scans were obtained at the resolution of 0.05 cm^{-1} over the region from 16,000 to 25,000 cm^{-1}. A total of 250 scans have been added together over 2 hrs. to obtain the final spectra shown in Figure 2. However, much longer integration times were not possible due to the deterioration of the discharge.

From the spectra obtained, the rotational fine structure is clearly seen in the P-branch region only. However, the R-branch peak does not show the rotational contours due to the limited cooling of benzyl radical compared to the resolution of the spectrometer. The ratio of signal to noise approaches about 100 in the spectra, which shows much improvement compared to about 7 of the previous report.[9]

In summary, the rotationally cooled benzyl radical has been generated in a jet by expansion with an inert buffer gas He from a high voltage electric *dc* discharge of the toluene. The high resolution spectra of the $6a_1^0$ and $6b_1^0$ vibronic bands of the 1^2A_2-1^2B_2 electronic transition of the benzyl radical have been obtained in emission using a high resolution Fourier transform visible spectrometer. From the comparison with the previous spectra reported,[9] the signal to noise ratio of the spectra has been substantially improved in this experiment. The quantitative analysis of the emission spectra observed will be published elsewhere.

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Photoaddition Reactions of Some Alkynes to Duroquinone and Photochemical Transformation of the Photoadducts

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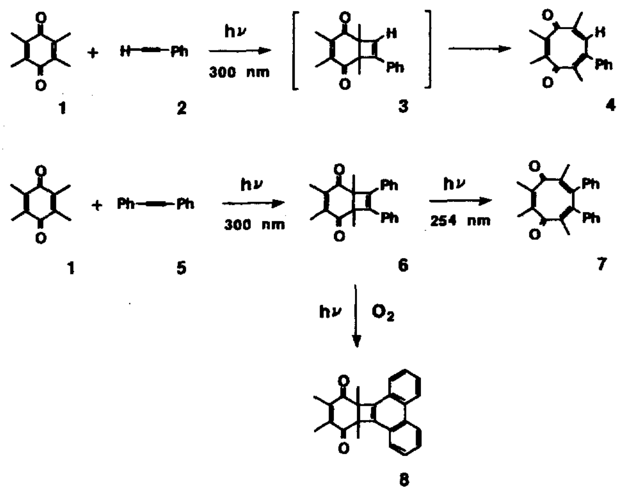
Quinones are an important class of compounds in organic synthesis, in industry, and in nature.[1] Due to their various spectroscopic properties and reactivities, the photochemistry of quinones has been a subject of interest in many areas.[2~4] Photoaddition of *p*-quinones to alkynes yields quinone methides, *via* an unstable intermediate spiro-oxetenes.[5~6] The *p*-quinones also add to a conjugated diyne such as 1,4-diphenylbutadiyne to give 1 : 1 adducts.[7]

In connection with our investigation of the scope of these reactions, we examined the photochemical reaction of duroquinone **1** having four electron-donating methyl groups with some alkynes, such as phenylacetylene **2**, diphenylacetylene **5**, 1,4-diphenylbutadiyne **9**, and 1,4-diethynylbenzene. It was observed that alkynes added to carbon-carbon double bond of duroquinone **1** to give [2+2] photocycloadducts, most of which are converted photochemically into their corresponding eight-membered compounds.

Preparative photochemical reactions were conducted in a photochemical reactor composed of a water-cooled system and a Pyrex (or a quartz) reaction vessel with 300 nm (or 254 nm) UV lamps (Rayonet Photochemical Reactor, Model RPR-208). Irradiation (300 nm) of duroquinone **1** (164 mg, 1.0 mmol) and excess of phenylacetylene **2** (2.0 mL) in dichloromethane (200 mL) for 25 h afforded the electrocyclic reaction product **4**[8] *via* [2+2]-photocycloadduct **3** which was not found in the photoreaction mixture using ^{1}H NMR spectroscopy. This reaction may reflect π, π^* activity in the excited duroquinone **1** having electron-donating methyl groups, the direction of addition being controlled by stabilization in the more stable 1,4-diradical intermediate. Flash column chromatography (silica gel, 230-400 mesh) using *n*-hexane and ethyl acetate (9 : 1, v/v) as the eluents gave the adduct **4** in 55% yield, in which *ca.* 30% of duroquinone **1** was recovered. ^{1}H NMR spectrum (CDCl$_3$) of 1 : 1 adduct **4** showed a vinyl proton in eight-membered ring at δ 7.57 ppm. The



Scheme 1.

