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Substituent effects on the photohydration of 1-aryl-5,5-dimethyl-1,3-hexadiynes

Sang Chul Shim [a,*], Yun Sook Chae [a], Eun Kyung Baek [a], Seung Ki Park [b]

[a] *Department of Chemistry, Korea Advanced Institute of Science and Technology, 373-1 Kusong-Dong, Yusung-Gu, Taejon, 305-701, South Korea*

[b] *Department of Chemistry, The University of Suwon, Kyungkido, 445-743, South Korea*

Abstract

The photohydration of 1-aryl-5,5-dimethyl-1,3-hexadiynes in aqueous sulfuric acid (10% H_2SO_4) yields two types of alkynyl (type A and type B) and allenyl ketones (type C and type D) through both S_1 and T_1 excited states when diynes are substituted by other than a nitro group. The electron-withdrawing substituents favor C_1 protonation giving type C allenyl ketones, while the electron-donating group yields C_4 protonation products, type D allenyl ketones. In contrast, nitro-substituted diynes gave only allenyl ketones (type C and type D) via T_1 excited states. © 1997 Elsevier Science S.A.

Keywords: Photohydration; Substituent effects

1. Introduction

The photohydration of substituted aromatic alkenes, alkynes, and allenes in aqueous sulfuric acid, in general, proceeds via a zwitterionic singlet excited state to give Markownikoff type addition products, as do the analogous thermal hydration reactions [1–4]. Exceptions are the nitro-substituted analogs which give anti-Markownikoff hydration products via a triplet excited state [2].

The photohydration reactions of 1-aryl-1,3-butadiynes have previously been reported from our laboratory [5–7]. 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_3O^+ addition mechanism for the formation of allenyl ketones.

The photohydration of 1-aryl-1,3-butadiynes is dependent on the substituent, but electron-donating or electron-withdrawing abilities of substituents in the excited state do not necessarily reflect their ground state σ values [8–11]. For example, the *meta*-fluoro group is strongly electron withdrawing ($\sigma^+ = 0.35$) in the ground state [12] but electron donating in the S_1 state ($\sigma^{hv} = -0.37$). The opposite appears to be true for the *para*-fluoro substituent [8]. In this paper we report substituent effects on the photohydration of 1-aryl-5,5-dimethyl-1,3-hexadiynes to give insight into the mechanism of the photohydration of conjugated 1-aryl-1,3-diynes.

2. Materials and methods

2.1. Instruments

^{1}H nuclear magnetic resonance (NMR) and ^{13}C NMR spectra were recorded on Bruker AM-300 and Bruker AC-200 spectrometers with chemical shifts being referenced against the signal of the solvent ($CDCl_3$). UV absorption spectra were recorded on a Shimadzu 3100S spectrophotometer. Fluorescence and phosphorescence emission spectra were recorded on a Perkin-Elmer LS-50 luminescence spectrophotometer with a gated photomultiplier detector at room temperature and 77 K with modification of the cell compartment. Melting points were determined in capillary tubes on a Thomas Hoover capillary melting point apparatus. Mass spectra were determined at 70 eV with a Hewlett-Packard 5985A GC/MS by the electron impact (EI) method. Fourier transform IR (FTIR) spectra were recorded on a Bomem MB-100 spectrophotometer in KBr pellets and NaCl cell. High-performance liquid chromatography (HPLC) was performed on a Waters Associates model 244 liquid chromatograph (Mildford, MA) equipped with a model 6000A solvent delivery system, model 440 UV absorbance detector fixed at 254 nm, and model U6K universal injector. Lichrosorb Si-60 column was used for preparative analyses.

2.2. Materials

3,3-Dimethyl-1-butyne, 4-iodoanisole, 3- and 4-iodobenzotrifluoride and 4-iodobenzoic acid were purchased from

* Corresponding author. Tel: +82 42 869 2815; fax: +82 42 869 2810; e-mail: scshim@sorak.kaist.ac.kr

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Aldrich Chemical Co. Diphenylacetylene (DPA), diphenyl-1,3-butadiyne (DPB), and 9-fluorenone-1-carboxylic acid were also purchased from Aldrich Chemical Co. and were used after recrystallization from methanol. Solvents of reagent grade for chromatography were used without further purification. Spectroscopic grade solvents (Tedia) were used for the HPLC measurements and absorption spectra.

2.3. Syntheses

1-(p-Methoxycarbonylphenyl)-5,5-dimethyl-1,3-hexadiyne (p-MCPDHD). *p*-Methoxycarbonylphenylacetylene and 1-bromo-3,3-dimethyl-1-butyne were prepared by the literature method [13,14]. The *p*-MCPDHD, a white solid, was prepared by the Cadiot–Chodkiewicz coupling method [15] and used after recrystallization from MeOH; m.p. 81–82 °C; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.91 (d, 2H), 7.50 (d, 2H), 3.88 (s, 3H), 1.26 (s, 9H) ppm; ^{13}C NMR (CD_3CN, 50 MHz) δ 166.8, 133.3, 131.2, 130.2, 127.1, 94.9, 77.2, 75.7, 64.0, 52.8, 30.4, 29.0 ppm; IR (NaCl) 2974, 2237, 1718, 1602, 1438, 1272, 1109, 766 cm^{-1}; UV (CH_3CN) λ_{max} 298 nm (ϵ = 26 700 M^{-1} cm^{-1}), 280 nm (ϵ = 29 800 M^{-1} cm^{-1}), 232 nm (ϵ = 19 500 M^{-1} cm^{-1}); MS *m/z* 240 (M^+, 29.7%), 225 (M^+-CH_3, 41.6%), 165 (M^+-$C_3H_7O_2$, 100.0%), 209 (M^+-CH_3O, 96.5%); HRMS (M^+)/EI calculated for $C_{16}H_{16}O_2$ 240.1150, found 240.1148.

