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16. The MS/MS spectra of LPA, LPC, and 1,2-DAG from gastric juice extract were compared and well matched with those of reference compounds obtained from commercial sources. The FAB-MS and MS/MS experiments were carried out on a JEOL HX110A/HX110A high resolution tandem mass spectrometer. The accelerating voltage was 10 kV with a mass resolution of 1 : 1000 (10% valley). The JEOL Cs^+ ion gun was operated at 25 kV. The collision cell potential was held at 3.0 kV and the ion collision energies were 7.0 kV. Helium collision gas was introduced into the collision chamber at a pressure sufficient to reduce the precursor ion signal by 50%.

Photoaddition Reactions of *o*-Benzoquinones to 1,4-Diphenylbut-1-en-3-yne : Formation of Phenanthrenes and Dihydrodioxins

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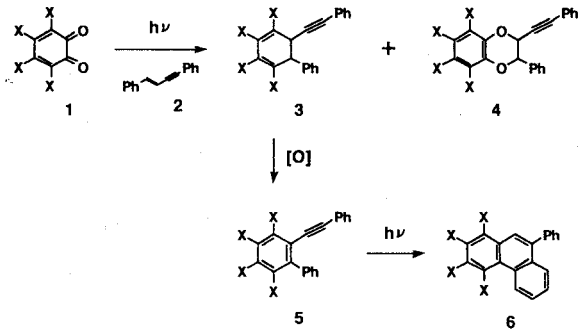
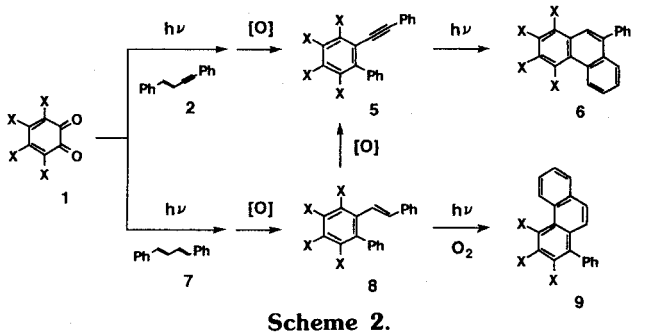
Quinones are an important class of compounds in organic synthesis, in industry, and in nature.[1] Due to their various spectroscopic properties and reactivities, the photochemistry of *o*-quinones has been a subject of interest in many areas.[2~6] Recently, we have found that *o*-benzoquinones can be utilized to synthesize 1-phenylphenanthrenes.[6] In connection with our investigation of the scope of these reactions, we examined the photochemical reactions of *o*-benzoquinones such as tetrachloro-1,2-benzoquinone (TCBQ) **1a** and tetrabromo-1,2-benzoquinone (TBBQ) **1b** with 1,4-diphenylbut-1-en-3-yne (BEY) **2**, having one carbon-carbon double bond and one carbon-carbon triple bond. In this paper, we provide another evidence for the utility of *o*-benzoquinones as starting materials for the synthesis of 9-phenylphenanthrenes.

Preparative photochemical reactions were conducted in dry nitrogen atmosphere 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 (300 nm) of TCBQ **1a** (X=Cl, 246 mg, 1.0 mmol) and BEY **2** (204 mg, 1.0 mmol) in dichloromethane (50 mL) for 24 h afforded 1,3-cyclohexadienes **3a** (X=Cl, 8%)[7] and their oxidized product **5a** (X=Cl, 5%),[6] as well as dihydrodioxins **4a** (X=Cl, 55%).[8] The photoproducts were isolated by flash column chromatography (silica gel, 230-400 mesh) using *n*-hexane and ethyl acetate (9 : 1, v/v) as the eluents.The starting material **2** (28%) was recovered first. Dihydrodioxins **4a** were then obtained as a mixture of two isomers (*cis/trans*) with a ratio of 1.0 : 1.4, as revealed by ^{1}H NMR. Two methine protons of *cis* isomer **4a** (*cis*) were observed at δ 5.15 (d, J=7.3 Hz) and 5.02 (d, J=7.3 Hz), whereas those of *trans* isomer **4a** (*trans*) were found at δ 5.50 (bs) and 5.36 (bs). The product could be further recrystallized from *n*-hexane to yield *cis* isomer **4a** (*cis*) in pure form (23%). The photoproduct **5a** was obtained as a mixture containing a small amount (8% of the two) of 9-phenylphenanthrene **6a** (X=Cl).[9] Rechromatography of the mixture over silica gel with *n*-hexane and ethyl acetate (from 97 : 3 to 9 : 1, v/v, gradient elution) afforded good separation of **5a** from **6a**. The latest fraction gave cyclohexadienes **3a**, which were also obtained as a mixture of two isomers (*cis/trans*) with a ratio of 1.3 : 1.0, as revealed by ^{1}H NMR. Two methine protons of **3a** (*cis*) were observed at δ 4.94 (d, J=7.3 Hz) and 4.87 (d, J=7.3 Hz), whereas those of **3a** (*trans*) were



