PHOTOHYDRATION REACTION OF 1-(p-NITROPHENYL)-5,5-DIMETHYL-1,3-HEXADIYNE
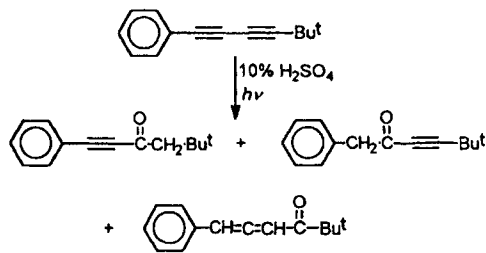
EUN KYUNG BAEK AND SANG CHUL SHIM*

Department of Chemistry, Korea Advanced Institute of Science and Technology, 373-1 Kusung-Dong, Yusung-Gu, Taejon 305-701, Korea

Irradiation of 1-(p-nitrophenyl)-5,5-dimethyl-1,3-hexadiyne (NDHD) in aqueous sulfuric acid yields conjugated allenyl ketones (1 and 2) and β-dicarbonyl compounds (3 and 4). The products 1 and 2 are primary photoproducts while 3 and 4 are secondary products formed by thermal hydration of the primary photoproducts showing the maximum quantum yield at $H_0 = -1·0$. A mechanism involving a synchronous addition of hydronium ion (H_3O^+) to a triplet state of NDHD is proposed.

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 S_1 state to give regiospecific hydration products in the Markovnikov sense, as do the analogous thermal hydration reactions. Exceptions are the *m*- and *p*-nitro derivatives, which add water via the T_1 state in the anti-Markovnikov directions.[2] A mechanism involving a synchronous addition of H_3O^+ to the T_1 state has been proposed for the photohydration of (nitrophenyl)-acetylenes. The driving force of the reaction was proposed to be the enhanced electron-withdrawing character of nitro groups in the T_1 state.

Scheme 1

The photohydration of conjugated diynes has previously been studied in our laboratory.[5,6] The photohydration of 1-phenyl-5,5-dimethyl-1,3-hexadiyne gives three photohydration products (Scheme 1) through both S_1 and T_1 excited states.[6] An allenyl ketone product is obtained as a minor product. The proposed mechanism involves the protonation step being the rate-limiting step in the formation of acetylenyl ketone products. On the other hand, the allenyl ketone product is formed by the synchronous addition mechanism of H_3O^+. In this paper, we report the photohydration of 1-(p-nitrophenyl)-5,5-dimethyl-1,3-hexadiyne, since a different reaction mechanism is expected due to the nitro effect (electron-withdrawing effect and enhanced intersystem crossing efficiency) on the excited state of diacetylenes.

RESULTS AND DISCUSSION

Irradiation of 1-(p-nitrophenyl)-5,5-dimethyl-1,3-hexadiyne (NDHD) in CH_3CN-H_2O (1/1, v/v) (10% sulfuric acid) gave four photoproducts (1–4) (Scheme 2).

Figure 1 shows the UV absorption spectra of NDHD and hydration products in acetonitrile. The absorption maximum of compound 2 is shifted to a longer wavelength than that of compound 1. The photoproducts (1 and 2) are conjugated allenyl ketones. The asymmetric absorption bands in IR for the allene moiety appear at 1944 and 1939 cm^{-1} in 1 and 2, respectively. In the ^{1}H NMR spectra, the allenic protons of photoproducts 1 and 2 appear between $\delta 5·5$ and $6·5$ ppm.[7,8]

---

* Author for correspondence.

Scheme 2
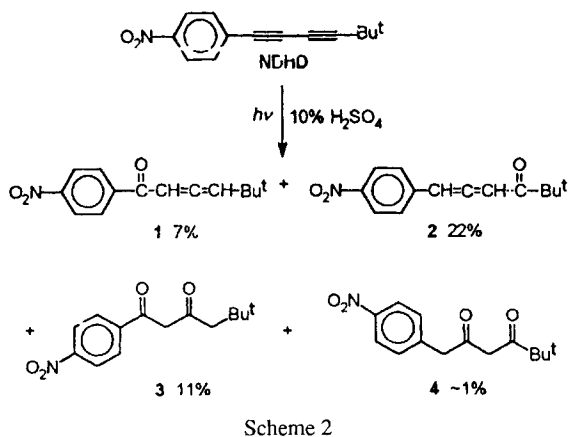
The photoproducts (**1** and **2**) are distinguished by the chemical shift of allenic protons. The structure of allenes is strongly supported by the extreme down-field chemical shift of the central carbon atom in ^{13}C NMR (δ215–216 ppm) and the carbonyl peaks appeared at δ198 and 203 ppm. In mass spectra, the M$^+$ peak at 245 indicates that the photohydration products are formed by the addition of one molecule of water.

