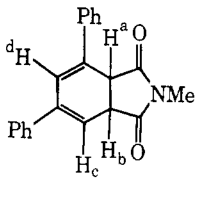
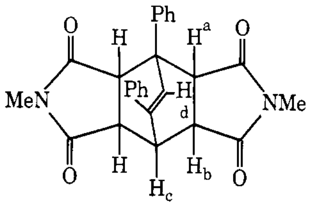
At this time we report a new example of eq 1 in which the olefin is an N-substituted maleimide and the acetylene is terminal or conjugated. Interestingly the reaction is catalyzed by $Ni(CO)_2(PPh_3)_2$ but not $PdCl_2$. Both these compounds catalyze the cyclotrimerization of acetylenes but probably *via* different mechanisms. While an intermediate such as I is possible in the former case, it is unlikely for $PdCl_2$.[3]

For the reaction between *N*-methylmaleimide and phenylacetylene the products of the reaction include not only the 2:1 adduct with the cyclohexadiene structure II but also a 1:1 adduct III which is the Diels–Alder product of II with a further mole of maleimide.

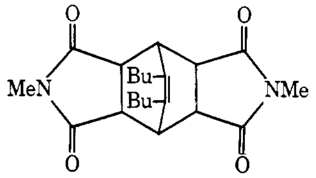


II



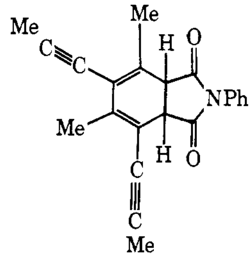
III

For the similar reaction between hexyne-1 and *N*-methylmaleimide a different stereochemistry was evident from the isolation of IV in 32% yield.

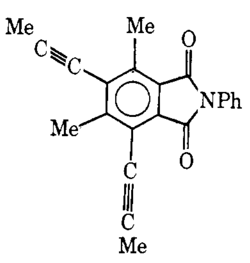


IV

Since $Ni(CO)_2(PPh_3)_2$ has recently been found to cyclotrimerize conjugated acetylenes,[6] the present reaction was also investigated for this class of acetylenes. Hexa-2,4-diyne and *N*-phenylmaleimide gave 20% V and 8% VI. Thus, the initial diene is apparently too sterically hindered to undergo a Diels–Alder reaction but does aromatize to some extent.



V



VI

It is of interest that Collman, *et al.*, have earlier attempted reactions such as eq 3 and found no reaction between maleic anhydride and an iridium metallocycle [I in which R = COOMe and M = $IrCl(PPh_3)_2$]. We have attempted the same reaction but substituted *N*-methylmaleimide for maleic anhydride and we were also unable to effect any reaction. It should be noted, however, that the presence of electron-withdrawing substituents on both diene and dienophile makes a Diels–Alder reaction unlikely in this case even if the reaction were to take place completely within the coordination sphere of the metal as seems likely in our catalytic examples.

Satisfactory elemental analyses, molecular weights (mass spectra), infrared spectra, and proton and C-13 nmr spectra were obtained for all the products cited. A typical reaction follows. *N*-Methylmaleimide (1.78 g, 16 mmol) and phenylacetylene (3.28 g, 32 mmol) were refluxed in 20 ml of benzene in the presence of $Ni(CO)_2(PPh_3)_2$ (0.064 g, 0.1 mmol) for 2.25 hr. On cooling, a white precipitate separated. It was removed by filtration, washed with benzene, and dried *in vacuo* to give 1.7 g (50% yield) of II. It was further purified by recrystallization from dimethyl sulfoxide (mp 349–351°). The filtrate was evaporated down and the resulting solid crystallized from a mixture of toluene and hexane to give 1.1 g (27% yield) of III (mp 150–155°). Their proton nmr spectra were consistent with the structures shown. In particular, the labeled protons in II gave the following δ values in $CDCl_3$: 4.50 (H_a, unresolved quartet), 4.05 (H_b, q), 5.85 (H_c, q), 6.74 (H_d, q), $J_{ab} = 11.6$, $J_{bc} = 3.8$, $J_{cd} = 1.1$, $J_{ad} =$ 1–2 Hz. The labeled protons in III gave the following δ values in dimethyl sulfoxide: 3.5 (H_a, d), 3.3 (H_b, q), 3.85 (H_c, sext), 6.65 (H_d, d), $J_{ab} = 8$, $J_{bc} = 2.8$, $J_{cd} = 1.7$ Hz. In addition both II and III gave C-13 nmr spectra (natural abundance) with 17 lines each consistent with the postulated structures.

