorn, and K. Hilpert, *Tetrahedron*, 2927 (1971).

(11) For a review and leading references, see: (a) H. G. Rickey, Jr., in "Carbonium Ions", Vol III, G. A. Olah and P. v. R. Schleyer, Ed., Wiley, New York, N.Y., 1972, p 1201; (b) K. B. Wiberg, B. A. Hess, Jr., and A. J. Ashe, III, *ibid.*, p 1295.

(12) P. G. Gassman, J. L. Marshall, and J. G. Macmillan, *J. Am. Chem. Soc.*, **95**, 6319 (1973).

(13) Ion **46** may be involved as a discrete intermediate which rearranges to **47**. If the rearrangement of **28** to **47** is a concerted process, the transition state should resemble **46**.

(14) (a) B. Capon, *Q. Rev., Chem. Soc.*, **18**, 45 (1964); (b) S. Winstein and R. B. Henderson, *J. Am. Chem. Soc.*, **65**, 2196 (1943); (c) S. Winstein and L. L. Ingraham, *ibid.*, **74**, 1160 (1952).

(15) P. Yates and R. J. Crawford, *J. Am. Chem. Soc.*, **88**, 1561 (1966).

(16) Y. Lin and Alex Nickon, *J. Am. Chem. Soc.*, **92**, 3496 (1970).

(17) G. R. Wenzinger and P. Benz, *Tetrahedron Lett.*, 727 (1976).

(18) J. D. Roberts and V. C. Chambers, *J. Am. Chem. Soc.*, **73**, 5034 (1951).

(19) S. Winstein, B. K. Morse, E. Grunwald, H. W. Jones, J. Corse, D. Trifan, and H. Marshall, *J. Am. Chem. Soc.*, **74**, 1127 (1952).

(20) P. v. R. Schleyer, M. M. Donaldson, and W. E. Watts, *J. Am. Chem. Soc.*, **87**, 375 (1965).

(21) R. H. Perry, *J. Org. Chem.*, **24**, 829 (1959).

(22) X. Creary, Ph.D. Thesis, The Ohio State University, 1973.

(23) A. Barco, G. DeGiuli, and G. P. Pollini, *Synthesis*, **11**, 626 (1972).

(24) X. Creary, *J. Org. Chem.*, **40**, 3326 (1975).

(25) X. Creary, *J. Am. Chem. Soc.*, **98**, 6608 (1976).

(26) H. Fiesselmann, *Chem. Ber.*, **75**, 881 (1942).

Photochemical Cycloadditions of Benzonitrile to Alkenes. Factors Controlling the Site of Addition

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The photochemical cycloaddition of benzonitrile to a diverse array of alkenes has been studied in order to determine the factors controlling the site of addition to the nitrile. The reaction course depends critically on the number and type of electron-donating groups on the alkene. Alkenes having four alkyl substituents, or two alkoxyls, or two alkyl and one alkoxyl, undergo addition to the C≡N triple bond, furnishing mainly 2-azabutadienes, together with varying amounts of their azetine precursors. With less electron-rich alkenes, i.e., those containing two or three alkyl groups, addition occurs at the 1,2 positions of the ring, furnishing 1-cyanobicyclo[4.2.0]octadienes. Both types of alkenes strongly quench benzonitrile fluorescence, indicating intermediacy of excited nitrile singlets. It is speculated that the difference in reaction sites for the two classes is the result of different sites of complexation at benzonitrile in singlet exciplexes.

Much of the vast amount of research performed during the past 15 years on the photochemical behavior of organic molecules has centered on carbonyl compounds, particularly ketones.[1] A wide array of interesting transformations have been observed, the reaction course depending on the exact structure of the ketone and upon the presence or absence of substrates or reactive solvents. In contrast, there have been very few reports on the photochemistry of nitriles and other carboxylic acid derivatives. In an early study, Buchi and colleagues showed that benzonitrile undergoes a [2 + 2] cycloaddition at the 1,2 positions of the benzene ring to certain alkenes, including 2-methyl-2-butene and ethoxyethylene, to yield 1-cyanobicyclo[4.2.0]octadienes.[2] Certain α,β-unsaturated nitriles, such as acrylonitrile,[3a] 2-cyanobutadiene,[3b] and 1-cyanocyclohexene,[3c] are reported to add alkenes across the C=C double bond and/or dimerize. Naphthonitriles have been observed to add certain alkenes at the 1,2 positions,[4a] as does naphthalene itself to acrylonitrile,[4b–d] via intermediate exciplexes. Two groups have observed [2 + 2] cycloaddition of 9-phenanthronitrile to alkenes at the 9,10 positions.[5] Since the publication of some of the present results, Yang and coworkers have very recently reported both 2-azabutadienes and azetines to be formed from benzonitrile and naphthonitriles with 2,3-dimethyl-2-butene.[6]

In a preliminary communication, it was reported that photochemically excited benzonitrile adds to certain electron-rich alkenes, such as 2,3-dimethyl-2-butene and 1,1-dimethoxy-2,2-dimethylethylene, across the cyano group to

Table I

Registry no.	Alkene	% yield of 2-azabutadienes and azetine[a]	% yield of bicyclo[4.2.0]-octadienes[a]	Ionization potentials, eV
5634-54-8	1,1-Dimethoxy-2,2-dimethylethylene (**2**)	45		
922-69-0	1,1-Dimethoxyethylene (**3**)	28		
931-57-7	1-Methoxycyclohexene (**4**)	46		
764-13-6	2,5-Dimethyl-2,4-hexadiene (**5**)	54		8.1
1674-10-8	1,2-Dimethylcyclohexene (**6**)	67[b]		8.5
563-79-1	2,3-Dimethyl-2-butene (**7**)	74		8.5
513-35-9	2-Methyl-2-butene (**8**)	6	65	8.80
142-29-0	Cyclopentene (**9**)		35	9.03
115-11-7	Isobutene (**10**)		46	9.3
121-46-0	Norbornadiene (**11**)		41	8.4
108-05-4	Vinyl acetate (**12**)		60	
116-11-0	2-Methoxypropene (**13**)		43	
156-60-5	*trans*-1,2-Dichloroethylene (**14**)		27	

[a] Yields given are of isolated products. [b] Includes product from hydrogen abstraction by CN.

Table II. Reaction of Benzonitrile with Alkenes of Type B

Alkene	Adduct(s)	Φ_{254}	Φ_{254} + diene	% isolated yield	Mp of NPM adduct, °C
8	**29**, **30**	0.18	0.13	63	247–248
9	**36**	0.11	0.07	27	214–215
10	**33**	0.02		40	184–185
11	**38**			36	
12	**35**	0.15	0.11	61	211–212
13	**34**	0.16		52	163–164
14	**37**	0.08		35	

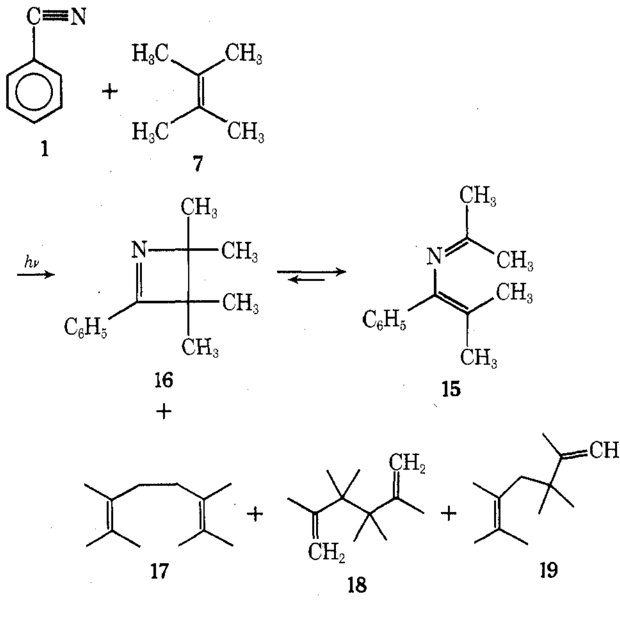
afford 2-azabutadienes, the products of electrocyclic ring opening of azetines produced by an initial [2 + 2] cycloaddition across the CN function.[7] Addition to alkenes of lower π-electron density, such as isobutene and cyclohexene, occurred at C(1)–C(2) of the aromatic ring to give substituted bicyclo[4.2.0]octadienes, in agreement with the results of Buchi et al.[2] Since the initial report, the author has extended the study to numerous other alkenes and has characterized some products not identified earlier, including the azetines in certain cases. Furthermore, additional information concerning the mechanism has now been obtained which requires a modification of the hypothesis presented in ref 7. There follows herewith the results of the detailed study.

