# Mechanistic Studies on the Photohydration of 1-Aryl-5,5-dimethyl-1,3-hexadiynes

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We have recently shown that irradiation of 1-aryl-5,5-dimethyl-1,3-hexadiynes substituted by other than nitro group in aqueous sulfuric acid yielded two types of alkynyl and allenyl ketones through both $S_1$ and $T_1$ excited states while nitro-substituted diynes gave only allenyl ketones *via* $T_1$ excited states (Scheme 1).[1] The diynes substituted by electron-withdrawing group such as p- $CO_2CH_3$, m- and p- $CF_3$ gave only type C allenyl ketones while diynes which have electron-donating groups such as p- $OCH_3$ yielded type D allenyl ketones regiospecifically.

In this paper we report substituent effects on the photohydration of 1-aryl-5,5-dimethyl-1,3-hexadiynes focusing on the multiplicity of the reactive excited state.

9-Fluorenone-1-carboxylic acid ($E_T$=50.0 kcal mol$^{-1}$)[2] efficiently quenched the photohydration of 1- (p- methoxy-carbonylphenyl)-5,5-dimethyl-1,3-hexadiyne (p- MCPDHD), 1- (p- methoxyphenyl)-5,5-dimethyl-1,3-hexadiyne (p- MPDHD), 1- (m- trifluoromethylphenyl)-5,5-dimethyl-1,3-hexadiyne (m- TPDHD), and 1- (p- rifluoromethylphenyl)-5,5-dimethyl-1,3-hexadiyne (p- TPDHD). The Stern-Volmer plots for the three photohydration products of p- MCPDHD (Type A, B and C) are curved reaching a plateau at about $\Phi^0_{pdt}/\Phi_{pdt}$=1.23, 1.48, and 1.54, respectively, supporting the contribution of both the singlet and triplet excited states to the photohydration (Figure 1).[3] Similar non-linear Stern-Volmer plots which have different convergence values ($\Phi^0_{pdt}/\Phi_{pdt}$= 1.18-3.5) were obtained for p- MPDHD, m- TPDHD, and p- TPDHD.

The total, singlet and triplet photohydration quantum yields ($\Phi^0$, $\Phi^0_s$ and $\Phi^0_T$) of the diynes were measured[4] and tabulated in Table 1 with the calculated and measured ratios of $\Phi^0_T/\Phi^0_s$. Most of the values of $\Phi^0_T/\Phi^0_s$ are less than

unity indicating that contribution of the singlet excited states to photohydration is greater than that of the triplet excited states.
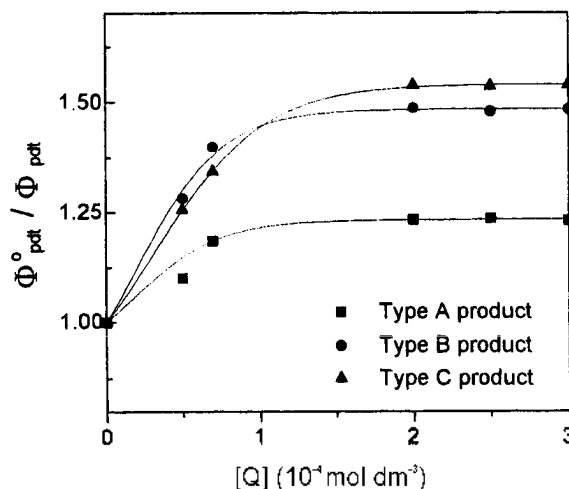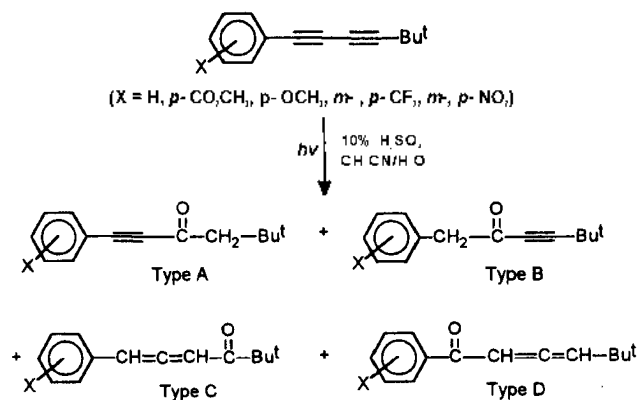


**Figure 1.** Stern-Volmer plots for the quenching of photohydration reactions of p- MCPDHD by 9-fluorenone-1-carboxylic acid.

