ISSN 1070-4280, Russian Journal of Organic Chemistry, 2017, Vol. 53, No. 12, pp. 1815–1821. © Pleiades Publishing, Ltd., 2017.
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Synthesis and Some Transformations of Polybrominated Quinone Diazides

V. A. Vasin,* M. V. Fadin, and I. V. Tarasova

Ogarev Mordovian State National Research University, ul. Bol'shevistskaya 68, Saransk, 430005 Russia
**e-mail: orgchem@mrsu.ru*

Received March 17, 2017

Abstract—The reduction of polybrominated *o*- and *p*-nitrophenols with granular tin in concentrated aqueous HCl gave polybrominated aminophenols which were diazotized with sodium nitrite in concentrated sulfuric acid at 0°C to obtain polybrominated *o*- and *p*-quinone diazides. Their thermolysis with elimination of nitrogen generated ketocarbenes which reacted with acetylacetone to form insertion products at the activated methylene group. Ketocarbenes generated from *o*-quinone diazides reacted with typical dipolarophiles such as acetonitrile, benzonitrile, styrene, and phenylacetylene to afford the corresponding [3+2]-cycloaddition products.

DOI: 10.1134/S1070428017120053

Quinone diazides have found wide application in various fields of practice [1, 2] such as microelectronics, printing, manufacture of dues, pyrotechnics, design of chemical sensors, etc. Due to diversity of chemical transformations of quinone diazides in combination with their relative accessibility, their use in organic synthesis opens wide prospects for preparation of various practically important phenol derivatives and heterocyclic compounds. Thermal or photolytic decomposition of quinone diazides involves elimination of nitrogen molecule with generation of ketocarbenes capable of participating in insertion, cyclopropanation, and 1,3-dipolar cycloaddition reactions. Ketocarbenes generated from polyfluorinated [3] and polychlorinated [4–7] quinone diazides are characterized by increased stability; in particular, polyhalogenated *o*-quinone diazides do not undergo ring contraction Wolff rearrangement [8]. These quinone diazides were used to synthesize various compounds containing a polyhalogenated aromatic ring.

Unlike polyfluorinated and polychlorinated quinone diazides, their bromine-containing analogs have been poorly studied, and they remain difficultly accessible. On the other hand, polybrominated quinone diazides attract interest as convenient precursors to structures possessing a polybromo(hydroxy)phenyl fragment, which cannot be obtained by direct bromination or via indirect routes. There are a few publications related to bromo-substituted quinone diazides [9–14], and no systematic studies of these compounds have been performed.

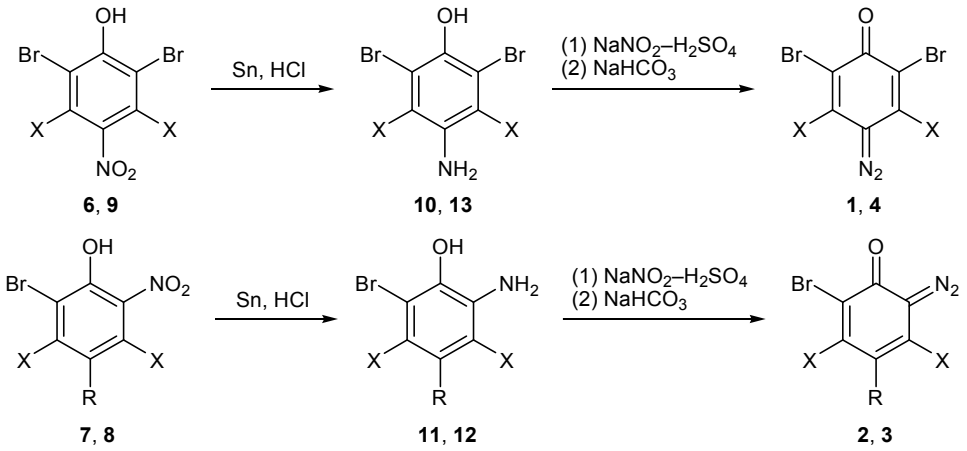
The goal of the present work was to develop preparative procedures for the synthesis of polybromo-substituted quinone diazides **1**–**5** with different numbers and positions of bromine atoms in the ring and study their thermal transformations in some reactive solvents.

Quinone diazides **1**–**4** were synthesized starting from 2,6-dibrom-4-nitro- and 2,4-dibromo-6-nitrophenols **6** [15] and **7** [16], 2,3,5-tribromo-4-methyl-6-nitrophenol (**8**) [17], and 2,3,5,6-tetrabromo-4-nitrophenol (**9**) [18], respectively. Nitro compounds **6**–**9** were smoothly reduced to the corresponding brominated amino phenols **10**–**13** with granular tin in concentrated aqueous HCl. Another convenient precursor to aminophenol **13** was 2,3,5,6-tetrabromo-1,4-benzoquinone oxime **14** [18] which was smoothly converted to **13** under analogous conditions (Scheme 1).