Results

The addition of photoexcited benzonitrile to carbon–carbon double bonds may proceed either across the cyano group or at the 1,2 positions of the benzene ring. The more electron-rich alkenes, such as 2,3-dimethyl-2-butene, react at the nitrile function to give varying amounts of 2-azabutadienes and their valence tautomers, the 1-azetines. Less electron-rich alkenes, including those with one to three alkyl substituents on the double bond, add to the benzene ring to give bicyclo[4.2.0]-octadienes. In all cases except those of alkenes possessing no allylic hydrogens, there are also formed products resulting from coupling of radicals produced by allylic hydrogen abstraction from the alkene, e.g., 2,3,6,7-tetramethylocta-2,6-diene from 2,3-dimethyl-2-butene. The chemical yields of the products obtained are given in Tables I and II. The results in some cases were previously noted,[7] for example, the formation of the major product with 2,3-dimethyl-2-butene. However, the earlier report did not metnion the minor product, azetine **16**, which had at that time escaped our notice. Since then we have conducted a thorough examination of the reaction mixtures for products of this type, and have examined the reactions of **1** with a number of other alkenes in order to delineate precisely the combination of structural features necessary to result in reaction at the cyano group. The first six alkenes (**2**–**7**) belong in the former category, group A, whereas the remainder (**8**–**14**) belong in the latter, group B. Brief inspection reveals that, in order for reaction at the cyano group to predominate, either four alkyl groups, or two alkyl and one alkoxy group, must be located on the doubly bonded carbons. The dramatic difference caused by a single methyl group is illustrated by the divergent results obtained with 2,3-dimethyl-2-butene (**7**), with which reaction of **1** occurs exclusively at the cyano group, and 2-methyl-2-butene (**8**), in which over 90% of the products result from addition to the benzene ring. The reaction of **1** with alkenes **4** and **13** illustrates the same striking difference caused by one alkyl group.

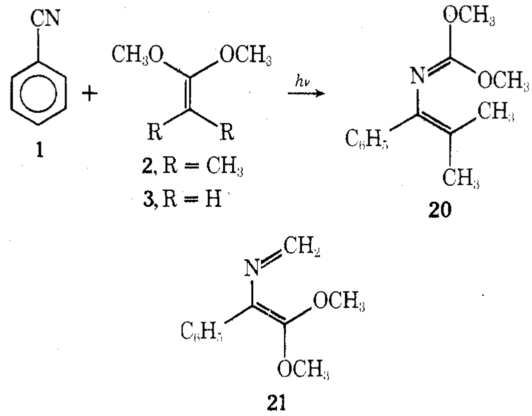
2,3-Dimethyl-2-butene. Irradiation through Vycor of hexane solutions of **1** with a two- to tenfold excess of 2,3-dimethyl-2-butene (**7**) until 50% of **1** was consumed gave two products (Scheme I): 2,5-dimethyl-3-phenyl-4-azahexa-2,4-diene (**15**; 66% based on unrecovered **1**), and its valence isomer, 2-phenyl-3,3,4,4-tetramethyl-1-azetine (**16**; 8%). The structure of azadiene **15** was deduced from its spectral properties, which include NMR singlets at τ 7.84, 8.08, 8.15, and 8.32, indicative of methyls on vinyl carbons, and was established conclusively by its rapid hydrolysis by cold aqueous acid

Scheme I



to isobutyrophenone and acetone. The quantum yield for **15** at 254 nm was 0.23. Photoproduct **16** escaped detection in the early experiments and hence was not mentioned in the preliminary communication. Its identity followed from its spectral features. Of particular help were two three-hydrogen singlets in the NMR spectrum at τ 8.62 and 8.66, a region characteristic of methyl groups on saturated carbon, and an infrared C=N band at 1580 cm^{-1}, which coincides exactly with that reported for 2-phenyl-1-azetine.[8] The manifest thermal stability of **16**, which allows it to survive gas chromatography at 170 °C, suggests that **15** is formed from it in a photochemical, rather than a thermal, ring opening. Indeed, direct reirradiation of purified **16** produces appreciable quantities of **15**; evidently the ratio of the two products, as isolated, reflects the equilibrium composition.[6] Also isolated from irradiation of mixtures of **1** and **7** was a mixture of hydrocarbons **17–19** in 62% yield. It proved to be possible to isolate **17** and **18** in pure form by GC; their identity was apparent from their NMR and mass spectra. These hydrocarbons evidently result from coupling of the allylic radical produced by abstraction of a hydrogen atom from alkene **7** by photoexcited benzonitrile. Coupling of two radicals in the head-to-head, tail-to-tail, or head-to-tail manner produces **17–19**, respectively.

Irradiation of **1** with excess 1,1-dimethoxy-2,2-dimethylethylene (**2**, the dimethyl acetal of dimethylketene)[9] until 40% of **1** was destroyed, followed by evaporation of the solvent and excess **2**, gave 45% of a single photoproduct, assigned structure **20** on the basis of its spectra properties and hydrolysis products. Compound **20** is an imidocarbonate ester, rather than a simple imine as was **15**, and proved to be more resistant to hydrolysis, in keeping with its chemical nature. Warming of 20–50 °C in acetic acid containing hydrochloric acid gave a fair yield of isobutyrophenone; long reaction times gave only products of aldolization of isobutyrophenone. In the reaction mixture with **20** were also detected small amounts of a mixture of incompletely characterized compounds produced by the coupling of radicals formed by hydrogen abstraction from **2**. Use of unsubstituted ketene dimethyl acetal gave 28% of the unstable imine **21**, not obtained analytically pure, but identifiable from its NMR and mass spectra.



1

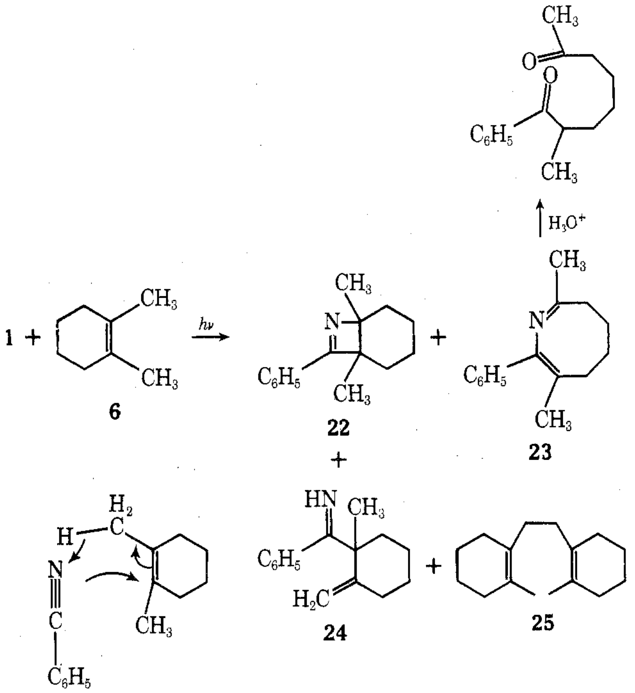
2, R = CH$_3$
3, R = H

20

21

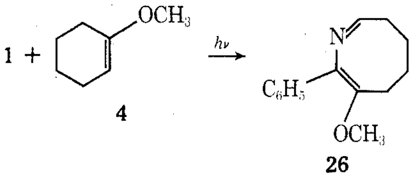
1,2-Dimethylcyclohexene. Irradiation of hexane solutions of **1** with excess 1,2-dimethylcyclohexene (**6**) afforded products **22** (17%), **23** (26%), **24** (24%), and **25** (16%) (Scheme II). Azacyclooctadiene **23** was identified by spectral data and by its hydrolysis to 1-phenyloctane-1,7-dione, whose spectral data and analytical data were in exact accord with expectation. Azetine **22**, identified from its NMR and mass spectral properties and an infrared band at 1568 cm^{-1}, constituted a significantly larger portion of the product mixture than did azetine **16**, derived from alkene **7**, also a tetraalkylalkene. Evidently azetine **22** is somewhat more stable with respect to isomerization to its azadiene isomer **23**, because of the reduced repulsion between the methyls and the α-methylene groups of **22** as compared with the two *gem*-dimethyl moieties of **16**.

