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Syntheses of 3,4-Bisaryl-3-cyclobutene-1,2-diones and Related Heterocycles

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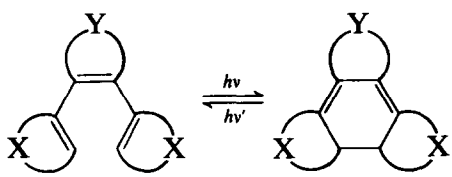
ABSTRACT

3,4-Dichloro-3-cyclobutene-1,2-dione was reacted with various aromatics to yield 3,4-bisaryl-3-cyclobutene-1,2-diones. Their naphthoquinone analogues were also synthesized.

1 INTRODUCTION

Diarylethenes, composed of 1,3,5-hexatriene cyclic systems, have been studied as photochromic systems (Scheme 1). Photochromic compounds can be applied as photo-erasable media in information recording and display systems.[1] Recently Irie and co-workers[2–4] reported the syntheses of various diarylethenes and their excellent photochromic properties. Some of them showed good heat- and photo-stability and thus have a good durability in photochromic applications.



X Heteroaromatic system
Y Heterocyclic system

Scheme 1

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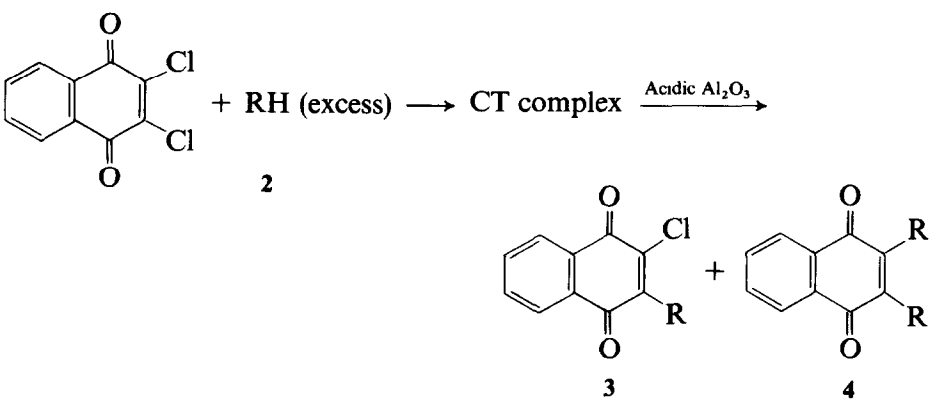
A diode laser which emits laser light in the range of 780–830 nm has been proposed as a light source for optical recording systems, and therefore the recording media should absorb in the near-IR region. The synthesized diarylethenes absorb up to 700 nm and a bathochromic shift of λ_{max} can be anticipated.

In this paper we report the syntheses of 3,4-bisaryl-3-cyclobutene-1,2-diones and 2,3-bisaryl-1,4-naphthoquinones as potential photochromic dyes. These compounds have an additional electron-accepting group in the diarylethene system, and a bathochromic shift of λ_{max} is indicated from the results of molecular-orbital calculations.

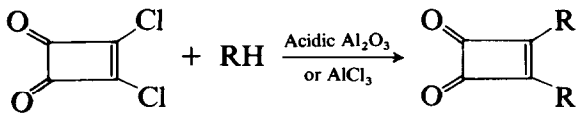
2 RESULTS AND DISCUSSION

It is well known that 1,4-naphthoquinones easily form charge-transfer (CT) complexes with electron-donating compounds.[5] Blackburn and Griffiths[6,7] reported a convenient route to 2-aryl-1,4-naphthoquinones by using the acidic alumina method, which converts the CT complex into donor-substituted quinones. For example, addition of 2,3-dichloro-1,4-naphthoquinone (**1**) to *N,N*-dimethyl-1-naphthylamine (**2a**) in dichloromethane produces the CT complex. Passing this CT complex solution through a column of acidic alumina using dichloromethane as eluent yielded the mono- (**3a**) and bisaryl (**4a**) derivatives.[6,7] Reaction of **1** with 1,2,5-trimethylpyrrole (**2b**) under similar reaction conditions gave the mono-substituted (**3b**) but not the bis-substituted (**4b**) derivative (Scheme 2). On the other hand, 3,4-dichloro-3-cyclobutene-1,2-dione (**5**) reacted with pyrrole



a R = 4-Me_2N-1-naphthyl
b R = 1,2,5-Me_3-3-pyrrolyl

Scheme 2



5 **6** **7**

a R = 1,2,5-Me_3-3-pyrrolyl
b R = 1,2-Me_2-3-indolyl
c R = 4-Cl-phenyl
d R = 2,4,6-Me_3-phenyl

Scheme 3

and indole to give the corresponding bisaryl derivatives (**7a**, **7b**), but did not react with furan and thiophene (Scheme 3, Table 1).

