REACTIONS OF SIX-MEMBERED RING α -DIAZOKETONES

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Photochemical reactions of 1-oxo-2-diazo-1,2-dihydrobenzene (DBQ), 1-oxo-2-diazo-1,2-dihydronaphthalene (DNQ) and 5-(4-tolyl)sulfonated DNQ (DNQ-5STL) are studied, as typical examples of six-membered ring α -diazoketones, by reverse-phase liquid chromatography. The obtained products under different reaction conditions, such as photochemical reactions of pure solid DNQ-5STL in air and in vacuo, are examined. The reactivity of the carboxy compounds produced in air or in a water-containing solution is also discussed. They exhibit decarboxylation, dimerization or azo formation in the presence of bases, being markedly dependent on the type of molecules. The azo formation rate constant of the 3-carboxyindene analogue from DNQ-5STL is much greater than that of its dimerization. Photochemical reactions of six-membered ring α -diazoketones from excitation to final product formation are also discussed.

1. Introduction

Most of α -diazoketones are known to produce reactive ketene intermediates when they are subjected to photochemical or thermal reactions. The formation of ketenes involves carbon-carbon 1,2-migration and is known as the Wolff rearrangement [1]. The ketenes undergo a variety of reactions depending upon the conditions as well as upon the type of molecules as shown in Fig. 1. For instance, some ketenes are reported to undergo dimerization [2], produce butenolides upon photolysis [3,4], or form 1,3-dioxoles in thermolysis in xylene [5,6]. Among these kinds of reactions, most interest is

Fig. 1 Reaction scheme after excitation of DNQ: KC, ketocarbene; OX, oxirene; and KE, ketene. The carbon atom migration of KC/OX to KE is called the Wolff rearrangement.

centered on the ring contraction through ester formation with hydroxy-group containing molecules. Especially, transformation of six-membered α -diazoketones into carboxy compounds is currently gathering a lot of attention, since it is used as a basis of microlithography.

However, fundamental aspects of the photochemical reactions of six-membered ring α -diazoketones and the

reactivity of the produced carboxy compounds are still not well understood. Recently we succeeded in elucidating the early stages of the photochemistry of six-membered ring α -diazoketones [7, 8]. In this paper we complete this study by analyzing the products of the photochemical reactions of 1-oxo-2-diazo-1,2-dihydrobenzene (DBQ), 1-oxo-2-diazo-1,2-dihydronaphthalene (DNQ) and one typical 5-sulfonated DNQ (4-tolyl 1-oxo-2-diazo-1,2-dihydronaphthalene-5-sulfonate:DNQ-5STL) by reverse-phase liquid chromatography. It will be shown that the carboxy compounds formed in photolysis of these molecules undergo decarboxylation, dimerization and azo formation, markedly depending upon the reaction conditions as well as substituents. The total reactions of six-membered ring α -diazoketones from excitation to final product formation will also be discussed.

2. Experimental

To 10 g of dioxane was dissolved 1g of DNQ-5STL, and was filtered with a 0.5 μ m filter. This solution was spun on a 2 inch glass substrate at a speed of 1000 rpm and baked at 80 $^{\circ}$ C for 30 min. The thickness of the film was 100 nm. This spin-coated film was exposed to UV light through UV-31 filter (Toshiba) with a BMO-100 super pressure Hg lamp (Wacom) at a distance of 1 m. The exposed sample was dissolved in 250 μ l tetrahydrofuran, 5 μ l of which was introduced into the CLC-OCD reverse-phase column of a LC-4A liquid chromatograph (Shimadzu). For the experiments in solution, 1 g of samples dissolved in dioxane-water (90:10) were exposed in a same fashion and were directly introduced into the column.

Solvent flow rate was 1.5 ml/min. As a mobile phase, gradient eluent of A: acetonitrile-aqueous phosphoric acid (PH=2.6) [20:80 by volume] and B: acetonitrile-aqueous phosphoric acid (PH=2.6) [80:20 by volume] was used. The composition of eluent was linearly changed from A-B [90:10 by volume] to B for the first 10 min and then was kept at B.

3. Results and discussion

Photochemical and thermal reactions of DBQ and DNQ have been reported by many researchers. First, we repeat these results from the side of reverse-phase chromatography study, and then discuss the reactions of DNQ-5STL under different conditions in detail.

A. Reactions of DBQ and DNQ

The photochemical reaction of DBQ is followed by liquid chromatography. DBQ in dioxane-water was photolyzed and the products were studied. The Figs. 2(a) and (b) show the chromatograms of DBQ before and after exposure to light. DBQ (1) converted into mainly three products. According to the product analysis study by other researchers [9, 10], the products can be assigned to carboxycyclopentadiene (2), the dimer of 2 and 6,6-dihydroxy-2-(2-hydroxyphenylazo)fulvene (3, 70% in yield). These assignments are consistent with the analysis for DNQ-5STL, being assessed in the next paragraph.

