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FEATURE ARTICLE

Photochemistry of conjugated poliynes

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Regio- and site-selectivity and product structure in the photocycloaddition of conjugated poliynes with various alkenes are dependent on the terminal groups, the number of triple bonds and the substrate alkenes. The reaction normally proceeds through cumulene-type triplet excited states. 1-Aryl-4-(pentamethyldisilanyl)buta-1,3-diynes add to methanol or acetone on irradiation through interesting silacyclopropene intermediates. Photohydration and photoaddition of 1-arylbuta-1,3-diynes to alcohols are also dependent on the other terminal group and the substituents on the aryl group.

Some linear poliynes have become important precursors to polymers possessing potentially useful physical properties such as nonlinear optical properties.[1] Furthermore, certain naturally occurring and synthetic linear poliynes, such as 1-phenylhepta-1,3,5-triyne (PHT) and 1,4-diphenylbutadiyne (DPB), have been reported to be phototoxic to a variety of microorganisms through membrane damage.[2] For example, 1-phenylhepta-1,3,5-triyne (PHT) and its biosynthetic derivative α-terthienyl (α-T) are phototoxic toward various organisms containing membranes, including eukaryotic cells, fungi, bacteria and viruses in the presence of UV-A light. The photobiological activity was directly dependent upon the number of thiophene rings and acetylene bonds. The mode of action of α-T was shown to be photodynamic in nature but that of PHT-type compounds was not clear.[2] The photophysical and photochemical behavior of conjugated linear poliynes have received relatively little attention in contrast to those of the corresponding conjugated polyenes, in spite of these important properties. The photochemistry of conjugated poliynes is reviewed, concentrating on the work carried out in our laboratory.

Photophysical properties of conjugated poliynes

A series of conjugated poliynes with two or three conjugated C≡C triple bonds and various terminal groups such as phenyl, naphthyl, *tert*-butyl, methyl and silyl groups has been synthesized in moderate to good yields by various methods.[3] All the poliynes, natural or synthetic, show characteristic spiky UV–VIS absorption bands separated by *ca.* 2300 $\mathrm{cm^{-1}}$ due to the C≡C stretching band. Aromatic groups at both ends are conjugated through the triple bonds between them. No fluorescence was observed from poliynes except naphthyl derivatives. According to Beer,[4] none of the poliynes with less than four triple bonds shows fluorescence except diphenylacetylene. Most of the poliynes show phosphorescence with the quantum yields shown in Table 1. In particular, these compounds show triplet–triplet absorption bands in the fluid solutions at room temperature with the triplet lifetime in the range of a few tenths of a microsecond in methanol and a few tenths of a second at liquid nitrogen temperature, unlike corresponding polyenes. For naphthyl conjugated poliynes, the fluorescence is observed and quenched by alkenes, particularly by electron deficient alkenes such as dimethyl fumarate and fumaronitrile, and sometimes exciplex emissions are observed as shown in Table 2.[5] Conjugated diynes can be either electron donors or acceptors in the excited state but they are more likely to be electron donors because no fluorescence quenching is observed with electron-rich alkenes such as 2,3-dimethylbut-2-ene. The results indicate that the conjugated poliynes have poor electron-accepting ability.[5]

Photoreactions with alkenes

Photoreaction of conjugated diynes with alkenes

Photolyses of 1,4-diphenylbutadiyne (DPB) with various alkenes such as 2,3-dimethylbut-2-ene,[5,6] dimethyl fumarate,[6,7] acrylonitrile[8] and ethyl vinyl ether[8] result in the formation of regio- and site-selective cyclobutene adducts, and unexpected novel cyclopropyl and oxirane adducts as shown in Table 3. Reactions proceed through a triplet excited state of DPB, and a plausible reaction mechanism involving a cumulene-type triplet excited state, a polar triplet structure of 1 : 1 cyclobutene adduct,

Table 1 Phosphorescence quantum yields of some conjugated poliynes at 77 K in methylcyclohexane

Conjugated poliynes	λ_{ex}/nm	$\phi_{ph}{}^{a}$
1-Phenylpenta-1,3-diyne	280	0.026
1-Phenyl-5,5-dimethylhexa-1,3-diyne	280	0.090
1,4-Diphenylbutadiyne	320	0.012
1-(1-Naphthyl)penta-1,3-diyne	330	0.002
1-(1-Naphthyl)-5,5-dimethylhexa-1,3-diyne	330	0.002
1-(1-Naphthyl)-4-phenylbuta-1,3-diyne	350	0.001
1,4-Di(1-naphthyl)buta-1,3-diyne	370	0.000
1-Phenylhepta-1,3,5-triyne	310	0.004
1,6-Diphenylhexa-1,3,5-triyne	360	0.004
1-(1-Naphthyl)-6-phenylhexa-1,3,5-triyne	377	0.001
1,6-Di(1-naphthylhexa-1,3,5-triyne	390	0.000

[a] Relative to anthracene (ϕ_f = 0.36 at 20–25 °C in cyclohexane).

