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A PRELIMINARY STUDY ON CHEMISTRY OF PHENOXYNAPHTHACENEQUINONES

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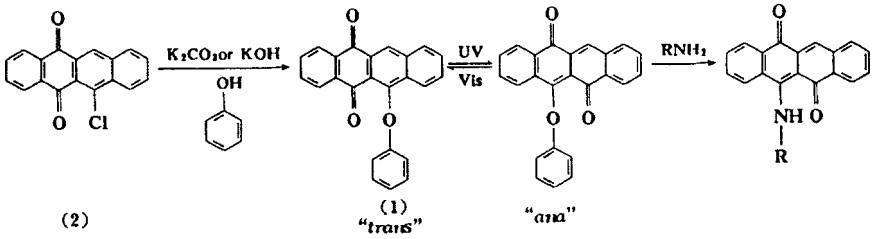
Abstract A preliminary study on the chemistry of 6-phenoxy-5,12-naphthacenequinone derivatives was reported. It was found that the main product was 6-(N,N-dimethylamino)-5,12-naphthacenequinone when a reaction of 6-chloro-5,12-naphthacenequinone with 4-hydroxyazobenzenes in DMF was carried out under certain reaction conditions. When the reaction of 6-[4-(4-hydroxyphenyl)isopropyl)phenoxy]-5,12-naphthacenequinone and epichlorohydrin was carried out in an acetone/DMF(V/V=2/1) mixed solvent and in the presence of K_2CO_3 and KI, a new phenoxynaphthacenequinone derivative,6,6'-[1-methylethylidenebis(4,1-phenyleneoxy)]bis(5,12-naphthacenequinone), was obtained.

INTRODUCTION

The possibility of employing photochromic 6-phenoxy-5,12-naphthacenequinone(**1**) and polymers with phenoxynaphthacenequinone side groups as materials for holographic recording has been explored [1,2]. Compound **1** and its derivatives can easily be synthesized by reacting 6-chloro-5,12-naphthacenequinone(**2**) with phenol or substituted phenols in the presence of a caustic catalyst, and their photochromism is due to the photoinduced isomerization of the yellow *trans* *p*-quinone form to the orange-colored *ana* *p*-quinone form [3-5]. The most significant features of these materials are their relatively low fatigue and

negligible *ana* to *trans* thermal back reaction[2]. The *trans* form is stable and does not react markedly with amines, while the *ana* form undergoes an irreversible reaction with them. The chemistry and photochemistry of **1** can be illustrated as below:



The above reactions of phenoxynaphthacenequinones involve the O-C_1(of benzene ring) and O-C_5(of naphthacenequinone ring) bonds. In study on synthesis of phenoxynaphthacenequinone derivatives and reagents, we have found two interesting reactions which are connected with the O-C_6(of naphthacenequinone ring) bond of the *trans* form.

EXPERIMENTAL DETAILS

Chemicals

Dimethylformide(DMF) was dried over CaH_2 and distilled. 6-Chloro-5,12-naphthacenequinone(**2**) and 6-[4-(2-(4-hydroxyphenyl)isopropyl)phenoxy]-5,12-naphthacenequinone(**3**) were synthesized as previously reported[4,5]. Other chemicals and solvents were of analytical grade and used as received.

Measurements

IR spectra were recorded on a BIO-RAD FTS-7 Infrared Spectrometer(KBr pellet). Measurements of ^1H NMR spectra were made in $CDCl_3$(using TMS as the internal standard) or DMSO-d_6(using the solvent peak at 2.62 as reference) with a JEOL Unity-400 NMR Spectrometer. A LDI 1700-TOF MS(Biomolecular comp. USA) was used to measure the molecular weights of components in a solution.

