The Reactions of Nitrile Oxide–Quinone Cycloadducts. II.[1] The Reactions of 2,5-Di-*t*-butyl-*p*-benzoquinone with Nitrile Oxides: 1:2 Cycloaddition and Base Induced Ring Transformation of the Cycloadducts

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The reactions of 2,5-di-*t*-butyl-*p*-benzoquinone with *p*-substituted benzonitrile *N*-oxides successfully gave 1:2 cycloadduct. The cycloadducts were proved to undergo base induced reactions in different patterns with aqueous sodium hydroxide or with triethylamine. Sodium hydroxide caused cleavage of cyclohexanedione ring to give γ-keto carboxylic acid derivatives, which take γ-hydroxy lactone form in solid state. On the other hand, triethylamine caused isoxazoline ring transformation reaction with elimination of one *t*-butyl group to give bis(isoxazole)-fused hydroxycyclohexadienone derivatives. The structure determination and the reaction mechanism are discussed.

Quinones and their hydrogenated compounds having fused polycyclic ring system are known as a structure component in some of antibiotics and the studies of their syntheses and the reactivities of those compounds have interested many organic chemists. Heterocycle-fused quinones and their related compounds often have strong antibiotic activity, e.g. mitomycins, and also function as electron acceptors with varied strength. Since 1,3-dipolar cycloaddition is one of the most useful methods of the preparation of the heterocyclic compounds, the dipolarophillic reactivities of quinones have been widely investigated.

The reactions of quinones with nitrile oxides were reported first by Quilico and co-workers[2] in 1950, and some works have been made up to date with nitrile oxide–quinone cycloadditions.[3] We also investigated the cycloaddtion reactions of aromatic nitrile oxides with several substituted *p*-benzoquinones[4,5] and found the reaction with the alkyl-substituted *p*-benzoquinones reacted with aromatic nitrile oxides at their C=C double bond to give isoxazoline-fused cyclohexenedione derivatives (**1**) in good yields.

In the presence of base, it is known that 2-isoxazolines lose their C^4 proton and some interesting reactions take place, substitution, rearrangment, ring cleavage, etc.[6] The adducts of the quinone–nitrile oxide cycloaddition have an activated proton at C^4 position of the isoxazoline ring by adjacent carbonyl moiety and some of the cycloadducts were proved to undergo novel rearrangement with catalytic action of base to give isomers of isoxazole-fused cyclohexadienone ring structures (Scheme 1).[1] Furthermore, it was found that the rearrangement products could be converted to isoxazole-fused catechol derivatives, which exhibited barnaclecide activity.[7] Thus this rearrangement was thought to be interesting from the point of view of biologically active compound syntheses, as well as heterocyclic ring system reactivities. The rearrangement reaction exhibited

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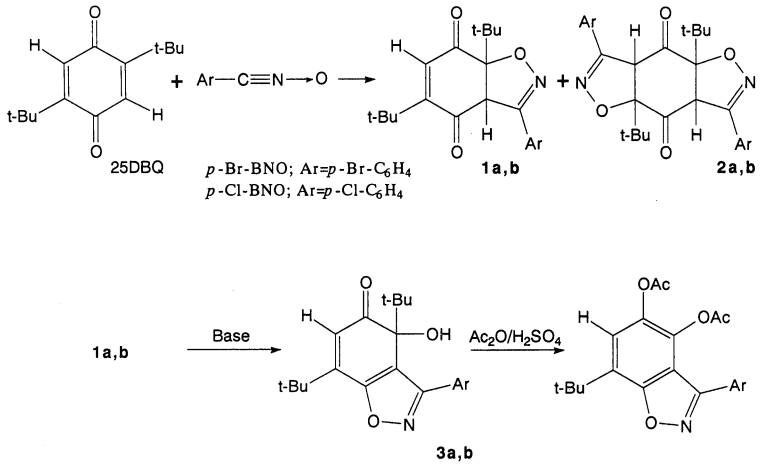


Scheme 1. 1,3-Dipolar cycloaddition reactions of 25DBQ with nitrile oxides and rearrangement reactions of the cycloadducts.

incomprehensible substituent effect, and the scope and the limitation of the reaction is still remain unclarified.