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Received May 3, 1972

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[6] A. J. Chalk, *Tetrahedron Lett.*, 61 (1972).

Divergent Pathways in the Photochemical Reactions of Benzonitrile

Sir:

The photochemical addition of benzonitrile to 2-methyl-2-butene and to ethoxyethylene was reported several years ago to occur at the 1,2 positions of the benzene ring to yield 1-cyanobicyclo[4.2.0]octadienes, to the exclusion of products from reaction at the cyano group.[1] Although aromatic ketones and aldehydes generally undergo photochemical 2 + 2 addition at the carbonyl group to give oxetanes, a process which is especially facile for those carbonyl compounds possessing lowest $n \rightarrow \pi^*$ triplet states,[2] analogous reactions of nitriles have not thus far been documented.[3]

We now report our observations that benzonitrile undergoes photochemical cycloaddition to certain electron-rich olefins at the nitrile function to yield 2-azabutadienes, the products of electrocyclic ring opening of initially formed azetines, and that this process proceeds *via* singlet excited states, in contrast to those additions occurring across the benzene ring,

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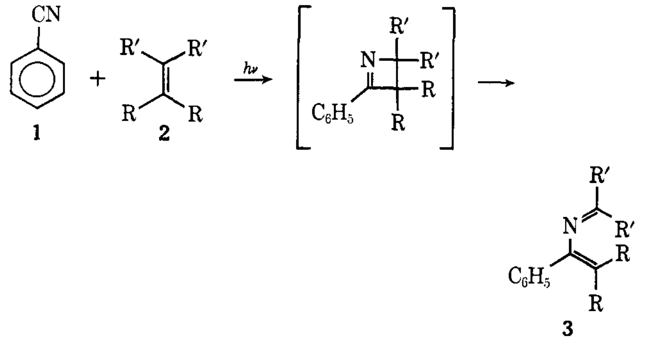
[1] J. G. Atkinson, D. E. Ayer, G. Buchi, and E. W. Robb, *J. Amer. Chem. Soc.*, **85**, 2257 (1963).

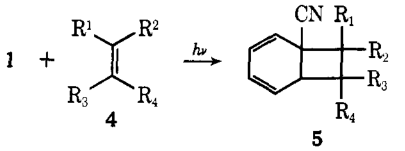
[2] (a) D. R. Arnold, *Advan. Photochem.*, **6**, 301 (1968); (b) N. C. Yang and W. Eisenhardt, *J. Amer. Chem. Soc.*, **93**, 1277 (1971).

[3] Photochemical reactions of unsaturated nitriles reported to date have involved transformation only of the hydrocarbon portion of the molecules: 2-cyanobutadiene (a) D. M. Gale, *J. Org. Chem.*, **35**, 970 (1970); acrylonitrile (b) S. Hosaka and S. Wakamatsu, *Tetrahedron Lett.*, 219 (1968); (c) J. A. Barltrop and H. A. J. Carless, *ibid.*, 3901 (1968); fumaronitrile (d) P. DeMayo, R. W. Yip, and S. T. Reid, *Proc. Chem. Soc.*, 54 (1963); (e) J. A. Barltrop and R. Robson, *Tetrahedron Lett.*, 597 (1963).

which appear to proceed from a benzonitrile triplet, probably the π → π* triplet.



a, $R = R' = CH_3$
b, $R = CH_3; R' = OCH_3$



a, $R_1 = R_2 = R_3 = CH_3; R_4 = H$
b, $R_1 = R_2 = CH_3; R_3 = R_4 = H$
c, $R_1 = R_3 = H; R_2 = R_4 = (CH_2)_3$
d, $R_1 = OAc; R_2 = R_3 = R_4 = H$
e, $R_1 = OCH_3; R_2 = CH_3; R_3 = R_4 = H$
f, $R_1 = R_3 = Cl; R_2 = R_4 = H$