Table 2 Stern–Volmer constants ($k_q\tau$) for fluorescence quenching of 1-(1-naphthyl)buta-1,3-diynes by some alkenes

	In acetonitrile			In diethyl ether		
Conjugated poliynes	DMB	DMFu	FN	DMB	DMFu	FN[a]
1-(1-Naphthyl)penta-1,3-diyne	0	17	37	0	20	3.6
1-(1-Naphthyl)-5,5-dimethylhexa-1,3-diyne	20.14[a]	156	130	0	129	157
1-(1-Naphthyl)-4-phenylbuta-1,3-diyne	0	9	6.9	0	9.8	2.3
1,4-Di(1-naphthyl)buta-1,3-diyne	0	14	5.4	0	14	1.7

[a] Exciplex emissions were observed. DMB: 2,3-dimethylbut-2-ene, DMFu: dimethyl fumarate, FN: fumaronitrile

and carbene intermediates for cyclopropyl and oxirane adducts is proposed (Scheme 1).

In the reaction with 2,3-dimethylbut-2-ene, a 1 : 1 cyclobutene adduct and a 1 : 2 cyclopropyl adduct are the primary photoproducts, while a 1 : 2 dicyclobutene adduct is the secondary photoproduct of the 1 : 1 cyclobutene adduct. Irradiation of DPB with dimethyl fumarate yields a primary 1 : 1 adduct *via* a triplet excited state, and further irradiation of the solution results in the formation of 1 : 2 oxirane adduct and 1 : 2 cyclopropyl adduct *via* singlet and triplet excited states of the 1 : 1 adduct, respectively. In the reaction with acrylonitrile and ethyl vinyl ether, the reactive centre for 1 : 1 photoadducts to give secondary 1 : 2 adducts is dependent on the electron density of alkenes, *i.e.* addition to the triple bond for acrylonitrile but to the double bond for ethyl vinyl ether, indicating that the lowest triplet excited state of 1 : 1 photoadducts has a polar character. The regioselectivity of these photocycloaddition reactions is attributed to stabilization of the α-position by substituents (CN, OEt) on the alkenes in diradical type intermediates. In the photolysis of DPB with ethyl vinyl ether, 1 : 2 1,5-diene products were obtained through thermal rearrangement of primary bicyclic[2.2.0.]hexane photoadduct.

In contrast to DPB, photolysis of 1-phenylpenta-1,3-diyne (PPD)[9] and 1-phenyl-5,5-dimethylbuta-1,3-diyne (PDB)[5] with 2,3-dimethylbut-2-ene, yields only a 1 : 1 cyclobutene adduct involving only the C-3 and C-4 triple bond (Scheme 2).

For DPB, the C-1 and C-4 positions are exactly the same, but for PPD and PDB the first addition should occur on C-4 due to the higher reactivity compared with C-1. In the triplet excited state, initial attack on the C-4 by the 2,3-dimethylbut-2-ene molecule gives a triplet diradical intermediate as shown in Scheme 3.

In this intermediate, ring closure to the cyclopropyl adduct will compete against the spin flip, which leads to a singlet diradical intermediate to form the cyclobutene ring. When R is an alkyl group, the spin flip is preferred to the ring closure. When R is phenyl, however, a significant portion of triplet diradical intermediate undergoes ring closure, leading to the formation of a 1 : 2 cyclopropyl adduct, probably *via* a carbene intermediate through the transition state stabilized by the group on C-4 as shown in Scheme 4. By delocalization of the unpaired electron over the phenyl ring, the phenyl group at C-4 stabilizes the transition state more than the alkyl groups.