Scheme 1.



Scheme 2.

found at δ 5.04 (bs) and 4.97 (bs).

Irradiation (300 nm) of TBBQ **1b** (X=Br, 424 mg, 1.0 mmol) and BEY **2** (204 mg, 1.0 mmol) in dichloromethane (50 mL) for 24 h yielded dihydrodioxins **4b** (X=Br),[8] a diphenylacetylene **5b** (X=Br),[6] and 9-phenylphenanthrene **6b** (X=Br)[9] in 45%, 7% and 13% yield, respectively. 1,3-cyclohexadiene derivatives, like **3a**, was not found in this photoreaction. The reaction mixture was chromatographed over silica gel with *n*-hexane and ethyl acetate as the eluent. The starting material **2** (30%) was recovered first. Dihydrodioxins **4b** were then obtained as an isomeric mixture, *i.e., cis* and *trans* isomer with a ratio of 1.0 : 1.2, as revealed by ^{1}H NMR. Two methine protons of *cis* isomer **4b** (*cis*) were observed at δ 5.16 (d, J=7.3 Hz) and 5.01 (d, J=7.3 Hz), whereas those of *trans* isomer **4a** (*trans*) were found at δ 5.45 (bs) and 5.35 (bs). The products could also be further recrystallized from *n*-hexane to yield **4b** (*cis*) in pure form (15%). In order to confirm the exact structure, ^{1}H-^{13}C correlation spectrum of **6b** was also obtained in chloroform-d. A carbon peak (δ 107.7) of C-10 in phenanthrene ring was correlated with a proton peak at δ 7.06 (s, 1H, aromatic).

As shown in the following scheme, a study on the photoaddition reactions of *o*-benzoquinones **1** and 1,4-diphenyl-1,3-butadiene **7** shows that 1,3-cyclohexadienes can initially be formed quantitatively, and that the adducts can be oxidized to stilbene derivatives **8** and then irradiated in the presence of molecular oxygen to give 1-phenylphenanthrenes **9**.[6] In sharp contrast, prolonged irradiation of diphenylacetylene **5a** (X=Cl) gives rise to 9-phenylphenanthrene **6a**, which may be produced *via* the initial formation of transoid excited intermediate of **5**, cyclization, and [1,5] hydrogen shift to yield aromatic system.

Interestingly, it was found that irradiation of **1a** and **2** in benzene, instead of dichloromethane, gave rise to **5a** in 48% yield as the major product . In this case, 1,3-cyclohexadienes **3a** and dihydrodioxins **4a** were obtained in 11% and 2% yield, respectively. It was also found that irradiation of tetrabromo-1,2-benzoquinone **1b** and an enyne **2** in benzene yielded **6b** (37%) as the major product in one-pot photoreaction, in which **4b** and **5b** were isolated in 8% and 6% yield, respectively.

In conclusion, we have shown that 9-phenylphenanthrenes **6** or their precursors, *i.e.*, substituted diphenylacetylenes **5** can be obtained from the photoreaction of *o*-benzoquinones **1** and an enyne **2**. This result makes an interesting contrast with our previous result that 1-phenylphenanthrenes **9** were obtained when irradiated substituted stilbenes **8** in the presence of molecular oxygen.[6] It was also found that tetrabromo-1,2-benzoquinone **1b** is more efficient than tetrachloro-1,2-benzoquinone **1a** to give the corresponding phenanthrenes **6**, where one-pot photochemical formation of a phenanthrene **6b** (37%) was observed when irradiated **1b** and **2** in benzene solution.