The products (**3** and **4**) show the M$^+$ peaks at 263, indicating that they are formed by the addition of two water molecules. In ^{1}H NMR spectra, the resonance peaks of hydrogen-bonded hydroxy protons in the enol form of β-dicarbonyl compounds appear as a broad singlet at δ15·5–16·5 ppm.[9] The olefinic protons appear at δ5·5–6·5 ppm. The β-dicarbonyl moiety is confirmed by the presence of two carbonyl peaks at δ180–200 ppm in ^{13}C NMR. Products **3** and **4** are
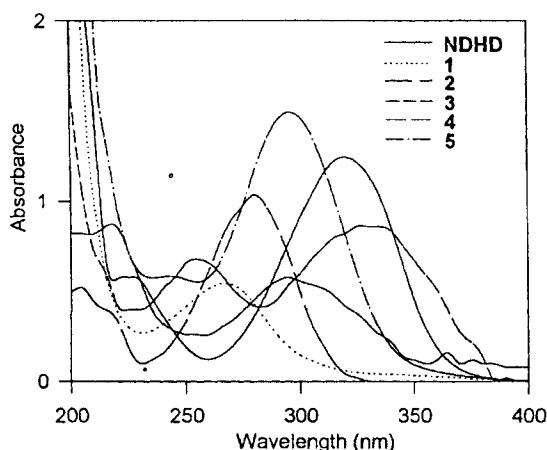
distinguished by the chemical shift differences of methylene protons in ^{1}H NMR.

In order to test the probable thermal hydration of NDHD, a control experiment in the dark was carried out in 10% and 50% sulfuric acid at room temperature. No reaction was observed from NDHD under these conditions.

Thermal hydration in 70% sulfuric acid for 30 minutes gives the products **3**, **4** and **5**. The unreacted NDHD (16%) is recovered (Scheme 3).

The products **3** and **4** are the two water molecule addition products and compound **5** is a dimerization product. Compound **5** shows one olefinic proton as a singlet at δ6·82 ppm in ^{1}H NMR. In ^{13}C NMR, two sp^2 carbons and one carbonyl carbon appear at δ143·3, 127·5 and 198·1 ppm, respectively. From the distortionless enhancement by polarization transfer (DEPT) experiment, the sp^2 carbon at δ143·3 ppm is assigned to be quarternary carbon, and the sp^2 carbon peak at δ127·5 ppm to be CH carbon. In mass spectra the molecular ion peak is not detected, but the peak shown at 246 is half the molecular weight of dimerization product, suggesting that compound **5** is the dimerization product with symmetrical structure. E,E and Z,Z isomers in symmetrical structure are possible. However, the two isomers could not be distinguished.

In 80% sulfuric acid, compound **6** is obtained instead of the dimerization product. In ^{13}C NMR spectrum of compound **6**, two acetylenic peaks and one carbonyl peak were confirmed. The thermal hydration of compound **6** gives compounds **3** and **5**.
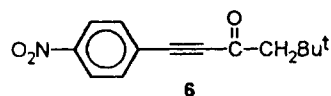
The dimerization of olefins in sulfuric acid was reported.[10] Carbocations are produced in a reaction medium by protonation of olefins, and attack the

Figure 1. UV absorption spectra of NDHD and hydration products (**1–5**) in acetonitrile

Scheme 3
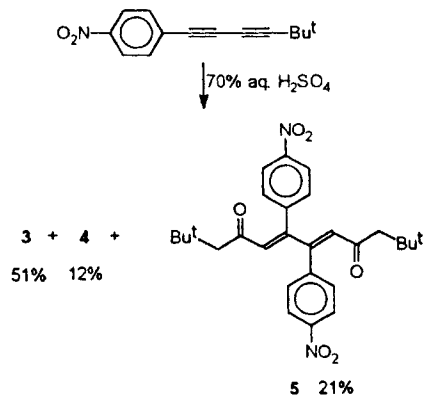
uncharged olefin to produce dimers, trimers and higher polymers. The dimerization of compound **6** may be proceeded by the similar mechanism.

