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PHOTOADDITION REACTIONS OF 1,4-DIPHENYLBUT-1-EN-3-YNE TO *p*-QUINONES

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Abstract — Photoaddition reactions of *p*-quinones to 1,4-diphenylbut-1-en-3-yne (BEY) have been investigated. Irradiation (300 nm) of BEY and 1,4-benzoquinones in dichloromethane afforded quinone methides. Irradiation of 1,4-naphthoquinone and BEY leaded to the formation of unstable spiro oxetene intermediate, followed by the rearrangement to give quinone methide, and finally the oxidative photocyclization. In contrast, irradiation 2,3-dichloro-1,4-naphthoquinone (or anthraquinone) and BEY yielded another type of quinone methides in one pot.

INTRODUCTION

Quinones are an important class of compounds in organic synthesis, in industry, and in nature.[1-2] Quinone methides are intermediates of relevance in a variety of areas.[3] Photoaddition of *p*-quinones to alkynes yields quinone methides, *via* an unstable intermediate spiro-oxetenes or cyclobutenes, depending on the character of the substituents.[4-7] The *p*-quinones also add to a conjugated diyne such as 1,4-diphenylbutadiyne to give 1:1 adducts.[8] Photoaddition reactions of conjugated diene, 1,4-diphenylbutadiene, to *p*-quinones were also studied, in which 1:1 adducts were isolated as the major product.[9]

In connection with our investigation of the scope of these reactions, we examined the photochemical reaction of *p*-quinones with a conjugated system, BEY **1**, having two reaction sites, *i.e.*, carbon-carbon double bond and triple bond. Here we report that a C=O bond of *p*-quinones added to carbon-carbon triple bond of **1** to give quinone methides *via* unstable intermediates, spiro-oxetenes.

MATERIALS AND METHODS

Materials. *p*-Quinones, such as 1,4-benzoquinone, chloranil, 1,4-naphthoquinone, 2,3-dichloro-1,4-naphthoquinone, and anthraquinone, were obtained from Aldrich Chemical Co. and used as received or recrystallized prior to use. BEY was synthesized from *β*-bromostyrene and phenylacetylene.[10] Dichloromethane, *n*-hexane, ethyl acetate, and methyl alcohol were distilled prior to use. Silica gel (Kieselgel 60 F254, Merck Co.) was used for thin layer chromatography and silica gel (Kieselgel 60, 230-400 mesh, Merck Co.) was used for column chromatography.

Instruments. ^{1}H and ^{13}C NMR spectra were recorded on a Jeol JMN EX NMR spectrometer. Proton chemical shifts, *δ*, were reported in parts per million (ppm) downfield from tetramethylsilane (TMS). IR spectra were recorded on a Nicolet 5-DX13 Fourier Transform spectrophotometer in KBr pellets or NaCl cells. UV spectra were obtained on a Hitachi 556 spectrophotometer. Fluorescence spectra were observed on a Jasco spectrofluorometer (Model FP-770). Mass spectra were determined on a Hewlett Packard 5985 GC/MS system using electron impact method.

General Procedure for Photocycoadditions of BEY to p-Quinones. Preparative photoreactions were conducted in a photochemical reactor composed of a water-cooled system and a Pyrex reaction vessel with 300 nm UV lamps (Rayonet Photochemical Reactor, Model RPR-208). Irradiation was carried out after degassing with dry nitrogen gas for 30 min. The reaction was followed by TLC. The residue obtained from the evaporation was chromatographed over silica gel with *n*-hexane and ethyl acetate as the eluent.