The cycloaddition reactions of 2,5-di-*t*-butyl-*p*-benzoquinone (25DBQ) with *p*-chlorobenzonitrile *N*-oxide(*p*-Cl–BNO) or with *p*-bromobenzonitrile *N*-oxide(*p*-Br–BNO) gave an 1 : 2 cycloadduct (**2**) as a by-product[5] (Scheme 1). These 1 : 2 cycloadducts have highly symmetrical bis(isoxazoline)-fused cyclohexanedione structure and have two activated isoxazoline C^4 protons. Investigation of the reactions of this compound with base relation to the rearrangement reaction of the 1 : 1 cycloadducts is expected to give a clue for the reaction mechanism of the rearrangement.

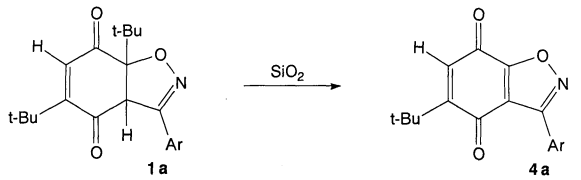
Useful preparative methods of the 1 : 2 cycloadducts of 25DBQ with *p*-Cl–BNO and *p*-Br–BNO were examined. The reaction cycloadducts were then reacted with base. It was found that the reactions proceeded in different ways with sodium hydroxide or with triethylamine. Either of the products was found to have unexpected structure. The structure determination and the reaction mechanism consideration are described.

Results and Discussion

1 : 2 Cycloaddition of 25DBQ with Nitrile Oxides. It is known that *p*-benzoquinones are very susceptible to bases[8] and therefore, the cycloaddition of nitrile oxide could not be conducted by usual in situ nitrile oxide generation procedure using triethylamine. The cycloaddition reactions were carried out by thermal decomposition of corresponding arenecarbohydroximoyl chloride in the presence of a quinone substrate in refluxing toluene. The reactions of 25DBQ with two equivalent of hydroximoyl chlorides gave 1 : 2 cycloadduct in low yields (**2a**; 34%, **2b**; 32%). An equimolar reaction of isolated 1 : 1 cycloadduct (**1a**) with preformed nitrile oxide in solution gave a better yield (overall yield of **2b** from 25DBQ, 48%). The reaction of 25DBQ with excess preformed nitrile oxide was not practical because of difficulty in separation of by-products. These 1 : 2 cycloadducts were identical to those reported before[5] and the structure was 3,7-diaryl-4a,8a-di-*t*-butyl-3a, 4a,7a,8a-tetrahydrobenzo[1,2-*d*: 4,5-*d'*]diisoxazole-4,8-dione (**2a, b**).

The second cycloaddition of nitrile oxide to 1 : 1 cycloadduct may proceed via *endo*- or *exo*-addition and two possible stereoisomers are conceivable for the 1 : 2 cycloadduct structure. The 1 : 2 cycloadducts obtained are considered to be a single compound from spectroscopic and chromatographic analyses. Diastereoselectivity of the second cycloaddition, however, was uncertain.

During the separation process of the products by silica-gel chromatography, it was found that **1a** underwent elimination of bridgehead *t*-butyl group and gave isoxazole-fused quinone **4a** (Scheme 2). It was confirmed that formation of **4a** took place by prolonged