1-(p-Methoxyphenyl)-5,5-dimethyl-1,3-hexadiyne (p-MPDHD). The *p*-MPDHD was obtained as a yellow oil by a method similar to that used for *p*-MCPDHD; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.35 (d, 2H), 6.81 (d, 2H), 3.76 (s, 3H), 1.26 (s, 9H) ppm; ^{13}C NMR ($CDCl_3$, 75 MHz) δ 160.0, 138.2, 133.9, 116.3, 114.0, 91.6, 76.1, 72.8, 63.9, 55.2, 30.5, 28.3 ppm; IR (NaCl) 2968, 2144, 1604, 1510, 1460, 1251, 1172, 831 cm^{-1}; UV (CH_3CN) λ_{max} 305 nm (ϵ = 23 000 M^{-1} cm^{-1}), 287 nm (ϵ = 23 800 M^{-1} cm^{-1}), 271 nm (ϵ = 14 300 M^{-1} cm^{-1}), 234 nm (ϵ = 19 300 M^{-1} cm^{-1}), 222 nm (ϵ = 15 300 M^{-1} cm^{-1}); MS *m/z* 212 (M^+, 73.3%), 197 (M^+-CH_3, 100.0%), 169 (M^+-C_2H_3O, 45.8%), 165 (M^+-C_2H_7O, 26.8%); HRMS (M^+)/EI calculated for $C_{15}H_{16}O$ 212.1201, found 212.1201.

1-(m-Trifluoromethylphenyl)-5,5-dimethyl-1,3-hexadiyne (m-TPDHD). The 5,5-dimethyl-1,3-hexadiyne was prepared by the Cadiot–Chodkiewicz coupling method [15]. The *m*-TPDHD was obtained as a yellow oil by the literature method [13,14]; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.69 (s, 1H), 7.58 (m, 2H), 7.44 (m, 1H), 1.28 (s, 9H) ppm; ^{13}C NMR ($CDCl_3$, 75 MHz) δ 135.4 (d, $^4J_{C\text{-}F}$ = 1.2 Hz) 131.3 (q, $^2J_{C\text{-}F}$ = 32.5 Hz) 129.2 (q, $^3J_{C\text{-}F}$ = 3.8 Hz), 129.0 (q, $^1J_{C\text{-}F}$ = 270.7 Hz), 125.2 (q, $^3J_{C\text{-}F}$ = 3.8 Hz), 123.3, 93.3, 75.8, 74.1, 63.5, 30.4, 28.3 ppm; IR (NaCl) 2973, 2240, 1585, 1487, 1434, 1344, 1300, 1134 cm^{-1}; UV (CH_3CN) λ_{max} 289 nm (ϵ = 21 500 M^{-1} cm^{-1}), 273 nm (ϵ = 26 500 M^{-1} cm^{-1}), 258 nm (ϵ = 16 400 M^{-1} cm^{-1}), 240 nm (ϵ = 11 300 M^{-1} cm^{-1}), 221 nm (ϵ = 46 900 M^{-1} cm^{-1}); MS *m/z* 250 (M^+, 31.3%), 235 (M^+-CH_3, 65.1%), 166 (M^+-$C_2H_3H_3$, 58.0%), 165 (M^+-$C_2H_4F_3$, 100.0%); HRMS (M^+)/EI calculated for $C_{15}H_{13}F_3$ 250.0969, found 250.0964.

1-(p-Trifluoromethylphenyl)-5,5-dimethyl-1,3-hexadiyne (p-TPDHD). The *p*-TPDHD was obtained as a white solid by the same method used for *m*-TPDHD and recrystallized from MeOH; m.p. 78–79 °C; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.54 (s, 4H), 1.28 (s, 9H) ppm; ^{13}C NMR (CD_2Cl_2, 75 MHz) δ 133.2, 130.9 (q, $^2J_{C\text{-}F}$ = 32.5 Hz) 126.6, 126.2 (q, $^1J_{C\text{-}F}$ = 270.4 Hz), 125.8 (q, $^3J_{C\text{-}F}$ = 3.8 Hz), 94.3, 76.9, 74.6, 63.8, 30.6, 28.8 ppm; IR (NaCl) 2976, 2234, 1613, 1405, 1363, 1323, 1167, 1127 cm^{-1}; UV (CH_3CN) λ_{max} 293 nm (ϵ = 30 000 M^{-1} cm^{-1}), 276 nm (ϵ = 33 800 M^{-1} cm^{-1}), 261 nm (ϵ = 20 100 M^{-1} cm^{-1}), 247 nm (ϵ = 8570 M^{-1} cm^{-1}), 223 nm (ϵ = 50 400 M^{-1} cm^{-1}), 213 nm (ϵ = 38 100 M^{-1} cm^{-1}); MS *m/z* 250 (M^+, 37.3%), 235 (M^+-CH_3, 69.3%), 166 (M^+-$C_2H_3F_3$, 53.1%), 165 (M^+-$C_2H_4F_3$, 100.0%); HRMS (M^+)/EI calculated for $C_{15}H_{13}F_3$ 250.0969, found 250.0964.

