Intermolecular Bromine Transfer of 2-Amino-7-bromotropone Derivatives Catalyzed by Strong Acid[1)]

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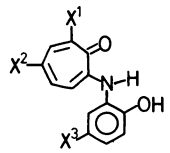
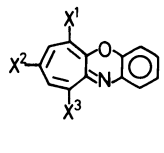
Upon heating acetic acid containg a trace amount of concd sulfuric acid at 120 °C under nitrogen, 2-bromo-7-(2-hydroxyanilino)tropone (**1a**) gave 6-bromocyclohepta[*b*][1,4]benzoxazine (**2a**) as the main product and cyclohepta[*b*][1,4]benzoxazine, its 6,8-dibromo derivative and trace amounts of other mono-, di-, and tribromo compounds. This reaction became much more complex in the presence of oxygen. A similar bromine transfer was observed for 2-bromo-7-(dimethylamino)-, 7-(2-hydroxy-5-methylanilino)-, and 7-(2-methoxyanilino)tropone although the cite of the intermolecular bromine transfer depended upon the structures of the substrates and the reaction conditions. In contrast, **2a** and 2-amino-5-bromotropone derivatives were completely stable towards the strong acid. Possible reaction pathways for this bromine transfer reaction are discussed.

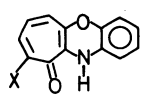
We previously reported that 2-bromo-7-(2-hydroxyanilino)tropone (**1a**) afforded an almost quantitative yield of 6-bromocyclohepta[*b*][1,4]benzoxazine (**2a**) upon heating at 120 °C in acetic acid containing a trace amount of concd sulfuric acid.[2)] However, upon repeating the preparation of **2a** and carefully separating the reaction products by chromatography, we isolated unexpected and interesting by-products. The structures of these compounds are reported in this paper together with a mechanistic study regarding the unique bromine transfer involved in the formation of these compounds. This can be regarded as another example of our frequent observation[3)] that a subtle change of reaction conditions causes a considerable alteration of product ratios.



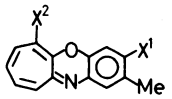
1	X^1	X^2	X^3
a	Br	H	H
b	H	H	H
c	Br	Br	H
d	H	Br	H
e	Br	H	Me
f	H	H	Me
g	Br	Br	Me



2	X^1	X^2	X^3
a	Br	H	H
b	H	H	H
c	Br	Br	H
d	H	Br	H
e	Br	H	Br
f	Br	Br	Br
g	Cl	H	H



3a : X=H
3b : X=Br

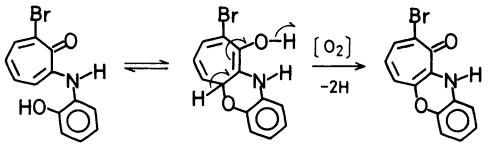


4a : X^1=H, X^2=Br
4b : X^1=X^2=H
4c : X^1=X^2= Br

Results and Discussion

When **1a** was heated at 120 °C for 2 h in acetic acid containing a trace amount of concd sulfuric acid, a detailed observation using HPLC showed that the reaction mixture contained, besides the main product **2a**, a large number of simultaneously formed by-products. The separation of these reaction products using silica-gel centrifugal chromatography afforded **2a**[2)] (55% yield), the parent cyclohepta[*b*][1,4]benzoxazine[2)] (**2b**, brown needles, 4% yield), the 6,8-dibromo derivative (**2c**, brown needles, 10% yield), cyclohepta[*b*][1,4]benzoxazin-10(11*H*)-one[4)] (**3a**, red needles, 3% yield), and its 9-bromo derivative (**3b**, red needles, 11% yield) as well as unreacted starting material (**1a**, 14% yield) and small proportions of 8-bromo (**2d**), 6,10-dibromo (**2e**), and 6,8,10-tribromo compound (**2f**). Furthermore, it was confirmed that 2-aminotropone derivatives **1b** and **1c** were also present in small quantities. Structures of these products were established either on the basis of their spectral data (see Experimental section) or by separate syntheses.