Compounds **10**–**13** were isolated as crystalline solids, and their structure was confirmed by IR, ^{1}H and ^{13}C NMR, and MALDI mass spectra.

Aminophenols **10**–**13** were diazotized with sodium nitrite in concentrated sulfuric acid at 0°C [19], and the reaction mixtures were then diluted with water to convert intermediate diazophenol sulfates to quinone diazides **1**–**4**. Quinone diazides **1**–**4** were isolated in the pure state, and their structure was confirmed by

Scheme 1.



1, **2**, **6**, **7**, **10**, **11**, X = H; **3**, **4**, **8**, **9**, **12**, **13**, X = Br; **3**, **7**, **12**, R = Me; **2**, **8**, **11**, R = Br.

elemental analyses and IR and ^{1}H and ^{13}C NMR spectra. The IR spectra of **1**–**4** displayed strong absorption bands at 2100–2200 and 1560–1655 cm^{-1} due to stretching vibrations of the conjugated diazo and carbonyl groups, respectively [20]. Quinone diazide **4** was also identified by comparison with an authentic sample [18].

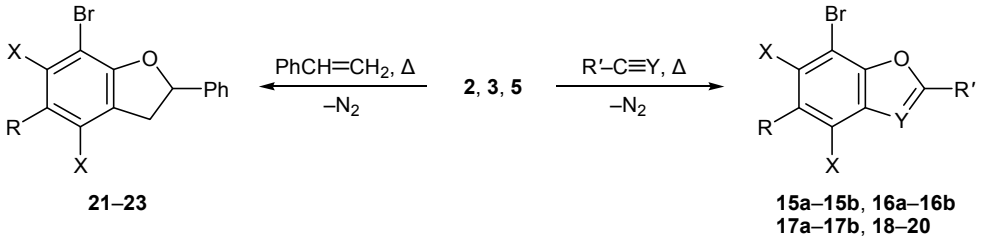
3,4,5,6-Tetrabromo-*o*-quinone diazide **5** was synthesized by reaction of tetrabromosalicylic acid with 10 equiv of sodium nitrite in glacial acetic acid according to the procedure described in [18].

Quinone diazides **2**, **3**, and **5** were subjected to thermolysis in sealed ampules at 150°C for 4 h in excess acetonitrile, benzonitrile, phenylacetylene, and styrene acting simultaneously as reagent and solvent. In each case, the corresponding heterocyclization products **15**–**23** were obtained in satisfactory yields (Scheme 2).

Compounds **15**–**23** were isolated and purified by flash chromatography on silica gel. Their structure was determined on the basis of their IR and ^{1}H and ^{13}C NMR spectra. Benzoxazole derivatives **15**–**17** characteristically showed in the IR spectra medium-intensity C=N stretching bands in the region 1630–1690 cm^{-1} [20]. The ^{1}H NMR spectra of **15a**, **16a**, **16b**, **17a**, **19**, and **22** contained singlets at δ ~2–3 ppm due to methyl protons. The phenyl substituent on C^2 in compounds **15b**–**17b** and **18**–**23** gave a five-proton multiplet signal at δ ~6–8 ppm. Two nonequivalent aromatic protons of the brominated aromatic ring in **15a**, **15b**, **18**, and **21** resonated in the same region as doublets with a coupling constant *J* of 2.3–2.8 Hz. In the ^{1}H NMR spectra of dihydrobenzofurans **21**–**23**, signals of diastereotopic protons of the CH_2 group appeared as two doublets of doublets at δ 3–4 ppm, while the 2-H proton resonated as a pseudotriplet at δ 5.5–6.5 ppm.

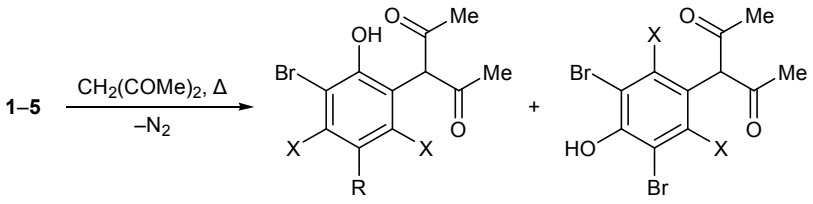
We also studied the reaction of polybrominated quinone diazides **1**–**5** with acetylacetone possessing an activated methylene group. The reactions were carried out by heating for 2 h at 90°C in 17 equiv of acetylacetone which simultaneously acted as solvent. *o*-Quinone diazides **2**, **3**, and **5** were thus converted in satisfactory yields to functionalized polybromophenols **24**–**26** as a result of insertion of intermediate ketocarbene into the C–H bond of acetylacetone. *p*-Quinone diazides **1** and **4** gave rise to polybromophenols

Scheme 2.