Photohydration of 1-aryl-5,5-dimethyl-1,3-hexadiynes. Deaerated water–MeCN solutions (1:1 v/v; H_2SO_4 10% (v/v)) of 1-aryl-5,5-dimethyl-1,3-hexadiynes 2 mM were irradiated with 300 nm UV light in a Rayonet photochemical reactor, model RPR-208, equipped with RUL 300 nm lamps (Southern New England Ultraviolet Co.). After irradiation for 2 h, the reaction mixture was extracted with diethyl ether. The organic phase was dried over $MgSO_4$ and then concentrated under vacuum.

Photohydration of 1-(p-methoxycarbonylphenyl)-5,5-dimethyl-1,3-hexadiyne (p-MCPDPHD). The photoproducts (**4**–**6**) and the unreacted starting material were isolated in 13.0%, 9.0%, 4.0%, and 67.3% yields respectively, by silica gel column chromatography using *n*-hexane–diethyl ether (12/1, v/v) as an eluent. The products were purified by normal phase HPLC using the following conditions. Eluents: **4** *n*-hexane–diethyl ether (12/1, v/v); **5** and **6** *n*-hexane–diethyl ether (10/1, v/v). **4**: m.p. 53–54 °C; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 8.00 (d, 2H), 7.61 (d, 2H), 3.91 (s, 3H), 2.58 (s, 2H), 1.09 (s, 9H) ppm; ^{13}C NMR ($CDCl_3$, 50 MHz) δ 187.4, 166.1, 132.6, 131.6, 129.1, 124.6, 91.08, 88.38, 58.2, 52.4, 31.9, 29.8 ppm; IR (NaCl) 2955, 2206, 1727, 1668, 1606, 1436, 1278, 1074, 769 cm^{-1}; UV (CH_3CN) λ_{max} 280 nm (ϵ = 28 200 M^{-1} cm^{-1}); MS *m/z* 258 (M^+, 0.1%), 202 (M^+-C_4H_8, 50.9%), 187 (M^+-C_5H_{11}, 100.0%), 100 (M^+-$C_8H_{14}O_3$, 4.5%). **5**: m.p. 54–55 °C; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.97 (d, 2H), 7.32 (d, 2H), 3.89 (s, 3H), 3.83 (s, 2H), 1.17 (s, 9H) ppm; ^{13}C NMR ($CDCl_3$, 50 MHz) δ 184.5, 166.8, 138.6, 129.9, 129.8, 129.1, 104.4, 79.0, 52.1, 52.0, 29.8, 27.7 ppm; IR (NaCl) 2969, 2212, 1723, 1674, 1611, 1436, 1279, 1111 cm^{-1}; UV (CH_3CN) λ_{max} 233 nm (ϵ = 23 900 M^{-1} cm^{-1}); MS *m/z* 258 (M^+, 1.8%), 227 (M^+-CH_3O, 4.9%), 109 (M^+-$C_9H_9O_2$, 100.0%), 81 (M^+-$C_{10}H_9O_3$, 42.5%). **6**: oil ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.95 (d, 2H), 7.33 (d, 2H), 6.57 (d, 1H, *J* = 6.4 Hz), 6.46 (d, 1H, *J* = 6.4 Hz), 3.89 (s, 3H), 1.22 (s, 9H) ppm; ^{13}C NMR ($CDCl_3$, 75 MHz) δ 214.5, 200.2, 166.7, 136.3, 130.1, 129.4, 127.2, 97.6, 95.3, 52.1, 44.7, 26.6

ppm; IR (NaCl) 2957, 1938, 1723, 1608, 1436, 1280, 1109 cm^{-1}; UV (CH_3CN) λ_{max} 273 nm ($\epsilon = 20\,700\ M^{-1}\ cm^{-1}$); MS m/z 258 (M^+, 0.1%), 114 (M^+-$C_7H_{12}O_3$, 52.8%), 85 (M^+-$C_{11}H_9O_2$, 29.8%), 57 (M^+-$C_{12}H_9O_3$, 56.0%).