Scheme II



Hydrocarbon **25** is analogous to **17**, formed from **1** and 2,3-dimethyl-2-butene; it is not clear why coupling products analogous to **18** and **19** were not observed. Interestingly, in the present case there was found, however, a significant quantity of **24**, possibly the product of cross-coupling of the two radicals produced via hydrogen abstraction from **6** by photoexcited **1**. The structure of imine **24** was deduced from spectral data, including, inter alia, an infrared C=N band at 1681 cm^{-1}, and NMR signals at τ 4.6 and 5.2 (1 H each, =CH$_2$), 6.1 (1 H, br, NH), 7.4–8.4 (8 H, m, CH$_2$), and 8.66 (3 H, d, J = 7.1 Hz, -C-CH$_3$); m/e 213. The formation of **24** was surprising, both because of the absence of an analogous product in the reaction of **1** and alkene **7**, and because it is the result of coupling of a benzimidyl radical to the tertiary more hindered site of the allylic radical derived from **6**. Imine **24** could also result from an ene reaction, as shown in Scheme II.

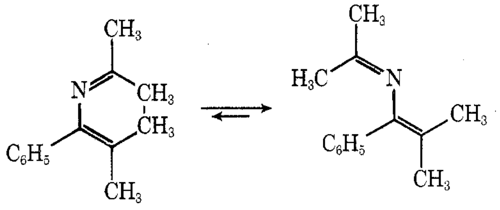
1-Methoxycyclohexene. Irradiation of mixtures of **1** and excess 1-methoxycyclohexene (**4**) produced 46% of azabutadiene **26**, identified by its spectral properties (see Experimental Section). There was also isolated 17% of a mixture which was not completely characterized but which, on the basis of spectral evidence, appeared to be composed of compounds derived from the combination of methoxycyclohexenyl radicals formed by hydrogen abstraction from alkene **4**. Thus, two alkyl groups and one alkoxyl attached to a carbon–carbon double bond provide sufficient electron density to cause photoexcited benzonitrile to react at the cyano group.



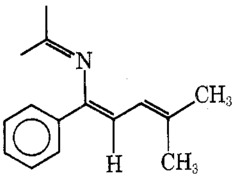
4

26

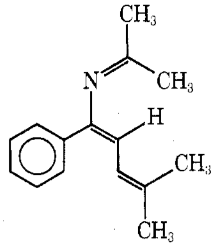
2,5-Dimethyl-2,4-hexadiene (5). Photolysis of **1** with excess **5** gave ~54% of a mixture of the geometric isomers **27a** and **27b** (ratio 57:43) in addition to small amounts of C$_{16}$ hydrocarbons formed via coupling of radicals derived from **5**. The *E* and *Z* isomers **27a** and **27b** could not be separated by the gas and thin-layer chromatographic techniques available, but were identified by the NMR signals in the spectrum of the mixture. Isomer **27a**, which exhibits an AB pattern at τ 3.78 and 4.30 (J = 11.4 Hz), is assigned the E geometry, since it shows four well-separated methyl singlets, whereas isomer **27b** shows a narrow six-hydrogen doublet at τ 8.18 and a six-hydrogen singlet at τ 8.27. Geometric isomer **27a** bears an alkyl group (isobutenyl) on C-4 of the 2-azahexatriene chain which is cis to the imine function. The same is true in azadiene **15**, whose NMR spectrum shows four well-separated methyl signals, the alkyl group which corresponds to the iso butenyl of **15** being one of those methyls. The fact that the methyls of the imine moiety of **15** exhibit different chemical shifts may be attributed to the existence of the compound predominantly in the transoid conformation, in which the methyl syn to the benzene ring will experience an environment different from the other, a consequence of the nearby phenyl group. It therefore seems likely that the transoid conformation of **27a** will be considerably more populated than in the case of **27b**, since in the cisoid form of **27b** (shown) only a hydrogen atom, rather than an alkyl, is syn to the imine proximate methyl group. On this basis, it seems more likely that **27a** will have its transoid conformer more highly populated than will **27b**, and consequently its imine methyls will exhibit significantly different chemical shifts.



15-cisoid 15-transoid

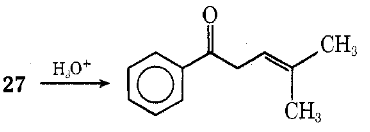


27a



27b

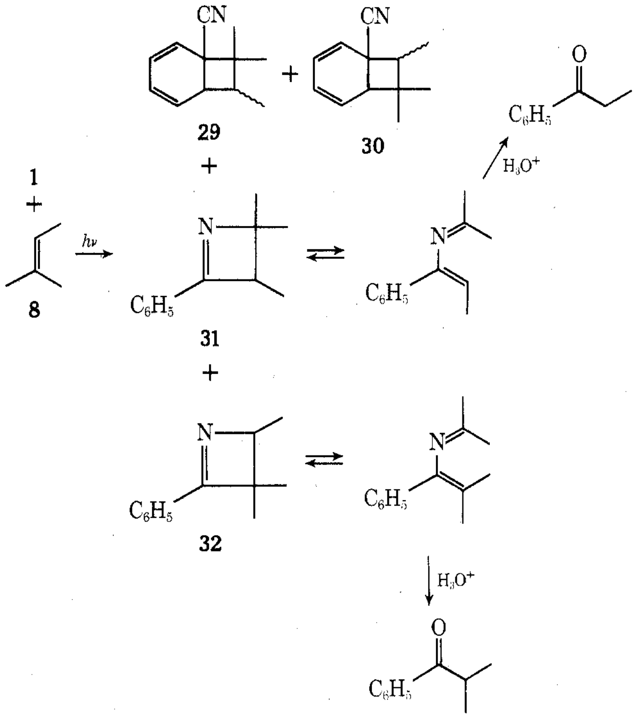
Acid hydrolysis of the **27a–b** mixture gave 2-methyl-5-phenyl-2-hexen-1-one (**28**), whose spectral properties were in agreement with expectation, thus further securing the gross structural assignment of **27**. It seems worth noting that the double bond of **28** shows no inclination to shift into conjugation with the ketonic carbonyl group; evidently the stabilizing effect of a trialkyl substitution vs. dialkyl outweighs the stability to be gained via conjugation with carbonyl.



28

2-Methyl-2-butene. Irradiation of **1** with either an equimolar amount or a tenfold excess of 2-methyl-2-butene (**8**) gave an identical mixture of adducts (Scheme III); the yield was 62% under the latter conditions (Φ = 0.17). The major (70% of the mixture) component has been shown by earlier workers[2] to be the 1-cyanobicyclo[4.2.0]octadiene **29**. Treatment of the mixture with N-phenylmaleimide (NPM) gave one pure product whose spectral properties were in accord with those expected of a Diels–Alder adduct of **29** and NPM. A small amount of a second adduct, possibly derived from the regioisomer **30**, was also observed.

