

1,3-DIPOLAR CYCLOADDITIONS OF 3-BROMO-1,5- AND 3-BROMO-1,7-AZULENEQUINONES WITH DIAZOMETHANE, DIPHENYLNITRILIMINE, AND BENZONITRILE OXIDE⁺

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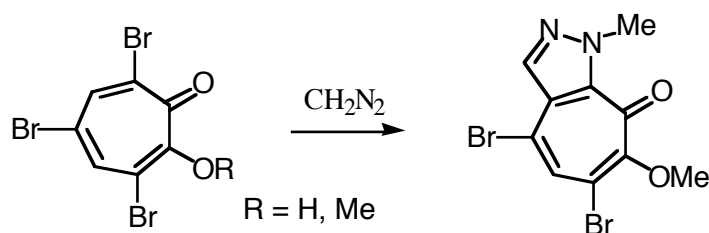
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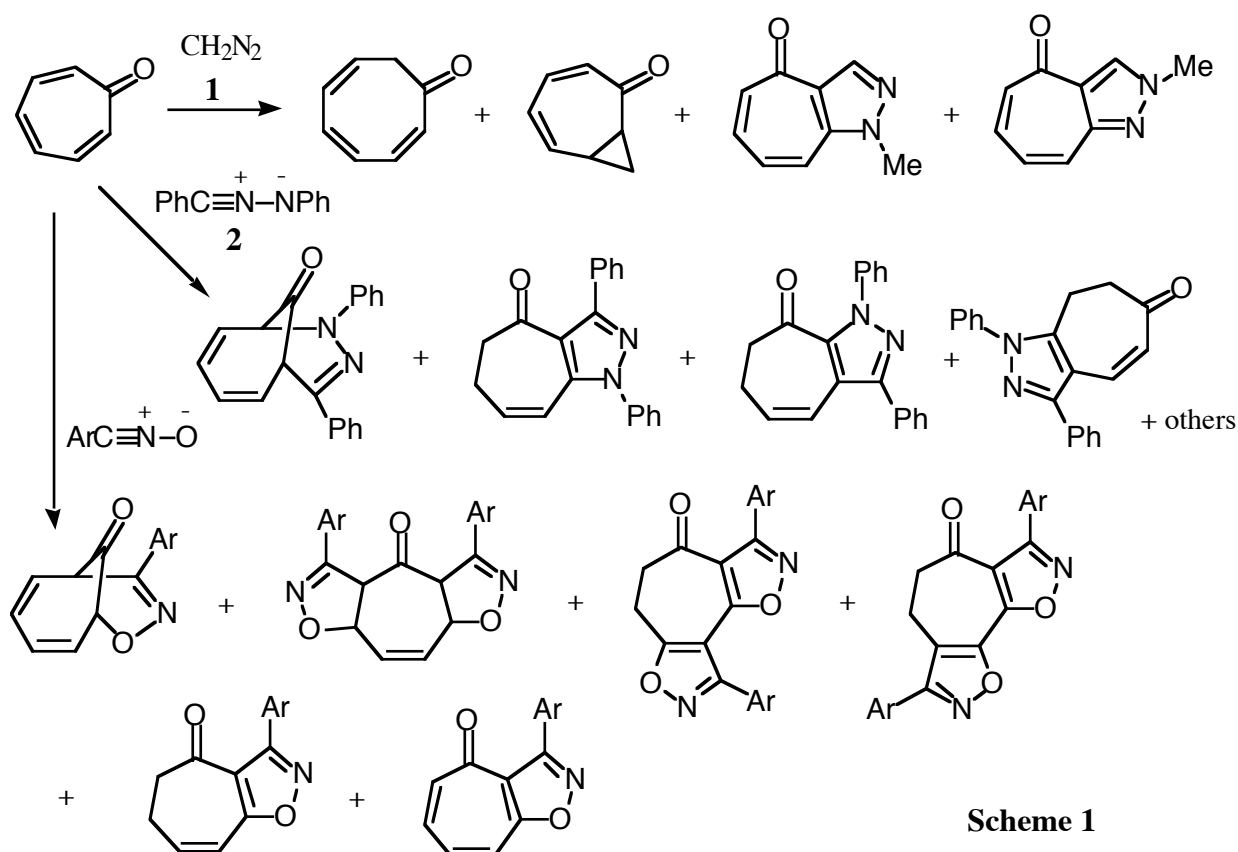
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Abstract—The reactions of 3-bromo-1,5- and 3-bromo-1,7-azulenequinones with diazomethane gave cyclooctatrienone derivatives and a [4+2] 1,3-dipolar adduct while they reacted with diphenylnitrilimine and benzonitrile oxide to give the corresponding [4+2] 1,3-dipolar adducts, showing the different site selectivities. 3-Bromo-1,5-azulenequinone reacted with the 1,3-dipoles dominantly to form the adducts on the cyclopentenone part while 3-bromo-1,7-azulenequinone reacted on the seven-membered ring.