15, **17**, **18**, **20**, **21**, **23**, R = Br; **16**, **19**, **22**, R = Me; **15a**–**17a**, R′ = Me; **15b**–**17b**, **18**–**20**, R′ = Ph; **15**, **18**, **21**, X = H; **16**, **19**, **20**, **22**, **23**, X = Br; **15**–**17**, Y = N; **18**–**20**, Y = CH.

Scheme 3.



24–26 **27**, **28**

24, **26**; R = Br; **25**, R = Me; **24**, **27**, X = H; **25**, **26**, **28**, X = Br.

27 and **28** (Scheme 3). Compounds **24**–**28** were isolated by flash chromatography on silica gel, and their structure was confirmed by IR, ^{1}H and ^{13}C NMR, and MALDI mass spectra.

As follows from the ^{1}H NMR data, diketones **24**–**26** in solution are almost completely enolized. Their ^{1}H NMR spectra displayed singlets in the region δ 1.5–2.9 ppm due to two nonequivalent methyl groups and singlets at δ 9.5–11.4 and 15.0–15.4 ppm, belonging to the phenolic and enolic hydroxy protons, respectively. Presumably, enolization of **24**–**26** is favored by intramolecular hydrogen bonding with participation of spatially close phenolic hydroxy group.

The ^{1}H NMR spectrum of **27** showed two singlets at δ 2.16 and 5.35 ppm with an intensity ratio of 6:1, which were assigned to two methyl groups and CH proton of the diketone fragment, as well as singlets at δ 1.86 and 7.48 ppm due to protons of the methyl groups and aromatic ring, respectively, and at δ 10.01 and 13.82 ppm due to phenolic and enolic hydroxyls. On the basis of signal intensities, the ratio of the diketone and enol tautomers of **27** was estimated at 1:5. Compound **28** was found to exist in solution exclusively as diketone tautomer. Its ^{1}H NMR spectrum contained singlets at δ 1.81 and 6.49 ppm, corresponding to protons of the two equivalent methyl groups and CH proton, respectively.

Thus, the behavior of quinone diazides **1**–**5** under thermolysis conditions is similar to their fluorinated and chlorinated analogs. Ketocarbenes generated by their decomposition react with typical dipolarophiles to afford five-membered heterocycles or insert into the activated C–H bond of acetylacetone.

EXPERIMENTAL

The ^{1}H and ^{13}C spectra were recorded on a Jeol JNM-ECX400 spectrometer at 400 and 100 MHz, respectively, using DMSO-d_6 or $CDCl_3$ (**3**, **19**, **22**, **25**, **28**) as solvent; the chemical shifts were measured relative to the residual proton and carbon signals of the deuterated solvent. The ^{1}H NMR spectra of some polybrominated amino phenols in DMSO-d_6 showed no OH and NH_2 signals because of exchange processes. The IR spectra were recorded in KBr on an InfraLYuM FT-02 spectrometer with Fourier transform; for each compound, frequencies of 10 most intense characteristic bands are given. Analytical thin-layer chromatography was performed on Silufol UV-254 plates using hexane–acetone (7:3) as eluent; spots were visualized by treatment with iodine vapor or under UV light. Silica gel Merk L (5–40 μm) was used for preparative flash chromatography (eluent light petroleum ether–acetone, 7:3. The elemental analyses were obtained with a Vario MICRO CHN analyzer.

The mass spectra (MALDI) were recorded on a Bruker Autoflex II instrument with a FWHM resolution of 18000 (nitrogen laser, λ 337 nm; time-of-flight mass analyzer, reflectron mode; accelerating voltage 20 kV; positive ion detection). Samples were applied onto a polished steel target plate. The resultant spectrum was the sum of 300 spectra recorded for different points on the target. 2,5-Dihydroxybenzoic acid (Acros, 99%) and α-cyano-4-hydroxycinnamic acid (Acros, 99%) were used as matrices. Given below are *m*/*z* values for ^{79}Br isotope ions.

Reduction of nitrophenols 6–9 and quinone oxime 14 (*general procedure*). Concentrated aqueous HCl, 20 mL, was added to a mixture of 10 mmol of compound **6**–**9** or **14** and 5.95 g (50 mmol) of granular tin. The mixture was kept for 1 h at 20°C, heated on a water bath at 70–80°C for 5 h with intermittent stirring, and left overnight. The precipitate was filtered off and washed with a small amount of cold water, and the filtrate was treated with s saturated aqueous solution of $NaHCO_3$ to pH 6–7 and extracted with diethyl ether. The combined extracts were dried over Na_2SO_4 and evaporated, and the residue was recrystallized from aqueous ethanol with addition of charcoal.