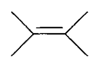
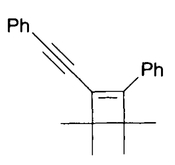
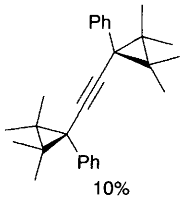
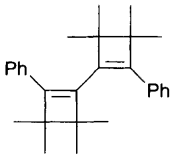
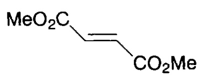
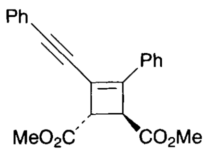
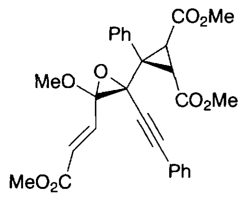
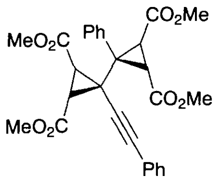
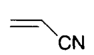
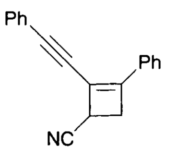
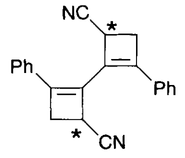
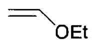
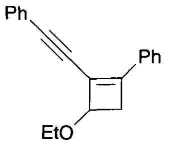
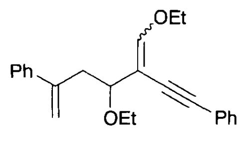
1-(1-Naphthyl)buta-1,3-diynes were photolyzed in 2,3-dimethylbut-2-ene to obtain [2 + 2] photoadducts (Scheme 5).[5] The reaction site is identified to be the acetylene moiety attached to the naphthyl group, and reactions proceed from both singlet and triplet excited states of diynes. Introduction of the 1-naphthyl group on the C-1 carbon causes participation of the singlet pathway and localization of electrons (or diradical character) on the C-1 and C-2 carbons and naphthyl ring in the excited state, while the phenyl group on the C-1 carbon causes the delocalization of electrons (or diradical character) throughout the conjugated system.

Photoreaction of conjugated triynes with alkenes

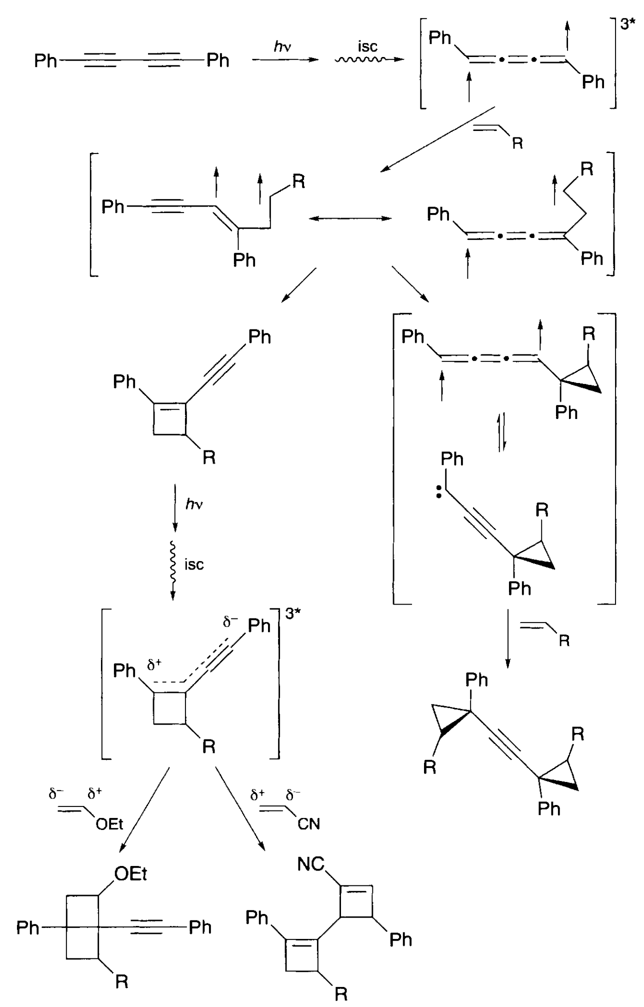
Irradiation of 1-phenylhexa-1,3,5-triynes (PHT) with various alkenes yields [2 + 2] type 1 : 1 photoadducts.[10–12] The photoreaction proceeds through a triplet excited state and shows

Table 3 Photoreaction of 1,4-diphenylbutadiyne with alkenes

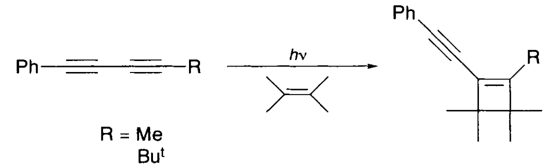
$$\mathrm{Ph{-}C{\equiv}C{-}C{\equiv}C{-}Ph} + \text{alkenes} \xrightarrow{h\nu} \text{products}$$