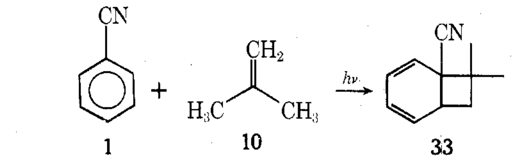
Scheme III



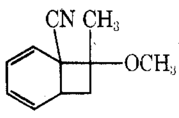
Because of the fishy amine-like odor of the distilled product mixture from **1** and alkene **8**, it was suspected that azetines and/or azadienes might be present therein. Extraction of a cold ether solution of the product mixture with ice-cold 10% hydrochloric acid, followed by immediate basification and reextraction, led to the isolation of an acid-soluble organic fraction, amounting to ~9% of the total product. By preparative GC one pure component, azetine **31**, was isolated in pure form (yield, 4%) and identified by spectral means. Allowing the acid extracts to stand at room temperature, followed by reextraction with ether, resulted in the isolation of propiophenone as its 2,4-dinitrophenylhydrazone. In the course of work described in part in ref 2, Ayer isolated from the acid-soluble fraction of the product mixture propiophenone, isobutyrophenone, and α,β-dimethyl-β-aminobutyrophenone, all in the form of derivatives.[10] The formation of all the products mentioned can reasonably be accounted for by the transformations shown in Scheme III, involving hydrolysis of azetines **31** or **32**, or of the ring-opened 2-azadiene valence isomers derived therefrom.

Isobutene. The photochemical addition of **1** to isobutene proceeded at a considerably slower rate than to the more highly alkylated alkenes; after 30 h of irradiation, only 25% of **1** had been destroyed. Workup gave a 42% chemical yield of a mixture of one major and two minor isomers. A pure sample of the major isomer, compound **33**, was obtained by repeated gas chromatography. It was additionally characterized by its Diels–Alder adduct with NPM.

2-Methyoxypropene, Vinyl Acetate, Cyclopentene, 1,2-Dichloroethylene, and Bicyclo[2.2.1]heptadiene. Irradiation of mixtures of **1** with all of these monoalkenes led to mixtures which, on the basis of their NMR and mass spectral properties, are formed by attachment of the substrate to the aromatic ring of **1**. The major isomer in each case must be a bicyclo[4.2.0]octadiene, since adducts with NPM could be obtained in the yields listed in Table II. It is likely that regio- and stereoisomers of the same gross structure (**34–38**) make up a large portion of the remainder of each mixture. In the case of the mixture obtained with 2-methoxypropene,



1 **10** **33**



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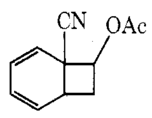

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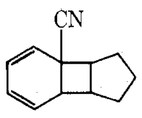

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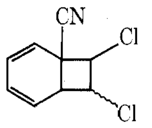

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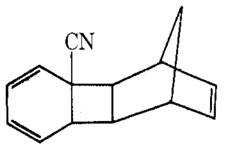

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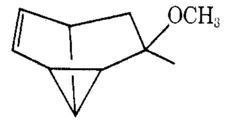
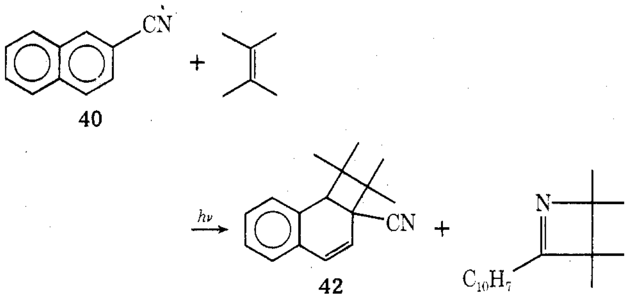
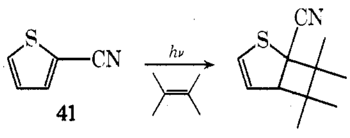


39

however, it appears that adducts from 1,3 addition across the benzene ring may comprise a major portion of the material remaining after treatment of the product mixture with NPM. The ratio of vinyl to saturated hydrogen in its NMR spectrum is too low to reconcile with a cyclohexadiene structure but is reasonable if some 1,3 addition to the benzene ring of **1** has occurred to give adducts of type **39.** The exact structure of the minor adducts from **1** and alkene **13** is still under investigation.



40 **42** **43**



41 **44**

The photolyses of β-naphthonitrile (**40**) and 2-thienonitrile [2-cyanothiophene (**41**)] with alkene **7** were briefly examined in order to determine the preference for cycloaddition site. In our hands, irradiation of **40** with excess **7,** followed by chromatography on silica gel, gave a 52% isolated yield of **42,** the product of ring addition. However, short-path distillation of the crude reaction mixture gave an oil whose NMR spectrum exhibited signals, besides those of **42,** at τ 8.68 and 8.79, which are ascribable to the methyls of azetine **43.** The distilled oil displayed an infrared band at 1585 cm^{-1}, similar to azetines **16** and **22.** The intensity of the NMR signals indicates a yield of ~20% of **43.**[11]

Discussion

The most remarkable feature of the present investigation is the dramatic dependence of the site of addition to **1** upon alkene structure. This is perhaps best illustrated by the divergence in reaction course caused by the presence or absence of one methyl group, as in the pair of alkenes 2,3-dimethyl-2-butene (**7**) and 2-methyl-2-butene (**8**). The preference shown by benzonitrile to add the latter alkene at C(1)–C(2) of the aromatic ring of **1** vs. addition at the nitrile function is ~12:1. Addition of **1** to alkene **7,** however, occurs exclusively at the nitrile group. A similar pair of alkenes are 2-methoxypropene (**13**) and 1-methoxycyclohexene (**4**). The latter bears one more alkyl group than **13.** Addition of **4** occurs exclusively to the cyano group of **1,** whereas reaction with **13** takes place only across the benzene ring.

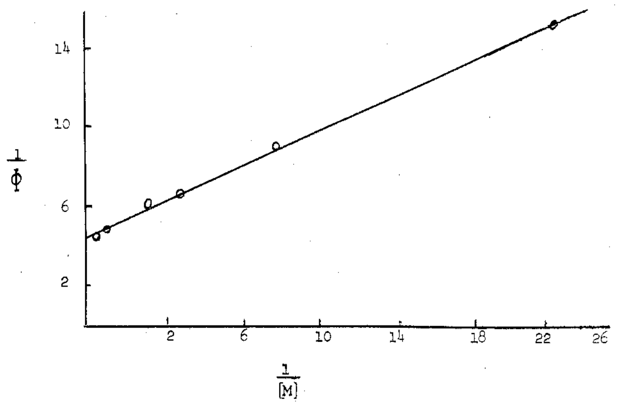


Figure 1.

Table III.

	$k_q\tau$	$k_q \times 10^{-9}$ [a]	$k_q \times 10^{-9}$ [b]
Benzonitrile + 7	10.2	1.06	1.3
Benzonitrile + 8	6.1	0.63	

[a] From fluorescence lifetime quenching. [b] From quantum yields.

In the preliminary communication[7] reporting some of the present results, the statement was made that addition of the less highly substituted alkenes to **1** apparently occurred via excited triplet benzonitrile, since addition to these alkenes could be partially quenched by added 1,3-dienes. However, subsequent experiments showed that this effect is smaller than originally thought. While there is a definite quenching observed with added 1,3-pentadiene, the maximum observed at larger quencher concentrations is a reduction in reaction efficiency to about 0.6–0.7 of that observed in the absence of added diene. This and other information is collected in Table II.

Studies subsequent to the earlier report have shown that 1,3-dienes of a low degree of alkyl substitution, such as 1,3-butadiene and *cis*-1,3-pentadiene (the latter was the quenching agent used earlier), do in fact add slowly to **1** to give adducts of bicyclo[4.2.0]octadiene type. When a correction is made for the reaction of **1** with the quencher, it is apparent that little if any triplet quenching is observed. In fact, we have now found that alkenes of both groups A and B, as well as simple dienes, quench benzonitrile fluorescence effectively. Benzonitrile exhibited a fluorescence lifetime in fluid solution at 25 °C of 9.6 ns. The k_q's for alkenes **7** and **8,** representatives of groups A and B, respectively, are given in Table III. The dependence of quantum yield of **15** and **16** (the products from **7**) on the concentration of alkene **7** was measured; the results are shown in Figure 1. The value of k_q obtained from these experiments via the equation

$$\frac{1}{\Phi_a} = \frac{1}{\Phi_I}\left[1 + \frac{1}{k_q\tau[A]}\right] \qquad (1)$$

where Φ_a is the quantum yield for addition and Φ_I is the quantum yield at infinite alkene concentration, is in reasonable agreement with the value obtained by fluorescence, indicating that the same excited state of **1** is involved in both emission and photochemical reactions. This value is probably the diffusion-controlled rate.