4-Amino-2,6-dibromophenol (10). Yield 45%, mp 187°C; published data [21]: 190°C. IR spectrum, ν, cm^{-1}: 3368 s, 3271 s, 3159 w, 1481 v.s, 1419 v.s, 1219 s, 1180 s, 887 s, 740 s. ^1H NMR spectrum, δ, ppm: 5.02 br.s (2H, NH_2), 6.76 s (2H, 3-H, 5-H), 8.68 br.s (1H, OH). ^{13}C NMR spectrum, δ_C, ppm: 113.6 (2C, C_{arom}), 117.3 (2C, C_{arom}), 140.6 (C_{arom}), 144.1 (C_{arom}). Found, %: C 26.91; H 1.75; N 4.91. $C_6H_5Br_2NO$. Calculated, %: C 27.00; H 1.89; N 5.25.

2-Amino-4,6-dibromophenol (11). Yield 50%, mp 96°C; published data [22]: mp 97–98°C. IR spectrum, ν, cm^{-1}: 3410 m, 3383 w, 3298 w, 1585 w, 1481 v.s, 1473 v.s, 1419 s, 1149 s, 871 s, 841 s. ^1H NMR spectrum, δ, ppm: 4.79 br.s (1H, OH), 5.40 br.s (2H, NH_2), 6.73 d (1H, 5-H, J = 2.52 Hz), 6.76 d (1H, 3-H, J = 2.52 Hz). ^{13}C NMR spectrum, δ_C, ppm: 115.8 (C_{arom}), 116.4 (C_{arom}), 118.6 (C_{arom}), 120.5 (C_{arom}), 138.5 (C_{arom}), 143.5 (C_{arom}). Found, %: C 26.79; H 1.65; N 4.99. $C_6H_5Br_2NO$. Calculated, %: C 27.00; H 1.89; N 5.25.

2-Amino-3,5,6-tribromo-4-methylphenol (12). Yield 60%, mp 144–145°C. IR spectrum, ν, cm^{-1}: 3494 m, 3425 m, 3344 m, 1604 m, 1446 v.s, 1269 m, 1172 v.s, 1026 m, 806 m, 678 m. ^1H NMR spectrum: δ 2.63 ppm, s (3H, CH_3). ^{13}C NMR spectrum, δ_C, ppm: 25.5 (CH_3), 109.0 (C_{arom}), 111.0 (C_{arom}), 114.0 (C_{arom}), 129.4 (C_{arom}), 136.9 (C_{arom}), 139.9 (C_{arom}). Mass spectrum: m/z 357.8063 $[M + H]^+$. $C_7H_7Br_3NO$. Calculated: M + H 357.8071.

4-Amino-2,3,5,6-tetrabromophenol (13). Yield 47% (from **9**), 50% (from **14**); mp 197°C (decomp.). IR spectrum, ν, cm^{-1}: 3409 m, 3375 m, 3328 m, 3294 m, 1596 s, 1438 s, 1380 v.s, 1276 s, 1195 s, 1134 m, 790 m. ^{13}C NMR spectrum, δ_C, ppm: 109.6 (2C, C_{arom}), 116.6 (2C, C_{arom}), 139.5 (C_{arom}), 143.1 (C_{arom}). Mass spectrum: m/z 421.7035 $[M + H]^+$. Found, %: C 17.03; H 0.64; N 3.26. $C_6H_3Br_4NO$. Calculated, %: C 16.97; H 0.71; H 3.30. M + H 421.7021.

Diazotization of amino phenols 10–13 (*general procedure*). A mixture of 5.8 mmol of amino phenol **10–13** and 20 mL of 70% H_2SO_4 was cooled to 0°C, and 4 g (5.8 mmol) of sodium nitrite was added in portions with vigorous stirring over a period of 15 min. The mixture was stirred for 1.5 h at that temperature and diluted with 40 mL of ice water. The precipitate was filtered off and dissolved in methylene chloride, the solution was washed with a saturated solution of $NHCO_3$ (3×5 mL) and dried over Na_2SO_4, the solvent was removed under reduced pressure (water-jet pump), and the crude product was analyzed by IR and NMR spectroscopy.