Entry	Alkene	Products		
1		 14%	 10%	 20%
2		 13%	 12%	 14%
3		 14%	 two diastereoisomers (15%), (14%)	
4		 5%	 *cis* (9%) and *trans* (8%)	

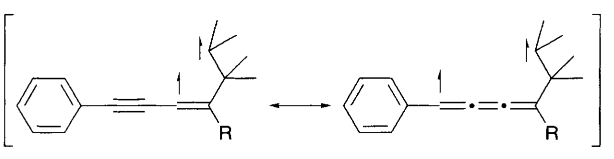
site- and regio-selectivity. Alkenes with electron-withdrawing substituents, such as dimethyl fumarate, fumaronitrile, acrylonitrile, methyl acrylate and styrene, are more reactive than electron rich olefins. The triplet excited state of 1,6-diphenylhexa-1,3,5-triyne (DPH) is quenched by olefins.[11] The quenching rate constants were determined by laser photolysis studies and turned out to be the rates for intermolecular addition of the DPH triplet excited state to the alkenes, because the rates are much slower than energy transfer quenching rates, which are usually in the range of diffusion control. The reaction rate constants for highly reactive alkenes, such as fumaronitrile, dimethyl fumarate, acrylonitrile, methyl acrylate and styrene, are in the range of 10^6–10^4 dm^3 mol^{-1} s^{-1}, unreactive or less-reactive alkenes such as ethyl vinyl ether, dihydrofuran, 2,3-dimethylbut-2-ene and *trans*-1,2-dichloroethylene show very small quenching rate constants, and tetrachloroethylene does not quench the triplet excited state of DPH at all, consistent with the lack of photochemistry. This can be explained on the basis of polar effects of electron-withdrawing substituents. The regioselectivity and reactivity of alkenes in the photoaddition reactions are in accord with that of the addition reaction of nucleophilic alkyl radicals to alkenes[13] and the results suggest that the triplet excited states of 1-phenylhexa-1,3,5-triynes have a nucleophilic radical character.



Scheme 1 A plausible reaction mechanism for photocycloaddition of 1,4-diphenylbutadiyne to alkenes



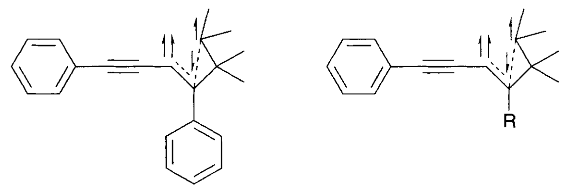
Scheme 2



Scheme 3

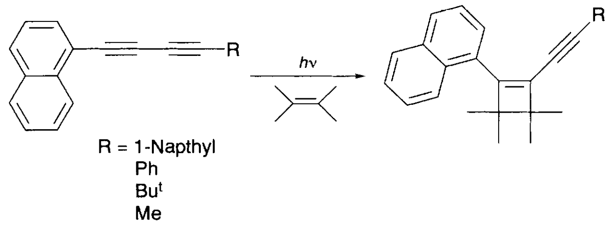
Photolysis of 1-phenylhexa-1,3,5-triynes (PHT) in 2,3-dimethylbut-2-ene gives dicyclopropyl photoadducts (Scheme 6).[12,14,15]

The reactions may proceed from the cumulene-type triplet excited states of triynes *via* carbene intermediates. Radical-stabilizing groups, such as the *tert*-butyldimethylsilyl group, on terminal carbons of conjugated hexatriynes control the photoaddition reactions of the compounds. Hydrogen and methyl groups on C-6 have little or no radical-stabilizing ability at C-6, while phenyl and *tert*-butyldimethylsilyl groups can stabilize the radical at C-6 by delocalization of the unpaired electron over the phenyl ring and empty d orbital of silyl group, respectively. Consequently, the radical at C-6 in 1-phenylhexa-1,3,5-triyne (PHT) and 1-phenylhepta-1,3,5-triyne is more reactive than the C-1 radical. However, when the R group is phenyl and *tert*-butyldimethylsilyl, the radicals at C-1 and C-6 will have similar reactivity.