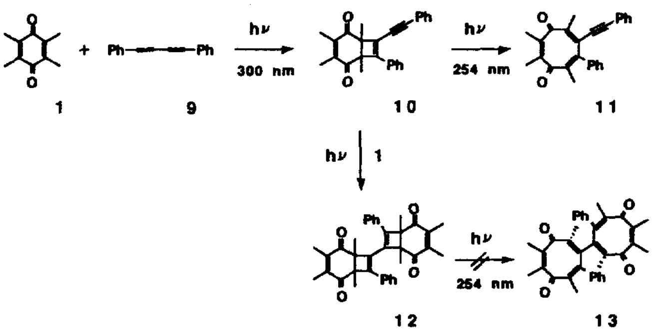
carbon signal containing the vinyl proton was also found at 158.6 ppm in ^{13}C NMR spectrum (CDCl$_3$). The EI mass spectrum gave a molecular ion peak at m/e 266.

On the other hand, irradiation (300 nm) of duroquinone **1** (164 mg, 1.0 mmol) and diphenylacetylene **5** (178 mg, 1.0 mmol) in dichloromethane (200 mL) for 65 h afforded [2+2] photocycloadduct **6** as the major product.[9] Flash column chromatography (silica gel, 230-400 mesh) using *n*-hexane and ethyl acetate (10 : 1, v/v) gave the adduct **6** in 45% yield, in which *ca.* 40% of the starting materials was recovered. The EI mass spectrum showed the molecular ion peak at m/e 342. ^{13}C NMR spectrum (CDCl$_3$) of **6** showed a carbon signal of carbonyl groups at δ 194.5 ppm due to the symmetrical structure. Irradiation (254 nm) of the 1 : 1 photoadduct **6** (20 mg) in dichloromethane (30 mL) for 5 h gave rise to the electrocyclic reaction product **7** in 17% yield as a sole product, which was also identified by EI mass spectrum, ^{1}H NMR spectrum, and UV spectrum.[10] The structure of **6** was also established by its oxidative photocyclization reaction to **8**. Irradiation (300 nm) of **6** (20 mg) in dichloromethane (30 mL), in the presence of O$_2$ for 10 h yielded **8** (52%), which was found to be fluorescent due to the phenanthrene moiety. The fluorescence emission bands were observed at 293, 320, 366, 383 and 405 nm in *n*-hexane (λ_{ex} 250 nm). Mass spectrum of **8** showed peaks at m/e 178, which is due to phenanthrene moiety, and m/e 340 (molecular ion).

Irradiation (300 nm) of **1** (164 mg, 1.0 mmol) and 1,4-diphenylbutadiyne **9** (202 mg, 1.0 mmol) in dichloromethane (200 mL) for 20 h gave 1 : 2 adduct **12** (35%) as well as 1 : 1 adduct **10** (27%).[11] The EI mass spectra of 1 : 1 adduct **10** and 1 : 2 adduct **12** showed molecular ion peaks at m/e 366 and m/e 530, respectively.

Irradiation of **10** with 254 nm UV light also yielded the electrocyclic reaction product **11** in *ca.* 54% yield,[11] whereas, irradiation (254 nm) of **12** did not give **13**. This fact may be explained by the steric hindrance between the methyl groups and phenyl groups of the structure **13**.

On the other hand, it was observed that 1 : 2 photoadduct of duroquinone **1** and 1,4-diethynylbenzene was converted photochemically into its corresponding isomer.[12] The steric hindrance in this 1 : 2 adduct decreases, in comparison with



Scheme 2.

13, because the two eight-membered rings are separated by the central benzene ring.

In conclusion, irradiation of duroquinone **1** and alkynes leads to [2+2] photocycloadducts. The photoadducts can be converted photochemically into their corresponding isomers depending on the steric hindrance. Extension of the photoaddition reactions of duroquinone to other systems will be investigated.