The 1,3-dipolar cycloadditions of troponoids have been reported by several groups almost two and three decades ago. Itô and his coworkers² reported that halotroponoids reacted with diazomethane to give pyrazolotropones; 3,5,7-tribromotropolone and its methyl ether gave 4,6-dibromo-7-methoxy-1-methyl-8(1*H*)-cyclohepta[*c*]pyrazolone. Tropone also gave the two isomeric *N*-methylpyrazolotropones together with cyclooctatrienone and 2,3-homotropone.³ With diphenylnitrilimine,⁴ tropone afforded a [6+4] and a [4+2] 1,3-dipolar cycloadduct. This reaction was reinvestigated⁵ to revise the structure of the [4+2] adduct to 5,6-dihydro-1,3-diphenylcycloheptapyrazol-4(1*H*)-one. The reaction of nitrile oxides with tropone yielded six 1,3-dipolar adducts; a [6+4] adduct, two mono [4+2] adducts, and three bis [4+2] adducts.⁶



⁺Dedicated to Professor Shô Itô on the occasion of his 77th birthday.



Scheme 1

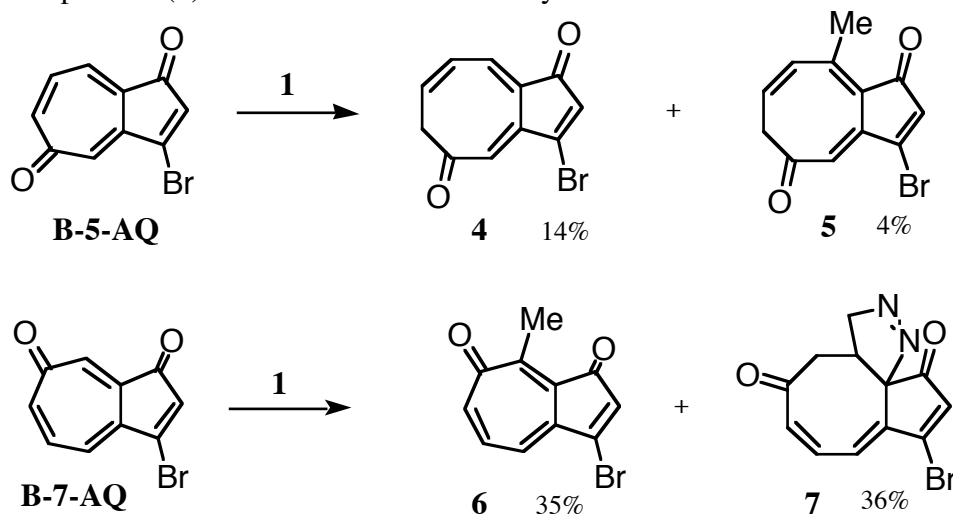
We recently reported the thermal cycloaddition reactions⁷ of 3-bromo-1,5-azulenequinone (**B-5-AQ**) and 3-bromo-1,7-azulenequinone (**B-7-AQ**),⁸ which have a tropone and a cyclopentenone chromophore, with monoolefins⁹ and dienes.¹⁰ Among them, the [4+2] cycloadducts were dominantly formed in the reactions with monoolefins avoiding the formation of an unstable cyclopentadienone moiety while dienes initially added on the cyclopentenone part and the subsequent [6+4] or [8+2] additions followed to give the 2 : 1 adducts.¹¹ With diphenylketene, bromoazulenequinones gave tetraphenylazulenequinodimethanes.¹²

On the other hand, photochemical reactions of **B-5-AQ** gave four dimeric products while **B-7-AQ** was unreactive.¹³ Thus, the thermal and photochemical reaction modes of bromoazulenequinones are similar to those of tropone. In this paper, we report the 1,3-dipolar cycloadditions of **B-5-AQ** and **B-7-AQ** with diazomethane (**1**), diphenylnitrilimine (**2**), and benzonitrile oxide (**3**), showing the different site selectivity.