When conducted under nitrogen, the above reaction yielded **2a** (71%), **2b** (7.4%), and **2c** (6.8%) along with trace amounts of **2d—f**, but no oxo derivatives, **3a** and **3b**. As compound **3a** was produced from **2b** upon exposure to air for a long period or upon airation at 120 °C in acetic acid, **3a** was apparently a secondary, autoxidation product of **2b**. On the other hand, compound **3b** was formed from **1a** by oxygenation at 120 °C in acetic acid, suggesting that **3b** was most likely produced by the autoxidation of the cyclic tautomer, as shown in Scheme 1.



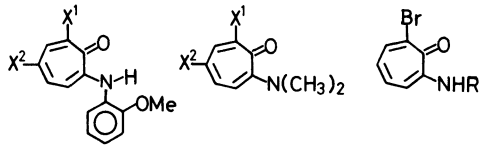
1a 3b

Scheme 1.

A similar acidic treatment of 2-bromo-7-(2-hydroxy-5-methylanilino)tropone (**1e**) under nitrogen resulted in a ring-closure to give **4a**[5)] (66% yield), the bromine-free compound (**4b**, 6.4% yield), and the 3,6-dibromo-2-methyl derivative (**4c**, 6.4% yield). The structures were based on their spectral data; the ABCX signal pattern

of the four protons on the seven-membered ring of **4c** in the ^{1}H NMR closely resembles those of **2a**. Thus, the cite of the second bromine atom on the benzene ring [at C-3 based on the small J value (<1 Hz) between the remaining two ring-proton signals] was established. It was confirmed that the 6-bromocyclohepta[*b*][1,4]benzoxazines **2a** and **4a** were completely stable under these conditions.

These results suggested that a bromine migration reaction under strongly acidic conditions had taken place at the stage of the anilinotropones (**1a**, **1e**) prior to the ring-closure. Indeed, when the methyl ether (**5a**)[2] that was prevented from cyclizing to the benzoxazine was subjected under the same conditions, 2-(2-methoxyanilino)tropone (**5b**)[6] and its dibromo derivative (**5c**) were obtained.



5	X^1	X^2
a	Br	H
b	H	H
c	Br	Br
d	H	Br

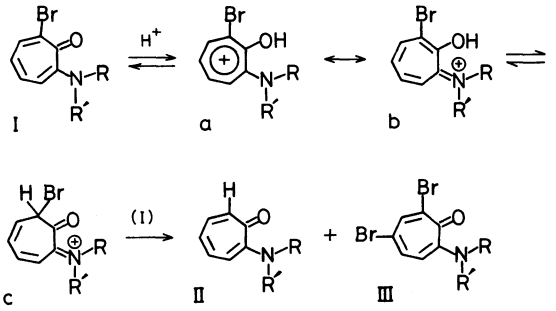
6	X^1	X^2
a	Br	H
b	H	H
c	Br	Br
d	H	Br

7a: R=H
7b: R=Me

Then, in order to examine the role of the arylamino group in this bromine-transfer reaction, 2-bromo-7-(dimethylamino)tropone (**6a**) was similarly treated with concd sulfuric acid-acetic acid at 120°C. The reaction was followed by time-dependent HPLC, which clearly showed the simultaneous formation of three main products. A spectroscopic analysis, as well as a comparison with the authentic specimens prepared separately, clarified the structures of these compounds to be bromine-free 2-(dimethylamino)tropone (**6b**),[7] its 5,7-dibromo (**6c**), and 5-bromo derivative (**6d**). Treatment of 2-amino- and 2-(methylamino)-7-bromotropone (**7a,b**)[8] with the same mixed acid afforded a similar type of products derived by the apparent disproportionation reaction.

The use of perchloric acid or phosphoric acid (instead of concd sulfuric acid) in acetic acid for the ring-closure of **1a** also caused a bromine transfer, but yields of products **2b** and **2c** became considerably lower. The use of concd hydrochloric acid afforded 6-chloro compound (**2g**) besides **2a—c**; **2g** was confirmed to be produced from the 6-bromo compound (**2a**) (but not from the ring-opened precursor **1a**) by the halogen-exchange reaction. It should be noted that, when **1a** was heated at 120°C under nitrogen in acetic acid containing concd hydrobromic acid, 8-bromocyclohepta[*b*][1,4]benzoxazine (**2d**) became the main product (47% yield) instead of **2a** (3% yield) or **2b,c** (8% yield each).