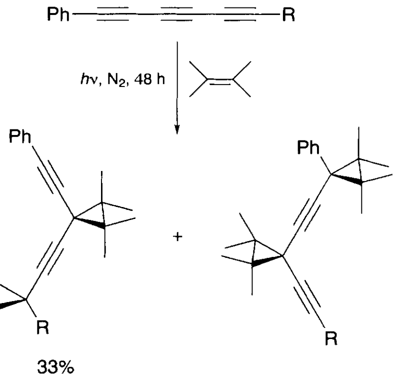


stabililized transition state non-stabililized transition state

Scheme 4



Scheme 5



R = Ph	33%	
Me	11%	
H	7%	
SiMeBu^t	11%	10%

Scheme 6

Four major photoadducts were isolated from the photoreaction of PHT with undecylenic acid methyl ester, an unsaturated fatty acid used as a model reaction for PHT phototoxicity *via* the viral membrane damage and PHT with hex-1-ene as a reference reaction.[16] Photoreactions occur through [2 + 2] photocycloaddition reaction between the double bond of the alkenes and C-1–C-2, C-3–C-4, and C-5–C-6 triple bonds of PHT. These reactions most likely result from the cumulene-type diradical species.

From these results, it is clear that photoaddition reactions of conjugated polyynes with alkenes are dependent on the number of conjugated triple bonds, the nature of terminal groups, and the structural properties of the alkenes.

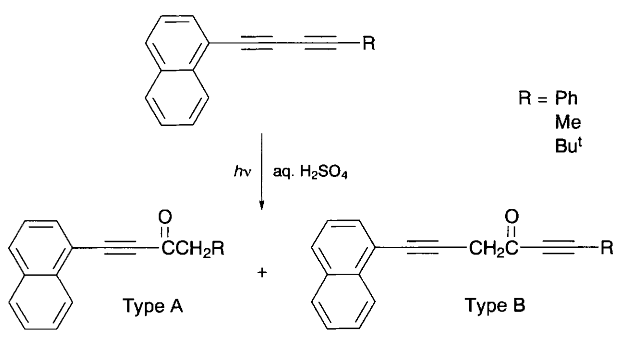
Photohydration reaction of conjugated diynes

It is well known that 1-arylacetylenes are generally not hydrated in neutral solution and very slowly hydrated in 25% (*m*/*m*) aqueous sulfuric acid at room temperature.[17] The compounds can, however, be easily hydrated photochemically under mild conditions due to their marked increase in basicity on excitation.[17,18] Irradiation of 1-(1-naphthyl)buta-1,3-diynes in aqueous acetonitrile (0–5% sulfuric acid) at 350 nm gave the type A and type B products in moderate yields (Scheme 7).[19] The singlet excited state yields both type A and type B photoadducts, while the triplet excited state yields only type B photoadducts.

The lowest excited singlet state of arylacetylenes (phenyl- or naphthyl-acetylenes) has zwitterionic character (positively charged C-1 and negatively charged C-2).[20] In 1-aryl-1,3-diynes, however, charge separation seems to be dichotomic (C-1 or C-4 is positively charged in the excited singlet state), the structure with a positively charged C-1 being dominant. The photohydration reaction appears to be a general reaction for nonhalogen-substituted aromatic alkenes and alkynes, and two photohydration mechanisms (involving the singlet excited state only or the triplet excited state only), in which the substituent on the aromatic ring leads to only one mechanism being operative, are proposed. On the other hand, in 1-(1-naphthyl)buta-1,3-diynes, a mixed mechanism involving both singlet and triplet excited states is operative. The substituents on C-4 of the diynes affect the photohydration quantum yield only, and not the product structure (reaction mechanism); in addition it is clear that the electron distribution of excited states of conjugated aryl-polyacetylenes is significantly influenced by the number of conjugated triple bonds.

Irradiation of 1-(*p*-nitrophenyl)-5,5-dimethylhexa-1,3-diyne in aqueous sulfuric acid yields conjugated allenyl ketones and β-dicarbonyl compounds (Scheme 8).[21] The conjugated allenyl ketones are primary photoproducts while β-dicarbonyl compounds are secondary products formed by thermal hydration of the primary photoproducts.