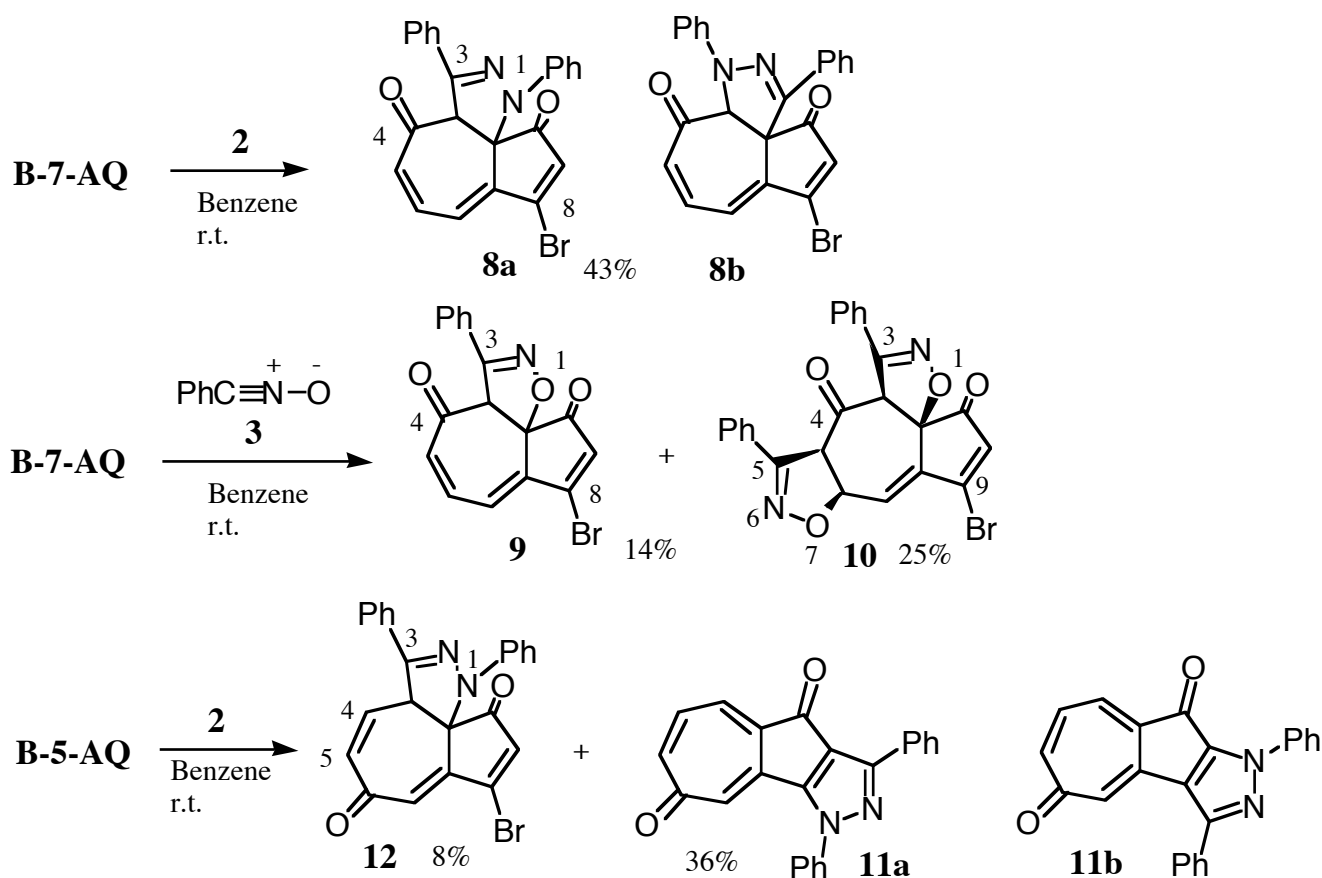
When an ether solution of **B-5-AQ** and **1** was reacted at 0 °C for 4 d, two products (**4** and **5**) were obtained in 14 and 4% yields, respectively. The main product (**4**) was a homologated derivative of **B-5-AQ** because a methylene unit appeared at δ 3.30 (2H, d, $J=8.8$ Hz), the neighboring olefinic proton was observed as a triplet at 6.10 (1H, dt, $J=10.3, 8.8$ Hz), and the rest of the signals was similar to the NMR data of **B-5-AQ**. When compared the NMR data of **4** with the minor product (**5**), **5** has a methyl group at δ 2.45 and one olefinic proton signal of the cyclooctatrienone ring of **4** disappeared. The structure of **5**, then, was determined to be a methyl derivative of **4**.

On the other hand, the reaction of **B-7-AQ** and **1** gave two products (**6** and **7**) in 35 and 36% yields. The structure of **6** was determined to be a methyl derivative of **B-7-AQ** from the NMR data. In the ¹H NMR

spectrum of the other product (**7**), there are two pairs of a methylene unit with a large coupling constant, which indicated that product (**7**) was an adduct of **1** and a cyclooctatrienone derived from **1** and **B-7-AQ**.



Scheme 2



Scheme 3

When a benzene solution of **B-7-AQ** and **2**, generated *in situ* from the reaction of *N*- α -chlorobenzylidene-*N'*-phenylhydrazine and triethylamine, was stirred for 5 h at room temperature, a single product (**8**) was obtained in 43% yield. The ¹H NMR spectrum of **8** indicated the presence of three

consecutive olefinic protons on the seven membered ring, a singlet olefinic proton at δ 6.44, and a methine proton at 5.02, which resulted that the reaction site was on the 8,8a double bond. There are two possibilities for the structure for **8**; one is **8a** and the other is **8b**. The ^{13}C NMR spectrum indicated that one of the two sp^3 -carbon atoms observed at δ 73.8 carried a hydrogen atom at 5.02, which coupled through the carbonyl group with an olefinic proton at 6.32. These data were consistent with the structure of **8a**, 8-bromo-3a,10a-dihydro-1,3-diphenylazuleno[4,3a-*d*]pyrazol-4,10-dione. This was confirmed by the X-Ray crystallographic study as shown in Figure 1.