The fact that the described acid-catalyzed bromine migration takes place only when the bromine atom is situated at C-7** of the 2-aminotropone form (**I**), suggests the following probable reaction pathways (Scheme 2).



Scheme 2.

The 2-(arylamino)- and 2-(dimethylamino)-7-bromotropone (**1a** and **6a**) give their protonated tropylium species (**a**). It was stabilized as an iminium form (**b**) and existed in equilibrium with the tautomeric keto form (**c**). The latter presumably reacts as an electrophilic reagent towards the unprotonated substrate (**I**), resulting in a transfer of the bromine atom to give 2-aminotropones (**II**) and the 5,7-dibromo derivatives **III** in a manner analogous to a disproportionation reaction. The reactive intermediate **c** is most likely to undergo electrophilic bromination at a position having the highest nucleophilicity in the molecule **I**.[9] This gives rise to a dibromo product in which, in some cases, the second bromine atom is on the benzene ring (*e.g.*, **4c**). The formation of a larger proportion of the 8-bromo compound **2d** from **1a** upon heating in HBr-AcOH could be explained by the transformation of the intermediate **c** (Scheme 2) to **II**, assisted by the bromide anion. This liberated a certain quantity of bromine atoms. Subsequently, this resulted in bromination at the 5-position of 2-aminotropones (**II**), followed by an acid-catalyzed ring-closure to afford **2d**. This pathway is supported by the fact that **1b** gave only **2b** under the same conditions.

Although the exact mechanisms of this unusual substitution and the ring-closure involving an interesting intermolecular bromine shift are currently under a detailed investigation, the present experimental results clearly demonstrate a further example of the diversity of chemical reactions and the intricate character of troponoid compounds.

Experimental

Melting points are uncorrected. The IR and electronic spectra were taken on a Shimadzu IR-450 and a Shimadzu UV-202 spectrometer, respectively. The UV spectra in acid and alkali were taken after adding a few drops of 3 M HCl or 3 M NaOH (1 M=1 mol dm^{-3}) to a sample solution. The

**2-Amino-5-bromotropones are stable under these acidic condition.

NMR spectra were measured in $CDCl_3$ (unless otherwise specified) on a JEOL JNM-PS/PFT (100 MHz) and a JEOL JNM-GX270 (270 MHz) spectrometer using TMS as an internal standard. The mass spectra were taken on a JEOL JMS-DX300 mass spectrometer and a Shimadzu LKB 9000 GC-mass spectrometer at 75 eV. The HPLC was carried out with Hitachi gel #3011 with MeOH–hexane (9:1) as a solvent. The centrifugal chromatography was performed with a Hitachi CLC-5 instrument in a Fuji silica-gel layer (KT-2151, 5-mm thick) using benzene as an eluant.

*Reaction of 2-Bromo-7-(2-hydroxyanilino)tropone (**1a**).*

A. Under Aerobic Conditions: A trace amount of concd sulfuric acid was added to a solution of **1a** (700 mg) in acetic acid (8 ml). The mixture was heated at 120 °C for 2 h and evaporated *in vacuo*. The residue was neutralized with aqueous $NaHCO_3$ and extracted with benzene. The combined extracts were washed with water, dried (Na_2SO_4), and concentrated *in vacuo*. The residual solid was chromatographed centrifugally in a layer of silica gel with benzene as the eluant, giving **2a**[2] (360 mg, 55% yield), **2b**[2] (20 mg, 4% yield), **2c** (see below, 85 mg, 10% yield), **3a**[4] (15 mg, 3%), **3b** (see below, 75 mg, 11%), **2d** (see below, 5 mg, 0.8%), **2e** (see below, <1%), and **2f** (see below, <1%). The starting material **1a** (≃100 mg, 14%) containing a small proportion of **1b**,[2] and **1c** (see below) were recovered by eluating the silica-gel layer with MeOH.

B. Under Nitrogen. A solution of **1a** (393 mg) in acetic acid (4 ml) containing a trace amount of concd sulfuric acid was heated under nitrogen at 120 °C for 2 h, followed by the same work-up procedures as above, giving **2a** (262 mg, 71%), **2b** (19.5 mg, 7.4%), **2c** (32.5 mg, 6.8%), and **2d—f** (6 mg, <2%), along with **1a** containing **1b** and **1c** (50 mg, 13%).