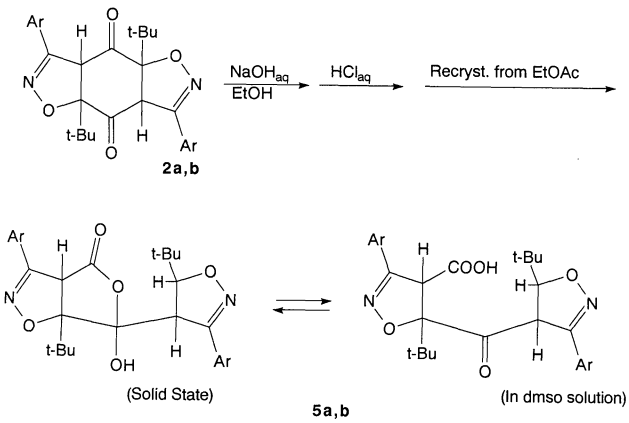


Scheme 2. The conversion of **1a** to an isoxazole-fused quinone **4**.

contact of **1a** with silica gel. The cycloaddition reaction of **4a** with another *p*-Br–BNO was examined and found that this isoxazole-fused quinone underwent second cycloaddtion. The details of this reaction will be discussed in the following section.

Hydroxide Induced Ring Conversion Reaction of 2. The reaction of **2a** with equimolar sodium hydroxide was carried out in ethanol at room temperature. The color of the solution changed immediately from pale yellow to yellow, brown, and reddish violet within ten minutes. The reddish violet state continued for about two hours and then slowly faded to pale yellow. The solution was allowed to stand for a day and was poured into ice water. Acidification with hydrochloric acid gave colorless solid.

The mass spectral data and elemental analyses of the products gave the molecular formula of $C_{28}H_{30}N_2O_5X_2$, which indicated that the product consisted of the starting adduct and one molecule of H_2O. IR spectrum (KBr disk) exhibits only one carbonyl absorption at 1798 cm^{-1}, and ν_{O-H} absorption around 3400 cm^{-1}. The wavenumber of the carbonyl group shifted upwards about 120 cm^{-1} compared with the starting adduct, suggesting the presence of a strained ring. But ^{13}C NMR spectrum, measured in dimethyl-d_6 sulfoxide (DMSO-d_6) solution, showed two carbonyl group absorptions at δ=208 and 170. These two peaks were assigned to nonaromatic ketone and carboxylic acid respectively, and neither of them shows IR absorbance around 1800 cm^{-1}. Therefore, the existence of structural reformation between in solid state and in solution was expected. The disappearance of one of the carbonyl groups, high wave-

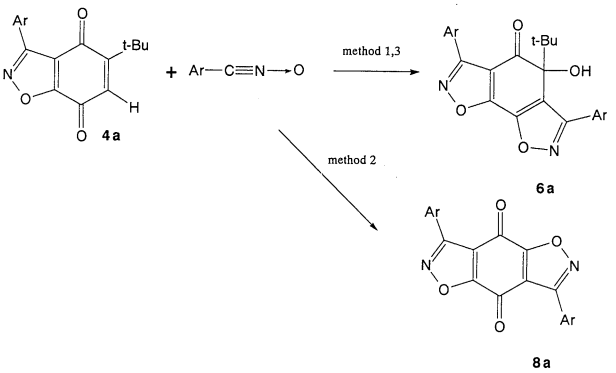


Scheme 3. The reactions of **2a**, **b** with sodium hydroxide.

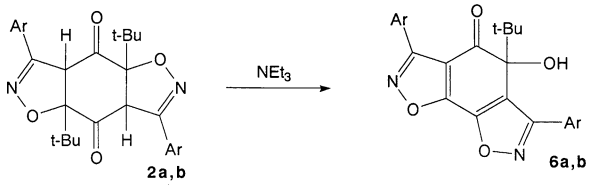
number of remaining carbonyl group, and the existence of hydroxyl group in solid state indicated that one of the carbonyl groups reacted with the other and the hydroxyl group was formed. From ^{13}C NMR spectra was apparent the existence of carboxyl group. The structure which satisfied all of these spectral data was considered to be **5**. (Scheme 3) In solid state, **5** was thought to take lactone form and in DMSO solution take keto carboxylic acid form. The structural change of **5** was confirmed to reversible by IR (solid state)–NMR (DMSO-d_6 solution)–IR (solid state) measurements. The mechanism of the reaction might be rationalized as nucleophilic attack of OH^- ion to the carbonyl group to cause C–C bond cleavage.

