

THE PHOTOHYDRATION OF 1-(NITROPHENYL)-5,5-DIMETHYL-1,3-HEXADIYNES: THE NITRO SUBSTITUENT EFFECT ON THE EXCITED STATES OF DIACETYLENES

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Abstract — The photohydration of 1-(*m*-nitrophenyl)-5,5-dimethyl-1,3-hexadiyne (*m*-NDHD) affords allenyl ketone compound (**1**) via triplet excited state which is converted into β -dicarbonyl compound (**2**) through thermal hydration. The allenyl ketone is formed by the synchronous addition of water with protonation at C₁ indicating that *m*-NDHD has the reverse polarization and greater electron withdrawing effect in the triplet excited state in comparison with *p*-NDHD.

INTRODUCTION

The photohydration of aromatic alkenes, alkynes and allenes in aqueous sulfuric acid has been previously investigated.¹⁻⁴ In general, these photohydration reactions are acid catalyzed and proceed via the S₁ state to give regiospecific hydration products in the Markownikoff sense, as do the analogous thermal hydration reactions. Exceptions are the *m*- and *p*-nitro derivatives, which add water via the T₁ state in the anti-Markownikoff directions.² The formation of *anti*-Markownikoff addition products is due to the enhanced electron-withdrawing character of nitro groups in the triplet excited state.

The photohydration of 1-(1-naphthyl)-1,3-butadiynes and 1-(*p*-nitrophenyl)-5,5-dimethyl-1,3-hexadiyne (*p*-NDHD) has previously been investigated in our laboratory.^{5,6} The protonation of *p*-NDHD gives two allenyl ketone compounds as primary products and two β -dicarbonyl compounds. The enhanced electron withdrawing character of nitro group in the triplet excited state of *p*-NDHD had almost no effect on the formation of hydration products. The enhancement of electron withdrawing character is greater in the *m*-isomer than the *p*-isomer.^{4,7} In this paper, we report the photohydration

of 1-(*m*-nitrophenyl)-5,5-dimethyl-1,3-hexadiyne (*m*-NDHD) in comparison with that of *p*-NDHD.

MATERIALS AND METHODS

General Methods. ¹H NMR and ¹³C NMR spectra were recorded on Bruker AM-300 and Bruker AC-200 spectrometers with chemical shifts being referenced against TMS as an internal standard or the signal of the solvent CDCl₃. Mass spectra were determined at 70 eV with a Hewlett-Packard 5985A GC/MS by the electron impact (EI) method. High-performance liquid chromatography was performed on a Waters Associates Model 244 liquid chromatography (Mildford, MA) equipped with a Model 6000A solvent delivery system, a Model 440 UV absorbance detector fixed at 254 nm, and a Model U6K universal injector. A Lichrosorb Si-60 column was used for preparative analyses.

Solvents of reagent grade for chromatography were used without further purification. Spectroscopic grade solvents (Tedia) were used for HPLC and absorption spectra.

Synthesis of 1-(*m*-nitrophenyl)-5,5-dimethyl-1,3-hexadiyne (*m*-NDHD). *m*-Nitrophenylacetylene and 1-bromo-3,3-dimethyl-1-butyne were prepared by the literature method.^{8,9} The *m*-NDHD was prepared by the Cadiot-Chodkiewicz coupling method¹⁰ and recrystallized from MeOH. *m*-NDHD; ¹H NMR (CDCl₃, 200 MHz) δ 8.02(m, 2H), 7.60(m, 1H), 7.41(t, 1H), 1.20(s, 9H) ppm; ¹³C NMR (CDCl₃, 50 MHz) δ 147.7, 137.5, 129.2, 126.6, 123.7, 123.0, 93.6, 76.6, 72.8, 63.1, 30.0, 28.0 ppm; IR (NaCl) 2969, 2242, 1534, 1456 cm⁻¹; UV (CH₂CN) λ_{\max} 289, 272, 258 nm; MS *m/z* 227(M⁺, 29.5%), 212(M⁺-CH₃, 35.2%), 165(M⁺-CH₃NO₂, 100%), 166(M⁺-CH₃NO₂, 88.5%); HRMS (M⁺) calcd for C_{subscript}14H₁₃NO₂ 227.0946, found 227.0949.

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† **Abbreviations** : Dedicated to Professor Pill-Soon Song for the occasion of his 60th birthday.