In the case of benzene derivatives, which are poor electron donors compared with five-membered heterocyclic aromatics, the Friedel–Crafts reaction is useful in the synthesis of the bisaryl cyclobutene-1,2-dione derivatives (**7c**, **7d**). Green and Neuse[8] reported the Friedel–Crafts reaction of **5** with benzene, giving 3,4-diphenyl-3-cyclobutene-1,2-dione. On the other hand, Ried and Schäfer[9] reported that similar reactions of 4-bromo-3-phenyl-3-cyclobutene-1,2-dione with aryl compounds gave the asymmetric 4-aryl-3-phenyl-3-cyclobutene-1,2-diones. We also synthesized 4-chlorophenyl- (**7c**) and 2,4,6-trimethylphenyl-analogue (**7d**) under similar conditions.

TABLE 1
Reaction of **1** or **5** with Various Aromatics

Entry number	*Reactant*	*Aromatics*	*Ratio*[a]	*Product (yield %)*
1	**1**	1,2,5-Trimethylpyrrole	1:6	**3b** (19)
2	**1**	1,2-Dimethylindole	1:6	[b]
3	**1**	2,5-Dimethylfuran	1:6	No reaction
4	**1**	2,5-Dimethylthiophene	1:6	No reaction
5	**5**	1,2,5-Trimethylpyrrole	1:7	**7a** (0·77)[c]
6	**5**	1,2-Dimethylindole	1:6	**7b** (0·67)[c]
7	**5**	2,5-Dimethylfuran	1:6	No reaction
8	**5**	2,5-Dimethylthiophene	1:6	No reaction
9	**5**	1,3,5-Trimethylbenzene	1:23	**7d** (7·2)
10	**5**	Chlorobenzene	1:7	**7c** (47·8)

[a] The ratio of reactant to aromatics. Reaction was carried out at room temperature.
[b] Many products in very small yields were observed on a column chromatography, but none of them can be isolated.
[c] Unreacted CT complexes were absorbed on the column.

The reactions of **1** and **5** with various aromatics are summarized in Table 1. When five equivalents of **2b** were added to a dichloromethane solution of **1**, the color of the solution immediately changed to purple, indicating the formation of the CT complex. The solution was passed through a column of acidic alumina, using dichloromethane as an eluent. The purple eluent was collected, the solvent evaporated and the residue was purified by column chromatography with dichloromethane and recrystallized from ethanol. This compound was identified as 2-chloro-3-(1,2,5-trimethyl-3-pyrrolyl)-1,4-naphthoquinone (**3b**). The bisaryl derivative (**4b**) was not obtained from this reaction.

This method could be applied to synthesis of 3,4-bisaryl-3-cyclobutene-1,2-diones (**7**). Commercially available 3,4-dihydroxy-3-cyclobutene-1,2-dione (squaric acid) is converted to the dichloro derivative (**5**) with thionyl chloride in the presence of small amounts of *N,N*-dimethylformamide.[10] When excess aromatics were added to a dichloromethane solution of **5**, the color of the solution immediately changed to purple, indicating the formation of the CT complex. This solution was passed through a column of acidic alumina, and the yellow eluent was collected and evaporated under reduced pressure. The yellow residue was purified by column chromatography to give 3,4-bis-(1,2,5-trimethyl-3-pyrrolyl)-3-cyclobutene-1,2-dione (**7a**). None of the mono-substituted product was obtained. Similar reaction of **5** with 1,2-dimethylindole (**6b**) gave 3,4-bis(1,2-dimethyl-3-indolyl)-3-cyclobutene-1,2-dione (**7b**). The reaction depends very much on the formation of the CT complex. 2,5-Dimethylthiophene or 2,5-dimethylfuran did not form a CT complex with **1** and **5**, and no substitution occurred, since they are weaker donors than pyrrole or indole (Table 1).