The Reaction of 2a with Triethylamine. The use of a less nucleophilic base was thought to cause different reactions. The reaction of **2** with triethylamine in place of sodium hydroxide was examined. No reaction proceeded at room temperature even after a week. Heating the reaction mixture up to 60 °C caused the color change of the solution from colorless to pale yellow and finally to pale red after 18 h. After the removal of the solvent, pale yellow flakes were obtained. TLC analyses showed some spots in addition to unreacted starting materials (**2a, b**). The main product was obtained as white flakes by column chromatography and/or recrystallization. The elemental analyses and chemical ionization mass spectra indicated that the composition of the product was $C_{24}H_{18}N_2O_4X_2$, which indicated the loss of C_4H_{10} from starting materials occurred. ^1H NMR spectra in DMSO-d_6 showed only one *t*-butyl group, one hydroxyl proton, and no C^4 proton. IR spectra also showed strong ν_{O-H} absorption. ^{13}C NMR and IR spectra were similar to those of **2**. The data indicate the structure to be **6a, b** (Scheme 4). In this reaction, the ring transformation is considered to proceed in a similar manner to the formation of **2** from **1**[1] but with the elimination of *t*-butyl group in basic conditions. The reaction mechanism was assumed as Scheme 5. The intermediate **7a** can be regarded as a cycloadduct of nitrile oxide with **4a**.

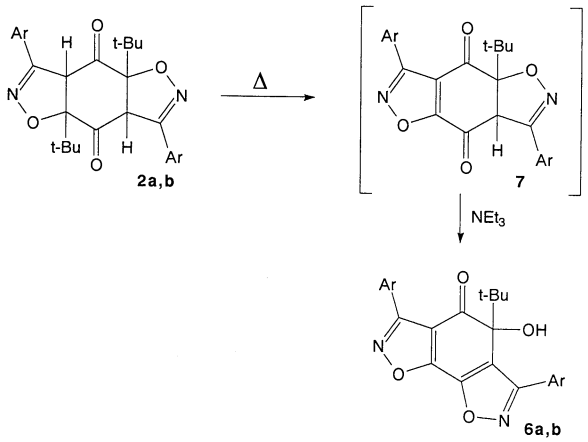
The Reaction of 4a with Another *p*-Br–BNO. The isoxazole-fused quinone **4a** was prepared by treating **2a** with silica gel. The cycloaddition of *p*-Br–BNO with **4a** was carried out by three different nitrile oxide generation methods; in situ formation of *p*-bromobenzonitrile *N*-oxide (method 1), thermal decomposition of *p*-bromobenzohydroximoyl chloride in refluxing toluene (method 2), and reaction with preformed *p*-Br–BNO (method 3).



Scheme 6. The reactions of **4** with *p*-Br–BNO.



Scheme 4. The reactions of **2a, b** with triethylamine.

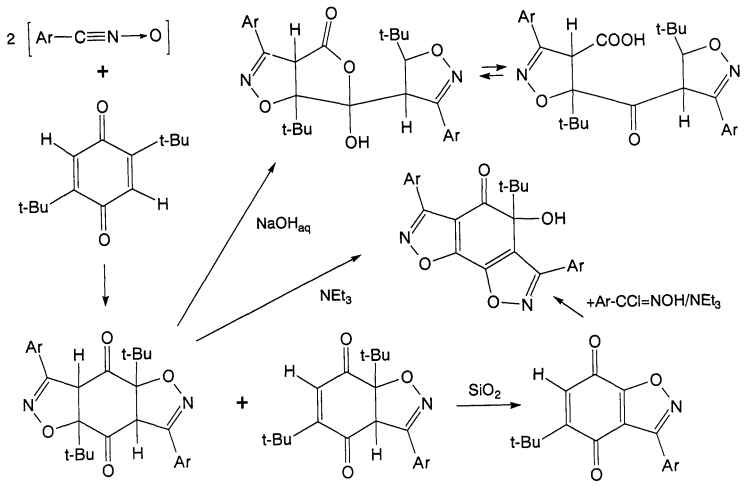


Scheme 5. Possible reaction mechanism of **2a, b** with triethylamine.