Irradiation of BEY and 1,4-benzoquinone. 204 mg (1.0 mmol) of **1** and 108 mg (1.0 mmol) of 1,4-benzoquinone **2** were dissolved in 100 mL of dichloromethane, and degassed with dry nitrogen gas for 30 min. The reaction mixture was irradiated with 300 nm UV light for 24 h. The residue obtained from the evaporation was chrmatographed over silica gel using *n*-hexane and ethyl acetate as the eluent: **6**, UV(MeOH) λ_{max} 327, 273, 228, 207 nm; Fluorescence(MeOH) λ_{max} 385 nm; IR(KBr), 3057, 2924,

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1604, 1509, 1446, 1257, 1221, 1175, 833, 765, 693 cm^{-1}; ^{1}H-NMR($CDCl_3$) δ 7.78(d, 2H, J=8.0Hz), 7.64(d, 2H, J=8.0Hz), 7.44(t, 3H, J=8.0Hz), 7.39-7.26(m, 5H), 7.34(d, 2H, J=8.0Hz), 6.91(d, 2H, J=8.0Hz); ^{13}C-NMR($CDCl_3$) δ 213.6(CO), 209.3(CO), 154.9, 131.2, 130.6, 126.8 (4C's), 109.5, 130.1, 128.7, 128.6, 128.4, 127.5, 127.3, 126.0, 123.8, 115.6; Mass(EI) m/e 77(Ph), 105(PhCO), 312(M).

Irradiation of BEY and Chloranil. A solution of 204 mg (1.0 mmol) of **1** and 245 mg (1.0 mmol) of chloranil **3** in 100 mL of dichloromethane was irradiated with 300 nm UV light for 48 h to yield the same type of quinone methide **7** in 25% yield: **7**, UV(MeOH)λ_{max} 345, 318, 234, 218, 212, 209 nm; ^{1}H-NMR($CDCl_3$) δ 7.87(d, 2H, J=8.0Hz), 7.44(d, 2H, J=8.0Hz), 7.40(d, 2H, J=8.0Hz), 7.33-7.25(6H); ^{13}C-NMR($CDCl_3$) δ 215.7(CO), 211.4(CO), 134.8, 130.0, 129.6, 128.8, 128.6, 128.3, 128.2, 127.9(C's), 128.7, 127.8, 124.5, 123.9, 117.2 (CH's), 109.2(=CH); Mass(EI) m/e 77(Ph), 105(PhCO), 450(M).

Irradiation of BEY and 1,4-Naphthoquinone. 204 mg (1.0 mmol) of **1** and 158 mg (1.0 mmol) of 1,4-naphthoquinone **10** (158 mg, 1.0 mmol) in 100 mL of dichloromethane (100 mL) was irradiated with 300 nm UV light for 24 h to give a quinone methide **13** in 43% yield: **13**, UV(MeOH)λ_{max} 395, 375, 335, 285, 264, 235, 206 nm; Fluorescence(MeOH) λ_{max} 430, 410 nm; IR(KBr), 3064, 2924, 1679, 1595, 1482, 1257, 1103, 1025, 786, 695 cm^{-1}; ^{1}H-NMR($CDCl_3$) δ 9.13(d, 1H, J=8.0Hz), 8.63(d, 1H, J=8.0Hz), 8.53(d, 1H, J=8.0Hz), 8.43(d, 1H, J=8.0Hz), 8.08(s, 1H), 8.10-7.20(11H); Mass(EI) m/e 77 (Ph), 360(M).

Irradiation of BEY and 2,3-Dichloro-1,4-naphthoquinone. 204 mg (1.0 mmol) of **1** and 227 mg (1.0 mmol) of 2,3-dichloro-1,4-naphthoquinone **14** in 100 mL of dichloromethane was irradiated with 300 nm UV light for 48 h to yield another type of photoproduct **17** (40%) in one-pot: **17**, UV(MeOH)λ_{max} δ 379, 368, 256, 238, 216 nm; Fluorescence(MeOH) λ_{max} 538, 438, 415 nm; IR(KBr), 3064, 2931, 2866, 1679, 1574, 1264, 1241, 1103, 906, 744, 702 cm^{-1}; ^{1}H-NMR($CDCl_3$) δ 8.90(d, 1H, J=8.0Hz), 8.40(d, 1H, J=8.0Hz), 7.90(d, 2H, J=8.0Hz), 7.83(t, 3H, J=8.0Hz), 7.58-7.31(m, 6H), 7.39(s, 1H); Mass(EI) m/e 77 (Ph), 105(PhCO), 430(M).