Photohydration of 1-(p-methoxyphenyl)-5,5-dimethyl-1,3-hexadiyne (p-MPDHD). The photoproducts (**7**–**9**) and the unreacted starting material were isolated in 8.5%, 5.0%, 5.0%, and 79.0% yields respectively, by silica gel column chromatography using *n*-hexane–diethyl ether (25/1, v/v) as an eluent. The products were purified by normal phase HPLC using the following conditions. Eluents: **7** and **8** *n*-hexane–diethyl ether (10/1, v/v); **9** *n*-hexane–diethyl ether (8/1, v/v). **7**: oil ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.47 (d, 2H), 6.87 (d, 2H), 3.80 (s, 3H), 2.54 (s, 2H), 1.08 (s, 9H) ppm; ^{13}C NMR ($CDCl_3$, 75 MHz) δ 187.6, 161.5, 134.9, 114.3, 111.9, 91.4, 89.5, 58.2, 55.3, 31.8, 29.8 ppm; IR (NaCl) 2954, 2193, 1659, 1603, 1511, 1466, 1255, 1170, 1088, 835 cm^{-1}; UV (CH_3CN) λ_{max} 303 nm ($\epsilon = 25\,900\ M^{-1}\ cm^{-1}$), 222 nm ($\epsilon = 13\,700\ M^{-1}\ cm^{-1}$); MS m/z 230 (M^+, 4.6%), 174 (M^+-C_4H_8, 33.8%), 159 (M^+-C_5H_{11}, 100.0%). **8**: oil ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.12 (d, 2H), 6.86 (d, 2H), 3.78 (s, 3H), 3.71 (s, 2H), 1.18 (s, 9H) ppm; ^{13}C NMR ($CDCl_3$, 75 MHz) δ 186.0, 158.8, 130.8, 125.5, 114.0, 103.7, 79.1, 55.2, 51.4, 29.7, 27.7 ppm; IR (NaCl) 2969, 2213, 1672, 1611, 1512, 1250, 1119, 1034 cm^{-1}; UV (CH_3CN) λ_{max} 275 nm ($\epsilon = 2770\ M^{-1}\ cm^{-1}$), 221 nm ($\epsilon = 22\,100\ M^{-1}\ cm^{-1}$); MS m/z 230 (M^+, 4.4%), 187 (M^+-C_2H_3O, 3.3%), 121 (M^+-C_7H_9O, 100.0%), 109 (M^+-C_8H_9O, 4.7%). **9**: oil ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.90 (d, 2H), 6.91 (d, 2H), 6.43 (d, 1H, $J = 6.1$ Hz), 5.62 (d, 1H, $J = 6.1$ Hz), 3.85 (s, 3H), 1.09 (s, 9H) ppm; ^{13}C NMR ($CDCl_3$, 75 MHz) δ 211.3, 189.6, 163.2, 130.9, 130.1, 113.4, 106.3, 95.3, 55.4, 30.0, 22.7 ppm; IR (NaCl) 2925, 1947, 1647, 1601, 1510, 1254, 1171 cm^{-1}; UV (CH_3CN) λ_{max} 288 nm ($\epsilon = 8700\ M^{-1}\ cm^{-1}$), 226 nm ($\epsilon = 9100\ M^{-1}\ cm^{-1}$); MS m/z 230 (M^+, 2.2%), 215 (M^+-CH_3, 2.3%), 135 (M^+-C_7H_{11}, 100.0%).

Photohydration of 1-(m-trifluoromethylphenyl)-5,5-dimethyl-1,3-hexadiyne (m-TPDHD). The photoproducts (**10**–**12**) and the unreacted starting material were isolated in 1.5%, 4.0%, 1.0%, and 78.5% yields respectively, by silica gel column chromatography using *n*-hexane as an eluent. The products were purified by normal phase HPLC using the following conditions. Eluents: **10** *n*-hexane–diethyl ether–methylene chloride (35/1/1, v/v/v); **11** and **12** *n*-hexane–diethyl ether–methylene chloride (30/1/1, v/v/v). **10**: oil ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.79 (s, 1H), 7.70 (m, 2H), 7.53 (m, 1H), 2.59 (s, 2H), 1.10 (s, 9H) ppm; ^{13}C NMR ($CDCl_3$, 75 MHz) δ 187.2, 135.8, 131.6 (q, $^2J_{C\text{-}F} = 32.9$ Hz), 129.5 (q, $^3J_{C\text{-}F} = 3.8$ Hz), 129.3, 127.1 (q, $^3J_{C\text{-}F} = 3.7$ Hz), 125.2 (q, $^1J_{C\text{-}F} = 270.8$ Hz), 121.2, 90.1, 87.6, 58.2, 31.9 29.8 ppm; IR (NaCl) 2958, 2206, 1669, 1480, 1434, 1334, 1134 cm^{-1}; UV (CH_3CN) λ_{max} 269 nm ($\epsilon = 15\,300\ M^{-1}\ cm^{-1}$) 200 nm ($\epsilon = 27\,600\ M^{-1}\ cm^{-1}$); MS m/z 268 (M^+, 0.6%), 212 (M^+-C_4H_8, 52.6%), 197 (M^+-C_5H_{11}, 100.0%), 184 (M^+-$C_2H_3F_3$, 7.2%), 183 (M^+-$C_2H_4F_3$, 2.6%). **11**: oil ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.42 (m, 4H), 3.83 (s, 2H), 1.17 (s, 9H) ppm; ^{13}C NMR ($CDCl_3$, 75 MHz) δ 184.5, 134.4, 133.2, 131.2 (q, $^2J_{C\text{-}F} = 32.0$ Hz) 129.0, 126.7 (q, $^3J_{C\text{-}F} = 3.8$ Hz), 125.8 (q, $^1J_{C\text{-}F} = 270.4$ Hz), 124.2 (q, $^3J_{C\text{-}F} = 3.7$ Hz), 104.8, 78.9, 51.9, 29.8, 27.7 ppm; IR (NaCl) 2974, 2212, 1676, 1452, 1332, 1188, 1128, 1077 cm^{-1}; UV (CH_3CN) λ_{max} 263 nm ($\epsilon = 14\,700\ M^{-1}\ cm^{-1}$), 206 nm ($\epsilon = 17\,600\ M^{-1}\ cm^{-1}$); MS m/z 268 (M^+, 0.3%), 159 (M^+-C_7H_9O, 52.6%), 109 (M^+-$C_8H_6F_3$, 100.0%), 81 (M^+-$C_9H_6OF_3$, 43.2%). **12**: oil ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.45 (m, 4H), 6.58 (d, 1H, $J = 6.4$ Hz), 6.48 (d, 1H, $J = 6.4$ Hz), 1.22 (s, 9H) ppm; ^{13}C NMR ($CDCl_3$, 75 MHz) δ 213.9, 203.4, 132.5, 131.6 (q, $^2J_{C\text{-}F} = 32.0$ Hz), 130.3, 129.33, 124.5 (q, $^3J_{C\text{-}F} = 3.7$ Hz), 123.9 (q, $^3J_{C\text{-}F} = 3.8$ Hz), 118.7 (q, $^1J_{C\text{-}F} = 270.8$ Hz), 97.3, 95.5, 44.6, 26.6 ppm; IR (NaCl) 2963, 1942, 1686, 1608, 1470, 1450, 1330, 1128, 1074 cm^{-1}; UV (CH_3CN) λ_{max} 250 nm ($\epsilon = 6000\ M^{-1}\ cm^{-1}$) 208 nm ($\epsilon = 14\,400\ M^{-1}\ cm^{-1}$); MS m/z 268 (M^+, 0.8%), 183 (M^+-C_5H_9O, 6.3%), 145 (M^+-$C_8H_{11}O$, 43.4%), 85 (M^+-$C_{10}H_6F_3$, 10.0%), 57 (M^+-$C_{11}H_6OF_3$, 30.8%).