The reaction by method 1 gave **6a**, which was considered as tandem cycloaddition–rearrangement reaction product. That is, the cycloaddition occurred at C=C double bond of the quinone and subsequent rearrangement caused by triethylamine, which remained in the solution.

Attempted reaction of **4a** with thermally generated *p*-Br–BNO (method 2) to obtain the cycloadduct was also examined. The product was a yellow solid and proved to be from analytical and spectral data as bis(isoxazole)-fused quinone **8**. The elimination of *t*-butyl group was thought to be caused by hydrochloric acid generated from *p*-bromobenzohydroximoyl chloride and/or the high temperature of these reaction conditions (110 °C). Another attempted reaction to obtain the cycloadduct **7a** using preformed *p*-Br–BNO (method 3) at 0 °C unexpectedly gave **6a**.

Isolation of **7a** was thus unsuccessful and tandem *t*-butyl elimination–rearrangement mechanism of the reaction of **2** with triethylamine was not proved. But the reactions of **4a** gave suggestions to the reactions of **2** with triethylamine. The reaction of **2** with triethylamine was rationalized as slow *t*-butyl elimination to give **7** which was followed by fast rearrangement of **7**. This fast rearrangement might be the reason why **7a** could not



Scheme 7. The summary of the reactions of cycloadducts.

be isolated in any reactions that were tried. It was reported that the rearrangement of **1** was fast and the reaction mixture exhibited obvious color change during the reaction (yellow to purple instantaneously, and finally colorless in a few seconds).[1] Therefore the reason why the reaction of **2** with triethylamine was slow and exhibited little color change may be the first step of the reaction, *t*-butyl elimination in basic conditions, was very slow and **7** reacted with base as soon as it was produced.

In conclusion, 1 : 2 cycloaddtion reaction of 25DBQ and 2,6-unsubstituted benzonitrile *N*-oxides satisfactorily gave the cycloadduct. This fused ring system reacts with bases in two ways, that is, nucleophilic attack to the carbonyl carbon by hydroxide ion in a case of aqueous sodium hydroxide, and 1 : 1 cycloadduct-like rearrangement with *t*-butyl elimination in a case of triethylamine. Also it was found that novel isoxazole-fused quinone **4a** reacted with nitrile oxide. All the reactions described are illustrated in Scheme 7.

Experimental

Melting points were measured with Yazawa Micro melting point measuring apparatus type BY-1 and are uncorrected. The IR spectra were recorded with a JASCO IRA-1 or IR-700 spectrometer. The ^{1}H NMR and ^{13}C NMR spectra were measured with GX-270 spectrometer, and chemical shifts were reported in ppm from internal tetramethylsilane. Mass spectra were recorded with Hitachi RMU-7M spectrometer or with JEOL DX-303 spectrometer. Column chromatography was performed with Wako-gel C-200 (Wako Chemicals Co., Ltd.).

Meterials. 2,5-Di-*t*-butyl-*p*-benzoquinone (25DBQ) was commercially obtained and purified by recrystallization from hexane. The hydroximic acid chlorides *p*-X-C$_6$H$_4$-CCl=NOH (X=Cl, Br) were synthesized from corresponding aldehyde oximes by chlorination using *N*-chlorosuccinimide[9] and used after recrystallization from ethanol–water mixture. Synthesis of 1 : 1 quinone–nitrile oxide cycloadduct (**1**) was described in the previous paper.[5] Sodium hydroxide was obtained commercially and used without further purification. Triethylamine was used after distillation with sodium hydride.