**Table 1.** The quantum yields ($\Phi^0$, $\Phi^0_s$ and $\Phi^0_T$) for the photohydration reaction of 1-aryl-5,5-dimethyl-1,3-hexadiynes and calculated and measured $\Phi^0_T$, $\Phi^0_s$.

| X | Products[a] | $\Phi^0$ ($\times 10^{-2}$) | $\Phi^0_s$ ($\times 10^{-2}$) | $\Phi^0_T$ ($\times 10^{-2}$) | $\Phi^0_T/\Phi^0_s$ (calcd.) | $\Phi^0_T/\Phi^0_s$ (measd.) |
|---|---|---|---|---|---|---|
| p- $CO_2CH_3$ | Type A | 1.6 | 1.3 | 0.30 | 0.23 | 0.24 |
| | Type B | 1.6 | 1.1 | 0.47 | 0.48 | 0.44 |
| | Type C | 0.31 | 0.18 | 0.13 | 0.54 | 0.76 |
| p- $OCH_3$ | Type A | 3.7 | 3.1 | 0.60 | 0.18 | 0.20 |
| | Type B | 2.4 | 1.6 | 0.75 | 0.44 | 0.47 |
| | Type D | 4.9 | 2.6 | 2.3 | 0.89 | 0.89 |
| m- $CF_3$ | Type A | 0.64 | 0.29 | 0.35 | 1.0 | 1.2 |
| | Type B | 5.0 | 1.4 | 3.6 | 2.4 | 2.5 |
| | Type C | 0.13 | 0.10 | 0.030 | 0.28 | 0.30 |
| p- $CF_3$ | Type A | 0.60 | 0.29 | 0.31 | 0.95 | 1.1 |
| | Type B | 0.50 | 0.26 | 0.24 | 0.90 | 0.90 |
| | Type C | 0.32 | 0.20 | 0.12 | 0.48 | 0.60 |

[a] $\Phi^0_s$ was measured from the quantitative analyses by HPLC after irradiation in the presence of a triplet quencher, 9-fluorenone-1-carboxylic acid. Light intensity was measured by ferrioxalate actinometry. $\Phi^0_T = \Phi^0 - \Phi^0_s$, where $\Phi^0$ is total photohydration quantum yield which is obtained after irradiation in the absence of a triplet quencher. See Scheme 1. Calculated $\Phi^0_T/\Phi^0_s$ was from the convergence value of the corresponding Stern-Volmer plots for the quenching of photohydration reactions by 9-fluorenone-1-carboxylic acid.



(X = H, p- $CO_2CH_3$, p- $OCH_3$, m- , p- $CF_3$, m- , p- $NO_2$)

$hv$ | 10% $H_2SO_4$
$CH_3CN/H_2O$

Type A

Type B

Type C

Type D

**Scheme 1.**

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As reported previously, the preference of protonation site in the photohydration reaction is dependent on the substituent on the aryl ring. Table 2 shows the ratios of total, singlet and triplet quantum yields for the photohydration through protonation at $C_4$ or $C_1$. It is evident that $C_4$ is protonated predominantly rather than $C_1$ when X is electron-donating OCH$_3$ group (($\Phi$ ")$_{c4}$/ ($\Phi$ ")$_{c1}$=3.6). On the other hand, the protonation occurs mainly at $C_1$ when X is electron-withdrawing group (($\Phi$ ")$_{c4}$/ ($\Phi$ ")$_{c1}$<1) and the preference of $C_1$ protonation is greater in *meta-* substituted than in *para-*substituted diynes when X is CF$_3$. This is in conform with the "meta-effect".[5,7] The electron-withdrawing effect of substituents in the photohydration is in the order of *m-* CF$_3$> *p-* CF$_3$> *p-* CO$_2$CH$_3$.