The photohydration of NDHD was monitored by studying the kinetics of the product formation and disappearance rate of the starting materials (Figure 2). The data clearly show that NDHD is initially converted into **1** and **2**. The products **3** and **4** are formed from **1** and **2**. The photohydration of pure **1** and **2** gives **3** and **4**, respectively, supporting strongly that **1** and **2** are primary photoproducts, **3** and **4** are secondary products.

Treatment of the primary photoproducts with 10% H_2SO_4 in the dark yields secondary products very rapidly and the thermal hydration of primary photoproducts gives the same results as photohydration, suggesting that the secondary hydration is thermal process. However, irradiation of **1** (with 254 nm) and **2** (with 300 nm) in 5% sulfuric acid at $-10\,°C$ gives compounds **3** and **4**, respectively, while thermal hydration did not proceed at all under the same condition. The thermal process, however, is dominant in the photohydrations of **1** and **2** at 350 nm in 10% sulfuric acid at room temperature, because of the weak absorbance at 350 nm and the faster thermal hydration.

The thermal hydration of (p-nitrophenyl)allene has already been reported.[3] Since (p-nitrophenyl)allene is thermally stable in 25% sulfuric acid, 83% sulfuric acid was used for the thermal hydration. However, conjugated allenyl ketones (**1** and **2**) in 10% sulfuric acid are converted into **3** and **4** very rapidly. The fast thermal hydration of allenyl ketones is probably due to the fast 1,4-addition of H_3O^+ (Scheme 4) as the unsaturated ketones.[11]

The oxygen effects on the photohydration of NDHD are summarized in Table 1. The quantum yields of the primary photoproducts (**1** and **2**) decreased to13% and 32% in aerated solutions, indicating that triplet excited

Table 1. Oxygen effects on the photohydration of NDHD

	Φ	Φ^*_{rel}
Photoproducts	De-aerated	Aerated
1	1	0·13
2	1	0·32

Compounds **1** and **2** are primary photohydration products.
* Relative quantum yields with respect to de-aerated solutions.

states are involved in the photohydration of NDHD to give the primary photoproducts (**1** and **2**). These results are supported by efficient intersystem crossing in nitro aromatics.[12]

Photohydration of NDHD ($E_T = 58$ kcal mol^{-1}) was quenched by 9-fluorenone-1-carboxylic acid ($E_T = 50$ kcal mol^{-1}).[13] The resulting linear Stern–Volmer plot (Figure 3) with a slope (Stern–Volmer constants, $k_q\tau$) of 5400 and 4700 dm^3 mol^{-1} in 10% sulfuric acid/ acetonitrile/water supported photohydration mechanism via the same triplet excited state.

The photohydration quantum yields were measured as a function of acidity for NDHD (Figure 4). The NDHD photohydration exhibits a maximum efficiency at $H_0 = -1.0$ for both primary photoproducts. The other example exhibiting a maximum had already been reported in the case of (nitrophenyl)acetylene.[2] The suggested mechanism involves the nucleophilic attack of water, synchronous with proton transfer. The decrease or leveling off in photohydration efficiency is most likely due to the depletion of water on going to strongly acidic media.