Photohydration of 1-(m-nitrophenyl)-5,5-dimethyl-1,3-hexadiyne (m-NDHD). Deaerated 2 mM solutions (water-MeCN)[1:1, v/v; H₂SO₄ 5% (v/v)] of *m*-NDHD were irradiated with 300 nm UV light in a Rayonet photochemical reactor, Model RPR-208, equipped with RUL 300 nm lamps. After irradiation for 30 min, the reaction mixture was extracted with diethyl ether. The organic phase was dried over MgSO₄, concentrated and separated by silica gel column chromatography using eluent; n-hexane/diethyl ether = 4/1 (v/v). The products were purified by normal phase HPLC using n-hexane/diethyl ether/methylene chloride (8/1/1, v/v/v) eluent. The compound **1** and **2** are obtained as oil. **1**: ¹H NMR (CDCl₃, 200 MHz) δ 8.12(m, 2H), 7.55(m, 2H), 6.66(d, 1H, J=6.4 Hz), 6.56(d, 1H, J=6.4 Hz), 1.25(s, 9H) ppm; ¹³C NMR (CDCl₃, 75 MHz) δ 214.0, 203.0, 148.7, 133.7, 132.8, 129.7, 122.5, 121.8, 96.9, 95.6, 44.6, 26.5 ppm; IR (NaCl) 2969, 1942, 1677, 1530, 1477 cm⁻¹; UV (CH₂CN) λ_{max} 238 nm; MS *m/z*: 245(M⁺, 2.8%), 114(M⁺-C₈H₉NO₂, 18.2%), 85(M⁺-C₇H₈NO₂, 34.6%); HRMS (M⁺) calcd for C₁₄H₁₇NO, 245.1052, found 245.0815. **2**: ¹H NMR (CDCl₃, 200 MHz) δ 15.56(s, 1H), 8.10(m, 2H), 7.52(m, 2H), 5.62(s, 1H), 3.70(s, 2H), 1.13(s, 9H), ppm. superscript C NMR (CDCl₃subscript, 75 MHz) δ 200.2, 191.9, 148.3, 137.1, 135.6, 129.4, 124.3, 122.1, 95.4, 45.0, 39.0, 27.2 ppm; IR (NaCl) 2969, 1598, 1530, 1479 cm⁻¹; UV λ_{max} (CH₂CN) 272 nm; MS *m/z*: 263(M⁺, 0.4%), 206(M⁺-C₈H₉, 20.8%), 136(M⁺-C₇H₇O₂, 13.8%), 127(M⁺-C₇H₇NO₂, 100%); HRMS (M⁺) calcd for C₁₄H₁₇NO, 263.1158, found 263.1151.

Thermal hydration. A solution of 50 mg *m*-NDHD in dioxane (20 ml) was added dropwise to 100 ml of 70 % aq. H₂SO₄ with rapid stirring. The solution was then stirred for 40 min to obtain a colored solution which was saturated with salt, extracted with diethyl ether, washed, dried and evaporated to get the crude product. The product was purified by normal phase HPLC using the eluent, n-hexane/ethyl ether (15/1, v/v). **3**: ¹H NMR (CDCl₃, 300 MHz) δ 8.37(m, 1H), 8.27(m, 1H), 7.84(m, 1H), 7.58(t, 1H), 2.59(s, 2H), 1.09(s, 9H) ppm; ¹³C NMR (CDCl₃, 75 MHz) δ 187.0, 148.1, 138.2, 129.8, 127.4, 125.1, 122.0, 90.5, 86.1, 58.1, 32.0, 29.7 ppm; IR (NaCl) 2954, 2206, 1689, 1534, 1473 cm⁻¹; UV λ_{max} (CH₂CN) 259 nm; MS *m/z*: 245(M⁺, 0.2%), 189(M⁺-C₈H₉, 100%), 174(M⁺-C₇H₁₁, 86.9%), 128(M⁺-C₇H₇NO₂, 42.1%); HRMS (M⁺) calcd for C₁₄H₁₇NO, 245.1052, found 245.1058.