Figure 2.

This evidence, together with the observed photochemistry of **1** and alkenes, supports the formation of exciplexes from excited singlet **1** and ground-state alkenes and dienes. Aryl nitriles such as naphthonitriles form fluorescent exciplexes with alkenes.[12] Exciplexes have been implicated as intermediates in numerous photochemical cycloaddition reactions of aromatic compounds.[4,5,13–15] Firm evidence for their intermediacy has been presented in some cases.[5,15] It appears, therefore, that singlet exciplexes are involved in the formation of both types of products observed in the present study.

An alternate explanation of the present observations involves charge-transfer complexes of ground-state **1** with various alkenes. Such a charge-transfer complex is believed to be an intermediate in the photochemical cycloaddition of benzene and maleic anhydride.[16] The most direct evidence for formation of charge-transfer complexes is nonadditivity in the UV–visible spectrum of mixtures of the two components. There does appear to be a slightly enhanced absorption area on the tail of the UV spectrum of benzonitrile when alkene **7** is added. However, this effect is small, and does not seem sufficient to justify invoking the intermediacy of charge-transfer complexes here.

There remains to be considered the reason for the great dependence on the site of addition to benzonitrile on alkene structure. It can be seen from the quantum yields for addition of **1** to alkenes **7** ($\Phi = 0.24$ at infinite alkene concentration), **8, 9,** and **10** (Table II) that the rates of conversion of the exciplexes to adducts vs. the rate of collapse to starting components is also a sensitive function of alkene structure. However, the differences in efficiencies of addition to **8–10** are of minor interest. Our concern here is in the difference in behavior of alkenes of categories A and B. One possibility is that the exciplexes formed with the two types of alkenes differ in the site of complexation with excited singlet **1**, i.e., in exciplex geometry. The more electron-rich alkenes, of category A, lie directly over the cyano group of excited **1**, as shown in Figure 2, whereas the less electron-rich alkenes, of category B, in the exciplex are located over the face of the benzene ring of **1**, the site of higher electron density. One piece of evidence which is consistent with this hypothesis is the observation of distinctly different exciplex emissions from mixtures of **1** with the two alkenes, **7** and **8**. Addition of either alkene results in enhanced emission in the 320–360-nm range, distinct from the fluorescence of **1**. While the effect is moderate in the case of **8** (a type of B alkene), the enhancement is enormous for alkene **7** (a type A alkene). Since the only gross structural difference of the components is one methyl group, the most likely explanation for the difference in exciplex emission is a considerably different geometry in the two exciplexes.

Since the behavior of various alkenic substrates toward excited singlet **1** depends on the π-electron density of the substrate, as determined by the number and kind of electron-donating substituents on the double bond, we should be able to predict whether still other alkenes will behave as a member of group A or B. One measure of π-electron density of alkenes is the ionization potential. Inspection of the ionization potentials of several of the alkenes used here (Table I) reveals those of IP of 8.6 eV or below add to the cyano group of **1** (group A), whereas those of IP 8.7 eV or above belong to group B. The exception to this is norbornadiene. Attempts have been made to correlate k_q with ionization potential, but with limited success.[18]

Studies are in progress on the behavior of substituted benzonitriles and related compounds.

Experimental Section

Irradiations were conducted in an annular apparatus using light from a Hanovia 450-W medium-pressure mercury arc lamp, filtered through Vycor (transmits >220 nm) and cooled by ice water in an immersion well. All photochemical reaction solutions were flushed with argon for 1 h prior to irradiation and an argon atmosphere was maintained during irradiation. NMR spectra were obtained on Varian A-60 and HR-220 instruments. Mass spectra were obtained on a Hitachi Perkin-Elmer Model RMU-6E. Gas chromatography was performed on the following columns: column A, 2 ft × 0.25 in., 10% SE-30 on Chromosorb W; column B, 2 ft × 0.25 in., 15% Carbowax 20M on Chromosorb W; column C, 6 ft × 0.25 in., 10% SE-30 column D, 6 ft × 0.25 in., 15% Carbowax 20M; column E, 6 ft × 0.375 in., 25% SE-30; and column F, 6 ft × 0.25 in., 15% Carbowax 20M on Chromosorb W + 2% KOH. Emission spectral data were obtained on a TRW Instruments Nanosecond Fluorescence Apparatus of Dr. Raymond Chen of the National Institutes of Health. Some of the quenching experiments were performed by Dr. Paul Engel at Rice University on an Aminco-Bowman Apparatus.

Irradiation of Benzonitrile with 2,3-Dimethyl-2-butene. A solution of **1** (4.0 g, 0.04 mol) and 2,3-dimethyl-2-butene (**7**, 20 g, 0.24 mol) in spectrograde hexane (80 mL) was irradiated through a Vycor filter for 4 h. Following evaporation of the solvent and excess alkene **7** from the yellow solution, the residue was fractionally distilled to give: (a) 1.4 g of recovered **1**, bp 35–38 °C (4 mm); (b) 1.8 g, bp 38–45 °C (0.2 mm); (c) a product mixture, bp 70–74 °C (0.1 mm) (3.3 g, 78%). Separation of fraction c on column F at 170 °C afforded pure **15** [retention time 5.2 min, 90% of total, 66% yield; IR (film) 1656 cm^{-1}; NMR τ 2.70 (5 H, s, br), 7.84 (3 H, s), 8.08 (3 H, s), 8.15 (3 H, s), 8.32 (3 H, s); *m/e* 187 (13, P), 172 (18), 148 (29), 131 (25), 105 (100), 77 (74). Anal. $C_{13}H_{17}N$: C, H, N] and **16** [retention time, 7.0 min, 10% of total, 8% yield; IR 1580 cm^{-1}; NMR τ 2.2 (2 H, m), 2.5–2.7 (3 H, m), 8.62 (6 H, m), 8.68 (6 H, m); *m/e* 187 (13, P), 172 (15), 131 (12), 104 (100), 103 (76), 91 (60), 84 (39). Anal. $C_{13}H_{17}N$: C, H]. There was present a third peak, of retention time 8.8 min (3% of total), which was not identified. Fraction b showed three peaks on column D at 120 °C, of retention times 4.5, 4.9, and 6.1 min, with relative areas of 28:15:57. The first and third peaks were sufficiently well separated to allow collection of pure samples. The third peak showed two slightly broadened NMR singlets at τ 7.8 and 8.3 in the ratio 2:9, and a mass spectral parent ion at *m/e* 166 with the major peak at 83, indicating structure **17**. The first peak showed a very similar mass spectrum, and NMR signals at τ 5.2 (4 H, s br), 8.2 (6 H, s br), and 8.7 (12 H, s), and hence is **18**.

Hydrolysis of 15. A mixture of imine **15** (0.97 g, 5.0 mmol), 15 mL of tetrahydrofuran, and 5 mL of 3% aqueous hydrochloric acid was allowed to stand at 10–15 °C for 2 h. Solid sodium bicarbonate was added until the solution was approximately neutral. The solution was distilled at 80 mm (bath temperature 35 °C) until the volume was reduced by two-thirds. Treatment of the distillate with 2,4-dinitrophenylhydrazine solution in the usual manner and recrystallization of the orange precipitate from ethanol gave the acetone 2,4-DNPH derivative (0.23 g), mp 126 °C, identical with an authentic sample. Extraction of the pot residue twice with ether, drying and evaporation of the combined extracts, and short-path distillation gave isobutyrophenone (0.42 g, 60%), identical in all respects with an authentic sample (IR, melting point, and mixture melting point of 2,4-DNPH).