RESULTS AND DISCUSSION

Reaction of 6-chloro-5,12-naphthacenequinone with 4-hydroxyazobenzene in dry DMF

As mentioned above, certain phenoxynaphthacenequinone derivatives can be synthesized by using reaction of 6-chloro-5,12-naphthacenequinone(**2**) with substituted phenols. 6-[4-(phenylazo)phenoxy]-5,12-naphthacenequinone(**4**) was synthesized by reacting **2** with 4-hydroxyazobenzene in dry DMF and in the presence of anhydrous potassium carbonate under the following procedures: a mixture of **2**(2.05 g, 7 mmol), 4-hydroxyazobenzene(1.67 g, 8.4 mmol), potassium carbonate(2.40 g, 17.4 mmol) in 30 mL DMF was heated at 115 °C for 3 h. It was then poured over potassium hydroxide aqueous solution, and the resulting precipitant was washed successively with 0.5 mol/L KOH solution, 0.5 mol/L HCl solution and water, and dried under vacuum. The crude product(2.91 g) was recrystallized twice from DMSO, yield 1.88 g (59.2%). IR, λ_{max}/cm^{-1}: 1669, 1582, 1491, 1428, 1398, 1346, 1278, 1236, 1139, 982, 833, 753, 714.

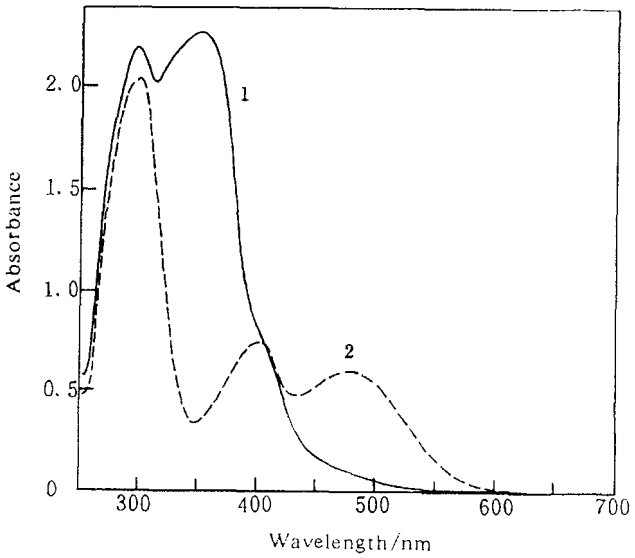


FIGURE 1 Absorption spectra of compound **4** and **5** in DMSO.
1---compound **4** ($C=1\cdot10^{-4}$ mol/L)
2---compound **5** (C=40 mg/L)

However, when the reaction conditions were changed to **2**(7 mmol), 4-hydroxyazobenzene(14 mmol), potassium carbonate(17.4 mmol), DMF(40 mL), 115 °C/4 h, and recrystallization twice from an ethanol/chloroform(V/V=3/2) mixed solvent, 1.13 g red crystals were obtained. As can be seen from Figure 1, this compound(**5**) has totally different spectral property from that of compound **4**. Furthermore, **5** has an IR spectrum different from that of **4**, λ_{max}/cm^{-1}: 2917, 2852, 1663, 1576, 1500, 1396, 1347, 1272, 1044, 981, 756, 711, indicating the absence of the characteristic peak of azobenzene. Compound **5** was further characterized with NMR analysis and proved to be 6-(N,N-dimethylamino)-5,12-naphthacenequinone. The details of NMR results will be published elsewhere[6], and the ^1H NMR spectra shown in Figure 2 indicate clearly that there did not exist an azobenzene moiety in compound **5** according to the disappearance of the peaks in the higher field(7.0-7.5 *ppm*), and that two different compounds were obtained under different reaction

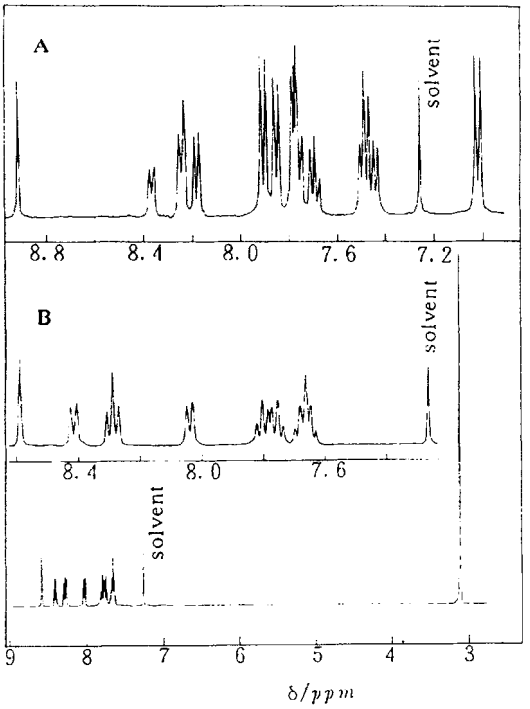


FIGURE 2 A comparison of two ^1H NMR spectra of compound **4**(A) and compound **5**(B) in $CDCl_3$.

conditions. In the later case, the yield of compound **5** was as high as 53.6% after twice recrystallization.