2,6-Dibromo-4-diazocyclohexa-2,5-dien-1-one (1). Yield 45%, mp 135°C (decomp.); published data [23]: mp 136–137°C (decomp.). IR spectrum, ν, cm^{-1}: 3078 v.w, 3055 v.w, 3024 v.w, 2141 m, 2114 s, 2102 s, 1581 m, 1558 v.s, 1149 m, 906 w, 752 w, 729 w. ^1H NMR spectrum, δ, ppm: 8.42 s (2H, 3-H, 5-H). ^{13}C NMR spectrum, δ_C, ppm: 80.3 (C^4), 114.9 (C^2, C^6), 133.4 (C^3, C^5), 169.2 (C=O). Found, %: C 26.11; H 0.57; N 9.91. $C_6H_2Br_2N_2O$. Calculated, %: C 25.93; H 0.73; N 10.08.

2,4-Dibromo-6-diazocyclohexa-2,4-dien-1-one (2). Yield 50%, mp 127°C (decomp.) [23]. IR spectrum, ν, cm^{-1}: 3062 w, 2148 s, 1604 m, 1558 v.s, 1550 v.s, 1481 m, 1184 m, 1110 m, 709 m. ^1H NMR spectrum, δ, ppm: 7.88 d (1H, 5-H, J = 2.53 Hz), 7.95 d (1H, 3-H, J = 2.53 Hz). ^{13}C NMR spectrum, δ_C, ppm: 89.0, 99.5, 121.3, 127.1, 143.3, 170.1 (C=O). Found, %: C 26.15; H 0.81; N 9.89. $C_6H_2Br_2N_2O$. Calculated, %: C 25.93; H 0.73; N 10.08.

2,3,5-Tribromo-6-diazo-4-methylcyclohexa-2,4-dien-1-one (3). Yield 74%, mp 130°C (decomp.). IR spectrum, ν, cm^{-1}: 2923 w, 2140 s, 1589 v.s, 1542 s, 1288 s, 1141 s, 968 s, 810 w. ^1H NMR spectrum: δ 2.47 s, ppm (3H, CH_3). ^{13}C NMR spectrum, δ_C, ppm: 24.6 (CH_3), 110.2, 125.0, 125.5, 141.5, 143.2, 170.5 (C=O). Mass spectrum: m/z 368.7864 $[M + H]^+$. Found, %: C 22.45; H 0.64; N 7.66. $C_7H_3Br_3N_2O$. Calculated, %: C 22.67; H 0.82; N 7.55. M + H 368.7869.

2,3,5,6-Tetrabromo-4-diazocyclohexa-2,5-dien-1-one (4). Yield 85%, mp 132–133°C (decomp.). The spectral characteristics of **4** coincided with those of a sample prepared by nitrosodecarboxylation of tetrabromo-4-hydroxybenzoic acid [18].

Reactions of polybrominated quinone diazides 2, 3, and 5 with dipolarophiles (*general procedure*). A solution of 1.8 mmol of quinone diazide **2**, **3**, or **5** in 2 mL of acetonitrile, benzonitrile, phenylacetylene, or styrene was heated for 4 h at 150°C in a sealed ampule. The ampule was cooled and opened, and the product was extracted with acetone and purified by flash chromatography on silica gel.

5,7-Dibromo-2-methyl-1,3-benzoxazole (15a). Yield 35%, mp 109°C (from acetone–petroleum ether). IR spectrum, ν, cm^{-1}: 3074 w, 2920 s, 1601 m, 1531 s, 1450 m, 1331 m, 1242 s, 1153 m, 887 m. ^1H NMR spectrum, δ, ppm: 2.91 s (3H, CH_3), 8.54 d (1H, 6-H, J = 2.5 Hz), 8.60 d (1H, 4-H, J = 2.5 Hz). Found, %: C 33.15; H 1.64; N 4.96. $C_8H_5Br_2NO$. Calculated, %: C 33.03; H 1.73; N 4.81.

4,6,7-Tribromo-2,5-dimethyl-1,3-benzoxazole (16a). Yield 28%, mp 173°C (from acetone–petroleum ether). IR spectrum, ν, cm^{-1}: 3080 w, 3029 w, 2980 w, 2955 w, 1664 s, 1385 m, 1235 m, 988 m. ^1H NMR spectrum, δ, ppm: 2.53 s (3H, CH_3), 2.81 s (3H, CH_3). Found, %: C 28.29; H 1.50; N 3.60. $C_9H_6Br_3NO$. Calculated, %: C 28.16; H 1.58; N 3.65.

4,5,6,7-Tetrabromo-2-methyl-1,3-benzoxazole (17a). Yield 26%, mp 185–187°C (from acetone–petroleum ether). IR spectrum, ν, cm^{-1}: 3110 v.w, 3045 v.w, 2935 w, 1653 s, 1593 m, 1423 m, 1205 m, 1011 m, 983 w. ^1H NMR spectrum: δ 2.71 ppm, s (3H, CH_3). Found, %: C 21.29; H 0.60; N 3.01. $C_8H_3Br_4NO$. Calculated, %: C 21.41; H 0.67; N 3.12.