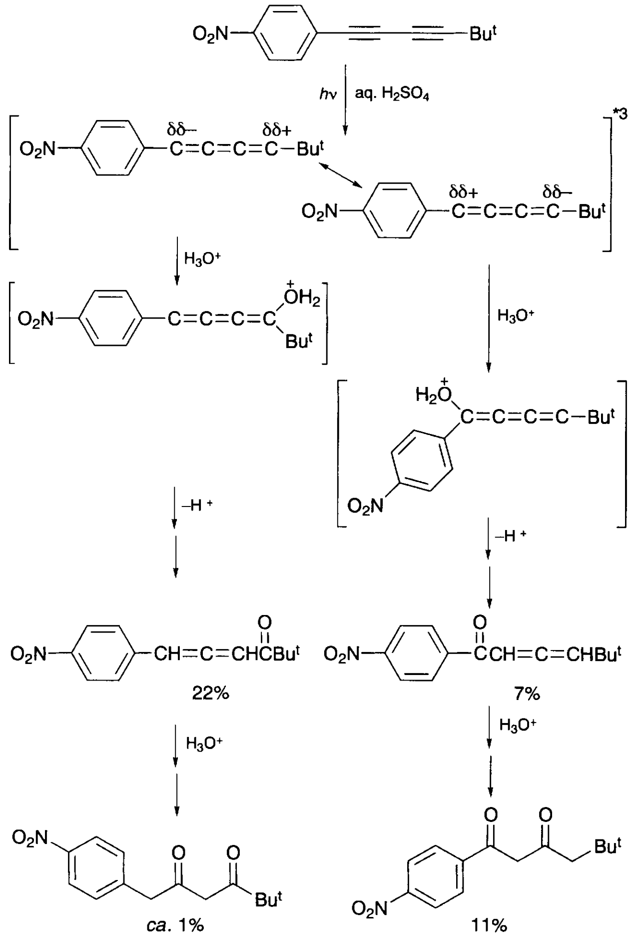
The photohydration reaction of 1-(1-naphthyl)buta-1,3-diynes proceeds *via* both singlet and triplet excited states, and the protonation step is the rate-limiting step. On the other hand, 1-(*p*-nitrophenyl)-5,5-dimethylhexa-1,3-diyne reacts *via* the triplet excited state only, and the allenyl ketone products are produced by the synchronous protonation and water addition mechanism. The protonation at C-1 of 1-(*p*-nitrophenyl)-5,5-dimethylhexa-1,3-diyne is greatly enhanced in the excited state compared to the ground state. Protonation of the ground state occurs predominantly at the C-4 position. However, the photohydration of 1-(*p*-nitrophenyl)-5,5-dimethylhexa-1,3-diyne does not yield the regiospecific hydration products given by nitrophenyl allenes and acetylenes.[17] In 1-(*p*-nitrophenyl)-5,5-dimethylhexa-1,3-diyne, the electron withdrawing effect of the nitro group is dispersed over the diacetylene group, weakening the effect compared to that dispersed over a single acetylene moiety only. The triplet excited state of 1-(*p*-nitrophenyl)-5,5-dimethylhexa-1,3-diyne, therefore, shows low regiospecificity for hydration.



Scheme 7

Photoreaction with alcohols

Photolysis of 1-arylbuta-1,3-diynes in methanol yields C-1 protonated polar photoaddition and photoreduction products.[22] The photoaddition and photoreduction products (*cis* form) undergo secondary photocyclization reactions to give phenanthrene derivatives on further irradiation. A plausible reaction mechanism involving both a highly dipolar singlet and a neutral or slightly charge separated triplet excited state is proposed. The reactions are influenced by the inductive effect of the groups attached to C-1 and C-4 of the conjugated diyne backbone. The singlet excited state is relaxed rapidly by losing a small amount of excitation energy to an intermediate. In this intermediate, the developed charge is on one of three sp^2 orbitals because the terminal carbons (C-1 and C-4) have sp^2 hybridization. The charge in this orbital cannot be delocalized over the aromatic ring because the p orbital is perpendicular to the aromatic π