Irradiation of 1 with 1,1-Dimethoxy-2,2-dimethylethylene (2). A solution of **1** (3.0 g, 0.03 mol) and ketene acetal **2** (20 g, 0.17 mol) in spectrograde hexane (110 mL) was irradiated for 7 h. The solvent was evaporated and the excess **2** was recovered by distillation under reduced pressure, bp 40–44 °C (12 mm). Fractional distillation of the residue gave two fractions. The first, bp 56–59 °C (0.1 mm), further purified by GC on column C, was dimethyl tetramethylsuccinate: IR (film) 1734 cm^{-1}; NMR τ 6.2 (6 H, s), 8.6 (12 H, s); *m/e* 202 (P, CI), 143 (58), 102 (100). The second fraction, bp 86–88 °C (0.08 mm), was almost pure imido carbonate **20:** IR (film) 1686 cm^{-1}; NMR τ 2.8 (5 H, s), 6.30, 6.34 (3 H each, s), 8.36 (6 H, s); *m/e* 219 (P, 92), 204 (32), 129 (100), 115 (78). Anal. $C_{13}H_{17}NO_2$: C, H.

Irradiation of 1 with 1,1-Dimethoxyethylene. Irradiation of 2 g of **1** with 10 g of ketene dimethyl acetal in 80 mL of spectrograde hexane at 2537 Å for 3 h gave a yellow solution. After evaporation of the solvent and excess reactants, short-path distillation gave 0.42 g of a yellow, unstable oil, bp 45–50 °C (bath, (0.06 mm) (**21**): IR (film) 1680, 1740 cm^{-}; NMR τ 2.8 (5 H), 5.3 (2 H, br); *m/e* 191 (30), 176 (21), 103 (46). A satisfactory analysis was not obtained, owing to the compound's instability.

Photochemical Reaction of 1 with 1,2-Dimethylcyclohexene (6). Irradiation of a solution of 1 (3.0 g, 0.03 mol) and 6 (22 g, 0.20 mol) for 6 h and workup in the usual manner gave 1.6 g of recovered 1 and 1.9 g of a product mixture, bp 102–105 °C (0.08 mm). Separation was readily accomplished by GC on column F at 190 °C. The first peak, of retention time 2.6 min, was hydrocarbon **25** (19% of total): NMR τ 7.5–8.4 (20 H, m, br), 8.3 (6 H, s); *m/e* 218 (CI), 110 (100), 109 (38). Anal. $C_{16}H_{26}$: C, H.

Peak 2, retention time 6.8 min, was imine **24**: IR 1650 cm^{-1}; NMR τ 2.1 (2 H, m), 2.6 (3 H, m), 4.61 (1 H, br), 5.12 (1 H, m), 6.1 (1 H, m, v br), 7.0–8.4 (8 H, m), 8.66 (3 H, s); *m/e* 213 (P, 8), 120 (18), 134 (43), 105 (100). Anal. $C_{15}H_{19}N$: C, H, N.

Peak 3, rentention time 8.7 min, was azetine **22**: IR 1568 cm^{-1}; NMR τ 2.2 (2 H, m, br), 2.6 (3 H, m), 7.9–8.7 (8 H, m), 8.70 (6 H, s); *m/e* 213 (P, 45), 198 (62), 189 (26), 120 (34), 104 (27), 84 (100). Anal. $C_{15}H_{19}N$: C, H, N.

Peak 4, retention time 11.5 min, was enamine **23**: IR 1647 cm^{-1}; NMR τ 2.73 (5 H, s), 7.6–8.9 (8 H, m), 7.83 (3 H, s), 8.21 (3 H, s); *m/e* 213 (P, 9), 170 (18), 134 (44), 105 (100), 91 (16). Anal. $C_{15}H_{19}N$: C, H.

Hydrolysis of Azadiene 23. A mixture of **23** (0.22 g, 1.0 mmol), tetrahydrofuran (15 mL), water (3 mL), and 2 drops of concentrated hydrochloric acid was stirred at 10 °C for 4 h. Concentration by rotary evaporation, dilution with water, and extraction with ether (2 × 15 mL), followed by drying of the combined extracts, evaporation of solvents, and short-path distillation gave 2-methyl-1-phenyloctane-1,7-dione (0.146 g, 62%): bp 110 °C (bath, 0.08 mm); IR 1680 cm^{-1}; NMR τ 2.3 (2 H, m), 2.7 (3 H, m), 7.1–8.4 (12 H, m), 7.78 (3 H, s); *m/e* 232 (P, 1.2), 134 (37), 105 (100). Anal. $C_{15}H_{20}O_2$: C, H.

Photochemical Reaction of 1 with 1-Methoxycyclohexene. A solution of 1 (3.0 g) and 1-methoxycyclohexene (4) (30 g) in spectrograde pentane (80 mL) was irradiated in the usual manner for 10 h. Workup gave 1.1 g of recovered 1, a low-boiling fraction [bp 64–76 °C (0.08 mm)] which appeared to consist of compounds formed by combination of radicals derived from hydrogen abstraction from alkene 4 (mass spectral parent ion at *m/e* 214; no C=N or C≡N bands in IR; methoxyls in NMR at τ 6.20–6.24) and a product fraction from which one pure compound (**26**) was isolated by GC (~85% of total, 1.8 g, 42%): bp 104–108 °C (0.08 mm); IR 1682 cm^{-1}; NMR τ 2.5–2.9 (5 H, m), 4.7 (1 H, t, J = 8 Hz), 6.1 (3 H, s), 7.6–8.5 (8 H, m); *m/e* 215 (36, P), 200 (52), 184 (50), 112 (49), 111 (60), 84 (100). Anal. $C_{14}H_{17}ON$: C, H.

Photochemical Reaction of Benzonitrile with 2,5-Dimethyl-2,4-hexadiene. A solution of 1 (3.0 g) and diene **5** (20 g) was irradiated through Vycor for 10 h. Workup in the usual manner gave, besides 1.5 g of recovered 1, 1.7 g of a mixture of geometric isomers **27a** and **27b**; bp 118–120 °C (0.08 mm) after a second fractional distillation; IR 1655 cm^{-1}; NMR τ 2.5–2.7 (5 H, m), 3.78, 4.30 (2 H, AB, J = 11.4 Hz, $\Delta\nu$ = 32, isomer A), 3.93, 4.22 (2 H, AB of isomer B further split by allylic coupling to CH_3), for isomer A, 3-H singlets at 7.78, 7.91, 8.10, 8.23; for isomer B, 6-H doublets (J ~1 Hz) at 8.18, 8.27; *m/e* 213 (P, 40), 198 (31), 157 (100), 104 (61). Anal. $C_{15}H_{19}N$: C, H, N.

Hydrolysis of 27a and 27b. A solution of **27a–b** (0.8 g) and 4 drops of concentrated hydrochloric acid in THF was allowed to stand at room temperature for 6 h. Dilution with water, extraction with ether (2 × 10 mL), drying and concentration of the extracts, and distillation of the residue gave 0.45 g (73%) of 1-phenyl-4-methyl-3-penten-1-one (**28**): bp 120 °C (bath, 0.08 mm); IR 1682 cm^{-1}; NMR τ 2.0 (2 H, m), 2.5 (3 H, m), 4.50 (1 H, 3q, J = 7.5, J' = 1.6 Hz), 6.38 (2 H, d, br, J = 7.5 Hz), 8.24, 8.72 (3 H each, s); *m/e* 162 (P, 2), 105 (100). Anal. $C_{12}H_{14}O$: C, H.

Photochemical Reaction of Benzonitrile with 2-Methyl-2-butene. A solution of 1 (3.0 g, 0.03 mol) and 2-methyl-2-butene (22 g, 0.3 mol) and spectrograde pentane (150 mL) was irradiated for 8 h. The usual workup gave a product fraction, bp 62–70 °C (0.1 mm) (1.8 g, 70%), in addition to recovered 1 (1.3 g). The combined product fractions from four such reactions were dissolved in 60 mL of ether, cooled in ice, and rapidly extracted with three 15-mL portions of ice-cold 10% hydrochloric acid.