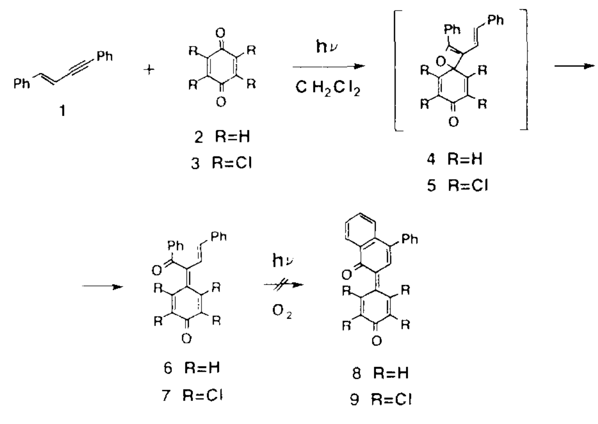
Irradiation of BEY and Anthraquinone. 204 mg (1.0 mmol) of **1** and 208 mg (1.0 mmol) of anthraquinone **18** in 100 mL of dichloromethane was irradieted with 300 nm UV light for 24 h to give a quinone methide **21** in 47% yield: **21**, UV(MeOH) λ_{max} 388, 305, 239, 209, 203 nm; Fluorescence(MeOH)λ_{max} 523, 433, 380 nm; IR(KBr), 3064, 2924, 2853, 1665, 1595, 1312, 1285, 1241, 1067, 778, 693 cm^{-1}; ^{1}H-NMR($CDCl_3$) δ 8.79(d, 1H, J=8.0Hz), 8.32(d, 1H, J=8.0Hz), 8.14(d, 1H, J=8.0Hz), 7.89(d, 2H, J=8.0Hz), 7.73(t, 3H, J=8.0Hz), 7.64-7.25(m, 9H), 7.38(s, 1H); ^{13}C-NMR(CDCl3) δ 195.6(CO), 192.8(CO), 141.9, 134.9, 134.0, 132.0, 131.7, 129.8, 129.3, 129.2, 128.7, 128.5, 127.7, 127.4, 127.1; Mass(EI) m/e 77 (Ph), 105(PhCO), 410(M).

RESULTS AND DISCUSSION

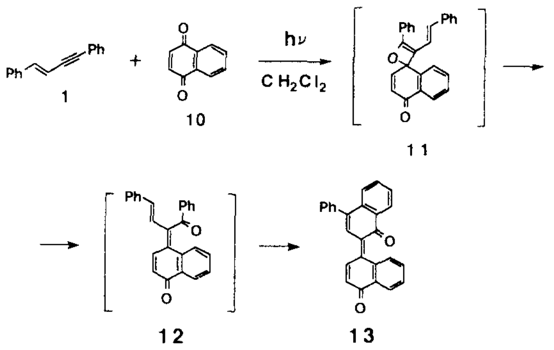
p-Quinones are known to add to olefins to give spiro-oxetanes or cyclobutanes depending on the character of the substituents. It also has been known that *p*-quinones added to alkynes to yield spiro-oxetenes or cyclobutenes, in which the former underwent rearrangement to give quinone methides. We have investigated the photoaddition reactions of diyne to *p*-quinones. The major products were found to be 1:1 adducts. Recently, we found that the carbon-carbon double bond of 1,4-diphenylbut-1-en-3-yne (BEY) **1** added to *o*-quinones to give 1,3-cyclohexadienes and dihydrodioxins, in which the former were oxidized and photocyclized to give 9-phenylphenanthrenes.[11] In order to compare the reactivity of carbon-carbon double bond and triple bond, we synthesized an enyne, *i.e.*, BEY **1** and irradiated with *p*-quinones in dichloromethane.