Photohydration of 1-(p-trifluoromethylphenyl)-5,5-dimethyl-1,3-hexadiyne (p-TPDHD). The photoproducts (**13**–**15**) and the unreacted starting material were isolated in 2.5%, 2.5%, 1.0%, and 80.0% yields respectively, by silica gel column chromatography using *n*-hexane as an eluent. The products were purified by normal phase HPLC using the following conditions. Eluents: **13** *n*-hexane–diethyl ether–methylene chloride (40/1/1, v/v/v); **14** and **15** *n*-hexane–diethyl ether–methylene chloride (30/1/1, v/v/v). **13**: oil ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.63 (d, 4H), 2.59 (s, 2H), 1.10 (s, 9H) ppm; ^{13}C NMR ($CDCl_3$, 75 MHz) δ 187.3, 133.0, 132.3 (q, $^2J_{C\text{-}F} = 32.8$ Hz) 125.6 (q, $^3J_{C\text{-}F} = 3.8$ Hz), 125.3 (q, $^1J_{C\text{-}F} = 270.7$ Hz), 124.0, 90.6, 87.6, 58.2, 31.9, 29.8 ppm; IR (NaCl) 2955, 2209, 1669, 1324, 1171, 1132, 1065 cm^{-1}; UV (CH_3CN) λ_{max} 264 nm ($\epsilon = 17\,600\ M^{-1}\ cm^{-1}$); MS m/z 268 (M^+, 0.2%), 212 (M^+-C_4H_8, 59.1%), 197 (M^+-C_5H_{11}, 100.0%), 184 (M^+-$C_2H_3F_3$, 6.6%), 183 (M^+-$C_2H_4F_3$, 2.0%). **14**: m.p. 44–45 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.57 (d, 2H), 7.36 (d, 2H), 3.84 (s, 2H), 1.18 (s, 9H) ppm; ^{13}C NMR ($CDCl_3$, 75 MHz) δ 1.84, 137.4, 130.2, 129.8 (q, $^2J_{C\text{-}F} = 32.3$ Hz) 125.9 (q, $^1J_{C\text{-}F} = 270.4$ Hz), 125.5 (q, $^3J_{C\text{-}F} = 3.7$ Hz), 104.6, 79.0, 51.8, 29.8, 27.7 ppm; IR (NaCl) 2980, 2210, 1674, 1412, 1326, 1161, 1114, 1067 cm^{-1}; UV (CH_3CN) λ_{max} 217 nm ($\epsilon = 18\,700\ M^{-1}\ cm^{-1}$); MS m/z 268 (M^+, 0.5%), 159 (M^+-C_7H_9O, 10.9%), 109 (M^+-$C_8H_6F_3$, 100.0%), 81 (M^+-$C_9H_6OF_3$, 38.8%). **15**: oil ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.55 (d, 2H), 7.38 (d, 2H), 6.58 (d, 1H, $J = 6.4$ Hz), 6.47 (d, 1H, $J = 6.4$ Hz), 1.23 (s, 9H) ppm; ^{13}C NMR ($CDCl_3$, 75 MHz) δ 214.2, 203.3, 135.4, 130.0 (q, $^2J_{C\text{-}F} = 32.3$ Hz), 127.4, 125.9 (q, $^3J_{C\text{-}F} = 3.8$ Hz), 122.2 (q, $^1J_{C\text{-}F} = 270.5$ Hz), 97.3, 95.3, 44.6, 26.6 ppm; IR (NaCl) 2953, 1941, 1678, 1616, 1325, 1165, 1124, 1068 cm^{-1}; UV (CH_3CN) λ_{max} 257 nm ($\epsilon = 8670\ M^{-1}\ cm^{-1}$), 208 nm ($\epsilon = 15\,000\ M^{-1}\ cm^{-1}$); MS m/z 268 (M^+, 4.1%), 183