The Reaction of 25DBQ with Two Equivalent *p*-X-BNO (X=Cl, Br). *p*-Bromobenzohydroximoyl chloride (2.34 g, 10 mmol) and 25DBQ (1.10 g, 5 mmol) were dissolved in 50 ml of toluene and the solution was allowed to reflux. The progress of the reaction was followed by TLC and evolution of HCl gas. After about 12 h, evolution of HCl gas almost ceased. After the reaction, the solvent was removed under reduced pressure. The reaction mixture was extracted with hexane and the residue was filtered off (crude **2**). The extract was concentrated and was subjected to column chromatography (benzene as an eluent). The product was eluted with nitrile oxide dimer (3,4-diarylfurazan 2-oxide). This mixture was subjected to column chromatography again (benzene–hexane 1 : 1 mixture as an eluent) and **2** was isolated. Combined **2** was recrystallized from ethanol twice. Yield **2a**; 34%, **2b**; 32%. All of the analytical data were identical to those were reported in the previous paper.[5]

In the reaction of 25DBQ with *p*-Br–BNO, isoxazole-fused quinone **4a** was also obtained. (See Text) The product was eluted with **1a** at first chromatogram. The mixture was separated by recrystallization from ethanol. Mp 160—161 °C. Found: C, 57.10; H, 3.77; N, 3.93%. Calcd for $C_{16}H_{14}NO_3Br$: C, 56.69; H, 3.92; N, 3.89%. High-resolution mass spectrum: Found: *m*/*z* 359.0163. Calcd for $C_{16}H_{14}NO_3Br$: M, 359.0157. IR (KBr) 2960 (ν_{C-H}), 1680 cm^{-1} ($\nu_{C=O}$); ^{1}H NMR δ=1.36 (s, 9H, *t*-Bu), 6.74 (s, 1H, vinyl) 7.79 (d-d, 4H, *p*-Br–Ph)

The Reaction of 1a with *p*-Br-BNO. Method A: To previously generated *p*-Br–BNO dichloromethane solution at 0 °C, dichloromethane solution containing equimolar **1a** was added and stirred for 18 h. The following procedure was the same above. Yield 48%.

Method B: Cycloadduct **1a** (1.0 g, 2.4 mmol) was dissolved to 50 ml of benzene and stirred at room temperature. To this solution 50 ml of benzene solution containing 0.56 g (2.4 mmol) of *p*-bromobenzohydroximoyl chloride was added. Triethylamine (0.24 g, 2.4 mmol), dissolved in 60 ml of benzene, was added dropwise. Addition required about 1.5 h. The progress of the reaction was followed by TLC analysis. After three days the reaction was completed. Isolation and purification

methods were the same as above described. Yield 38%.

The Reaction of 2(a,b) with Sodium Hydroxide. To the 50 ml of ethanol solution containing 0.24 mmol of **2**, 2 ml of 10% sodium hydroxide ethanol solution was added dropwise. The reaction solution was stirred at room temperature. The color of the solution changed immediately to yellow, brown, and reddish violet. This violet color persisted for several hours and then slowly faded. The stirring was continued for a day, and the solution became almost colorless. The solution was concentrated under reduced pressure, and to the residue about 100 ml of ice-water was poured. After the neutralization with dilute hydrochloric acid, the curdy precipitate of **5** was filtered. The precipitate was recrystallized from ethyl acetate. yield **5a** 75%, **5b** 68%.

5a: Mp 263—264 °C. Found: H, 4.76; C, 52.97; N, 4.17%. Calcd for $C_{28}H_{30}N_2O_5Br_2$: H, 4.64; C, 51.56; N; 4.29%. IR (KBr) 3210 (ν_{O-H}), 2964 (ν_{C-H}), 1798 cm^{-1} ($\nu_{C=O}$); ^1H NMR (DMSO-d_6) δ=1.0 (9H, s), 1.1 (9H, s), 2.6 (1H, d), 5.5 (1H, s), 7.1—7.5 (8H, m), 8.7 (1H, s); ^{13}C NMR (DMSO-d_6) δ=208, 170; mass spectrum (FAB, *m*-nitrobenzylalcohol as matrix) 635 (Calcd for $C_{28}H_{30}N_2O_5Br_2$, 634, M+1$^+$).