Furthermore, in the case of dichlorodicyanobenzoquinone (DDQ), which is a very strong acceptor, the CT complex was formed, but it is too stable because of the strong donor–acceptor interaction, and no reaction occurred. Adequate combination of a donor and an acceptor is necessary for the success of this reaction. For the poor electron-donating aryl compounds the Friedel–Crafts reaction is useful to synthesize 3,4-bisaryl-3-cyclobutene-1,2-diones (**7c**, **7d**). Compound **5** was dissolved in a large excess of chlorobenzene and two equivalents of sublimed aluminum chloride was added. The reaction mixture was poured into water and extracted with ether. The ether layer was evaporated and the residue was purified by column chromatography to give 3,4-bis(4-chlorophenyl)-3-cyclobutene-1,2-dione (**7c**). The very sterically hindered 3,4-bis(2,4,6-trimethylphenyl)-3-cyclobutene-1,2-dione (**7d**) could also be synthesized by this method. It was found that the acidic alumina method and the Friedel–Crafts method could be applied to the synthesis of bisaryl heterocycles, depending on the strength of the donor properties of the reactant.

The synthesized bisaryl heterocycles have a 1,3,5-hexatrien system in the molecule and are expected to show photochromism as shown in Scheme 1. Solutions of **7a**–**7d** were irradiated with a mercury lamp with color-glass filters, and the absorption spectra changes were monitored. In the case of **7d**, the absorption spectra did not change at all. It is concluded that a 2,4,6-trimethylphenyl group is too bulky to change into the closed ring form. In the case of **7c**, the absorption spectra changed and reached the photostationary state after 0·5 h of irradiation. It was found that the spectra changes were not caused by photochromism, and a photooxidation process, reported by Bird,[8] is proposed. In the cases of **7a** and **7b**, the absorption maxima were gradually degenerated by irradiation, and visible-light irradiation did not induce the reverse reaction, and consequently no photochromism was observed. The reason for this is now being investigated by means of the molecular-orbital method.

3 EXPERIMENTAL

All melting points are uncorrected. ^{1}H-NMR spectra were recorded on a JEOL JNM-GX270 spectrometer. Mass spectra were recorded on a Shimadzu LKB-9000 spectrometer operating at 80 eV. The visible spectra were measured using a Shimadzu UV-240 spectrophotometer. Elemental analyses were recorded on a Yanaco CHN recorder MT-2. 2,3-Dichloro1,4-naphthoquinone (**1**) was commercial grade and 3,4-dichloro-3-cyclobutene-1,2-dione (**5**) was prepared according to the literature method.[10]

3.1 2-Chloro-3-(1,2,5-trimethyl-3-pyrrolyl)-1,4-naphthoquinone (3b)

To a solution of **1** (1·00 g, 4·40 mmol) in dichloromethane (10 ml), 1,2,5-trimethylpyrrole (**2b**) (2·90 g, 26·6 mmol, 6 equivalents) was added at room temperature. The color of the solution changed immediately from yellow to purple. The solution was slowly passed through a column of 80 g of acidic alumina (ICN Biomedicals, activity grade 1). The solution of **2b** (1·48 g, 13·6 mmol) in dichloromethane (50 ml) was used as first eluent, and this was followed with dichloromethane. The purple eluent was collected and evaporated. Four compounds were detected by thin-layer chromatography (chloroform). The major purple compound was separated by column chromatography on silica gel using chloroform as eluent, giving **3b** (yield 19%) with a melting point of 195–196°C (ethanol); ^{1}H-NMR (deuteriochloroform) δ, 8·2–8·1 (m, 2H, 5-H and 8-H), 7·8–7·7 (m, 2H, 6-H and 7-H), 6·0 (s, 1H, pyrrolyl-H), 3·4 (s, 3H, N-CH_3), 2·3 (s, 3H, 2-CH_3) and 2·1 (s, 3H, 5-CH_3); *m/z* 299 (M^+), 264 (M^+–Cl); UV/visible (chloroform) 539 nm.

For $C_{17}H_{13}NO_2Cl$ the calculated values were 68·12, 4·71 and 4·67 for C, H and N, respectively; the experimentally found values were 67·85, 4·68 and 4·58.