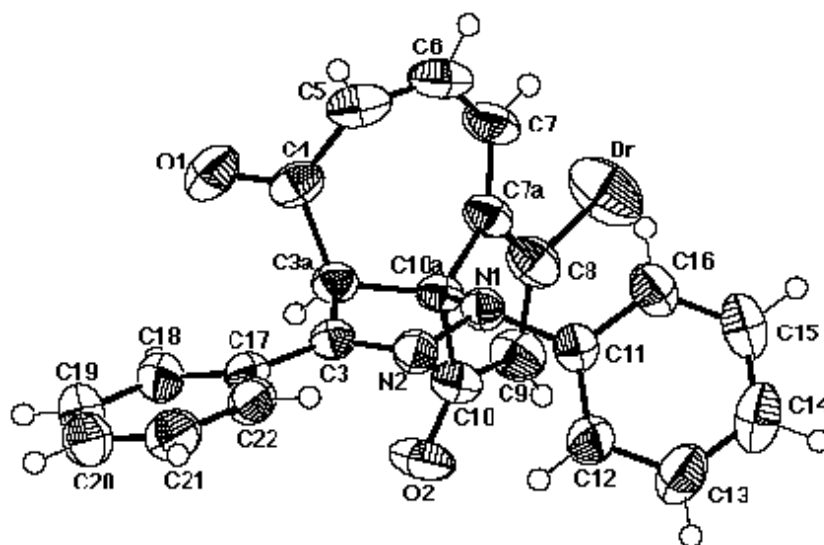


Figure 1. ORTEP drawing of compound (**8a**).

While a benzene solution of **B-7-AQ** and **3**, generated *in situ* from benzhydroxamic acid chloride and triethylamine, was stirred for 5 h at room temperature, two products (**9** and **10**) were obtained in 14 and 25% yields. The minor product (**9**) was a 1 : 1 adduct from the MS spectrum. Since the splitting pattern in the ^1H NMR spectrum of **9** was similar to that of **8a**, the structure was determined to be 8-bromo-3a,10a-dihydro-3-phenylazuleno[4,3a-*d*]isoxazole-4,10-dione. The major product (**10**) was a 2 : 1 adduct from the MS spectrum. The position of the isoxazole rings of **10** was determined from the observation of a W-letter coupling between H_{3a} and H_{4a} . At the same time, the observation of the W-letter coupling deduced that the stereochemistry of the two isoxazole rings was *cis*. The structure of **10** was, thus, determined to be 9-bromo-3a,10a,4a,7a-tetrahydro-3,5-diphenylazuleno[4,3a-*d*:5,6-*d'*]diisoxazole-4,11-dione.

Next, the reaction of **B-5-AQ** and **2** gave two products (**11** and **12**) in 36 and 8% yields, respectively although the reaction of **B-5-AQ** and **3** did not give any product. The ^1H NMR spectrum of the minor product (**12**) showed the presence of the two olefinic protons with a small coupling constant at δ 6.36 and 6.78. The former was assigned to the proton on the cyclopentenone ring and the latter was the proton at the peri-position of the bromine atom. Since the hydrogen atom on a sp^3 -carbon atom appeared at δ 4.61 with a poor splitting pattern in CDCl_3 , we changed the solvent to C_6D_6 to observe as a doublet of doublets at 3.73 ($J=3.4, 2.4$ Hz). Therefore, product (**12**) was 8-bromo-3a,10a-dihydro-3-phenylazuleno[4,3a-*d*]-pyrazole-4,10-dione. The H_4 of **12** appeared at the higher magnetic field (δ 6.26 in CDCl_3 and 5.57 in

C₆D₆) than H₅ (δ 6.33 in CDCl₃ and 6.01 in C₆D₆). These rather unusual chemical shifts must be due to the anisotropic effect of the neighboring phenyl group.

Since the major product (**11**) had no bromine atom, the reaction site should be on the cyclopentenone ring. After the 1,3-dipolar addition, hydrogen bromide was removed from a 1:1 adduct. There are two possibilities for the structure of **11**; one is **11a** and the other is **11b**. The structure of **11a** should be preferred from molecular orbital consideration. Table 1 shows coefficients of the selected molecular orbitals of **B-5-AQ** and **B-7-AQ** (PM3). It has already been reported that the interaction of the LUMO of nitrilimines and nitrile oxides with the HOMO of tropone determines the preferred regioselectivity.¹⁴ Although the regioselectivity of the reaction of **B-7-AQ** and **2** was explained by the interaction of the HOMO of **B-7-AQ** and the LUMO of **2**,¹⁴ the site selectivity was not explained by the interaction of the frontier orbitals. In the case of the reaction of **B-5-AQ** and **2**, however, the site selectivity was interpreted by the interaction of the LUMO of **B-5-AQ** and the HOMO of **2**,¹⁴ which would also determine the regioselectivity to lead structure (**11a**).

Table 1. Coefficients of the Selected Molecular Orbitals of **B-5-AQ** and **B-7-AQ**

		E/eV	C2	C3	C4	C8	C8a	C3a
B-5-AQ	LUMO+1	-1.378	-0.316	0.181	-0.514	-0.445	0.341	0.347
	LUMO	-1.519	0.331	-0.370	0.137	-0.228	0.308	-0.226
	HOMO	-9.781	0.227	0.124	-0.466	0.362	0.380	-0.286
B-7-AQ	LUMO+1	-1.197	0.011	-0.166	-0.307	-0.558	0.474	0.154
	LUMO	-1.625	-0.414	0.347	-0.395	-0.107	-0.037	0.395
	HOMO	-9.601	-0.339	-0.185	0.414	-0.306	-0.162	0.422

On the other hand, the interaction of the HOMO of the highly nucleophilic **1** with the LUMO of tropone determined the regioselectivity.¹⁴ The formation of product (**6**) from **B-7-AQ** and **1** indicated that the reaction occurred at the 8,8a double bond. The orbital coefficients at the 8,8a double bond of the LUMO of **B-7-AQ** are, however, small and the signs mismatched to those of the HOMO of **1**.¹⁴ The next LUMO of **B-7-AQ** has the large orbital coefficients on the 8,8a double bond to determine the site selectivity and the regioselectivity of the reaction between **B-7-AQ** and **1**.