When 4-hydroxy-4'-ethoxyazobenzene was used instead of 4-hydroxyazobenzene, two different products were also prepared just depending on the reaction conditions. Compound **5** was the main product under the following reaction conditions: **2**(7 mmol), 4-hydro-4'-ethoxyazobenzene(14 mmol), potassium carbonate(17.4 mmol), DMF(40 mL), and 115 °C/4 h, yield: 1.01 g(47.9%) after twice recrystallization from an ethanol/chloroform(V/V=3/2) mixed solvent.

We supposed that compound **5** was formed by a further reaction of compound **4** with DMF. In order to prove this idea, LDI 1700 MALDI-TOF MS was used to monitor the reaction of compound **4** with DMF. When **4** was added to DMF, the colour change of the solution from yellow to red may be observed even at room temperature. When the solution was treated at 115 °C for 2 h, the peak of compound **4** (M=454) completely disappeared, and only the peak of M=301 left, which is in agreement with the formation of compound **5** (see Figure 3).

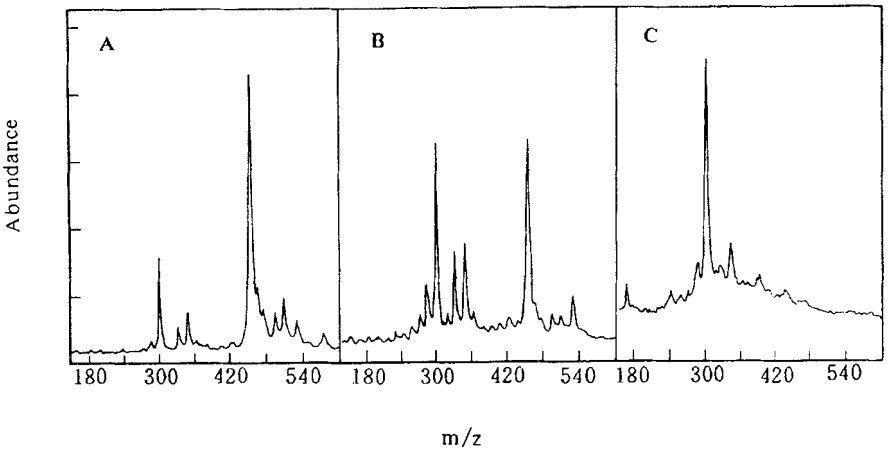


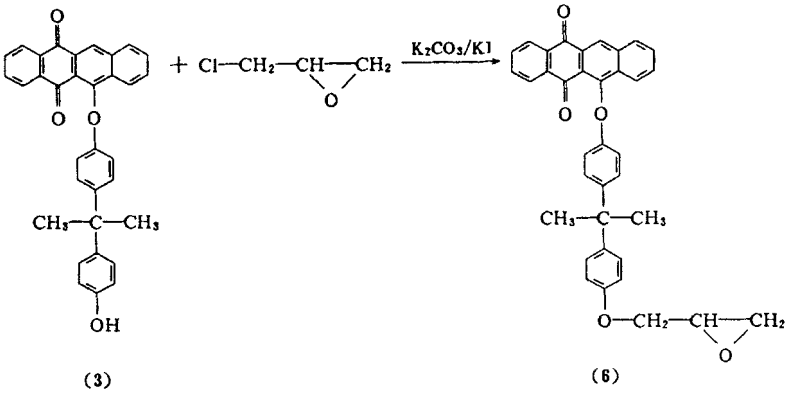
FIGURE 3 MALDI-TOF MS spectra (polarity:positive) of compound **5** in DMF. A---freshly prepared solution; B---after ca. 1 h; C---reacted for 2 h at 115 °C

In fact, the reaction of phenoxynaphthacenequinone derivatives with DMF was first observed in a previous work[5]: when the solution of 6-[4-(2-(4-hydroxyphenyl)isopropyl)phenoxy]-5,12-naphthacenequinone(**3**)

in DMF was kept in the dark for 1 week before UV irradiation, there was an apparent spectral change, and the solution did not exhibit photochromism on UV irradiation anymore. At that time, we were not sure whether the reaction occured between **3** and DMF or between **3** and impurities in DMF. The spectrum of DMF solution of compound **3** kept in the dark for 1 week is almost the same as that of compound **5** in DMSO. Now, we are certain that this spectral change indicates that the reaction proceeds between the *trans* form of compound **3** and DMF.