Then, the photochemical reaction of DNQ was analyzed. DNQ was photolyzed in dioxane-water and the liquid chromatograms of DNQ before and after exposure to light were examined. DNQ (4) produced mainly 3-carboxyindene (5) after exposure as shown in Figs. 2(c) and (d). This is in good agreement with the literature [11-13].

The 3-carboxyindene (5) was very stable, in contrast to the case of carboxycyclopentadiene (2) from DBQ. Actually, 3-carboxyindene did not change into any other species even by addition of the bases at room temperature. Sus reported that the 3-carboxyindene analogue from the 4-sulfonated DNQ easily undergoes decarboxylation with the addition of potassium carbonate [11], but this is not the case for 3-carboxyindene (5) produced from DNQ as reported by MacDonald et al. [13], for which high temperature of ca. 100 °C is needed. We followed the MacDonald's result concerning the base catalyzed decarboxylation of 3-carboxyindene (5) at 100 °C by liquid chromatography. Fig. 2(e) shows the liquid chromatogram of 3-carboxyindene (5) mixed with triethylamine after being kept at

Fig. 2 LC chromatograms of DBQ and DNQ reacted under different conditions. (a): DBQ, (b): DBQ after exposure in dioxane-water, (c): DNQ, (d): DNQ after exposure in dioxane-water, (e) after addition of triethylamine into 3-carboxyindene and being kept 100 °C for 30 min.

100. °C for 30 min. The formation of indene through decarboxylation is clearly observed. The difference in the features of the base catalyzed decarboxylation between DNQ and its 4-sulfonated analogue indicates that the reactivity of carboxyindenes are influenced to a great extent by substituents.

B. Reactions of DNQ-5STL

As demonstrated for DBQ and DNQ, reverse-phase liquid chromatography is very useful technique to study the reactions of six-membered α -diazoketones and the reactivity of their products. Here, the reaction of DNQ-5STL under different conditions is studied in detail by applying this technique.

Photolysis of DNQ-5STL under various conditions First the photolytical reaction of DNQ-5STL in pure solid is compared with that in water-containing solution. Pure solid of DNQ-5STL spun on a glass substrate was exposed to UV light and the

formed products were studied by liquid chromatography, while DNQ-5STL in dioxane-water (90:10 by volume) was also studied in a same fashion. The measured liquid chromatograms are shown in Figs. 3(b) and (c) together with that of the parent DNQ-5STL in Fig. 3(a). DNQ-5STL (7) converted into the corresponding 3-carboxyindene analogue (8) with the conversion yields of more than 90 % for the pure solid DNQ-5STL and of more than 70 % for DNQ-5STL in dioxane-water. The formation of 8 is easily confirmed by ^1H -NMR and IR spectroscopies. DNQ-5STL (7): ^1H -NMR (D^6 -acetone) δ : 8.6 (1H, dd, $J=1.6$ Hz and 8 Hz), 8.1 (1H, dd, $J=1.6$ Hz and 8 Hz), 7.2-7.7 (3H, m), 6.5-7.2 (4H, m), 2.2 (3H, s); IR (cm^{-1}): 2120 (=N=N), 1614 (=C=O), 1374, 1205, 868, mp=131-134 dec. 4-Tolyl-3-carboxyindene-7-sulfonate (8): ^1H -NMR (D^6 -acetone) δ : 8.3 (1H, m), 7.6 (3H, m), 6.7-7.2 (4H, m), 3.8 (2H, d, $J=4.2$ Hz). IR (cm^{-1}): 3000 (-OH), 1698 (=C=O), 1374, 1193, 868. mp=150-152. The 3-carboxy compound formation is in agreement with other reports in literature [12, 13]. Only the yield of the carboxy compound (8) is slightly different between solid and liquid phase.

As can be recognized from the reaction scheme in Fig. 1, the presence of water plays an important role in the formation of these carboxy compounds from ketene (KE). We could expect that different products are formed in the absence of water. To eliminate trace amount of water in the samples, pure solid DNQ-5STL on a glass substrate was also exposed to UV light in vacuum (6.7×10^{-4} Pa) and the photo-induced products were examined. DNQ-5STL in vacuum gave a product (12, ca. 50 % yield) different from that in the presence of water as shown in Fig. 3(h). Small amount of 8 was still detected, probably due to residual water adsorbed in the matrix. The product shows no significant IR spectrum peak in the region of over 1650 cm^{-1} . Furthermore, the ^1H -NMR spectrum of the formed product indicates the chemical shift of $\delta=3.3$ that is assigned to the methylene of indene analogues. From IR and ^1H -NMR data, the formed product can be assigned to 4-tolyl indene-7-sulfonate (12): ^1H -NMR (D^6 -acetone) δ : 8.3-6.6 (9H, m), 3.3 (6H, s), 2.2 (3H, s); IR (cm^{-1}): 1503, 1380, 1200, 870.