Irradiation through Corex[4] of benzonitrile (**1**) in the presence of excess 2,3-dimethyl-2-butene (**2a**) or of 1,1-dimethoxy-2,2-dimethylethylene (**2b**) gave the products shown, *i.e.*, 4-phenyl-2,5-dimethyl-3-aza-2,4-hexadiene [**3a**; 71% based on unrecovered **1**, bp 72–73° (0.1 mm); ir^{film} 1664 cm^{-1}; nmr ($CDCl_3$) τ 2.7 (5 H, s) and 7.84, 8.08, 8.15, and 8.32 (all 3 H, s); *m/e* (parent) 187] and 1,1-dimethoxy-3-phenyl-5-methyl-2-aza-1,3-pentadiene [**3b**; 45%; ir^{film} 1686 cm^{-1}; nmr ($CDCl_3$) τ 2.85 (5 H, s), 6.33, and 8.37 (both 6 H, s)], respectively. The structures of **3a** and **3b** follow from their spectral characteristics and from their hydrolysis on treatment with aqueous acid to isobutyrophenone (**6**). Imine **3a** is converted to **6** in 0.5 hr at 5–10° in 2% hydrochloric acid; compound **3b**, an imidocarbonate, requires refluxing in acetic acid–aqueous hydrochloric acid to effect hydrolysis.[5]

The additions of **1** at the 1,2 positions of the benzene ring to 2-methyl-2-butene and to ethoxyethylene, including an elegant structure proof of the major adduct from the former olefin, have been reported by Büchi and coworkers. We have now observed that this type of 2 + 2 addition to the aromatic ring of **1** also takes places with several other olefins, including isobutene, cyclopentene, vinyl acetate, 2-methoxypropene, and 1,2-dichloroethylene (**4a–e**), to produce the analogous adduct mixtures of gross structures **5a–5e**. The spectral properties of these substances show that they are composed, primarily,[6] of 1-cyanobicyclo[4.2.0]octadienes, with none of the isomeric 2-azabutadienes present. *N*-Phenylmaleimide adducts of the major isomers were obtained in most cases, as listed in Table I.

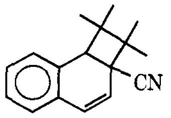
Table I

Olefin	Adducts	Φ_{2537}	Yield, %[a]	Mp of *N*-phenylmaleimide derivative,[b] °C
2a	**3a**	0.20	71	
2b	**3b**	0.048	45	
4a	**5a**	0.18	63	247–248
4b	**5b**	0.02	40	184–185
4c	**5c**		27	214–215
4d	**5d**	0.15	61	211–212
4e	**5e**	0.16	52	163–164
4f	**5f**		35	

[a] Isolated. [b] Of major isomer.

The formation of compounds **3a** and **3b** could not be quenched by added 1,3-dienes at concentrations up to 1 *M*. On the other hand, formation of adduct mixtures **5a**, **5d**, and **5e** in solutions 0.5 *M* in *cis*-1,3-pentadiene occurs at a rate only *ca.* one-fourth that in the absence of added quencher. Sensitization proved impractical because of the high energy of the lowest triplet of benzonitrile (77 kcal);[7] however, the quenching results, at least, suggest the intermediacy of excited *singlet* benzonitrile in the additions taking place at the nitrile group, *i.e.*, formation of **3a** and **3b**, whereas the additions to the benzene ring apparently proceed *via* triplet excited states. The lowest triplet of benzonitrile is known from studies of its phosphorescence spectrum to be π → π* in nature.[7] It is tempting to postulate that the additions across the cyano group occur *via* an n* singlet state, perhaps by way of singlet exciplexes with the very electron-rich olefins. In the presence of olefins of only moderate π-electron density, the excited singlet decays to the lowest triplet, whose longer lifetime enables it to cycloadd to the less electron-rich olefins. The lowest triplet of **1**, being of π → π* character, might well be expected to be more reactive at the ring than at the nitrile function.[8] Similar behavior has also been observed for certain aromatic carbonyl compounds whose lowest triplet is of predominantly π → π* character.[9]

This difference in reactivity of benzonitrile toward various olefins does not extend to β-naphthonitrile (**7**); irradiation of **7** in the presence of 2,3-dimethyl-2-butene gave as the only tractable product the 2 + 2 adduct **8** [ir 2246 cm^{-1}; nmr τ 2.7–3.1 (4 H, m), 3.49 and 4.28 (AB, J = 9.6 Hz), 6.30 (1 H, s, br), 8.52 (3 H, s), 8.90 (6 H, s), and 9.21 (3 H, s)].