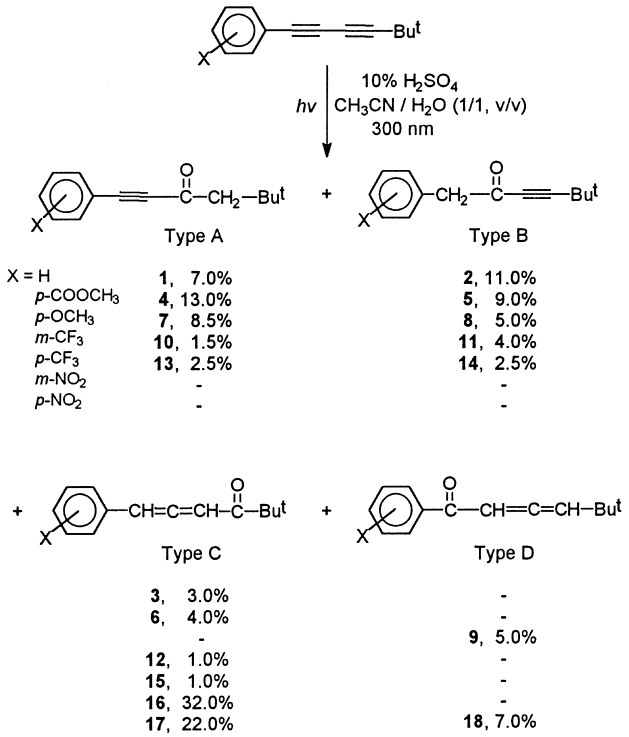
(M^+-C_5H_9O, 33.3%), 145 (M^+-$C_8H_{11}O$, 31.5%), 85 (M^+-$C_{10}H_6F_3$, 40.1%), 57 (M^+-$C_{11}H_6OF_3$, 100.0%).

Effect of 9-fluorenone-1-carboxylic acid. Sample solutions (MeCN–water (1/1, v/v), 4 ml) containing various concentrations (0–3.0×10^{-4} mol dm^{-3}) of 9-fluorenone-1-carboxylic acid were deaerated by Ar bubbling and irradiated for 3 min with 300 nm UV light in a Rayonet photochemical reactor, model RPR-208, equipped with RUL 300 nm lamps. DPA (for *p*-MCPDHD and *p*-MPDHD) and DPB (for *m*-TPDHD and *p*-TPDHD) were used as internal standards. The quantitative analyses were carried out by HPLC under the following conditions. Column, Lichrosorb RP-18 (5 μm). Eluents: *p*-MCPDHD and *p*-MPDHD methanol–water (2/1, v/v); *m*-TPDHD methanol–water (3/1, v/v); *p*-TPDHD methanol–water (5/2, v/v).

3. Results and discussion

The photohydration of 1-(*m*-nitrophenyl)-5,5-dimethyl-1,3-hexadiyne (*m*-NDHD) and its *para*-analog (*p*-NDHD) was previously reported to give allenyl ketones (**16** for *m*-NDHD and **17, 18** for *p*-NDHD) unlike that of 1-phenyl-5,5-dimethyl-1,3-hexadiyne (PDHD) which gave the two alkynyl ketones (**1** and **2**) and an allenyl ketone **3** as photohydration products [6,7].

Irradiation of 1-aryl-5,5-dimethyl-1,3-hexadiynes in 10% sulfuric acid acetonitrile–water (1/1, v/v) solution afforded four types of hydration product (Scheme 1).



Scheme 1. Photohydration of 1-aryl-5,5-dimethyl-1,3-hexadiynes. The yields are the isolated yields of the corresponding photohydration products.

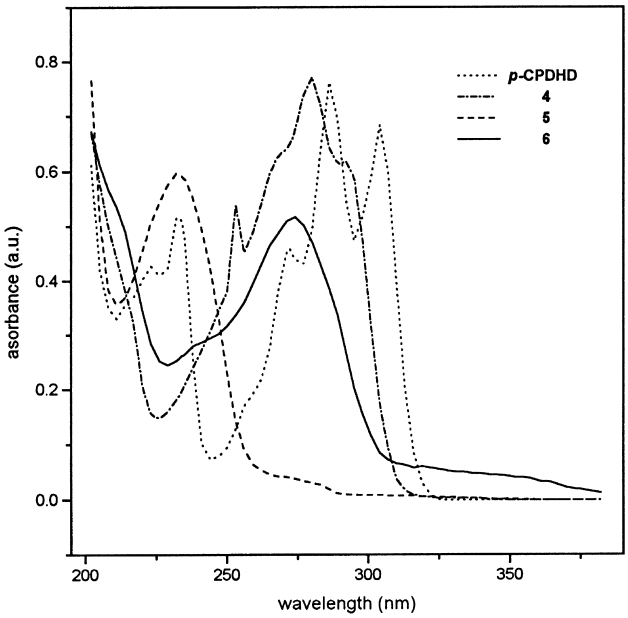


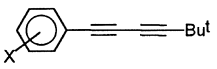
Fig. 1. The UV absorption spectra of *p*-MCPDHD and photohydration products (**4, 5** and **6**) in acetonitrile.

The reaction is stopped after 2 h irradiation to avoid secondary photoreactions. Most of the unreacted starting material was recovered (ca. 67.3%–80.0%) along with a small amount of unidentified byproducts which are probably oligomers and decomposition products to account for the material balance of the reactions.