Figure 2. Kinetics of photohydration of NDHD and hydration products (**1–4**)
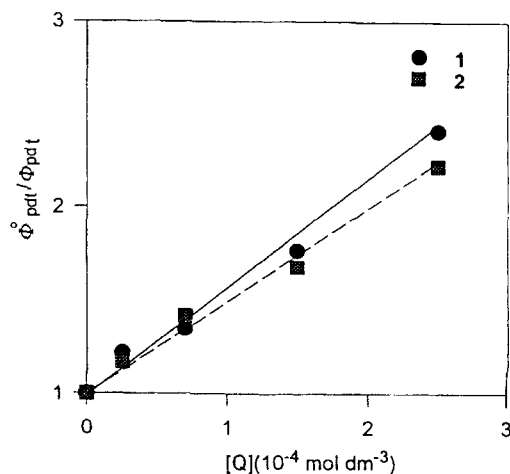
Figure 3. Quenching of photohydration reaction of NDHD by 9-fluorenone-1-carboxylic acid. The compounds **1** and **2** are primary photohydration products
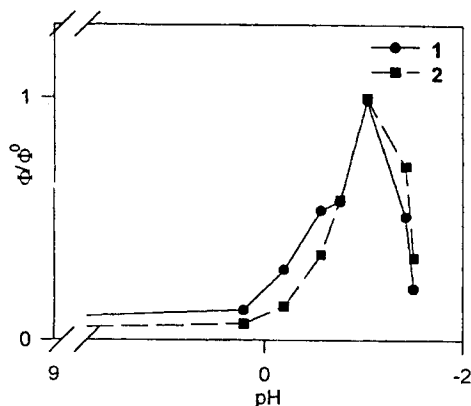
Figure 4. Relative quantum efficiency (Φ/Φ^0) as a function of acidity for NDHD. Φ^0 is quantum yield of compound 2 at $H_0 = -1\cdot0$

Photohydration mechanism

In the triplet excited state, the charge of 1,3-diynes seems to be delocalized throughout the conjugate system.[5] A possible charge distribution of the excited state is shown in Scheme 4. The previous studies showed that the photohydration of 1-phenyl-5,5-dimethyl-1,3-hexadiyne proceeds through both S_1 and T_1 excited states, and two kinds of mechanisms are involved. The photohydration of 1-(1-naphthyl)buta-1,3-diyne gives the two acetylenyl ketone products via both S_1 and T_1 excited states, and the protonation step is the rate-limiting step. On the other hand, NDHD reacts via the T_1 state only, and the allenyl ketone products are produced by the synchronous addition mechanism.

The protonation at C_1 of NDHD is increased in hydration of excited state in comparison with hydration of ground state. The protonation of ground state is dominant at the C_4 position. However, the photohydra-

Scheme 4

tion of NDHD does not give the regiospecific hydration product in the anti-Markovnikov sense as nitrophenyl alkenes and acetylenes. In general, the degree of reverse polarization due to the nitro group appears to be greater for the alkenes than the alkynes. It is expected that the electron-withdrawing effect of the nitro group will be dispersed all over the diacetylene group and will be weaker than the effect on the single acetylene moiety. Therefore, the triplet excited state of NDHD has a weak partial charge character, and cannot produce the regiospecific hydration product in the anti-Markovnikov sense.

The primary product in the photohydration of NDHD is allenyl ketone, while acetylenyl ketone in the thermal hydration. It is suggested that the excited states of NDHD have the cumulene type structures. The photohydration of 1-phenyl-5,5-dimethyl-1,3-hexadiyne and 1-(1-naphthyl)-1,3-butadiynes give the acetylenyl ketone products, while the allenyl ketones are produced in the photohydration of NDHD. In the photohydration of NDHD, the formation of allenyl ketone may be due to the synchronous addition of H_3O^+. In other words, the rearrangement of cation 7 to the cation 8 competes with the addition of water, and the addition of water is faster in the photohydration of NDHD. In 1-phenyl- and 1-(1-naphthyl)-1,3-butadiynes, the rearrangement of cation 7 to 8 is fast, and the acetylenyl ketones are produced.

$$\left[Ar\text{-}CH\text{=}C\text{=}\overset{+}{C}\text{-}Bu^t \overset{\longleftarrow}{\longrightarrow} Ar\text{-}CH\text{=}\overset{+}{C}\text{-}C\equiv C\text{-}Bu^t \right]$$

$$\quad\quad\quad\quad\ 7 \quad\quad\quad\quad\quad\quad\quad\quad\quad\quad 8$$

The mechanism may be more clarified by studying the substituent effects which is presently under study in our laboratory.