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[4] Preparative irradiations were performed with Corex-filtered light from a 450-W medium-pressure mercury arc; quantum yield determinations were done in a Rayonet chamber reactor with 2537-Å lamps.

[5] The orientation of **3b** is analogous to that observed by us in the oxetane from benzophenone and 1,1-dimethoxy-2,2-dimethylethylene.

[6] One of the three products from **1** and 2-methoxypropene, whose exact structure has not been determined, is a member of neither group **3** nor **5**.

[7] K. Takei and Y. Kanda, *Spectrochim. Acta*, **81**, 1201 (1962).

[8] Excited 2-cyanobutadiene has been found to undergo the cyclization reactions characteristic of the parent hydrocarbon, which necessarily possesses only π → π* excited states.[3a]

[9] (a) D. R. Arnold, *Advan. Photochem.*, **6**, 301 (1968), and references given therein; (b) T. S. Cantrell, *Chem. Commun.*, 155 (1972); (c) T. S. Cantrell, unpublished results.

We are intensively pursuing further studies of the photochemical behavior of aromatic nitriles and related compounds.

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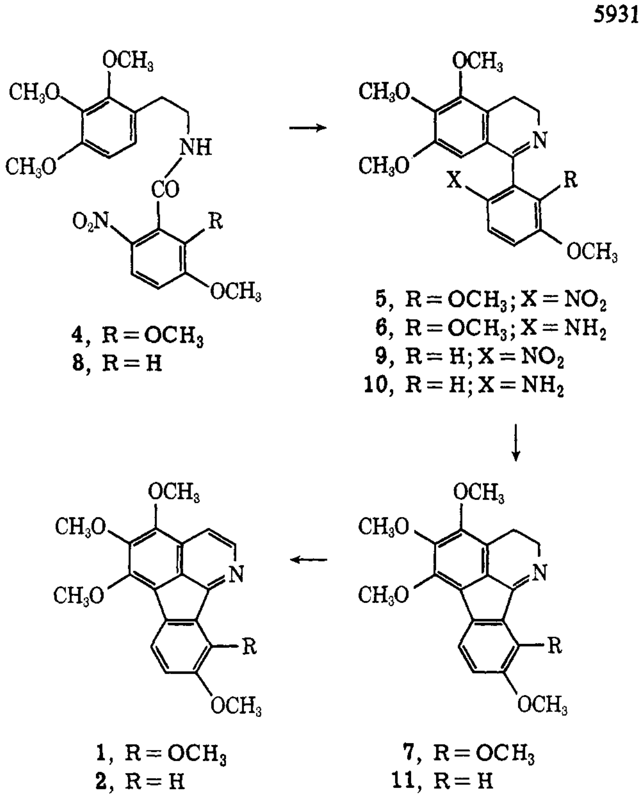
Azafluoranthene Alkaloids. A New Structural Type

Sir:

We wish to report the isolation, characterization, and structural confirmation of the first representatives of a new class of natural products, the azafluoranthene alkaloids.[1]

Two nonphenolic yellow bases imeluteine (**1**, $C_{20}H_{19}NO_5$, mp 146–147°) and rufescine (**2**, $C_{19}H_{17}NO_4$, mp 88–90°) were isolated (ptlc) from the stem alkaloid fractions of the Amazonian vines *Abuta imene* and *Abuta rufescens* (Menispermaceae).[2,3] Neither **1** nor **2** shows hydroxyl or carbonyl absorption in the infrared. Their uv–visible spectra are quite similar and are indicative of a highly conjugated system. For **1**, λ_{max}^{EtOH} 233 nm (log ϵ 4.48), 253 (4.49), 288 (4.43), 317 (3.75), 365 (sh) (3.72), 380 (3.85), 400 (sh) (3.72); for **2**, 247 (4.52), 285 (sh) (4.31), 295 (4.34), 304 (4.29), 315 (sh) (3.84), 356 (3.65), 373 (3.78), 400 (sh) (3.32). The 100-MHz nmr spectrum ($CDCl_3$) of imeluteine shows only five aromatic methoxyls (δ 3.94, 4.02, 4.08, 4.10, and 4.17) and two aromatic AB quartets (δ 6.91, 7.60, J = 8 Hz; δ 7.57, 8.65, J = 6 Hz), consistent with structure **1**. The corresponding nmr spectrum ($CDCl_3$) of rufescine shows four aromatic methoxyls (δ 3.94, 4.05, 4.11, and 4.13), an aromatic AB quartet (δ 7.63 and 8.59, J = 6 Hz), and an aromatic ABC system (δ 7.82, 7.68, and 6.96; J_{AC} = 8 Hz, J_{BC} = 2 Hz), consistent with structure **2**.