The site selectivity of the 1,3-dipolar reactions of **B-5-AQ** and **B-7-AQ** with the 1,3-dipoles was different from each other and from the cycloaddition reactions with dienophiles and dienes, in which they reacted at the double bond on the cyclopentenone part not to form an unstable cyclopentadienone structure.⁹⁻¹¹

The authors thank Professor Dr. Klaus Hafner, Darmstadt Technischen Hochschule, for generous donation of the starting material, azulene.

EXPERIMENTAL

Elemental analyses were performed at Kyushu University. The melting points were obtained on a Yanagimoto Micro Melting Point Apparatus and are uncorrected. The NMR spectra were measured on

JEOL GSX 270H, LA 400, and LA 600 spectrometers in CDCl₃; the chemical shifts are expressed in δ units. The MS spectra were measured with JEOL 01SG-2 and JMS-700 spectrometers. The IR spectra were recorded on a JASCO IR-A102 spectrophotometer with KBr disks. The UV spectra were measured in CHCl₃ using Hitachi U-3200 and U-3410 spectrophotometers. The stationary phase for the column chromatography was Wakogel C-300 and the elution solvents were mixtures of hexane and ethyl acetate.

Reaction of B-5-AQ and diazomethane (1)

To an ether solution (500 mL) of **B-5-AQ** (103 mg, 0.43 mmol), **1** (0.5 mmol) was added at 0 °C. The mixture was kept at 0 °C for 4 d. The solvent was removed and the residue was chromatographed on a silica gel column (dichloromethane) to give **4** (15 mg, 14%) and **5** (4 mg, 4%). **4**: yellow crystals, mp 163-165 °C (hexane-AcOEt). ¹H NMR δ 3.30 (2H, d, J =8.8 Hz), 6.10 (1H, dt, J =10.3, 8.8 Hz), 6.63 (1H, dd, J =10.3, 5.9 Hz), 6.80 (1H, d, J =0.7 Hz), 6.99 (1H, s), and 7.32 (1H, d, J =5.9 Hz). ¹³C NMR δ 44.3, 129.5, 130.3, 132.1, 133.1, 133.7, 134.4, 144.0, 155.5, 189.3, and 190.5. IR ν 1697, 1656, 1543, 1257, 1195, 1105, 1024, 893, 805, and 703. MS m/z (%): 252 (M^{++1} for ⁸¹Br, 28), 250 (M^{++1} for ⁷⁹Br, 28), 224 (23), 222 (23), 144 (11), 143 (100), 115 (83), and 89 (15). FABHM m/z (%) Found: 250.9708 (M^{++1} for ⁷⁹Br) and 252.9699 (M^{++1} for ⁸¹Br). Calcd for C₁₁H₈O₂Br: 250.9708 ($M+1$ for ⁷⁹Br) and 252.9688 ($M+1$ for ⁸¹Br). **5**: yellow crystals, mp 108-110 °C (hexane-AcOEt). ¹H NMR δ 2.45 (3H, s), 3.23 (2H, d, J =8.8 Hz), 5.87 (1H, dt, J =10.6, 8.8 Hz), 6.36 (1H, d, J =10.6 Hz), 6.68 (1H, d, J =0.7 Hz), and 6.79 (1H, s). ¹³C NMR δ 20.8, 43.9, 105.6, 115.4, 128.5, 131.0, 135.0, 135.8, 145.6, 159.3, 191.1, and 191.8. IR ν 1690, 1657, 1632, 1555, 1434, 1262, 1191, 1112, 891, 819, 775, and 553 cm⁻¹. MS m/z (%): 266 (M^{+} for ⁸¹Br, 12), 264 (M^{+} for ⁷⁹Br, 13), 238 (14), 236 (15), 158 (12), 157 (100), 129 (74), 128 (71), and 127 (33). HM (EI) Found: 263.9787 (M^{+} for ⁷⁹Br) and 265.9771 (M^{+} for ⁸¹Br). Calcd for C₁₂H₉O₂Br: 263.9786 (M for ⁷⁹Br) and 265.9766 (M for ⁸¹Br).