EXPERIMENTAL SECTION

General methods

^1H NMR and ^{13}C 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 $CDCl_3$. 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 system (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.

Diphenyl-1,3-butadiyne (DPB) and 9-fluorenone-1-carboxylic acid were purchased from Aldrich Chemical Co. and were used after recrystallization. Solvents of reagent grade for chromatography were used without

further purification. Spectroscopic grade solvents (Tedia) were used for HPLC and absorption spectra, respectively.

Synthesis of 1-(p-nitrophenyl)-5,5-dimethyl-1,3-hexadiyne (NDHD)

p-Nitrophenylacetylene and 1-bromo-3,3-dimethyl-1-butyne were prepared by the literature method.[14,15] The NDHD was prepared by the Cadiot–Chodkiewicz coupling which is a convenient method of preparation of asymmetrical polyacetylenes.[16] The NDHD was used after recrystallization in MeOH, m.p. 106–107 °C; ^1H NMR ($CDCl_3$, 200 MHz) δ 8·10 (d, 2H), 7·52 (d, 2H), 1·24 (s, 9H) ppm; ^{13}C NMR ($CDCl_3$, 50 MHz) δ 147·1, 133·0, 129·0, 123·4, 95·3, 79·3, 73·6, 63·2, 30·2, 28·3 ppm; ν_{max} (NaCl) 2971, 2232, 1591, 1518, 1340; UV (CH_3CN)$_{lmax}$ 319 nm; m/z 227 (M^+, 27·6%), 212 (M^+-CH_3, 34·8%), 165 (M^+-CH_4NO_2, 100%); HRMS (M^+) calculated for $C_{14}H_{13}NO_2$ 227·0946, found 227·0936.

Photohydration reaction of 1-(p-nitrophenyl)-5,5-dimethyl-1,3-hexadiyne (NDHD)

De-aerated 2 mM solutions (water/MeCN)[1/1, v/v; H_2SO_4 10% (v/v)] of NDHD were irradiated with 350 nm UV light in a Rayonet photochemical reactor, Model RPR-208, equipped with an RUL 350 nm lamp. After irradiation for 30 minutes, the reaction mixture was extracted with diethyl ether. The organic phase was dried over $MgSO_4$ and separated by silica gel column chromatography using the eluent n-hexane/diethyl ether, 6/1 (v/v). The products were purified by normal phase HPLC using the following conditions. Eluents: (1), n-hexane/diethyl ether/methylene chloride (12/1/1, v/v/v); (3), n-hexane/diethyl ether/methylene chloride (16/1/1, v/v/v); (2, 4), n-hexane/diethyl ether/methylene chloride (14/1/1, v/v/v). The compounds 1 and 3 are obtained as solids and 2 and 4 as oils. 1: m.p. 39–40 °C; ^1H NMR ($CDCl_3$, 200 MHz) δ 8·26 (d, 2H), 7·95 (d, 2H), 6·36 (d, 1H, J = 6·0 Hz), 5·65 (d, 1H, J = 6·0 Hz), 1·05 (s, 9H) ppm; ^{13}C NMR ($CDCl_3$, 50 MHz) δ 215·7, 190·7, 149·8, 142·8, 129·4, 123·4, 107·2, 96·5, 33·1, 29·9 ppm; ν_{max} (NaCl) 2962, 1944, 1658, 1602, 1526, 1348, 1277; UV (CH_3CN) λ_{max} 265 nm; m/z 245 (M^+, 3·6%), 230 (M^+-CH_3, 15·5%), 150 (M^+-C_7H_{11}, 100%), and 104 (M^+-$C_7H_{11}NO_2$, 21·9%); HRMS (M^+) calculated for $C_{14}H_{15}NO_3$ 245·1052, found 245·1070. 2: ^1H NMR ($CDCl_3$, 200 MHz) δ 8·17 (d, 2H), 7·40 (d, 2H), 6·63 (d, 1H, J = 6·4 Hz), 6·53 (d, 1H, J = 6·4 Hz), 1·22 (s, 9H) ppm; ^{13}C NMR ($CDCl_3$, 50 MHz) δ 214·8, 202·9, 147·1, 138·7, 127·7, 124·2, 97·1, 95·3, 44·7, 26·4 ppm; ν_{max} (NaCl) 2969, 1939, 1677, 1596, 1518, 1343; λ_{max}