The combined extracts were made basic with 20% NaOH, keeping the temperature below 5 °C by cooling with an ice–salt bath. Reextraction with ether (3 × 10 mL) gave 0.51 g of acid-soluble material which was short-path distilled to afford 0.26 g of colorless oil. Purification by GC on column F gave azetine **31**: IR 1576 cm^{-1}; NMR τ 2.3–2.8 (5 H, m), 7.1 (1 H, q, J ~7 Hz), 8.6 (3 H, d, J ~7 Hz), 8.8 (6 H, s); *m/e* 173 (P, 4), 158 (13), 103 (100), 70 (38).

The neutral material remaining in the ether layer after acid extraction was a mixture of three major components in the ratio 7:2:1. The NMR spectrum of the mixture exhibited peaks in agreement with the assignment of **29** as the major product. Warming of the nitrile mixture (0.30 g) with *N*-phenylmaleimide in benzene at 40 °C for 4 h, followed by addition of half a volume of hexane and cooling overnight at 5 °C, led to formation of a yellowish solid. Filtration and recrystallization from chloroform–hexane gave colorless needles (0.18 g): mp 247–248 °C; IR 1705 cm^{-1}; NMR τ 2.7 (5 H, s, br), 3.5–3.9 (2 H, br), 6.4–7.9 (H, m), 8.71 (3 H, d, J = 6 Hz), 9.00 (6 H, s). Anal. $C_{22}H_{22}N_2O_2$: C, H, N.

Photochemical Reaction of Benzonitrile with Isobutene. A solution of 1 (3.0 g) and isobutene (30 mL) in spectrograde pentane was cooled externally with a dry ice–acetone bath while a glycol–water mixture at −30 °C was circulated through the immersion well. The solution was irradiated through Vycor for a total of 62 h, interrupting the irradiation three times to allow the apparatus to cool off overnight. Evaporation of solvent and fractional distillation of the residue gave 0.94 g of almost colorless oil **33**: bp 60–62 °C (0.2 mm); IR (film) 2242 cm^{-1}; NMR τ 3.8–4.3 (4 H, m), 6.7–8.2 (3 H, m), 8.85 (3 H, s), 8.97 (3 H, s); *m/e* 159 (P, 31), 144 (70), 117 (48), 104 (71), 103 (100), 77 (49). Anal. Calcd for $C_{11}H_{13}N$: C, 83.04; H, 8.27. Found: C, 82.74; H, 8.01. Analysis on column G at 160 °C shows one major component with ~4% of a second.

Warming of a solution of **33** (0.20 g) and *N*-phenylmaleimide (0.22 g) in benzene at 40 °C for 3 h, followed by cooling at 0 °C overnight gave a precipitate which was recrystallized from benzene–hexane to give colorless blades (0.23 g): mp 184–185 °C; IR (KBr) 1705, 2238 cm^{-1}; NMR τ 2.7–2.8 (5 H), 4.1–4.3 (2 H, m), 6.1–8.2 (5 H, m), 8.72, 8.80 (3 H each, s); *m/e* 334 (P). Anal. $C_{21}H_{20}N_2O_2$: C, H.

Photochemical Reaction of Benzonitrile with 2-Methoxypropene (13), Vinyl Acetate (12), Cyclopentene (9), 1,2-Dichloroethylene (14), and Norbornadiene (11). Solutions of 3.0 g of 1 (0.03 mol) and a tenfold excess of each alkene were irradiated and worked up in the usual fashion. Listed below are the irradiation times, yields of products (**33–38**), and pertinent spectral features of the mixture. All gave satisfactory C and H analyses unless so designated.

2-Methoxypropene: 30 h; 52%; bp 82–85 °C (0.1 mm); IR 2238 cm^{-1}; NMR τ 3.9–4.5 (4 H, m), 6.70 and 6.78 (singlets, total 3 H), 7.9 (2 H, AB, J = 13 Hz), 8.41 and 8.53 (singlets, total 3 H); *m/e* 175 (21), 160 (11), 104 (100), 103 (44). *N*-Phenylmaleimide adduct of major component (**34**): mp 163–164 °C; IR (KBr) 2240 (m), 1698 (s) cm^{-1}; NMR τ 2.6–2.8 (5 H, m), 3.9 (2 H, m), 6.8–7.5 (3 H, m), 6.83 (3 H, s), 8.07 (2 H, AB, J = Hz), 8.41 (3 H, s); *m/e* 348 (P).

Vinyl acetate: 12 h, with cleaning of polymer from apparatus after 6 h; 61% bp 96–99 °C (0.08 mm); IR (film) 2237 (m), 1732 (s) cm^{-1}; NMR τ 3.8–4.3 (4 H, m), 5.1 (1 H, m), 6.5–7.7 (3 H, m), 7.90, 8.04, 8.07 (all s, total, 3 H); *m/e* 189 (74), 129 (100); 104 (23), 103 (26). *N*-Phenylmaleimide adduct of major component (**35**): mp 211–212 °C; IR 2236 (m), 1736, 1700 (s) cm^{-1}; NMR τ 2.8 (5 H), 4.1 (2 H, m), 5.1 (1 H, m), 6.6–7.9 (4 H, m), 7.88 (3 H, s); *m/e* 362.

Cyclopentene: 24 h; 35%; bp 94–96 °C (0.1 mm); IR (film) 2240 cm^{-1}; NMR τ 4.1–4.5 (~2.6 H), 6.4–8.7 (9 H, m, br); *m/e* 171 (P, 45), 170 (26), 143 (29), 142 (36), 104 (41), 103 (87), 81 (100). *N*-Phenylmaleimide adduct of major component (**36**): mp 214–215 °C; IR 1700, 2240 cm^{-1}; NMR τ 2.8 (5 H), 3.9–4.1 (2 H, m), 6.7–6.8 (2 H, m), 7.2–8.4 (10 H, m); *m/e* 344.

1,2-Dichloroethylene: 30 h, with cleaning of polymer from the surfaces of the immersion well on three occasions during that time; 27%; bp 93–96 °C (bath, 0.06 mm); IR 2242 cm^{-1}; NMR τ 3.9–4.3 (~4 H, m, br), 5.8–6.9 (3 H, m, br); *m/e* 203, 201, 199 (parent, dichloro compound isotope distribution), 164 (100), 103 (22). A satisfactory analysis could not be obtained for this material (**37**).

Norbornadiene: 20 h; 42%; bp 108–110 °C (0.08 mm); IR (film) 2240 cm^{-1}; NMR τ 3.6–4.2 (6 H, m), 6.4–8.7 (7 H, m); *m/e* 195 (P, 17), 103 (40), 92 (26), 91 (100). Anal. $C_{14}H_{13}N$: C, H.

Irradiation of 2-Cyanothiophene (41) and Alkene 7. A solution of 2-cyanothiophene (1.1 g, 0.01 mol) and tetramethylethylene **7** (20 g) made up to 120 mL in spectrograde pentane was irradiated through Vycor for 6 h. Workup in the usual manner gave, besides 0.4 g of recovered **41**, adduct **44** (0.28 g, 24%): bp 76–79 °C (0.1 mm); IR 2230 cm^{-1}; NMR τ 3.70 (1 H, 2d, J' ~1 Hz), 4.52 (1 H, 2d, J = 6, J' ~3 Hz), 6.42 (1 H, m), 8.63, 8.68, 8.80, 8.95 (3 H each, s); *m/e* 193 (P, 0.6), 178 (14), 109 (61), 84 (100). Anal. $C_{11}H_{15}NS$: C, H.

Photolysis of 2-Cyanonaphthalene (40) with 2,3-Dimethyl-2-butene. A solution of **40** (1.2 g) and alkene **7** (20 g) in 80 mL of spectrograde pentane was irradiated through Corex for 10 h. Evaporation of excess alkene, followed by short-path distillation, gave almost pure adduct **42** (0.56 g): bp 120 °C (0.06 mm); IR 2235 cm^{-1}; NMR τ 2.7–3.1 (4 H, m), 3.49, 4.28 (2 H, AB, J = 9.6 Hz), 6.30 (1 H, s, br), 8.52 (3 H, s). 8.90 (6 H, s), 9.21 (3 H, s); *m/e* 237 (P, 0.4), 153 (60), 105

(100), 84 (73). Anal. $C_{17}H_{19}N$: C, H. When the crude oil remaining after evaporation of excess alkene was chromatographed on silica gel, elution with mixtures of benzene and ethyl acetate gave fractions containing first 0.3 g of **42**, followed by fractions which on evaporation gave 0.16 g of an oil which appears to be azetine **43**: IR 1660 cm^{-1}; NMR τ 2.2–2.7 (7 H, m), 8.62 (6 H, s), 8.69 (6 H, s); *m/e* 237 (Parent).