*2,4-Dibromo-7-(2-hydroxyanilino)tropone (**1c**).* A mixture of 2,4-dibromo-7-methoxytropone[10] (500 mg, 1.70 mmol) and *o*-aminophenol (287 mg, 2.63 mmol) in 1-butanol was heated at 120 °C for 2 h. After cooling, the precipitates were filtered off and recrystallized from methanol to give 565 mg (90%) of **1c** [2,4-dibromo-7-methoxytropone (30 mg, 6%) was recovered from the filtrate]: yellow needles; mp 198—199 °C; UV λ_{max} (MeOH) 264 (log ε, 4.20), 359 (3.89), and 438 nm (4.00); IR (KBr) 3400 (OH), 3350 (NH), and 1588 cm^{-1} (C=O); ^1H NMR (100 MHz) δ=8.65 (1H, bs, NH), 8.42 (1H, d, $J_{3,5}$=2.0 Hz, H-3), 7.50 (1H, dd, $J_{5,6}$=11.2 Hz, H-5), 7.0—7.2 (4 H, m, H-3′, 4′, 5′, 6′), and 6.59 (1H, d, H-6).

Found: C, 42.10; H, 2.49; N, 3.78%; M^+, 373. Calcd for $C_{13}H_9NO_2Br_2$: C, 42.08; H, 2.48; N, 3.78%; M, 373.

*6,8-Dibromocyclohepta[b][1,4]benzoxazine (**2c**).* A solution of **1c** (161 mg) in acetic acid (5 ml) containing a trace amount of concd sulfuric acid was heated at 120 °C for 1.5 h under nitrogen, followed by the same procedures as those described for **1a**. The residual solid was recrystallized from benzene to give 132 mg (86%) of **2c**: brown needles; mp 165—166 °C; UV λ_{max}(MeOH) 262 (log ε, 4.47), 306 (3.66), and 415 nm (3.86); IR (KBr) 3080 (CH) and 1637 cm^{-1} (C=N); ^1H NMR (270 MHz) δ=6.8—6.9 (3H, m, H-1, 2, 3), 6.79 (1H, d, $J_{7,9}$=2.2 Hz, H-7), 6.60 (1H, m, H-4), 6.19 (1H, dd, $J_{9,10}$=12.9 Hz, H-9), and 5.89 (1H, d, H-10), ($CDCl_3$+CF_3COOD) δ=8.00 (1H, d, $J_{7,9}$=2.2 Hz, H-7), 7.44 (1H, dd, $J_{9,10}$=11.9 Hz, H-9), 7.05 (1H, td, J=8.0 and 1.5 Hz, H-2 or 3), 6.96 (1H, td, J=8.0 and 1.5 Hz, H-3 or 2), 6.70—6.85 (2H, m, H-1, 4), and 6.75 (1H, d, H-10).

Found: C, 44.43; H, 2.13; N, 3.77%; M^+, 355. Calcd for $C_{13}H_7NOBr_2$: C, 44.23; H, 2.00; N, 3.97%; M, 355.

*9-Bromocyclohepta[b][1,4]benzoxazin-10(11H)-one (**3b**)*: Red needles (from benzene); mp 223—224 °C; UV λ_{max} (MeOH) 240 (log ε, 4.22), 270 (4.08), 294 (4.04), 330 (3.80), and 500 nm (3.79); IR (KBr) 3300 (NH) and 1574 cm^{-1} (C=O); ^1H NMR (270 MHz) δ=7.79 (1H, dd, $J_{6,8}$=1.0 and $J_{7,8}$=9.5 Hz, H-8), 6.79 (1H, dd, $J_{6,7}$=11.1 Hz, H-6), 6.5—6.8 (4H, m, H-1, 2, 3, 4), and 6.42 (1H, dd, H-7).

Found: C, 53.55; H, 2.83; N, 4.91%; M^+, 291. Calcd for $C_{13}H_8NO_2Br$: C, 53.82; H, 2.78; N, 4.83%; M, 291.