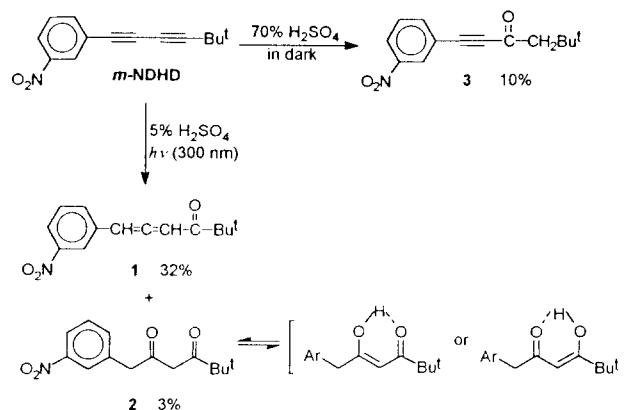
Effect of the medium acidity. Samples of acetonitrile-water (1/1, v/v) solutions of *m*-NDHD (2 mM) in the presence of various concentrations of sulfuric acid (0-30%) were purged with argon gas and irradiated with 350 nm UV light. Quantitative analyses were carried out by reverse phase HPLC after saturation with NaCl utilizing the following conditions, column: Lichrosorb RP-18(5μM), eluent; methanol-water (6/1, v/v), and internal standard; diphenyl acetylene (Aldrich).

Oxygen effect. The relative quantum yields of the photoreaction of *m*-NDHD (2μM) to give photoadduct (**1**) were measured in the presence of oxygen (bubbled with oxygen) and compared with that obtained in the deaerated

condition (degassed by N₂ bubbling). The samples were irradiated for 5 min with 350 nm UV light in a Rayonet photochemical reactor, Model RPR-208, equipped with RUL 350 nm lamps. The quantitative analysis was carried out by reverse phase HPLC after saturation with NaCl.

RESULTS AND DISCUSSION

Two photohydration products (**1** and **2**) were obtained on irradiation of 1-(*m*-nitrophenyl)-5,5-dimethyl-1,3-hexadiyne (*m*-NDHD) in CH₂CN-H₂O (1/1, v/v) (5% sulfuric acid) (Scheme 1).



In the ¹H NMR spectra of compound **1**, the allenic protons appear at δ 6.56 and 6.66 ppm. The allenyl ketone structure is supported by the central carbon atom of allene at δ 214 ppm and the carbonyl peak at δ 203 ppm in ¹³C NMR. The characteristic absorption band of allene moiety in IR also appears at 1942 cm⁻¹. In mass spectra, the M⁺ peak at 245 indicates that the photohydration product is formed by the addition of one molecule of water to the diacetylene.

In ¹H NMR spectra of compound **2**, the resonance peak of hydrogen bonded hydroxyl proton in the enol form of β-dicarbonyl compound appears as a broad singlet at δ 15.56 ppm. The olefinic proton appears at δ 5.62 ppm. The β-dicarbonyl moiety is confirmed by the presence of two carbonyl peaks at δ 200.2 and 191.9 ppm in ¹³C NMR. The product (**2**) shows the M⁺ peak at 263 indicating that product (**2**) is formed by the addition of two water molecules to the diacetylene.

The photohydration of *m*-NDHD at 5°C gave only the primary photohydration product **1**, and the hydration of compound **1** in dark at room temperature gives compound **2** indicating that compound **2** is a secondary product formed through a thermal process.

The thermal hydration of allenyl ketone has already been reported in the study on the photohydration of 1-(*p*-nitrophenyl)-5,5-dimethyl-1,3-hexadiyne.⁶

The thermal hydration of *m*-NDHD at ambient temperature in 70 % aqueous sulfuric acid yields only the compound **3** (Scheme 1). In the ¹³C NMR spectra, two acetylenic peaks and one carbonyl peak were observed. The peak at 2.59 ppm in ¹H NMR spectra indicates that the compound **3** is formed via the protonation at C₄ carbon. Thermal hydration of conjugated dialkyl substituted diacetylenes has shown