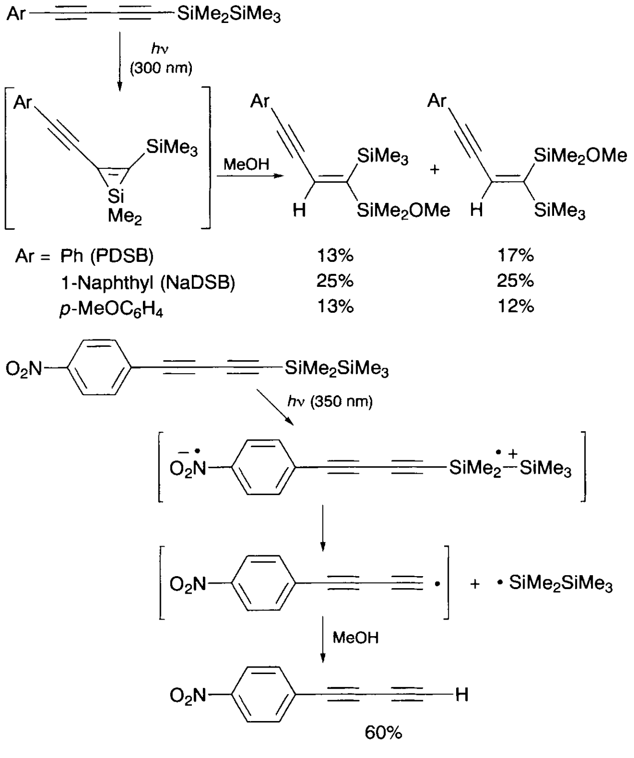


Scheme 8

orbital system; therefore the inductive effect only contributes to the charge separation of the intermediate. The photoreduction products seem to originate from the triplet excited state. Upon irradiation, conjugated polyynes react also with tetrahydrofuran (THF) to give photoaddition and photoreduction products.[23]

Photochemistry of 1-aryl-4-(pentamethyldisilanyl)-buta-1,3-diynes

The excited state chemistry of aryldisilanes has been extensively studied because these compounds show interesting photophysical and photochemical properties.[24–26] Aryldisilanes show dual fluorescence, local and intramolecular charge-transfer fluorescence. This intramolecular charge-transfer state has a strongly polar structure with complete charge separation, which plays an important role in the photochemical reaction.[25] Interestingly, photolysis of alkynyl-substituted disilane derivatives give highly reactive silacyclopropene intermediates.[26]



Scheme 9

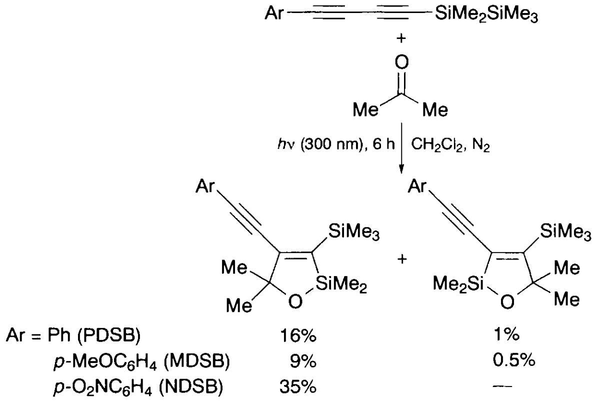
Photophysical properties of 1-aryl-4-(pentamethyldisilanyl)-buta-1,3-diynes

No fluorescence was observed from 1-phenyl-4-(pentamethyldisilanyl)buta-1,3-diyne (PDSB), 1-(*p*-methoxyphenyl)-4-(pentamethyldisilanyl)buta-1,3-diyne (MDSB), 1-(*p*-nitrophenyl)-4-(pentamethyldisilanyl)buta-1,3-diyne (NDSB) even at 77 K but 1-(1-naphthyl)-4-(pentamethyldisilanyl)buta-1,3-diyne (NaDSB) shows fluorescence with a maximum at 353 nm in methanol.[27] No charge-transfer emission is observed in any of these compounds. All the 1-aryl-4-(pentamethyldisilanyl)buta-1,3-diyne derivatives show strong phosphorescence with strong 0-0 bands around 460–550 nm at 77 K in organic glasses, indicating that the triplet energies of these compounds lie around 218–260 kJ mol^{-1}. Laser photolysis of NDSB in ethanol results in the formation of an interesting transient (zwitterion) species which is observed 500 ns after laser pulsing and quenched by oxygen (electron acceptor) and *N,N*-dimethylaniline (electron donor).[27] The transient is probably formed by an intramolecular electron transfer from the disilanyl to the nitro group in the triplet excited state in polar solvents such as ethanol and acetonitrile.