Reaction of B-7-AQ and diazomethane (1)

To an ether solution (100 mL) of **B-7-AQ** (36.5 mg, 0.15 mmol), **1** (0.18 mmol) was added at 0 °C. The mixture was kept at 0 °C for 4 d. The solvent was removed and the residue was chromatographed on a silica-gel column (dichloromethane) to give **6** (13 mg, 35%) and **7** (16 mg, 36%). **6**: colorless crystals, mp 128 °C (decomp) (hexane-AcOEt). ¹H NMR δ 2.65 (3H, s), 6.70 (1H, s), 6.86 (1H, d, J =12.1 Hz), 7.02 (1H, d, J =8.1 Hz), and 7.12 (1H, dd, J =12.1, 8.06 Hz). ¹³C NMR δ 14.9, 126.2, 131.4, 133.9, 134.5, 137.8, 142.6, 150.0, 152.0, 189.1, and 193.5. IR ν 1704, 1584, 1547, 1433, 1367, 1277, 1147, 1018, 868, 822, and 632 cm⁻¹. MS m/z (%): 252 (M^{++1} for ⁸¹Br, 58), 250 (M^{++1} for ⁷⁹Br, 58), 224 (7), 222 (8), 221 (6), 144 (15), 143 (100), 115 (54), 89 (12), and 63 (8). FABHM m/z (%) Found: 250.9709 (M^{++1} for ⁷⁹Br) and 252.9696 (M^{++1} for ⁸¹Br). Calcd for C₁₁H₈O₂Br: 250.9708 ($M+1$ for ⁷⁹Br) and 252.9688 ($M+1$ for ⁸¹Br). **7**: colorless crystals, mp 128-130 °C (decomp) (hexane-AcOEt). ¹H NMR δ 2.32 (1H, ddd, J =12.9, 6.6, 1.9 Hz), 2.89 (1H, m), 2.91 (1H, dd, J =12.9, 2.4 Hz), 4.62 (1H, dd, J =17.8, 7.8 Hz), 5.03 (1H, dd, J =17.8, 1.2 Hz), 5.89 (1H, dd, J =12.9, 1.2 Hz), 6.67 (1H, s), 6.67 (1H, dd, J =12.9, 6.6 Hz), and 6.95 (1H, d, J =6.6 Hz). ¹³C NMR δ 42.4, 43.0, 80.5, 100.6, 128.3, 131.8, 133.5, 134.5, 141.6, 157.6, 194.2, and 198.7. IR ν 3462, 3128, 1712, 1648, 1538, 1433, 1138,

900, 856, 779, and 620. MS m/z (%): 266 ($M^+ - 28$ for ^{81}Br , 17), 264 ($M^+ - 28$ for ^{79}Br , 18), 236 (12), 185 (75), 157 (89), 129 (100), 128 (92), and 127 (42). Anal. Calcd for $\text{C}_{12}\text{H}_9\text{N}_2\text{O}_2\text{Br}$: C, 49.17; H, 3.09; N, 9.56. Found: C, 48.90; H, 3.10; N, 9.26.

Reaction of B-7-AQ and diphenylnitrilimine (2)

An anhydrous benzene solution (10 mL) of *N*- α -chlorobenzilidene-*N'*-phenylhydrazine (20 mg, 0.087 mmol), triethylamine (0.5 mL), and **B-7-AQ** (24 mg, 0.1 mmol) was reacted at rt for 5 h. The precipitate was filtered off and the benzene solution was washed with water, dried on MgSO_4 , and evaporated. The residue was purified by column chromatography to give **8** (16 mg, 43%). **8**: reddish crystals, mp 191–192 °C (hexane-chloroform). ^1H NMR δ 5.02 (1H, d, $J=1.1$ Hz), 6.32 (1H, dd, $J=11.7$, 1.1 Hz), 6.44 (1H, s), 6.61 (1H, d, $J=5.5$ Hz), 6.68 (1H, dd, $J=11.7$, 5.5 Hz), 7.02 (1H, tt, $J=7.3$, 1.1 Hz), 7.10 (2H, ddm, $J=7.7$, 1.1 Hz), 7.21 (2H, dm, $J=7.3$ Hz), 7.38 (3H, m), and 7.81 (2H, m). ^{13}C NMR δ 73.8, 75.2, 119.3 (2C), 124.0, 126.8 (2C), 127.9, 128.6 (2C), 129.0 (2C), 129.5, 130.0, 132.6, 134.2, 136.1, 141.6, 142.7, 143.8, 155.3, 194.8, and 197.2. IR ν 1708, 1659, 1596, 1561, 1528, 1490, 1446, 1401, 1343, 1285, 1263, 1227, 1165, 1138, 1079, 1061, 1028, 1008, 992, 964, 916, 895, 855, and 826 cm^{-1} . UV λ 248.3 nm (ϵ 28810), 289.0 (16850, sh), 329.6 (16960), and 378.7 (6720, sh). MS m/z (%) 432 (M^+ for ^{81}Br , 2), 431 ($M^+ + 1$, 1), 430 (M^+ for ^{79}Br , 2), 351 (17), 327 (83), 325 (81), 295 (38), 245 (42), 218 (65), 191 (73), 190 (79), 165 (43), 147 (43), 133 (9), 104 (6), 91 (41), 77 (100), and 75 (9). Anal. Calcd for $\text{C}_{23}\text{H}_{15}\text{O}_2\text{N}_2\text{Br}$: C, 64.05; H, 3.51; N, 6.50. Found: C, 63.83; H, 3.76; N, 6.34.