5,7-Dibromo-2-phenyl-1,3-benzoxazole (15b). Yield 20%, mp 125°C (from acetone–hexane). IR spectrum, ν, cm^{-1}: 3098 m, 3062 w, 1670 s, 1610 m, 1490 m, 920 s, 730 s. ^1H NMR spectrum, δ, ppm: 7.44 d (1H, 6-H, J = 2.0 Hz), 7.48 d (1H, 4-H, J = 2.0 Hz), 7.61–7.95 m (5H, H_{arom}). Found, %: C 44.30; H 2.09; N 3.88. $C_{13}H_7Br_2NO$. Calculated, %: C 44.23; H 2.00; N 3.97.

4,6,7-Tribromo-5-methyl-2-phenyl-1,3-benzoxazole (16b). Yield 25%, mp 186°C (from acetone–hexane). IR spectrum, ν, cm^{-1}: 3067 v.w, 2940 w, 1667 s, 1590 m, 1489 m, 1274 s, 1055 s, 996 s. ^1H NMR spectrum, δ, ppm: 2.70 s (3H, CH_3), 7.46–7.55 m (3H, H_{arom}), 7.79–7.85 m (2H, H_{arom}). Found, %: C 37.79; H 1.74; N 3.21. $C_{14}H_8Br_3NO$. Calculated, %: C 37.71; H 1.81; N 3.14.

4,5,6,7-Tetrabromo-2-phenyl-1,3-benzoxazole (17b). Yield 23%, mp 210°C (from acetone–hexane); published data [24]: mp 219–220°C. IR spectrum, ν, cm^{-1}: 3067 v.w, 3035 v.w, 2920 w, 1655 s, 1483 m, 1240 m, 1035 m, 843 m. ^1H NMR spectrum, δ, ppm: 7.24–7.56 m (3H, H_{arom}), 7.91–8.04 m (2H, H_{arom}). ^{13}C NMR spectrum, δ_C, ppm: 119.4 (C_{arom}), 123.1 (C_{arom}), 124.5 (C_{arom}), 127.3 (2C, C_{arom}), 128.9 (C_{arom}), 129.3 (C_{arom}), 130.1 (2C, C_{arom}), 132.4 (C_{arom}), 143.8 (C_{arom}), 151.6 (C_{arom}), 165.1 (C^2). Found, %: C 30.65; H 0.91; N 2.87. $C_{13}H_5Br_4NO$. Calculated, %: C 30.57; H 0.99; N 2.74.

5,7-Dibromo-2-phenyl-1-benzofuran (18). Yield 23%, mp 109°C (from acetone–hexane). IR spectrum, ν, cm^{-1}: 3078 w, 3059 v.w, 2924 v.w, 1570 w, 1450 m, 1169 m, 841 m, 733 s. ^1H NMR spectrum, δ, ppm: 7.42–7.61 m (3H, H_{arom}), 7.52 s (1H, 3-H), 7.73 d (1H, 7-H, J = 1.77 Hz), 7.78 d (1H, 4-H, J = 1.77 Hz), 7.90–7.96 m (2H, H_{arom}). ^{13}C NMR spectrum, δ_C, ppm: 102.4 (C^3), 115.8 (C_{arom}), 123.2 (C_{arom}), 125.0 (2C, C_{arom}), 128.5 (C_{arom}), 128.9 (C_{arom}), 129.2 (C_{arom}), 129.8 (2C, C_{arom}), 131.8 (C_{arom}), 150.4 (C^2). Found, %: C 47.65; H 2.21. $C_{14}H_8Br_2O$. Calculated, %: C 47.77; H 2.29.

4,6,7-Tribromo-5-methyl-2-phenyl-1-benzofuran (19). Yield 26%, mp 172–173°C (from acetone–hexane). IR spectrum, ν, cm^{-1}: 3059 v.w, 3036 v.w, 2920 w, 1489 m, 1288 m, 1022 m, 837 m, 763 s. ^1H NMR spectrum, δ, ppm: 2.36 s (3H, CH_3), 6.96 s (1H, 3-H), 7.31–7.42 m (3H, H_{arom}), 7.73–7.85 m (2H, H_{arom}). ^{13}C NMR spectrum, δ_C, ppm: 21.7 (CH_3), 102.0 (C^3), 114.3 (C_{arom}), 125.0 (2C, C_{arom}), 128.9 (C_{arom}), 128.7 (C_{arom}), 128.8 (2C, C_{arom}), 129.1 (C_{arom}), 131.8 (C_{arom}), 133.3 (C_{arom}), 149.5 (C_{arom}), 156.9 (C^2). Found, %: C 40.40; H 2.10. $C_{15}H_9Br_3O$. Calculated, %: C 40.49; H 2.04.