The photohydration reactions of conjugated diynes normally proceed through cumulene-type singlet and/or triplet excited state.[8-10] In 1-aryl-1,3-diynes, charge separation of the lowest singlet excited state seems to be dichotomic ($C_1$
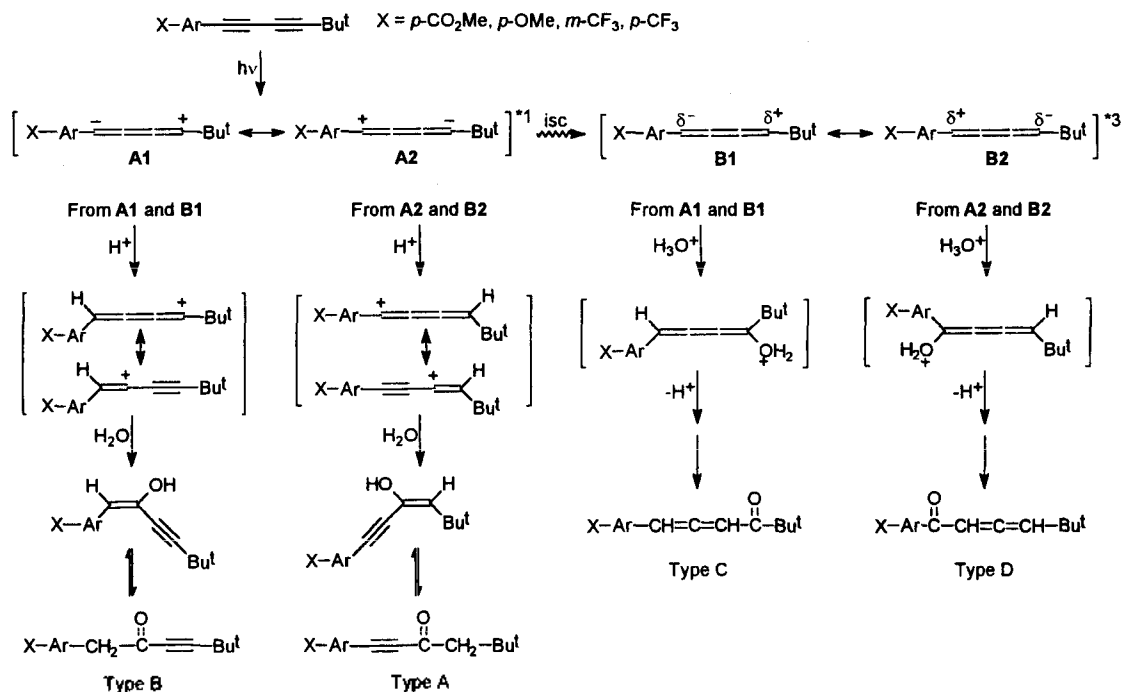
**Table 2.** The ratios of total, singlet and triplet quantum yields for the photohydration of 1-aryl-5,5-dimethyl-1,3-hexadiynes proceeding *via* protonation at $C_4$ or $C_1$

| X | ($\Phi$ )$_{c4}$/ ($\Phi$ )$_{c1}$[a] | ($\Phi'$ )$_{c4}$/ ($\Phi'$ )$_{c1}$[b] | ($\Phi''_r$)$_{c4}$/ ($\Phi''_r$)$_{c1}$[c] |
|---|---|---|---|
| *p-* CO$_2$CH$_3$ | 0.84 | 1.0 | 0.5 |
| *p-* OCH$_3$ | 3.6 | 3.6 | 3.9 |
| *m-* CF$_3$ | 0.12 | 0.19 | 0.097 |
| *p-* CF$_3$ | 0.73 | 0.63 | 0.86 |

[a] ($\Phi$ )$_{c4}$/ ($\Phi$ ")$_{c1}$=$\Phi$"(Type AandD) / $\Phi$"(Type B and C) where $\Phi$" is a total photohydration quantum yield shown in Table 1. For each type of photohydration product, see Scheme 1. [b]($\Phi'$)$_{c4}$/ ($\Phi'$)$_{c1}$ =$\Phi'_s$ (Type A and D) / $\Phi'_s$ (Type B and C) where $\Phi'_s$ is a photohydration quantum yield *via* singlet excited state. [c]($\Phi'_r$)$_{c4}$/ ($\Phi'_r$)$_{c1}$= $\Phi'_r$ (Type A and D)/ $\Phi'_r$ (TypeB and C) where $\Phi'_r$ is a photohydration quantum yield *via* triplet excited state.

or $C_4$ is positively charged) while $S_1$ state of arylacetylenes has zwitterionic character with positively charged $C_1$ and negatively charged $C_4$.[11,12] The $T_1$ state of 1-aryl-1,3-diynes is weakly charged[9] even though $T_1$ of acetylenes is normally considered to be similar to that of diradicals. The proposed mechanism for the reactions involves the protonation step being the rate determining step in the formation of alkynyl ketone products and synchronous H$_2$O[+] addition mechanism for the formation of allenyl ketones.[9,10]