X-Ray crystallographic analysis of 8a

A dark violet crystal of $\text{C}_{23}\text{H}_{15}\text{BrN}_2\text{O}_2$ ($M_r = 431.28$) having approximate dimensions of 0.60 x 0.45 x 0.30 mm was mounted on a glass fiber in a random orientation. Preliminary examination and data collection were performed with Cu $K\alpha$ radiation ($\lambda = 1.54184$ Å) on an Enraf-Nonius FR590 computer controlled kappa axis diffractometer equipped with a graphite crystal, incident beam monochromator. Cell constants and an orientation matrix for data collection were obtained from least-squares refinement, using the setting angles of 25 reflections in the range $18 < \theta < 42^\circ$, measured by the computer controlled diagonal slit method of centering. There were no systematic absences and the space group was determined to be triclinic $P\bar{1}$. The data were collected at a temperature of 23 °C using the ω - 2θ scan technique. A total of 3879 reflections were collected, of which 3597 were unique. An empirical absorption correction *via* ψ scans was applied to the data. The structure was solved by direct method (*SIR92*)¹⁵ and difference Fourier syntheses. Using the all 3597 reflections for 253 variable parameters, the structure was refined in full-matrix least-squares on F^2 (*SHELXL93*).¹⁶ All H atoms were located at ideal positions and were included in refinement, but restrained to ride on the atom to which they are bonded. Isotropic thermal factors of H atoms were held fixed to 1.2 times U_{eq} of the riding atoms. Atomic scattering factors were taken from International Tables for X-ray Crystallography. The highest peak in the final difference Fourier had a height of 0.979 $\text{e}/\text{\AA}^3$ and the minimum negative peak had a height of -1.088 $\text{e}/\text{\AA}^3$.

Crystal data of **8a**: $a = 10.611(3)$ Å, $b = 13.108(3)$ Å, $c = 7.916(2)$ Å, $\alpha = 104.05(2)^\circ$, $\beta = 110.85(2)^\circ$, $\gamma = 68.83(2)^\circ$, $V = 951.2(4)$ Å³, $Z=2$, $D_x = 1.506$ gcm^{-3} , $R[F^2 > 2\sigma(F^2)] = 0.0539$, $wR(F^2) = 0.1502$

Reaction of B-7-AQ and benzonitrile oxide (3)

To an anhydrous benzene solution (10 mL) of benzohydroxamic acid chloride (30 mg, 0.19 mmol) and **B-7-AQ** (24 mg, 0.1 mmol) was added triethylamine (0.5 mL) at rt. The reaction mixture was kept at rt for 1 d. The precipitate was filtered off and the benzene solution was washed with water, dried on MgSO₄, and evaporated. The residue was purified by column chromatography to give **9** (5 mg, 14%) and **10** (12 mg, 25%). **9**: pale yellow crystals, mp 162-164 °C (hexane-chloroform). ¹H NMR δ 5.08 (1H, s), 6.18 (1H, m), 6.62 (3H, m), 7.39-7.46 (3H, m), and 7.79 (2H, m). ¹H NMR (C₆D₆) δ 4.97 (1H, s), 5.55 (1H, dd, *J*=12.2, 5.5 Hz), 5.58 (1H, d, *J*=12.2 Hz), 5.73 (1H, s), 5.78 (1H, d, *J*=5.5 Hz), 7.00 (3H, m), and 7.91 (2H, m). ¹³C NMR δ 70.7, 84.8, 127.0, 127.6, 127.8 (2C), 128.9 (2C), 131.1, 132.4, 132.8, 134.6, 140.5, 152.8, 155.9, 194.1, and 194.9. IR ν 1716, 1678, 1599, 1564, 1535, 1495, 1445, 1398, 1327, 1286, 1237, 1179, 1149, 1103, 1023, 970, 920, 854, and 838 cm⁻¹. UV λ 255.0 nm (ε 20240), 290.4 (9920), and 326.6 (7220, sh). MS *m/z* (%) 357 (M⁺ for ⁸¹Br, 3), 355 (M⁺ for ⁷⁹Br, 2), 276 (7), 248 (18), 198 (12), 189 (38), 144 (87), 117 (32), 101 (34), 95 (24), 89 (85), 77 (100), 75 (39), and 63 (21). FABHM *m/z* (%) Found: 355.9909 (M⁺+1 for ⁷⁹Br) and 357.9874 (M⁺+1 for ⁸¹Br). Calcd for C₁₇H₁₀O₃NBr; 355.9922 (M+1 for ⁷⁹Br) and 357.9904 (M+1 for ⁸¹Br). **10**: colorless crystals, mp 240 °C (decomp) (hexane-chloroform). ¹H NMR δ 4.59 (1H, dd, *J*=9.5, 1.5 Hz), 4.89 (1H, d, *J*=1.5 Hz), 5.45 (1H, dd, *J*=9.5, 7.3 Hz), 6.76 (2H, d, *J*=8.1 Hz), 6.88-7.04 (5H, m), 7.12 (1H, ddm, *J*=7.3, 1.8 Hz), and 7.23-7.35 (4H, m). ¹³C NMR δ 64.8, 65.9, 78.9, 84.7, 126.6 (2C), 126.7, 127.1 (2C), 127.4, 127.8, 128.3 (2C), 128.4 (2C), 130.4, 130.5, 134.4, 143.9, 153.2, 155.3, 155.9, 195.0, and 196.5. IR ν 1712, 1666, 1600, 1572, 1531, 1500, 1446, 1378, 1337, 1309, 1272, 1228, 1202, 1159, 1117, 1026, 973, 930, 894, 863, and 846 cm⁻¹. UV λ 247.4 nm (ε 26560) and 277.0 (20955). MS *m/z* (%) 476 (M⁺ for ⁸¹Br, 1), 474 (M⁺ for ⁷⁹Br, 2), 303 (4), 276 (4), 250 (5), 222 (24), 214 (7), 194 (19), 189 (25), 176 (13), 163 (19), 144 (100), 116 (32), 102 (12), 89 (40), 77 (79), and 63 (10). Anal. Calcd for C₂₄H₁₅O₄N₂Br: C, 60.65; H, 3.18; N, 5.89. Found: C, 60.45; H, 3.22; N, 5.99.