3.2 3,4-Bis(1,2,5-trimethyl-3-pyrrolyl)-3-cyclobutene-1,2-dione (7a)

To a solution of squaric acid (0·50 g, 4·38 mmol) in benzene (20 ml) thionyl chloride (1·13 g, 9·50 mmol, 2·17 equivalents) and four drops of *N,N*-dimethylformamide were added, and the mixture was heated at 65°C for 2 h. Benzene and excess thionyl chloride were removed by distillation under reduced pressure. The residue (**5**) was dissolved in chloroform (5 ml) and **2b** (3·25 g, 29·8 mmol, 6·90 equivalents) was added at room temperature, the color of the solution immediately changing to purple. The solution was passed through a column of acidic alumina, and the yellow eluent was collected and evaporated. The crude product was purified by column chromatography on silica gel using dichloromethane. Most of the CT complexes were not converted to the aryl derivatives in this process. The yield of **7a** was 0·01 g (0·77%) with a melting point >200°C (decomposed); ^{1}H-NMR (deuteriochloroform) δ, 6·3 (s, 2H, 4-H), 3·5 (s, 6H, N-CH_3), 2·6 (s, 6H, 2-CH_3) and 2·2 (s, 6H, 5-CH_3); *m/z* 296 (M^+), 240 ($M^+-2\times C{=}O$), 148; UV/visible (chloroform) 385 nm.

For $C_{18}H_{20}N_2O_2$ the calculated values were 72·95, 6·80 and 9·45 for C, H and N, respectively; the experimentally found values were 73·29, 7·00 and 9·32.

3.3 3,4-Bis(1,2-dimethyl-3-indolyl)-3-cyclobutene-1,2-dione (7b)

To a solution of **5** (2·02 mmol) in dichloromethane (3 ml) 1,2-dimethylindole (**6b**) (1·8 g, 12·4 mmol, 6·14 equivalents) was added at room temperature. The procedures following were the same as in the case of **7a**. The yield of **7b** was 0·005 g (0·67%) with a melting point >200°C (decomposed); ^{1}H-NMR (deuteriochloroform) δ, 7·3 (m, 4H, 4-H and 7-H), 7·2 (m, 2H, 5-H), 7·0 (m, 2H, 6-H), 3·8 (s, 6H, N-CH_3) and 2·5 (s, 6H, 2-CH_3); *m/z* 368 (M^+), 312 ($M^+-2\times C{=}O$); UV/visible (chloroform) 406 nm.

For $C_{24}H_{20}N_2O_2$ the calculated values were 78·24, 5·47 and 7·64 for C, H and N, respectively; the experimentally found values were 76·98, 5·72 and 7·34.

3.4 3,4-Bis(4-chlorophenyl)-3-cyclobutene-1,2-dione (7c)

To squaric acid (3·04 g, 26·6 mmol) thionyl chloride (6·42 g, 54·0 mmol) and four drops of *N,N*-dimethylformamide were added, and the mixture was

heated at 65°C for 2 h. To the resultant solution of **5**, chlorobenzene (**6c**) (20 ml) and freshly sublimed aluminum chloride (8·50 g, 63·8 mmol, 2·4 equivalents) were added and the mixture was stirred for 30 h at room temperature (under closed conditions with a calcium chloride tube to protect from moisture). The mixture was poured into water (20 ml) and extracted with ether. The ether layer was dried with magnesium sulfate and then evaporated. The crude residue was purified by column chromatography on silica gel using chloroform. The yield of **7c** was 3·85 g (47·8%) with a melting point of 146–148°C; ^{1}H-NMR (deuteriochloroform) δ, 8·0 (dt, 4H, 2-H and 6-H) and 7·5 (dt, 4H, 3-H and 5-H); *m/z* 302 (M^+), 246 ($M^+-2 \times C{=}O$) 176, 123; UV/visible (chloroform) 340 nm.

For $C_{16}H_8O_2Cl_2$ the calculated values were 63·39 and 2·66 for C and H, respectively; the experimentally found values were 63·01 and 2·65.

3.5 3,4-Bis(2,4,6-trimethylphenyl)-3-cyclobutene-1,2-dione (7d)

Similar reaction of **5** with 1,3,5-trimethylbenzene (**6d**) in the presence of aluminum chloride gave **7d**, yield 7·2% with a melting point of 202–203°C; ^{1}H-NMR (deuteriochloroform) δ, 6·9 (s, 4H, 4-H and 6-H), 2·3 (s, 6H, 5-CH_3) and 2·1 (s, 12H, 1-CH_3 and 3-CH_3); *m/z* 318 (M^+), 262 ($M^+-2 \times C{=}O$); UV/visible (chloroform) 315 nm.

For $C_{22}H_{22}O_2$ the calculated values were 82·99 and 6·96 for C and H, respectively; the experimentally found values were 82·63 and 6·93.

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