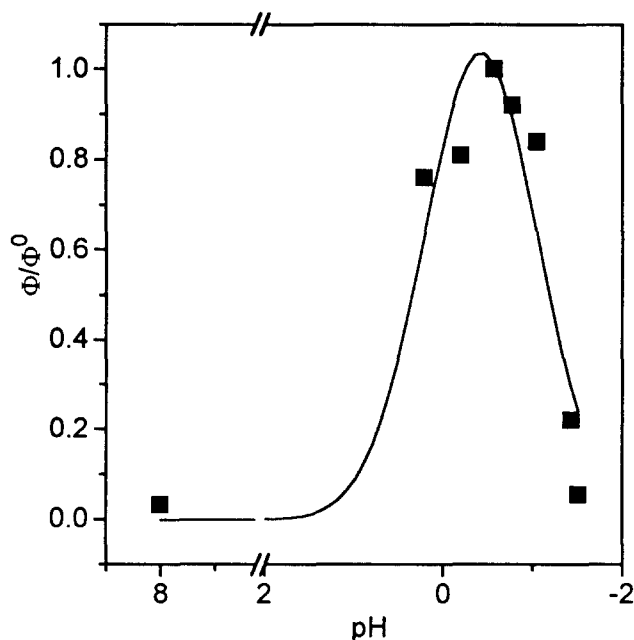
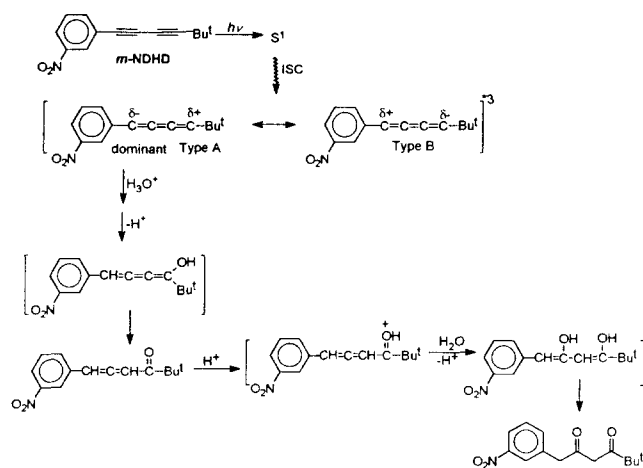


Figure 1. Relative quantum efficiency (Φ/Φ°) as a function of acidity for *m*-NDHD. Φ° is the maximum quantum yield of compound **1**.



that one molecule of water is added to C₂ or C₃ carbon of the acetylenic group attached to the more branched alkyl group, i.e., Markownikoff-type addition.¹¹

The quantum yield of the primary photoproduct (**1**) decreased to 2.5 % in oxygenated (aerated) solution indicating that triplet excited states are involved in the photohydration of *m*-NDHD to give the primary photoproduct (**1**). The result is supported by efficient intersystem crossing in nitro aromatics.^{6,12,13}

The photohydration quantum yields were measured as a function of acidity (Figure 1) and found a maximum efficiency at $H_0 = -0.6$ for the primary photoproduct. This optimum acidity value is lower than that of *p*-NDHD ($H_0 = -1.0$), and the photohydration of *m*-NDHD proceeded in weak acid solutions, even at pH7 in contrast to *p*-NDHD which is not photohydrated at pH7. These results indicate that the enhancements of electron withdrawing effect and basicity in the excited states of *m*-NDHD are greater than those of *p*-NDHD. The similar acidity effect had already been reported for (nitrophenyl)acetylene² and 1-(*p*-nitrophenyl)-5,5-dimethyl-1,3-hexadiyne.⁶ Synchronous addition of water with protonation is proposed as a plausible mechanism. Decrease in photohydration efficiency in highly acidic media is attributed to the depletion of neutral water on going to strongly acidic media.

The thermal hydration of 3- and 4-nitrophenyl alkenes and alkynes in aq. sulfuric acid is very slow, and yields Markownikoff-type addition products in sufficiently strong acid solutions. On the other hand, the photochemical addition of water gives rise to the anti-Markownikoff-type products *via* triplet excited state in weak acid solutions.^{2,4} The facile protonation of the excited state was attributed to the enhanced basicity of the alkene and alkyne moieties in the excited states. The reversed polarization (anti-Markownikoff addition) in comparison with ground state and considerable charge separation as well as the enhanced reactivity in the excited state are attributed to the strong electron withdrawing effect of nitro group (*meta* > *para*) in the excited state.

In photohydration of *p*-NDHD, two allenyl ketones are obtained via both type A and type B excited states.⁶ On the other hand, only the type A allenyl ketone is obtained on photohydration of *m*-NDHD, indicating that *m*-NDHD has greater enhancement of electron withdrawing effect than that of *p*-NDHD. The results are in good agreement with the previous reports of Zimmerman^{7,14} and Yates.^{2,4,15}

This is so-called *meta* effect in photochemical reactions, originally noted by Zimmerman,^{7,14} Wherry¹⁶ and Yates¹⁵ have attempted to estimate this effect

semiquantitatively by using the Taft equation¹⁷:

$$\alpha = \frac{\rho, \sigma_1 - \log(k^*/K_s)_{\text{meta}}}{\rho, \sigma_1 - \log(k^*/K_s)_{\text{para}}}$$

The α assesses the relative importance of conjugative effects at *meta* and *para* positions in ground and excited states. They suggested that *meta* conjugation in excited states is perhaps more important than *para* conjugation. The *meta* effect in nitro-substituted diacetylene is confirmed by the comparison of *m*-NDHD with *p*-NDHD in photohydration.

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