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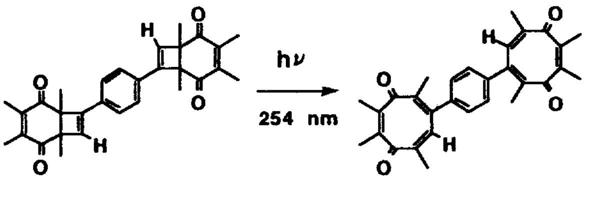
8. Spectral data of **4**; IR (KBr), 3057, 2966, 1700, 1644, 1447, 1377, 786, 695 cm^{-1}; UV (MeOH), λ_{max} 329, 288, 251, 227 nm; ^{1}H NMR (CDCl$_3$), δ 7.68-7.32 (5H), 7.57 (1H, s), 2.11(3H, s), 1.67 (3H, s), 1.38 (3H, s), 1.37 ppm (3H, s); ^{13}C NMR (CDCl$_3$), δ 206.1 and 204.6 (C=O's), 158.6 (=CH), 129.2, 128.2 and 127.2 (aromatic CH's), 16.87, 15.99, 12.88 and 9.73 ppm (Me's); MS (EI), m/e 77, 189, 266 (M).
9. Spectral data of **6**; IR (KBr), 3064, 2931, 1672, 1588, 1447, 1377, 793, 716 cm^{-1}; UV (MeOH), λ_{max} 288, 260 nm; ^{1}H NMR (CDCl$_3$), δ 7.99-7.51 (10H), 2.16 (6H, s), 2.05 ppm (6H, s); ^{13}C NMR (CDCl$_3$), δ 194.5 (C=O), 134.9, 129.9,

and 128.7 (aromatic CH's), 12.44 and 12.19 ppm (Me's); Mass (EI), m/e 77, 178, 342 (M).

10. Spectral data of **7**; UV (MeOH), λ_{max} 320, 253 nm; ^{1}H NMR (CDCl$_3$), δ 7.98-7.45 (10H), 2.08 (6H, s), 1.39 ppm (6H, s); Mass (EI), m/e 342 (M).
11. Spectral data of **10**; IR (KBr), 3057, 2924, 2185, 1665, 1447, 1376, 758 cm^{-1}; UV (MeOH), λ_{max} 248, 312 nm; ^{1}H NMR (CDCl$_3$), δ 7.89-7.28 (10H), 2.00 (3H), 1.97 (3H), 1.66 (3H), 1.52 ppm (3H); ^{13}C NMR (CDCl$_3$), δ 194.1 and 193.5 (C=O's), 131.9, 128.8, 128.6, 128.4, 128.2 and 126.5 (aromatic CH's), 16.50, 15.41, 13.93 and 13.66 ppm (Me's); Mass (EI), m/e 202, 366 (M).
    Spectral data of **11**; UV (MeOH), λ_{max} 320, 281, 272, 252, 244 nm; ^{1}H NMR (CDCl$_3$), δ 7.80-7.38 (10H), 2.12 (3H, s), 1.67 (3H, s), 1.41 (3H, s), 1.40 ppm (3H, s); Mass (EI), m/e 202, 366 (M).
    Spectral data of **12**; IR (KBr), 3064, 2931, 1658, 1447, 1377, 786, 695 cm^{-1}; UV (MeOH), λ_{max} 259, 270 nm; ^{1}H NMR (CDCl$_3$), δ 7.28-7.04 (2 x 5H), 2.04 (6H, s), 1.89 (6H, s), 1.66 (6H, s), 1.58 ppm (6H, s); ^{13}C NMR (CDCl$_3$), δ 200.2 and 198.0 (C=O's), 128.7, 128.0 and 126.1 (aromatic CH's), 16.28, 16.10, 13.21 and 13.53 (Me's), 150.7, 141.9, 141.8, 138.7, 132.2, 59.24 and 56.75 ppm (7 C's); Mass (EI), m/e 202, 530 (M).
12. 1 : 2 [2+2]-Photoadduct (see below) was obtained from the photoreaction of duroquinone and 1,4-diethynylbenzene in dichloromethane with 300 nm UV light. Spectral data; IR (KBr), 3057, 2973, 1700, 1665, 1454, 1377, 835 cm^{-1}; UV (MeOH), λ_{max} 290, 280, 257 nm; ^{1}H NMR (CDCl$_3$), δ 7.38 (4H, s, ArH), 6.49 (2 x 1H, s, 2=CH's), 1.97 (2 x 3H, s, 2 Me), 1.93 (2 x 3H, s, 2Me), 1.60 (2 x 3H, s, 2Me), 1.48 ppm (2 x 3H, s, 2Me); ^{13}C NMR (CDCl$_3$), δ 200.4 and 199.8 (C=O's), 134.5 (=CH's), 125.8 (aromatic CH's), 16.93, 16.55, 13.80 and 13.56 (Me's), 152.6, 142.6, 142.5, 132.0, 58.25, 56.08 ppm (6C's); Mass (CI), m/e 455 (M+1).
    Spectral data of the electrocyclic reaction product; IR (KBr), 3043, 2924, 1700, 1644, 1454, 1377, 842 cm^{-1}; UV (MeOH), λ_{max} 336, 294, 254, 240 nm; ^{1}H NMR (CDCl$_3$), δ 7.72 (4H, s, ArH), 7.61 (2H, s, 2=CH'), 2.14 (6H, s, 2Me), 1.71 (6H, s, 2me), 1.41 (6H, s, 2Me), 1.40 ppm (6H, s, 2me); ^{13}C NMR (CDCl$_3$), δ 206.0 and 204.5 (C=O's), 158.9 (=CH's), 127.3 (aromatic CH's), 16.90, 16.29, 12.91 and 8.34 ppm (Me's); Mass (CI), m/e 455 (M+1).