4,5,6,7-Tetrabromo-2-phenyl-1-benzofuran (20). Yield 33%, mp 185°C (from acetone–hexane). IR spectrum, ν, cm^{-1}: 3109 v.w, 3055 v.w, 2959 v.w, 1489 w, 1373 m, 1280 w, 1161 w, 1022 w, 760 m. ^1H NMR spectrum, δ, ppm: 7.55–7.63 m (3H, H_{arom}), 7.92–8.05 m (3H, H_{arom}). Found, %: C 32.85; H 1.25. $C_{14}H_6Br_4O$. Calculated, %: C 32.98; H 1.19.

5,7-Dibromo-2-phenyl-2,3-dihydro-1-benzofuran (21). Yield 24%, mp 97°C (from acetone–hexane). IR spectrum, ν, cm^{-1}: 3063 m, 2932 m, 1446 v.s, 1365 m, 1230 s, 976 s, 914 s, 717 s. ^1H NMR spectrum, δ, ppm: 3.27 d.d (1H, 3-H, J = 7.8, 8.6 Hz), 3.79 d.d (1H, 3-H, J = 6.8, 8.6 Hz), 5.95 t (1H, 2-H, J = 8.3 Hz), 7.39 m (5H, H_{arom}), 7.42 br.s (1H, 4-H), 7.55 br.s (1H, 6-H). Found, %: C 47.63; H 2.79. $C_{14}H_{10}Br_2O$. Calculated, %: C 47.50; H 2.85.

4,6,7-Tribromo-5-methyl-2-phenyl-2,3-dihydro-1-benzofuran (22). Yield 25%, mp 168°C (from acetone–petroleum ether). IR spectrum, ν, cm^{-1}: 3036 v.w, 2920 w, 1593 m, 1415 s, 1365 s, 1176 m, 968 s, 760 v.s, 702 s. ^1H NMR spectrum, δ, ppm: 2.60 s (3H, CH_3), 3.28 d.d (1H, 3-H, J = 7.7, 8.8 Hz), 3.74 d.d (1H, 3-H, J = 6.8, 8.8 Hz), 5.90 t (1H, 2-H, J = 7.6 Hz), 7.36–7.40 m (5H, H_{arom}). ^{13}C NMR spectrum, δ_C, ppm: 24.7 (CH_3), 41.9 (C^3), 84.1 (C^2), 120.1 (C_{arom}), 125.6 (C_{arom}), 126.0 (C_{arom}), 127.9 (2C, C_{arom}), 128.3 (C_{arom}), 128.4 (C_{arom}), 128.8 (2C, C_{arom}), 131.0 (C_{arom}), 134.4 (C_{arom}), 140.6 (C_{arom}), 155.8 (C_{arom}). Found, %: C 40.22; H 2.51. $C_{15}H_{11}Br_3O$. Calculated, %: C 40.31; H 2.48.

4,5,6,7-Tetrabromo-2-phenyl-2,3-dihydro-1-benzofuran (23). Yield 30%, mp 183°C (from acetone–

hexane). IR spectrum, ν, cm^{-1}: 3059 v.w, 3020 v.w, 2909 w, 1404 s, 1265 m, 1157 m, 937 m, 763 s, 703 s. ^1H NMR spectrum, δ, ppm: 3.20 d.d (1H, 3-H, J = 7.6, 8.8 Hz), 3.83 d.d (1H, 3-H, J = 6.9, 8.8 Hz), 5.86 t (1H, 2-H, J = 8.2 Hz), 7.55 m (5H). Found, %: C 32.93; H 1.64. $C_{14}H_8Br_4O$. Calculated, %: C 32.85; H 1.58.

Reaction of polybrominated quinone diazides 1–5 with acetylacetone (*general procedure*). A mixture of 3.5 mmol of quinone diazide **1–5** and 17 equiv of acetylacetone was heated for 2 h at 90–95°C and was then refluxed for 2 h until nitrogen no longer evolved. Excess acetylacetone was distilled off under reduced pressure (water-jet pump), and the residue was purified by flash chromatography on silica gel.