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Registry No.—**1**, 100-47-0; **15**, 37771-71-4; **16**, 61838-76-4; **17**, 18495-18-6; **18**, 62816-34-6; **20**, 37771-72-5; **21**, 63704-25-6; **22**, 63704-26-7; **23**, 63704-27-8; **24**, 63704-28-9; **25**, 63704-29-0; **26**, 63704-30-3; **27a**, 63704-31-4; **27b**, 63704-32-5; **28**, 36597-09-8; **29**, 37771-73-6; **29** NPM adduct, 63704-33-6; **31**, 63704-34-7; **33**, 37771-74-7; **33** NPM adduct, 63704-35-8; **34**, 37771-77-0; **34** NPM adduct, 63704-36-9; **35**, 37771-76-9; **35** NPM adduct, 63704-37-0; **36**, 37771-75-8; **36** NPM adduct, 63704-38-1; **37**, 63704-39-2; **38**, 63704-40-5; **40**, 613-46-7; **41**, 1003-31-2; **42**, 37771-79-2; **43**, 63765-57-1; **44**, 63704-41-6; NPM, 941-69-5; dimethyl tetramethylsuccinate, 17072-58-1; 2-methyl-1-phenyloctane-1,7-dione, 63704-42-7; acetone 2,4-DNPH, 1567-89-1.

References and Notes

(1) (a) N. J. Turro in "Energy Transfer and Organic Photochemistry," A. A. Lamola and N. J. Turro, Ed., Wiley- Interscience, New York, N.Y., 1969, Chapter 3; (b) W. M. Horspool, "Organic Photochemistry", Academic Press, New York, N.Y., 1976, Chapter 6.

(2) G. Buchi, J. G. Atkinson, D. E. Ayer, and E. W. Robb, *J. Am. Chem. Soc.*, **85**, 2257 (1963).

(3) (a) S. Hosaka and S. Wakamatsu, *Tetradedron Lett.*, **219** (1968); (b) D. M. Gale, *J. Org. Chem.*, **35**, 970 (1970); (c) T. S. Cantrell, *ibid.*, **40**, 1447 (1975).

(4) (a) J. J. McCullough, R. C. Miller, D. Fung, and W. S. Wu, *J. Am. Chem. Soc.*, **97**, 5942 (1975); (b) R. M. Bowman, C. Calvo, J. J. McCullough, R. C. Miller, and I. Singh, *Can. J. Chem.*, **51**, 1060 (1973); (c) T. R. Chamberlain and J. J. McCullough, *ibid.*, **51**, 2578 (1973); (d) R. M. Bowman, T. R. Chamberlain, C. W. Huang, and J. J. McCullough, *J. Am. Chem. Soc.*, **96**, 692 (1974).

(5) (a) K. Mizumo, C. Pac, and H. Sakurai, *J. Am. Chem. Soc.*, **96**, 2993 (1974); (b) R. A. Caldwell and L. Smith, *ibid.*, **96**, 2994 (1974).

(6) N. C. Yang, B. Kim, W. Chiang, and T. Hamada, *J. Chem. Soc., Chem. Commun.*, 729 (1976). We are grateful to Professor Yang for informing us of these results prior to publication.

(7) T. S. Cantrell, *J. Am. Chem. Soc.*, **94**, 5929 (1972).

(8) G. Sziemies, U. Siefkin, and R. Rinck, *Angew. Chem., Int. Ed. Engl.*, **12**, 161 (1973).

(9) S. M. McElvain and W. R. Davie, *J. Am. Chem. Soc.*, **73**, 1400 (1951).

(10) (a) D. E. Ayer, Ph.D. Dissertation, Massachusetts Institute of Technology, 1958; (b) we are grateful to Professor Buchi for communicating these results to us.

(11) See, however, ref 6.

(12) (a) W. R. Ware, D. Watt, and J. D. Holmes, *J. Am. Chem. Soc.*, **96**, 7853 (1974); (b) W. R. Ware, J. D. Holmes, and D. R. Arnold, *ibid.*, **96**, 7861 (1974).

(13) (a) C. Pac, T. Sugioka, and H. Sakurai, *Chem. Lett.*, 39 (1972); (b) *ibid.*, 667 (1973); (c) C. Pac, T. Sugioka, K. Mizuno, and H. Sakurai, *Bull. Chem. Soc. Jpn.*, **46**, 238 (1973).

(14) N. C. Yang, K. Srinavaschar, B. Kim, and J. Libman, *J. Am. Chem. Soc.*, **97**, 5006 (1975).

(15) F. D. Lewis and R. H. Hirsch, *J. Am. Chem. Soc.*, **98**, 5914 (1976).

(16) W. H. Hardham and G. S. Hammond, *J. Am. Chem. Soc.*, **89**, 3200 (1967).

(17) D. A. Deneo and M. A. El-Sayed, *J. Chem. Phys.*, **52**, 2622 (1970).

(18) D. A. Labianca, G. N. Taylor, and G. S. Hammond, *J. Am. Chem. Soc.*, **94**, 3679 (1972).

α- and β-Rearrangement Products, Benzoylpyridyltriphenylphosphonium Methylides and Phenylethynylpyridines, from Pyridine *N*-Oxides and Phenylethynyltriphenylphosphonium Bromide

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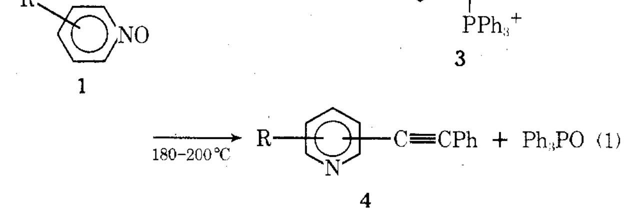
Pyridine *N*-oxides and phenylethynyltriphenylphosphonium bromide react in chloroform to produce α- and β-benzoylpyridyltriphenylphosphonium methylides. When sublimed at ca. 200 °C, these enol phosphoranes yield triphenylphosphine oxide and α- and β-phenylethynylpyridines.

Recently we have been exploring the chemistry of ethynylphosphonium salts (**2**).[1] Here we report on process 1 which juxtaposes steps which have separately become familiar. By bringing together pyridine *N*-oxides (**1**) with **2** (eq 1), we have



obtained some new enol phosphoranes (**3**) and pyridylacetylenes (**4**) which are collected in Table I.

Michael additions of ylides, e.g., $\equiv N^+—N^-—$, $=S^+—N^-—$, $\equiv N^+—O^-$, to alkynes are known and have been reviewed both generally[2a] and in the context of specialized topics, e.g., nitrone,[2b] azomethine ylide[2c] and other dipolar cycloadditions,[2d] indolizine synthesis,[2e] and nuclear substitution in heteroaromatic *N*-oxides.[3,4] Pertinent here is the specific area of *N*-oxide attacks on activated alkynes. Although apparent rearrangements in pyridine *N*-oxide chemistry yield numerous α-substituted pyridines, those which give β-pyridines have few precedents but are not unknown.[3-5] Indeed, the recent elucidation of possible mechanisms and products of the reaction of pyridine (or quinoline) with phenylpropionitrile, described by Abramovitch's group, stimulated our interest in this area (eq 2):[3]

Now there are other syntheses which appear to be related to those of eq 1, at least in overall effect. Pyridine *N*-oxides and pyridines, usually as salts, and metal acetylides give 2- and occasionally 4-ethynylpyridines;[6a-d] pyridine, benzoyl chloride, and silver phenylacetylide yield *N*-benzoyl-2-phenylethynyl-1,2-dihydropyridine.[6e] The thermal conversion of the phosphorane enolate, **3** to **4**, has ample precedent in other alkyne syntheses.[7]