(CH₃CN) 296 nm; m/z 245 (M⁺, 3·6%), 85 (M⁺-C₉H₆NO₂, 27·8%), and 57 (M⁺-C₁₀H₆NO₃, 100%); HRMS (M⁺) calculated for C₁₄H₁₅NO₃ 245·1052, found 245·1045. **3**: m.p. 58–59 °C; ¹H NMR (CDCl₃, 200 MHz) δ 16·14 (s, 1H), 8·28 (d, 2H), 8·02 (d, 2H), 6·14 (s, 1H), 2·31 (s, 2H), 1·05 (s, 9H) ppm. ¹³C NMR (CDCl₃, 75 MHz) δ 196·5, 181·1, 149·8, 140·9, 128·0, 123·8, 99·2, 52·7, 32·1, 30·0 ppm; ν_{max} (NaCl) 2957, 2869, 1619, 1585, 1526, 1474, 1346; λ_{max} (CH₃CN) 254·3, 332 nm; m/z 263 (M⁺, 4·9%), 207 (M⁺-C₄H₈, 66·8%), 192 (M⁺-C₅H₁₁, 100%), and 150 (M⁺-C₇H₁₃O, 30·8%); HRMS (M⁺) calculated for C₁₄H₁₇NO₄ 263·1158, found 263·1098. **4**: ¹H NMR (CDCl₃, 200 MHz) δ 15·56 (s, 1H), 8·17 (d, 2H), 7·41 (d, 2H), 5·59 (s, 1H), 3·70 (s, 2H), 1·31 (s, 9H) ppm; ¹³C NMR (CDCl₃, 50 MHz) δ 200·2, 191·8, 147·0, 142·7, 130·2, 123·8, 95·41, 45·3, 39·0, 27·2 ppm; ν_{max} (NaCl) 2969, 1606, 1595, 1521, 1346; λ_{max} (CH₃CN) 280 nm; m/z 263 (M⁺, 3·6%), 206 (M⁺-C₄H₉, 32·3%), 127 (M⁺-C₇H₃NO₂, 100%), and 57 (M⁺-C₁₀H₈NO₄, 28·5%); HRMS (M⁺) calculated for C₁₄H₁₇NO₄ 263·1158, found 263·1150.

Thermal hydration

A solution of 100 mg NDHD in dioxane was added dropwise to 200 ml of 70% H₂SO₄ with rapid stirring. The solution was then stirred for 30 minutes. A colored solution was obtained and saturated with salt, extracted with diethyl ether, washed, dried and evaporated to get the crude product. Routine analyses were then carried out on this product. The products were purified by normal phase HPLC using the following conditions. Eluents: **5**: n-hexane/diethyl ether/methylene chloride (14/1/1, v/v/v); **6**: n-hexane/methylene chloride (2/1, v/v); **5**: ¹H NMR (CDCl₃, 200 MHz) δ 8·25 (d, 2H), 7·81 (d, 2H), 6·82 (s, 1H), 2·56 (s, 2H), 1·06 (s, 9H) ppm; ¹³C NMR (CDCl₃, 75 MHz) δ 198·1, 148·7, 143·3, 138·4, 128·2, 127·5, 123·8, 56·9, 31·8, 29·8 ppm; ν_{max} (NaCl) 2955, 1690, 1587, 1522, 1490, 1348; λ_{max} (CH₃CN) 296 nm. **6**: ¹H NMR (CDCl₃, 200 MHz) δ 8·23 (d, 2H), 7·69 (d, 2H), 2·60 (s, 2H), 1·09 (s, 9H) ppm; ¹³C NMR (CDCl₃, 50 MHz) δ186·9, 148·4, 133·4, 126·6, 123·7, 92·2, 86·2, 58·2, 31·9, 29·7 ppm; ν_{max} (NaCl) 2958, 2209, 1668, 1595, 1524, 1345; m/z 245 (M⁺, 0·1%), 189 (M⁺-C₄H₈, 100·0%), 174 (M⁺-C₅H₁₁, 82·1%), and 128 (M⁺-C₅H₁₁NO₂, 43·3%); HRMS (M⁺) calculated for C₁₄H₁₅NO₃ 245·1052, found 245·1036.