3-(3,5-Dibromo-2-hydroxyphenyl)-4-hydroxypent-3-en-2-one (24). Yield 55%, mp 176°C. IR spectrum, ν, cm^{-1}: 3222 br.w, 3086 w, 2924 w, 1655 v.s, 1516 v.s, 1365 m, 1300 s, 1138 m, 937 m. ^1H NMR spectrum, δ, ppm: 1.57 s (3H, CH_3), 1.64 s (3H, CH_3), 6.68 d (1H, H_{arom}, J = 2.3 Hz), 6.85 d (1H, H_{arom}, J = 2.3 Hz), 9.67 s (1H, OH), 13.42 s (1H, OH, enol). ^{13}C NMR spectrum, δ_C, ppm: 26.6 (CH_3), 31.4 (CH_3); 112.9, 113.1, 116.4, 129.8, 133.9, 142.5 (C_{arom}, C^3); 196.5, 197.2 (C^2, C^4). Mass spectrum: m/z 348.9083 $[M + H]^+$. $C_{11}H_{11}Br_2O_3$. Calculated: M + H 348.9070.

3-(3,4,6-Tribromo-2-hydroxy-5-methylphenyl)-4-hydroxypent-3-en-2-one (25). Yield 30%, mp 156–157°C. IR spectrum, ν, cm^{-1}: 3456 br.m, 2429 m, 1678 v.s, 1624 s, 1512 s, 1354 s, 1180 s, 929 m, 810 m. ^1H NMR spectrum, δ, ppm: 2.45 s (3H, CH_3), 2.66 s (6H, CH_3), 11.41 s (1H, OH), 14.7 s (1H, OH, enol). ^{13}C NMR spectrum, δ_C, ppm: 25.6 (CH_3), 27.0 (CH_3), 32.0 (CH_3); 113.3, 115.2, 123.7, 124.5, 130.74, 131.7, 145.6 (C_{arom}, C^3); 194.2, 198.3 (C^2, C^4). Found, %: C 32.45; H 2.34. $C_{12}H_{11}Br_3O_3$. Calculated, %: C 32.54; H 2.50.

3-(3,4,5,6-Tetrabromo-2-hydroxyphenyl)-4-hydroxypent-3-en-2-one (26). Yield 25%, mp 160–161°C. IR spectrum, ν, cm^{-1}: 3406 br.m, 2970 v.w, 2916 v.w, 2854 v.w, 1670 s, 1508 v.s, 1358 m, 1176 m, 929 w. ^1H NMR spectrum, δ, ppm: 2.55 s (3H, CH_3), 2.61 s (3H, CH_3), 11.01 s (1H, OH), 14.10 s (1H, OH, enol). ^{13}C NMR spectrum, δ_C, ppm: 27.1 (CH_3), 31.6 (CH_3); 114.7, 115.7, 124.4, 127.5, 127.7, 141.9, 148.0 (C_{arom}, C^3); 195.8, 197.8 (C^2, C^4). Found, %: C 26.10; H 1.55. $C_{11}H_8Br_4O_3$. Calculated, %: C 26.02; H 1.59.

3-(3,5-Dibromo-4-hydroxyphenyl)pentane-2,4-dione (27). Yield 45%, mp 109°C. IR spectrum, ν, cm^{-1}: 3321 m, 3059 w, 2924 w, 1589 s, 1481 v.s, 1300 s, 1149 s, 922 w, 879 w, 744 s. ^1H NMR spectrum ($CDCl_3$ or DMSO-d_6, 25°C; a mixture of diketone and enol tautomers at a ratio of 1:5), δ, ppm: diketone tautomer: 2.16 s (6H, CH_3), 5.34 s (1H, CH), 7.36 s (2H, H_{arom}); enol tautomer: 1.86 s (6H, CH_3), 7.48 s (2H, H_{arom}), 10.01 s (1H, OH), 13.82 s (1H, OH, enol). ^{13}C NMR spectrum, δ_C, ppm: 23.9, 26.4, 30.1 (CH_3); 111.8, 112.6, 120.1, 122.5, 127.1, 130.6, 133.1, 134.8, 150.0, 150.3, 190.1, 196.1, 202.8. Found, %: C 37.69; H 2.92. $C_{11}H_{10}Br_2O_3$. Calculated, %: C 37.75; H 2.88.

3-(2,3,5,6-Tetrabromo-4-hydroxyphenyl)pentane-2,4-dione (28). Yield 26%, mp 167–168°C. IR spectrum, ν, cm^{-1}: 3356 br.w, 2920 v.w, 1597 s, 1543 v.s, 1331 v.s, 1257 s, 1157 v.s, 918 m. ^1H NMR spectrum, δ, ppm: 1.81 s (6H, CH_3), 6.49 s (1H, CH); OH signal was not observed. ^{13}C NMR spectrum, δ_C, ppm: 23.3 (2C, CH_3), 113.1, 118.1, 129.4, 132.7, 151.4 (C_{arom}, C^3); 190.6 (C^2, C^4). Mass spectrum: m/z 504.7276 $[M + H]^+$. $C_{11}H_9Br_4O_3$. M + H 504.7280.

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