The structure of the photoproducts was determined by various spectroscopic analyses. The UV absorption spectra (Fig. 1) of *p*-MCPDHD and hydration products (**4, 5** and **6**) in acetonitrile show that the absorption maximum of **4** is slightly longer than that of **6** which in turn is at a longer wavelength than **5** owing to the extended conjugation. The same phenomena were observed for *m*-TPDHD and *p*-TPDHD. The type A and type B products show the methylene proton peaks at δ 2.54–2.59 and 3.71–3.84 ppm in ^{1}H NMR respectively. The difference in chemical shifts clearly differentiates the position of protonation in the diacetylene. The ^{13}C NMR spectra show one carbonyl carbon and two acetylenyl carbon peaks. The type C and type D photoproducts are conjugated allenyl ketones. Asymmetric absorption bands of the allene moiety in the IR spectra appear at 1938–1942 and 1947 cm^{-1} for type C and type D products respectively. In the ^{1}H NMR spectra, the allenic protons of type C products appear at δ 6.5–6.6 ppm (J = 6.4 Hz) and those of type D at δ 5.6–6.4 ppm (J = 6.1 Hz) [16,17]. The presence of the allene moiety of **6, 12** and **15** is strongly supported by an extreme down-field resonance peak of the central carbon atom at δ 212–215 ppm and carbonyl peaks at δ 200–203 ppm. The M^+ peaks at 258, 230, 268, and 268, indicate the photohydration products to be formed by addition of one molecule of water to *p*-MCPDHD, *p*-MPDHD, *m*-TPDHD, and *p*-TPDHD respectively.

None of the starting materials shows fluorescence in ethanol at room temperature. The phosphorescence emission

Table 1
The phosphorescence emission of 1-aryl-5,5-dimethyl-1,3-hexadiynes in ethanol



X	λ_{ex} (nm) [a]	λ^{p}_{max} (nm) [b]	E_T (kcal mol^{-1}) [c]
p-$COOCH_3$	297.0	469.0	61.0
p-OCH_3	305.0	446.5	64.1
m-CF_3	289.0	447.0	64.0
p-CF_3	293.0	449.5	63.6
p-NO_2 [d]	319.0	491.0	58.0

[a] The longest λ_{max} in the UV–visible absorption spectra.
[b] The shortest λ^{p}_{max} of the emission band assigned as the 0-0 band.
[c] Calculated from the λ^{p}_{max}.
[d] Ref. [6].

data of 1-aryl-5,5-dimethyl-1,3-hexadiynes in ethanol at 77 K are shown in Table 1. Triplet energies of substituted diynes are similar to each other ($E_T = 61.0$–64.1 kcal mol^{-1}) but that of *p*-NDHD is relatively low ($E_T = 58.0$ kcal mol^{-1}) indicating that the nitro group stabilizes the T_1 state better than other substituents. We did not attempt to deduce substituent constants in the excited states by spectral analysis.

To investigate the triplet reaction pathway of photohydration, a triplet quenching experiment with 9-fluorenone-1-carboxylic acid ($E_T = 50.0$ kcal mol^{-1}) [18] was carried out. The Stern–Volmer plots for three photohydration products, **4**, **5**, and **6** (Fig. 2) are curved reaching a plateau at about $\Phi^{o}_{pdt}/\Phi_{pdt} = 1.23$, 1.48, and 1.54 respectively, supporting the contribution of both singlet and triplet excited states. Similar non-linear Stern–Volmer plots were also obtained for *p*-MPDHD, *m*-TPDHD, and *p*-TPDHD. The ratios of the quantum yields of photohydration reaction proceeding from both the singlet and triplet excited state ($\Phi^{T*}_{pdt}/\Phi^{S*}_{pdt}$) can be obtained from the convergence value of the corresponding non-linear Stern–Volmer plots [19] and the calculated ratios for the photohydration products are tabulated in Table 2. Most of the values of ($\Phi^{T*}_{pdt}/\Phi^{S*}_{pdt}$) except those of **13** and **14** are less than unity, indicating that the contribution of singlet excited states is greater than that of triplet excited states.

The photohydration of PDHD, *p*-MCPDHD, *p*-MPDHD, *m*-TPDHD, and *p*-TPDHD gives two types of alkynyl ketone and one of the two types of allenyl ketone depending on the

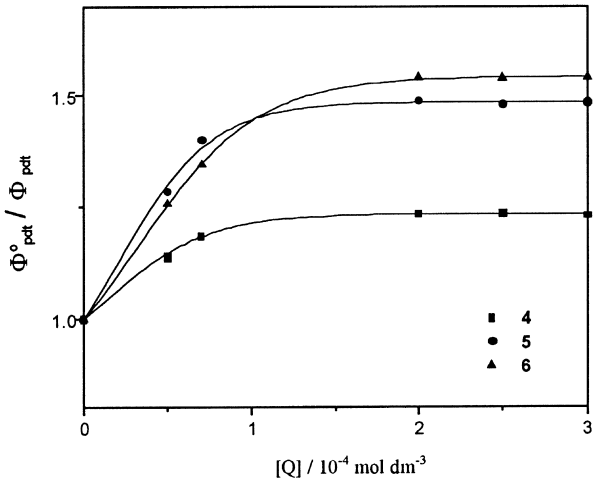
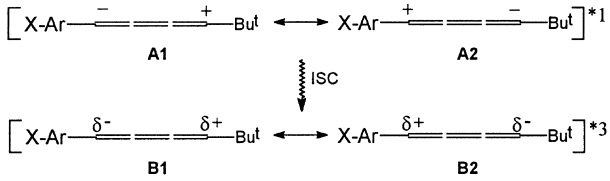