Fig. 3 Liquid chromatograms of DNQ-5STL reacted under different conditions: R=tolyl group. (a): DNQ-5STL, (b): after exposure in dioxane-water, (c): after exposure on a glass substrate in air, (d): 5 min after addition of triethylamine into the 3-carboxyindene analogue, (e): 1 day after addition of triethylamine into the 3-carboxyindene analogue, (f): 1 min after addition of triethylamine into a mixture of DNQ-5STL and the 3-carboxyindene analogue (1:1, by mol fraction), (g): 1 day after addition of triethylamine into a mixture of DNQ-5STL and the 3-carboxyindene analogue (1:1, by mol fraction), (h) after exposed on a glass substrate in vacuo, (i) after thermally reaction in refluxed xylene.

Reactivity of the carboxyindene analogue (8) The 3-carboxyindene analogue (8) produced from DNQ-5STL was stable in a normal condition, but it reacted very easily in the presence of bases even at room temperature. It gave rise to two very stable products after the addition of bases, such as triethylamine, triethanolamine, imidazole, as shown in Figs. 3 (d) and (e). The formation of these two products proceeded at a same rate. This is contrast to the case of 3-carboxyindene (5) from DNQ, as explained in previous section, which is very stable at room temperature even in the presence of these bases. 3-Carboxyindene (5) undergoes decarboxylation in the presence of the bases over 70 °C and it was confirmed by the liquid chromatography in the previous section. In this experiment, however, the sample was kept at room temperature, furthermore, no $^1\text{H-NMR}$ signal indicating the presence of indene

analogues was observed after conversion. Therefore, from the reaction features, the two products formed with almost the same chromatogram intensities could be assigned to the dimerization isomers (9 and 10) of 8.

The 3-carboxyindene analogue (8) was also found to react with the parent DNQ-5STL in the presence of the bases. The isolated 8 was mixed with the same amount of DNQ-5STL (7) in tetrahydrofuran, and the reaction was followed by liquid chromatography after the addition of the bases. Figures 3(f) and (g) show that the carboxyindene analogue (8) immediately converts into single product through the reaction with DNQ-5STL, where the liquid chromatogram peak intensities of 8 and 7 decreases quantitatively and a single chromatogram peak appears. The product is assigned to an azo compound, in analogy with the study on the photolysis of DBQ by Yagihara et al. [10]. When DNQ-5STL is present together with the 3-carboxyindene analogue (8) in equal quantity, the yield of the dimerization products (9 and 10) was very small. Thus, the azo formation rate constant for the 3-carboxyindene analogue (8) with DNQ-5STL is much greater than that of the dimerization reaction (i.e., yield of 11 >> yield of 9 and 10).

As a result, one can recognize that the carboxy compounds produced from six-membered ring α -diazoketones undergo three types of reactions, i.e., decarboxylation, dimerization and azo formation, especially in the presence of bases. The reaction rate constants vary depending upon the molecular structure as well as upon the reaction conditions. The results indicate that the base catalyzed decarboxylation mechanism, which is believed to be a reason for the image reversal process of positive resists, might be slightly modified by the type of molecules used.

Reactions of six-membered ring α -diazoketones

The reactions of six-membered ring α -diazoketones are now discussed. As studied by liquid chromatography, DBQ, DNQ and DNQ-5STL mainly give rise to carboxy products under irradiation except for the case of DBQ, where the dimerization and the azo formation occur under a normal condition. The carboxy product

formation results from ketene intermediates. Existence of ketene intermediates was first confirmed by Rodionova et al. [14] and was spectroscopically identified by other researchers [15-20]. We also reported that several kinds of strain-free six-membered ring α -diazoketones give rise to ketene intermediates through the Wolff rearrangement by using low-temperature matrix isolation technique [8], and also showed that the Wolff rearrangement for these α -diazoketones occurs through oxirene intermediates [7, 8].

As demonstrated for DNQ and DNQ-5STL, the reactivity of the formed 3-carboxyindene analogues is very dependent upon substituents. Generally they exhibit decarboxylation, dimerization, and azo compound formation in the presence of bases, depending upon reaction conditions. For instance, the reaction rate constant of the azo formation for DNQ-5STL is much greater than that of the dimerization. Azo formation is also observed for the photolysis of DBQ. In the literature [10], the azo formation for DBQ has been considered to result from the reaction of cyclopentadienoketene (6-oxofulvene) with the parent DBQ. However, our laser flash photolysis study [8] shows that the lifetime of the ketene is mainly determined by the solvent water, and no effect of [DBQ] was detected. Therefore, in agreement with Sus [9], the azo formation must proceed via carboxycycloheptadiene (2) with DBQ but not via cyclopentadienoketene, such as in the case of DNQ-5STL.

4. Conclusion

The photolytical reactions of six-membered ring α -diazoketones under several conditions were studied in detail by means of reverse-phase liquid chromatography technique. Especially, the reactivity of the produced carboxy compounds was precisely discussed. It was demonstrated that they undergo decarboxylation, dimerization and azo formation in the presence of bases, depending greatly upon molecular structure. The result indicates that base catalyzed decarboxylation mechanism of 3-carboxyindene, which is believed to be a reason for the image reversal process of positive resists, might be modified slightly by varying the type of molecules.

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