A possible charge distribution of excited states is shown in Scheme 2. We can propose the A1 and A2 structures for $S_1$ state and B1 and B2 structures for $T_1$ state from the fact that four types of products are formed through both $S_1$ and $T_1$ excited states which are known to have a cumulene-type structure. Type A and B products ($C_4$ protonation products) would be formed from A2 and B2 and type B and C products ($C_1$ protonation products) would be formed from A1 and B1. The preference of $C_1$ protonation for electron-withdrawing groups and $C_4$ protonation for electron-donating groups is due to the degree of stabilization of negative charge on $C_1$ in the A1 structure. However, the stabilization effect on the diynes is much smaller than that of arylacetylene because of the delocalization of charge through the conjugated system and the regiospecific formation of alkynyl ketones is not observed. The exact reasons why the formation of allenyl ketone is regiospecific but that of alkynyl ketones is not and why allenyl ketones are only formed in the case of X= NO$_2$ are not clear. However, the results observed evidently show that regioselectivity and multiplicity of the reactive state in the photohydration of 1-aryl-5,5-dimethyl-1,3-hexadiynes are dependent on the substituents on the aryl ring. The substituents such as *p-* CO$_2$CH$_3$, *m-* and *p-* CF$_3$, *m-* and *p-* NO$_2$ groups showed electron-withdrawing effects on the photohydration reaction and the strength of electron-withdrawing effect was *m-* NO$_2$> *p-* NO$_2$> *m-* CF$_3$> *p-* CF$_3$> *p-* CO$_2$CH$_3$



**Scheme 2.**

while *p*-OCH₃ group showed electron-donating effect. Most of the substituents favored the singlet excited state in the photohydration of diynes but nitro group favored triplet excited state due to the efficient intersystem crossing.[13]

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# Synthesis and Ionophoric Properties of Mono-Penta Type Mixed-Functionalized Ligands Based-upon *p-tert*-Butylcalix[6]arene

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Ester, amide, and ether functional groups have been ingeniously utilized by nature for the construction of many bioactive molecules having ionophoric properties. Representative of such ingenuity are valinomycin and related antibiotics.[1] There have been many attempts to mimic the ionophoric properties of these natural antibiotics for the development of new host systems.[2] Calixarenes are one of the most attractive and widely studied compounds for this purpose and many effective ligating groups have been incorporated into their molecular frameworks.[3] However, in order to design more versatile calixarene-based host molecules useful for practical purposes, such as preparation of separation media and sensory materials, more elaborate structural transformations are necessary.[4] In view of this, we prepared a series of mono-penta type mixed ligating ionophores based upon pentaethyl ester of *p-tert*-butylcalix[6]arene and investigated their ionophoric behaviors toward alkali metal cations.

Mono-penta type mixed ligands were prepared by selective monoalkylation for the introduction of mono-part substituent followed by exhaustive alkylation with ethyl bromoacetate (Scheme). Monoalkylation was performed by reacting with one or two equivalents of required methyl bromoacetate, chloroacetone, or *N,N*-diethyl bromoacetamide in

the presence of $K_2CO_3$ in THF according to the reported procedure to obtain monomethyl or monobenzyl ether of *p-tert*-butylcalix[6]arene (yield: 42-58%).[5] The desired mixed-functionalized derivatives **2a-2c** were prepared by exhaustive alkylation of the appropriate mono-functionalized derivatives with a large excess of ethyl bromoacetate in refluxing acetone (yield: 69-82%).

To have a more versatile procedure for the synthesis of mono-penta type mixed ligands, the monophenol pentaester **3** was chosen as a key intermediate with the intent of utilizing benzyl ether moiety as a protecting group. Monobenzyl ether pentaethyl ester **2d** was prepared from monobenzyl ether of *p-tert*-butylcalix[6]arene[6] by exhaustive alkylation with ethyl bromoacetate ($K_2CO_3$/acetone). Subsequent removal of benzyl group by treatment with trimethylsilyl bromide[6] yield monophenol-pentaester **3** (65%). We attempted to introduce the desired functional group into the remaining phenol group of the *p-tert*-butylcalix[6]arene by alkylation with a suitable reagent but to no avail partly due to the steric congestion in monophenol **3**. For all the prepared ligands, ethoxycarbomethyl substituent was chosen as penta-part because of their widely investigated and relatively well-defined ionophoric properties toward many interesting guests.[7]