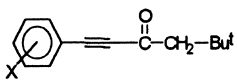
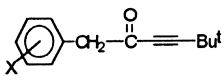
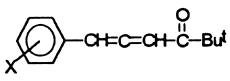
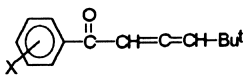
Fig. 2. Stern–Volmer plot of the quenching of the photohydration reaction of *p*-MCPDHD by 9-fluorenone-1-carboxylic acid.

substituents via both singlet and triplet excited states, while only allenyl ketones are produced in the photohydration of *m*- and *p*-NDHD which was reported to proceed via triplet excited states [6,7]. The S_1 state of these molecules probably possesses a high degree of charge-transfer character, while the T_1 state possesses lower charge-transfer character than the S_1 state [5]. Electron-withdrawing substituents such as *p*-methoxycarbonyl, *m*-, *p*-trifluoromethyl, and *m*-, *p*-nitro groups favor protonation on C_1 (type B and C products) owing to the stabilization of negative charge on C_1 in both **A1** and **B1** structures as shown below. However, the electron-donating *p*-methoxy group favors protonation on C_4 (type A and D products) since the substituent stabilizes **A2** and **B2** structures.



The regiospecific formation of allenyl ketones **6**, **9**, **12**, and **15** from *p*-MCPDHD, *p*-MPDHD, *m*-TPDHD, and *p*-TPDHD respectively, can be due to the larger contribution of S_1 state than the T_1 state in the reaction ($\Phi^{T*}_{pdt}/\Phi^{S*}_{pdt}$ value less than unity in Table 2). The stabilization effect of negative charge on C_1 in the **A1** structure by COOMe, OMe, and CF_3

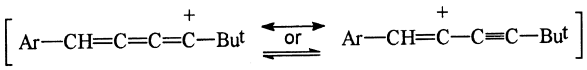
Table 2
The calculated $\Phi^{T*}_{pdt}/\Phi^{S*}_{pdt}$ for the photohydration reaction of 1-aryl-5,5-dimethyl-1,3-hexadiynes

Substituent	Type A	Type B	Type C	Type D
				
p-COOMe	0.23	0.48	0.54	—
p-OMe	0.18	0.44	—	0.89
m-CF_3	1.01	2.44	0.28	—
p-CF_3	0.95	0.90	0.48	—

groups is large enough to give type C allenyl ketones regiospecifically.

The photohydration of *m*-NDHD gives **16** regiospecifically while *p*-NDHD gives both **17** and **18**. The *meta*-nitro group has been shown to be more electron-withdrawing than the *para*-nitro group in the excited state relative to the ground state (*meta* effect) [20,21]. Therefore, a larger contribution of **B1** than **B2** to the triplet excited state of *m*-NDHD is expected leading to the regiospecific C_1 protonation and formation of **16**.

Although the diynes substituted by other than the nitro group also show a strong regiospecific preference for the formation of allenyl ketones, the nitro group in the *para* position, a strong electron-withdrawing group, does not show regiospecificity. This seemingly inconsistent result can be rationalized by the involvement of different multiplicities of excited states which is supported by quenching experiments. The charge stabilization effect of substituents will be greater when the reaction proceeds through the S_1 excited state than T_1 excited state since charge-separation of the S_1 excited state is relatively greater than that of T_1 excited state. The photohydration of *p*-NDHD proceeds via the T_1 excited state only and the products **17** and **18** are formed through both **B1** and **B2** structures not through **A1** or **A2** structures. Although the *para*-nitro group is a strong electron-withdrawing group, regiospecific formation of the allenyl ketone cannot be achieved since the charge stabilization effect on both **B1** and **B2**, which are less charge-separated than **A1** and **A2**, is not efficient. However, the electron-withdrawing nitro group still gives allenyl ketone **17** regioselectivity (22% of **17** vs. 7% of **18**) which is formed by C_1 protonation of **B1**.



Cations formed by a protonation can rearrange into other carbons competing with addition of water. If the rearrangement is faster than water addition, alkynyl ketones are obtained as major photoproducts. Substituents other than the nitro group give alkynyl ketones as major products and allenyl ketones as minor products. On the contrary, the addition of water is much faster than the rearrangement in the case of NDHD to give only allenyl ketones. This is in agreement with the proposed mechanism for the photohydration of PDHD and NDHD. The photohydration of PDHD proceeds through both S_1 and T_1 excited states and two kinds of mechanism are involved, the rate-determining protonation for alkynyl ketones and synchronous addition of H_3O^+ for allenyl ketones. However, NDHD reacts via the T_1 state only and the allenyl ketones are produced by the synchronous addition mechanism showing *meta* effect [6,7].

The substituent effect in the excited states is very complicated since the electronic structure, inductive and mesomeric effect, and conformational changes are not well defined in the excited states compared with those of the ground state. The multiplicity of the excited states makes it more complex and it is very difficult to derive any quantitative substituent constants in the photohydration reactions.

Acknowledgements

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