Further studies are in progress to prepare analogues of **6** or **9**.

Acknowledgment. This work was supported by the Organic Chemistry Research Center (OCRC) sponsored by the Korea Science and Engineering Foundation (KOSEF). This work was also in part supported by the Ministry of Education, Project No. BSRI-96-3431.

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7. Spectral data of **3a** (*cis*) : ^{1}H NMR ($CDCl_3$), δ 7.51-7.29 (10H), 4.94 (d, 1H, J=7.3 Hz), 4.87 (d, 1H, J=7.3 Hz); IR (KBr), 3057, 2968, 2926, 2229, 1556, 1441, 1384, 1285, 1015, 760, 695 cm^{-1}; UV (MeOH), λ_{max} 301, 252, 242, 235, 219 nm; Mass (EI), m/e 392 (M), 77.
8. (a) For the photochemical additions of tetrachloro-1,2-benzoquinone **1** to conjugated alkenynes, see Koster, R. J. C.; Streefkerk, D. G.; Oudshoorn-Van Veen, M. J.; Bos, H. J. T. *Recl. Trav. Chim. Pays-Bas*, **1974**, *93(6)*, 157-159. (b) According to ref. 8(a), tetrachloro-1,2-benzoquinone **1** added to the double bond of alkenynes to give dihydrodioxins, like **4a**. The photoaddition occurred nonstereospecifically. (c) Spectral data of **4a** (*cis*) : ^{1}H NMR ($CDCl_3$), δ 7.51-7.30 (10H), 5.15 (d, 1H, J=7.3 Hz), 5.02 (d, 1H, J=7.3 Hz); IR (KBr), 3064, 2966, 2924, 2235, 1257, 1025, 751, 688 cm^{-1}; UV (MeOH), λ_{max} 301, 253, 242, 234, 218 nm; Mass (EI), m/e 448 (M), 204, 77. (d) Spectral data of **4b** (*cis*) : ^{1}H NMR ($CDCl_3$), δ 7.53-7.31 (10H), 5.16 (d,

1H, J=7.3 Hz), 5.01 (d, 1H, J=7.3 Hz); IR (KBr), 3064, 2966, 2924, 2235, 1257, 1025, 751, 688 cm^{-1}; UV (MeOH), λ_{max} 302, 280, 253, 243, 224 nm; Mass (EI), m/e 624 (M), 204, 77.

9. (a) Spectral data of **6a**: ^1H NMR ($CDCl_3$), δ 7.88 (d, 1H, J=7.3 Hz), 7.87 (d, 1H, J=7.3 Hz), 7.79 (dd, 2H, J=7.3 Hz, J=1.5 Hz), 7.49-7.43 (5H), 7.05 (s, 1H); Mass (EI), m/e 390 (M), 77. (b) Spectral data of **6b**: ^1H NMR ($CDCl_3$), δ 7.88 (d, 1H, J=7.3 Hz), 7.87 (d, 1H, J=7.3 Hz), 7.78 (dd, 2H, J=7.3 Hz, J=1.5 Hz), 7.49-7.43 (5H), 7.06 (s, 1H); ^{13}C NMR ($CDCl_3$), δ 129.6 (CH), 129.3 (CH), 129.1 (2CH's), 128.6 (3CH's), 124.8 (2CH's), 107.7 (CH); IR (KBr), 3064, 1553, 765, 667 cm^{-1}; UV (MeOH), λ_{max} 395, 389, 272, 212 nm; Mass (EI), m/e 566 (M), 77.