The structures of imeluteine and rufescine were established by the following unambiguous syntheses. Reaction of β-(2,3,4-trimethoxyphenyl)ethylamine (**3**)[4] with the acid chloride of 2,3-dimethoxy-6-nitrobenzoic acid[5] gave the corresponding amorphous amide **4**, which was converted by phosphorus oxychloride in acetonitrile into the dihydroisoquinoline **5**, mp 168–170° (55% from amine **3**). Reduction of **5** with hydrazine and 10% palladium/charcoal in ethanol gave amine **6**, isolated as the crystalline hydrochloride, mp 199–200° dec (81%). Diazotization of **6** in 60% sulfuric acid, followed by treatment with activated copper, gave dihydroimeluteine (**7**), mp 105–106° (67%). Dehydrogenation of **7** by 10% palladium/charcoal in refluxing *p*-cymene afforded imeluteine (**1**) (48%), identical (ir, mixture melting point) with the natural base. Rufescine (**2**) was similarly synthesized from **3** and 3-methoxy-6-nitrobenzoic acid[6] by an analogous route, by way of the corresponding intermediates **8**, **9**, **10**, and **11**.



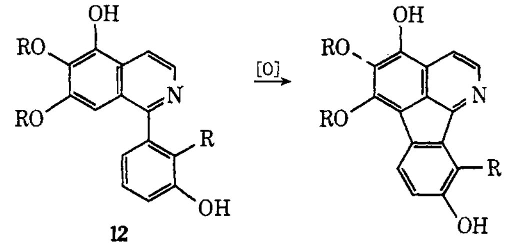
4, R = OCH_3
8, R = H

5, R = OCH_3; X = NO_2
6, R = OCH_3; X = NH_2
9, R = H; X = NO_2
10, R = H; X = NH_2

1, R = OCH_3
2, R = H

7, R = OCH_3
11, R = H

The azafluoranthene alkaloids **1** and **2** probably arise biogenetically from phenolic 1-phenylisoquinoline precursors (**12**) by oxidative cyclization, followed by methylation. The recent report of the natural occurrence of 1-phenyl-1,2,3,4-tetrahydroisoquinoline alkaloids[7,8] lends some support to this hypothesis.



12

Acknowledgment. We are grateful to the National Institutes of Health for a grant (CA-11445) in support of this work. We also thank Dr. Charles A. Hetzel of Wyeth Laboratories for the determination of high resolution mass spectra.

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[1] The systematic name for the ring system found in these alkaloids is indeno[1,2,3-*i,j*]isoquinoline.

[2] The isolation of the novel aporphine alkaloid imenine from *A. imene* has been reported earlier: M. D. Glick, R. E. Cook, M. P. Cava, M. Srinivasan, J. Kunitomo, and A. I. daRocha, *Chem. Commun.*, 1217 (1969).

[3] The empirical formulas of **1** and **2** were determined by mass spectrometry. Found for **1**: *m/e* 353.1235. Found for **2**: *m/e* 323.1135. Satisfactory elemental analyses were obtained for all other compounds reported except for the amorphous **4** and **8**.

[4] S. Kubota, T. Masui, E. Fujita, and S. M. Kupchan, *J. Org. Chem.*, **31**, 516 (1966).

[5] W. H. Perkin, Jr., R. Robinson, and S. W. Stoyle, *J. Chem. Soc.*, **125**, 2358 (1924).

[6] I. M. Heilbron, F. N. Kitchen, E. B. Parkes, and G. D. Sutton, *ibid.*, **127**, 2167 (1925).

[7] K. Leander, B. Luning, and E. Ruusa, *Acta Chem. Scand.*, **23**, 244 (1969).

[8] A. Brossi and S. Teitel, *Helv. Chim. Acta*, **54**, 1564 (1971).

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