Irradiation (300 nm) of an enyne **1** (10^{-2} *M*) and 1,4-benzoquinone **2** (10^{-2} *M*) in dichloromethane (100 mL) for 24 h afforded quinone methide **6** in 38% yield, as shown in Scheme 1. The photoadduct was isolated by flash column chromatography on silica gel using *n*-hexane and ethyl acetate (9:1, v/v) as the eluent. In order to confirm the structure of **6**, ^{1}H-^{1}H correlation spectrum was obtained in chloroform-d. The peaks (d, 2H, overlapped) at δ 6.91 were correlated with the peaks (d's, 2H, overlapped) at δ 7.34. Vinyl protons of ethenylbenzene moiety appeared at δ 7.64 (d's, overlapped). Oxidative photocyclization reaction of **6** was attempted in vain, in the presence of molecular oxygen, to give **8**. Irradiation of BEY **1** (10^{-2} *M*) and chloranil **3** (R=Cl, 10^{-2} *M*) in dichloromethane (100 mL) for 48 h also yielded the same type of quinone methide **7** in 25% yield

Irradiation (300 nm) of BEY **1** (10^{-2} *M*) and 1,4-naphthoquinone **10** (10^{-2} *M*) in dichloromethane (100 mL) for 24 h gave rise to a quinone methide **13** in

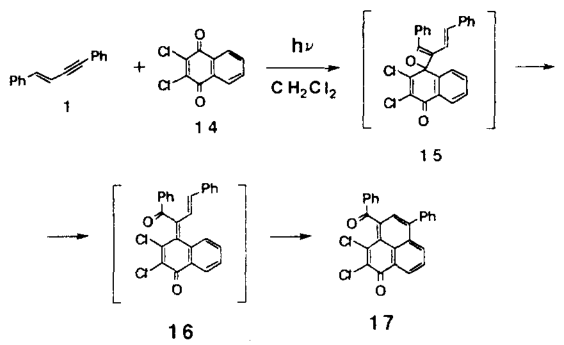


Scheme 1



Scheme 2

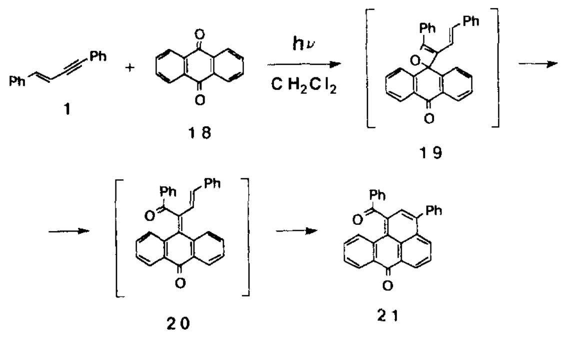
43% yield, which may be formed *via* the formation of unstable intermediate, spiro oxetene **11**, followed by the rearrangement to give quinone methide **12** and finally the oxidative photocyclization as shown in Scheme 2. It is interesting to note that the final product **13** is produced in one-pot photoreaction in a moderate yield.



Scheme 3

In contrast, irradiation (300 nm) of BEY **1** (10^{-2} *M*) and 2,3-dichloro-1,4-naphthoquinone **14** (10^{-2} *M*) in dichloromethane for 48 h yielded another type of photoproduct **17** (40%) in one-pot, as shown in Scheme 3. However, the final oxidative photocycliza tion process occurred at ethenylbenzene and naphthoquinone moiety.

In the case of anthraquinone **18**, the same type of photoproduct **21**, like **17**, was also produced in one pot, as shown in Scheme 4. Irradiation (300 nm) of **1** (10^{-2} *M*) and **18** (10^{-2} *M*) in dichloromethane for 24 h gave **21** in 47% yield.



Scheme 4

In conclusion, we have shown here that carbon-carbon triple bond of BEY **1** adds to C=O bond of the *p*-quinones to give quinone methides *via* the corresponding spiro-oxetenes, in which some of those undergo further photocyclization reaction to give the corresponding final products, such as **13**, **17**, and **21**. Interestingly, the cyclization of the intermediate **12** occurs at benzoyl / ethenylbenzene moiety to yield **13**. On the other hands, those of the intermediates, **16** and **20**, occurs at ethenylbenzene / quinone moiety to yield **17** and **21**, respectively.

Extension of the chemical properties of the photoproducts will be investigated.

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