Reaction of B-5-AQ and diphenylnitrilimine (2)

An anhydrous benzene solution (10 mL) of *N*-α-chlorobenzilidene-*N'*-phenylhydrazine (20 mg, 0.087 mmol), triethylamine (0.5 mL), and **B-5-AQ** (24 mg, 0.1 mmol) was reacted at rt for 5 h. The precipitate was filtered off and the benzene solution was washed with water, dried on MgSO₄, and evaporated. The residue was purified by column chromatography to give **11** (8 mg, 36%) and **12** (3 mg, 8%). **11**: pale yellow crystals, mp 295 °C (decomp) (hexane-chloroform). ¹H NMR δ 6.82 (1H, dd, *J*=2.6, 0.7 Hz), 6.95 (1H, ddd, *J*=12.1, 2.6, 0.7 Hz), 7.16 (1H, dd, *J*=12.1, 8.1 Hz), 7.42-7.53 (2H, m), 7.57 (1H, dd, *J*=8.1, 0.7 Hz), 7.59-7.66 (6H, m), and 8.36-8.41 (2H, m). ¹³C NMR δ 125.2 (2C), 125.7, 127.5 (2C), 128.9 (2C), 129.3, 130.0, 130.1 (2C), 130.2, 130.3, 130.9, 134.5, 134.6, 138.0, 143.8, 145.8, 149.7, 156.3, 178.9, and 186.8. IR ν 1709, 1642, 1623, 1587, 1511, 1486, 1463, 1429, 1382, 1318, 1284, 1263, 1222, 1100, 1077, 933, 902, 859, and 834 cm⁻¹. UV λ 268.0 nm (ε 27980, sh), 280.6 (32330), 289.8 (31410), 321.4 (11770, sh), and 373.9 (5900, sh). MS *m/z* (%) 351 (M⁺+1, 1), 350 (M⁺, 4), 322 (46), 321 (41), 190 (37), 161 (20), 111 (11), 97 (25), 83 (35), 77 (100), 69 (37), and 55 (36). Anal.

Calcd for C₂₃H₁₄O₂N₂: C, 78.84; H, 4.03; N, 8.00. Found: C, 79.12; H, 4.30; N, 7.91. **12**: pale yellow crystals, mp 175-177 °C (hexane-chloroform). ¹H NMR δ 4.61 (1H, d, *J*=1.1 Hz), 6.26 (1H, br d, *J*=13.5 Hz), 6.33 (1H, dd, *J*=13.5, 1.1 Hz), 6.36 (1H, d, *J*=0.7 Hz), 6.78 (1H, d, *J*=1.1 Hz), 7.14 (3H, m), 7.21 (1H, d, *J*=0.7), 7.24 (1H, m), 7.35 (3H, m), and 7.80 (2H, m). ¹H NMR (C₆D₆) δ 3.73 (1H, dd, *J*=3.4, 2.4 Hz), 5.57 (1H, dd, *J*=12.8, 3.4 Hz), 5.60 (1H, d, *J*=0.5 Hz), 6.01 (1H, dt, *J*=12.8, 2.4 Hz), 6.68 (1H, d, *J*=2.4 Hz), 6.81 (1H, tm, *J*=7.3 Hz), 6.93 (2H, dd, *J*=8.2, 7.5 Hz), 7.08-7.13 (5H, m), 7.26 (2H, m), and 7.67 (2H, m). ¹³C NMR δ 50.6, 70.0, 122.9 (2C), 126.2, 126.8 (2C), 128.9 (2C), 129.1 (2C), 130.0, 130.1, 130.2, 131.7, 134.4, 136.9, 143.8, 144.7, 148.4, 155.5, 189.1, and 198.0. IR ν 1709, 1680, 1655, 1595, 1570, 1527, 1493, 1452, 1354, 1273, 1241, 1205, 1178, 1145, 1098, 1072, 981, 919, 861, and 836 cm⁻¹. UV λ 251.7 nm (ε 24200, sh), 341.6 (9410), and 373.8 (7500, sh). MS *m/z* (%) 432 (M⁺ for ⁸¹Br, 3), 431 (M⁺⁺1, 2), 430 (M⁺ for ⁷⁹Br, 3), 351 (1), 324 (2), 295 (7), 218 (3), 191 (12), 189 (12), 165 (3), 105 (6), 91 (100), 77 (72), and 64 (11). Anal. Calcd for C₂₃H₁₅O₂N₂Br: C, 64.05; H, 3.51; N, 6.50. Found: C, 63.74; H, 3.55; N, 6.41.

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