5b: Mp 243—245 °C. Found: H, 5.54; C, 61.50; N, 4.84%. Calcd for $C_{28}H_{30}N_2O_5Cl_2$: H, 5.54; C, 61.66; N, 5.14%. IR (KBr) 3222 (ν_{O-H}), 2964 (ν_{C-H}), 1799 cm^{-1} ($\nu_{C=O}$); ^1H NMR (DMSO-d_6) δ=0.91 (s, 9H), 1.05 (s, 9H), 2.6 (d, 1H), 3.6 (d, 1H), 5.4 (s, 1H), 7.8—8.2 (m, 8H); ^{13}C NMR (DMSO-d_6) δ=208, 170; mass spectrum (FAB, *m*-nitrobenzylalcohol as matrix) 545 (Calcd for $C_{28}H_{30}N_2O_5Cl_2$, 544, M+1$^+$)

The Reaction of 2(a,b) with Triethylamine. To the solution of **2** in absolute ethanol (200 mg/50 ml), 2 ml of 10% triethylamine solution was added dropwise. The reaction mixture was warmed to 70 °C and stirred. The reaction was continued for about 16 h. The color of the solution slowly turned to pale red. The solvent was removed under reduced pressure, and the crude product was obtained. The crude product was recrystallized from benzene, and **6** was obtained as white flakes. Yields, **6a** 35%, **6b** 34%.

6a: Mp 263—264 °C (decomp). Found: H, 3.13; C, 51.30; N, 5.34%. Calcd for $C_{24}H_{18}N_2O_4Br_2$: H, 3.25; C, 51.64; N, 5.02%. IR (KBr) 3382 (ν_{O-H}), 2962 (ν_{C-H}), 1680 cm^{-1} ($\nu_{C=O}$); ^1H NMR (DMSO-d_6) δ=0.78 (s, 9H, *t*-Bu), 7.58—7.98 (m, 9H, *p*-Br-Ph and -OH); mass spectrum (CI, isobutane as ionization gas), 557 (Calcd for $C_{24}H_{18}N_2O_4Br_2$, 556, M+1$^+$).

6b: Mp 250 °C (decomp). Found: H, 4.20; C, 61.98; N, 5.64%. Calcd for $C_{24}H_{18}N_2O_4Cl_2$: H, 3.87, C, 61.42; N, 5.97%. IR (KBr) 3382 (ν_{O-H}), 2962 (ν_{C-H}), 1679 cm^{-1} ($\nu_{C=O}$); ^1H NMR (DMSO-d_6) δ=0.78 (s, 9H), 7.2—7.8 (m, 9H); mass spectrum (CI, isobutane as ionization gas), 469 (Calcd for $C_{24}H_{18}N_2O_4Cl_2$, 468, M+1$^+$)

Silica Gel Induced Conversion of 1a to 4a. The benzene solution of **1a** (200 mg/10 ml) was absorbed completely to 10 g of silica gel (Wako-gel C-300, Wako Chemicals Co., Ltd.) and allowed to stand for 3 d. The gel was subjected to Soxlet extractor for 4 h with 95% ethanol. The extract was concentrated under reduced pressure and the residue was subjected to column chromatogram (benzene as an eluent). The product was recrystallized from hexane and **4a** was obtained as yellow needles. Yield 32%. The characterization data of **4a** were already described.

Cycloaddition Reactions of 3 with *p*-Br-BNO. The procedure of the reaction was the same as the cycloaddition reactions of **1a**.