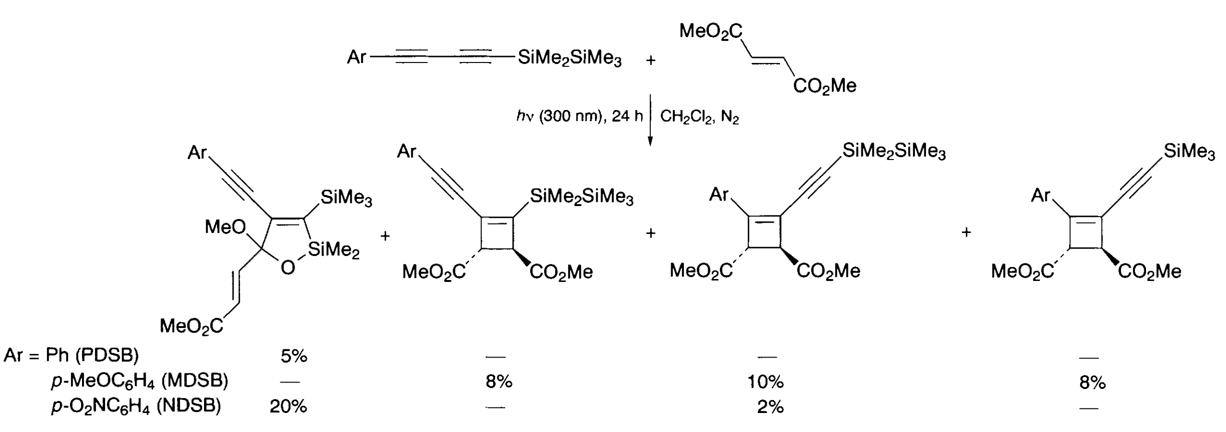
Photochemical reactions of 1-aryl-4-(pentamethyldisilanyl)-buta-1,3-diynes

Upon irradiation 1-aryl-4-(pentamethyldisilanyl)buta-1,3-diyne gives silacyclopropene intermediates in the singlet excited state except for NDSB, which gives silacyclopropenes from the triplet excited state.[27–29] Irradiation of 1-aryl-4-(pentamethyldisilanyl)buta-1,3-diynes (PDSB, NaDSB, and MDSB) in methanol gives 1 : 1 photoadducts *via* silacyclopropene intermediates (Scheme 9).[27]

The reaction of the silacyclopropene with methanol proceeds *via* an ionic reaction path.[27,28] On the other hand, photolysis of NDSB in methanol and ethanol results in the formation of 1-(*p*-



Scheme 10



Scheme 11

nitrophenyl)buta-1,3-diyne through C–Si bond cleavage.[27] This photoproduct is formed from the triplet excited state of NDSB, and the plausible reaction mechanism involves an intramolecular electron-transfer to give a long-lived transient (zwitterion) species in polar solvents. The C–Si bond is cleaved homolytically from the transient, and the radical abstracts a hydrogen from the methyl group of methanol.

Irradiation of 1-aryl-4-(pentamethyldisilanyl)buta-1,3-diynes (PDSB, MDSB, NDSB) with acetone yields site specific and regioselective 1 : 1 adducts having 1-oxa-2-sila-cyclopent-3-ene structure through two-atom insertion of acetone to silacyclopropene intermediates (Scheme 10).[29]

Experiments to quench the triplet excited state of acetone selectively confirmed that the silacyclopropene formed from the photolysis of 1-aryl-4-(pentamethyldisilanyl)buta-1,3-diynes reacts with ground state acetone *via* the triplet excited state of the silacyclopropene, not the acetone triplet state. The triplet energy of the silacyclopropene lies around 62–68 kcal mol^{-1}.[28,29]

Photoreaction of 1-aryl-4-(pentamethyldisilanyl)buta-1,3-diynes (PDSB, MDSB, NDSB) with dimethyl fumarate gives two-atom insertion products *via* silacyclopropene intermediates and/or [2 + 2] photocycloaddition products (Scheme 11).[29]

MDSB, which has a electron-donating group, yields only [2 + 2] photocycloaddition products, while NDSB, which has a nitro group, gives both a two-atom insertion product *via* silacyclopropene intermediates and a [2 + 2] photocycloaddition product, the former in higher yields. These results can be attributed to the stabilization of silacyclopropene intermediates by substituents, and also to the nucleophilic character of the 1-aryl-4-(pentamethyldisilanyl)buta-1,3-diyne radicals in the [2 + 2] photocycloaddition reaction. The silacyclopropene formed from MDSB is rather unstable and the triplet radical has enhanced nucleophilic character due to the electron donating methoxy group; therefore only [2 + 2] photocycloaddition products are formed. On the other hand, in NDSB, due to the electron withdrawing nitro group, silacyclopropene is stable and the triplet radical has sustained nucleophilic character to give a two-atom insertion product in high yields *via* silacyclopropene intermediate. The high efficiency of intersystem crossing may play another important role.

In conclusion, the triplet excited states of conjugated poliynes can be explained by cumulene-type diradical having nucleophilic character. The electronic distribution of excited states of conjugated polyynes is significantly influenced by the number of conjugated triple bonds and terminal groups. Further studies on the geometry and properties of the excited states of conjugated polyynes are in progress in our laboratory.

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