Novel Migration of Aryl Group in 3-Trifluoromethylpyrazolyl Aryl Ether

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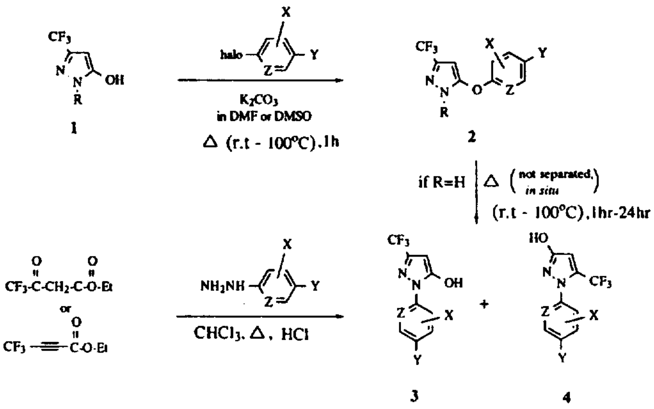
3-Trifluoromethylpyrazolyl aryl ethers **2** have been reported to exhibit a potent herbicidal activity[1] and also used as intermediates for the synthesis of insecticides.[2] In the synthesis of their analogues, the aryl group was usually introduced by the reaction of compound **1** with an appropriate aryl halide under basic conditions (Scheme 1).

Surprisingly, in case of R=H, we found that the above reactions initially gave the *O*-arylated pyrazole compound **2** as an intermediate and eventually resulted in the aryl group migrated pyrazole compound **3** with a concomitant formation of regioisomer **4** as a minor product. The progress of reaction can be simply checked by T.L.C. The regioisomers of the reaction products can be assigned by comparing the physical properties and spectral data of the isomers with the ones of the authentic samples, which were synthesized by other methods,[3-8] such as using aryl hydrazine derivatives shown in Scheme 1. The general solubilities[3,5] of the two isomers were reported. So the separation of the two regioisomers was facile since the 5-hydroxy isomer **3** was soluble in aqueous NaHCO$_3$ solution while the 3-hydroxy isomer **4** was not.

Of the several intramolecular rearrangement reaction of aryl group from oxygen to nitrogen atoms, the Chapman Rearrangement,[9] which is the thermal reaction of aryl imidates to *N,N*-diaryl amides, is typical. Just like the Chapman Rearrangement, the strong electron-withdrawing groups of the aryl ring in the above reactions facilitate its migration from oxygen to nitrogen atoms (Table 1). Contrary to the aryl group, no alkyl group migration was observed at all.



Scheme 1.