Method 1: Isoxazole-fused quinone **4a** (0.55 g, 1.5 mmol) was dissolved in 10 ml of benzene and stirred at room temperature, and to this solution, 10 ml of the solution containing *p*-bromobenzohydroximoyl chloride *p*-Br-C_6H_4-CCl=NOH (0.36 g, 1.5 mmol) was added. Triethylamine solution (1.5 mmol/40 ml) was added dropwise over a 1 hour period. The color of the solution changed slowly to orange and the white precipitate appeared. The solution was continued stirring for a day and the precipitate was filtered. The crude product was obtained as slightly colored powder. After recrystallization from benzene, **5** was obtained as white crystals. Yields 78%. Mp 263—364 °C. All spectral and analytical data were similar with those of the triethylamine-induced rearrangement product of **2a(6a)**.

Method 2: Isoxazoloquinone **4a** (200 mg, 0.56 mmol) and equimolar *p*-bromobenzohydroximoyl chloride were dissolved in 20 ml of toluene and the solution was heated to reflux. The progress of the reaction was followed by evolving HCl gas. After 16 h, evolution of HCl gas ceased. After the reaction, solvent was distilled off under reduced pressure, and extracted with benzene. From the extract 45% of starting **4a** was recovered. The residue was recrystallized from benzene-hexane mixture. Yield 36%. Mp 250 °C (decomp). High-resolution mass spectrum: Found: *m/z* 497.8852. Calcd for $C_{26}H_8N_2O_4Br_2$: M, 497.8851. IR 1690 cm^{-1} ($\nu_{C=O}$); ^1H NMR (DMSO-d_6) δ=7.8—8.2 (d-d).

Method 3: To previously generated *p*-Br-BNO dichloromethane solution (from corresponding benzohydroxamic acid chloride and triethylamine at 0 °C), dichloromethane solution of equimolar **4a** was added dropwise. The temperature was slowly raised to room temperature. After 16 h, the mixture was concentrated under reduced pressure. The residue was extracted with benzene and triethylammonium chloride was separated from the reaction mixture as precipitate. The extract was concentrated again and the mixture was dissolved in benzene. The insoluble product was collected and recrystallized from hexane-benzene mixture. Yield 35%. All the characterization data were identical to those of **6a**.

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References

1) Part I, S. Shiraishi, B. S. Holla, K. Imamura, and Y. Inoue, *Bull. Chem. Soc. Jpn.*, **65**, 2480 (1992).

2) A. Quilico and G. Stagno d'Alcontres, *Gazz. Chim. Ital.*, **80**, 140 (1950).

3) P. Caramella and P. Grunanger, in "1,3-Dipolar Cycloaddition Chemistry," ed by A. Padwa, John Wiley & Sons, New York (1984), Vol. 1, Chap. 3, p. 360, and references sited therein.

4) T. Hayakawa, K. Araki, and S. Shiraishi, *Bull. Chem. Soc. Jpn.*, **57**, 1643 (1984).

5) S. Shiraishi, B. S. Holla, and K. Imamura, *Bull. Chem. Soc. Jpn.*, **56**, 3457 (1983).

6) S. A. Lang, Jr. and Y.-i Lin, in "Comprehensive Heterocyclic Chemistry," ed by A. R. Katritzky and C. W. Rees, Pergamon Press, New York (1984), Vol. 6, p. 36.

7) S. Shiraishi, B. S. Holla, K. Imamura, and Y. Inoue, in preparation. A part of the data was presented in 16th Congress of Heterocyclic Chemistry, Osaka, Japan, 1984, Abstr., 2B-15; S. Shiraishi, The Japanese–United States Congress of Pharmaceutical Sciences, Honolulu, Hawaii, 1987, Symposia Abstr., p. 130.

8) K. T. Finley, in "The Chemistry of the Quinonoid Compounds," ed by S. Patai, John Wiley & Sons Inc., New York (1974), Part 2, Chap. 17, p. 880.

9) K.-C. Liu, B. R. Shelton, and R. K. Howe, *J. Org. Chem.*, **45**, 3916 (1984).