Effect of the medium acidity

Samples of acetonitrile/water (1/1, v/v) solutions of NDHD in the presence of various concentrations of sulfuric acid (0–30%) were purged with nitrogen gas. These samples were irradiated at 350 nm. Quantitative analyses were carried out by reverse phase HPLC after

saturation with NaCl, using nitrobenzene as an internal standard, Lichrosorb RP-18 (5 μm), and methanol/water (3/1, v/v) solvent. The amounts of the primary photoproducts are calculated from the amounts of secondary photoproducts.

Oxygen effect

The relative quantum yields of the photoreactions of NDHD (2 mM) to give photoadducts (**1** and **2**) were measured in the presence of oxygen (bubbled with oxygen) and compared with those obtained in the de-aerated condition (degassed by N₂ bubbling). The 350 nm UV light in a Rayonet photochemical reactor, Model RPR-208, equipped with RUL 350 nm lamps was shone for 5 minutes. The quantitative analysis was carried out by reverse phase HPLC after saturation with NaCl.

Effect of 9-fluorenone-1-carboxylic acid

A sample solution [MeCN/water (1/1, v/v); 3 ml] in Pyrex ampoules containing various concentrations of 9-fluorenone-1-carboxylic acid $(0-2\cdot5 \times 10^{-4}$ mol dm⁻³) and DPB as internal standard were degassed with three freeze–pump–thaw cycles with cooling in liquid nitrogen and were then sealed. These samples were irradiated in a merry-go-round apparatus with 366 nm monochromatic UV light. The 366 nm was isolated by Corning glass filters #0-52 and #7-37. Quantitative analysis was carried out by HPLC using Lichrosorb RP-18 (5 μm) and methanol/water (3/1, v/v) solvent. The amounts of the primary photoproducts is calculated from the amounts of secondary photoproducts.

REFERENCES

1. P. Wan and K. Yates, J. Org. Chem. **48**, 869–876 (1983).
2. P. Wan, S. Culshaw and K. Yates, J. Am. Chem. Soc. **104**, 2509–2515 (1982).
3. K. Rafizadeh and K. Yates, J. Org. Chem. **49**, 1500–1506 (1984).
4. P. Wan, M. J. Davis and M. A. Teo, J. Org. Chem. **54**, 1354–1359 (1989).
5. S. C. Shim and T. S. Lee, J. Chem. Soc. Perkin Trans. 2 1739–1743 (1990).
6. E. K. Baek, S. T. Lee and S. C. Shim, unpublished results.
7. R. F. Gunico, Tetrahedron Lett. **35**, 2291–2294 (1994).
8. P. Clerc and S. Simon, Tables of Spectral Data for Structure Determination of Organic Compounds, Springer-Verlag, New York and London (1983).

9. C. J. Pouchert and J. Behnke, *The Aldrich Library of ^{13}C and ^{1}H FT NMR Spectra*, Vol. 1, pp. 661–663, Aldrich Chemical Company Inc. (1993).
10. M. Liler, *Reactions in Sulphuric Acid and Other Strong Acid Solutions*, Vol. 23, pp. 300–301, Academic Press, London and New York (1971).
11. R. P. Bell, J. Preston and R. B. Whitney, *J. Chem. Soc.* 1166–1170 (1962).
12. (a) H. A. Morrison, *The Chemistry of the Nitro and Nitroso Groups*, pp. 165–213, Wiley, New York (1969).

(b) R. Hurley and A. C. Testa, *J. Am. Chem. Soc.* **90**, 1949–1952 (1968).
13. J. C. Scaiano, *CRC Handbook of Organic Photochemistry*, pp. 382, CRC Press Inc., Florida (1989).
14. Y. Zhang and J. Wen, *J. Chem. Research (S)* 20–21 (1991).
15. L. Brandsma, *Preparative Acetylenic Chemistry*, pp. 219, Elsevier, New York (1988).
16. R. Eastmond and D. R. M. Walton, *Tetrahedron* **28**, 4591–4599 (1972).