Rhodium(II)-catalyzed Cycloaddition of Diazodicarbonyl Compounds with Vinyl Sulfides. Synthesis of 3-Acylfurans

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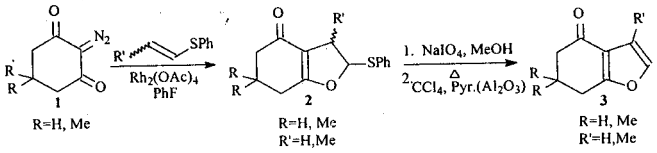
Furans are one of the most important heteroaromatic compounds with widespread occurrence in nature.[1] They are frequently found in many natural products arising from plants and marine organisms.[2] Possessing a variety of biological activities, they are used as pharmaceutical, flavor, insecticidal, and fish antifeedant agents.[3] Their important biological activities and usefulness as synthetic intermediates of natural products have prompted a search for better methods. Although a number of synthetic methods for preparation of 3-acylfurans have been reported, simple and efficient approaches still remain scarce.[4] In particular, the known direct furannulation of a 1,3-diketone by phenylthionitroolefin or an allenic sulfonium salt is limited to a 3-acyl-4-methylfuran substitution pattern.[5]

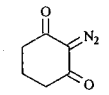
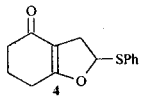
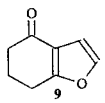
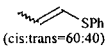
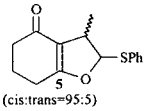
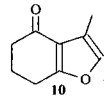
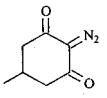
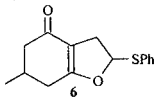
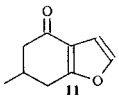
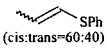
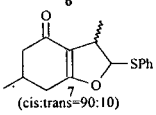
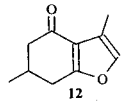
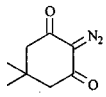
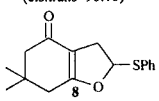
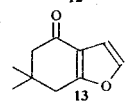
The rhodium-mediated decomposition of diazocarbonyl compounds has become an important method in synthesis of heterocyclic frameworks such as furans.[6] We have been interested in dipolar cycloadditions of 2-diazocyclohexane-1,3-diones with vinyl ethers.[7] We have reported that reactions of these diazoketones with vinyl acetates followed by acid-catalyzed dehydration is a route to benzofuran derivatives.[8] Thus, we have also reported total syntheses of natural products based on the preparation of furo[2,3-b] furan ring catalyzed by rhodium acetate.[9] We describe here the efficient synthesis of 3-acylfurans by rhodium-mediated dipolar cycloaddition of cyclic diazo carbonyl compounds with vinyl sulfides followed by $NaIO_4$ oxidation and syn-elimination under mild conditions.

The sequence that we have developed begins with the



Scheme 1.

Table 1. Synthesis of Dihydrofurans and Furans

2-Diazo-1,3-dicarbonyl compound	Vinyl sulfide	Dihydrofuran	Yield	Furan	Yield
			50		80
	 (cis:trans=60:40)	 (cis:trans=95:5)	56		54
			49		87
	 (cis:trans=60:40)	 (cis:trans=90:10)	45		61
			57		89

reaction of the cyclic 2-diazo-1,3-dicarbonyl compound **1** with a vinyl sulfide present in 5-fold excess (Scheme 1). The cyclic 2-diazo-1,3-dicarbonyl compound **1** was allowed to react with vinyl sulfides under rhodium acetate catalysis (2 mol %) in fluorobenzene to give dihydrofuran 2 in moderate yields.

The intermediate dihydrofurans were characterized spectroscopically.[10] The intermediate dihydrofurans of **5** and **7** demonstrates an interesting aspect of this process. The dihydrofurans were isolated as a major of *cis* isomer despite the use of a 3 : 2 mixture of stereoisomers of the vinyl sulfide. There is thus kinetic discrimination against the *trans* isomer in the cycloaddition. The stereochemical assignment of *cis*- and *trans*-isomers was defined by observation of coupling constants between vicinal protons. It is also suprising to note that none of the formation of sulfonium ylides and C-H insertion products was observed. The results of synthesized dihydrofurans are summarised in Table 1.

The intermediate dihydrofurans were treated with sodium periodate in aqueous methanol at room temperature for 24 h to form the corresponding sulfoxide, which on directly refluxing for 2 h with pyridine in carbon tetrachloride delivers the 3-acylfurans in high yield. Both stereoisomers of **5** and **7** were also similarly transformed into 3-acyl-4-methylfuran in moderate yield; although, active alumina had to be added in the elimination step to cause epimerization of the *cis*-sulphoxide prior to *syn*-elimination of the sulphenic acid. These transformations had been reported by Yoshikoshi in a 3-me-