Reaction of compound **3** and epichlorohydrin

We tried to synthesize a new reagent with phenoxynaphthacenequinone photochrome and oxirane group by reacting compound **3** with epichlorohydrin:



(3) (6)

Thus, a mixture of **3**(7.83 g, 15 mmol), epichlorohydrin(5.0 mL, 62 mmol), K_2CO_3(2.30 g, 16.7 mmol), KI(0.001 g), acetone(120 mL), and DMF(60 mL) was reacted at 72 °C for 48 h. It was found that fine yellow powders were formed during the reaction. The precipitant was separated from the dark-red mother liquor by filtration, washed with water, and then dried under vacuum. This crude product(4.0 g) was recrystallized from DMSO, yield 3.2 g (compound **7**). **7** is insoluble in DMF, THF, acetone and xylene etc., IR, λ_{max}/cm^{-1}: 2966(very weak), 1674, 1581, 1503, 1426, 1397, 1344, 1274, 1233, 1217, 1175, 985, 828(weak), 754,716. These results of solubility and IR demonstrate that **7** is different from compound **3**. The ^1H NMR spectrum of compound **7** is shown

in Figure 4, which gives very good evidence that compound **7** is 6,6'-[1-methylethylidenebis(4,1-phenyleneoxy)]bis(5,12-naphthacenequinone).A reasonable interpretation for the formation of compound **7** could

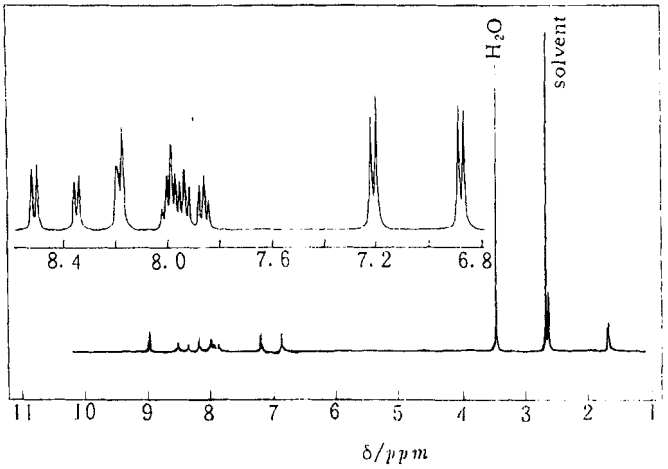
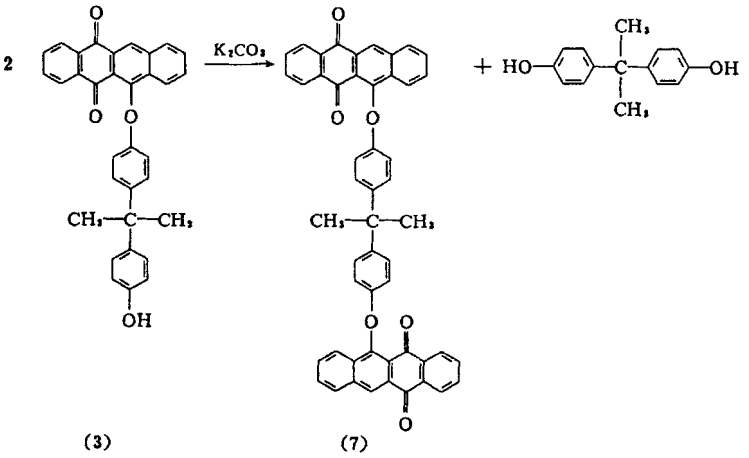


FIGURE 4 'H NMR spectrum of compound **7**.

be based on S_N2 reaction between two **3** molecules with the phenoxy anion as the attacking nucleophile which was formed in the basic medium:



Based on the procedures mentioned above, the yield of compound **7** was 57.7% after recrystallization.

ACKNOWLEDGMENTS

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