*8-Bromocyclohepta[b][1,4]benzoxazine (**2d**)*: Red brown needles (from benzene); mp 163—164 °C; UV λ_{max} (MeOH) 262 (log ε, 4.43), 271 (4.35), 298 (3.93), and 414 (4.12), (MeOH+3 M HCl) 265 (log ε, 4.43), 273 (4.35), 325 (3.95), and 447 nm (4.06); IR (KBr) 1580 cm^{-1} (C=N); ^1H NMR (270 MHz) δ=6.7—6.8 (3H, m, H-1, 2, 3), 6.38 (1H, m, H-4), 6.24 (1H, dd, $J_{7,9}$=2.0 and $J_{6,7}$=10.2 Hz, H-7), 6.21 (1H, dd, $J_{9,10}$=13.2 Hz, H-9), 5.84 (1H, d, H-10), and 5.12 (1H, d, H-6).

Found: C, 56.92; H, 3.22; N, 5.13%; M^+, 275. Calcd for $C_{13}H_8NOBr$: C, 56.96; H, 2.94; N, 5.11%; M, 275.

*6,10-Dibromocyclohepta[b][1,4]benzoxazine (**2e**)*: Red brown solid; UV λ_{max} (MeOH) 261, 270, 313, and 414 nm, (MeOH+3 M HCl) 268, 273, 325, 448, and 480 nm; M^+, 355.

*6,8,10-Tribromocyclohepta[b][1,4]benzoxazine (**2f**)*: Red brown solid; UV λ_{max} (MeOH) 238, 263, 271, 400, 416, and 445 nm, (MeOH+3 M HCl) 258, 309, and 393 nm; M^+, 435.

*Reaction of 2-Bromo-7-(2-hydroxy-4-methylanilino)tropone (**1e**).* A similar treatment (to that for **1a**) of **1e** (500 mg) with acetic acid (10 ml) containing a trace amount of concd sulfuric acid at 120 °C for 1.5 h under nitrogen gave **4a**[5] (310 mg, 66%), **4b** (see below, 22 mg, 6.4%), and **4c** (see below, 38 mg, 6.4%), besides the recovered **1e** (100 mg, 20%) containing **1f** and **1g** (<2% each).

*2-Methylcyclohepta[b][1,4]benzoxazine (**4b**).* A mixture of 2-chlorotropone (370 mg, 2.63 mmol) and 2-amino-4-methylphenol (486 mg, 3.95 mmol) in acetic acid (5 ml) was heated at 120 °C for 3 h, followed by the same work-up procedures as for **1a**. This gave 280 mg (51%) of **4b**: red brown needles (from benzene); mp 86—87 °C; UV λ_{max} (MeOH) 256 (log ε, 4.28), 264 (4.35), 273 (4.31), 305 (3.73), and 415 nm (4.01), (MeOH+3 M HCl) 226 (log ε, 4.38), 268 (4.38), 275 (4.40), 326 (3.88), and 440 (3.98); IR (KBr) 2930 (CH) and 1600 cm^{-1} (C=N); ^1H NMR (270 MHz) δ=6.61 (1 H, d, $J_{1,3}$=2 Hz, H-1), 6.55 (1H, dd, $J_{3,4}$=8 Hz, H-3), 6.28 (1H, d, H-4), 6.16 (2H, m, H-9, 10), 5.99 (1H, ddd, $J_{7,8}$=10.7, $J_{6,7}$=9.4, and $J_{7,9}$=1.5 Hz, H-7), 5.79 (1H, td, $J_{8,10}$=3.9 and $J_{8,9}$=10.7 Hz, H-8), 5.46 (1H, d, H-6), and 2.12 (3H, s, CH_3).

Found: M^+, 209.0813. Calcd for $C_{14}H_{11}NO$: M, 209.0840.

*3,6-Dibromo-2-methylcyclohepta[b][1,4]benzoxazine (**4c**)*: Red brown needles (from benzene); mp 121—122 °C; UV λ_{max} (MeOH) 232 (log ε, 4.20), 268 (4.28), 275 (4.25), 305 (3.83), and 415 nm (3.94), (MeOH+3 M HCl) 235 (log ε, 4.18), 275 (4.25), 281 (4.26), 325 (3.84), and 450 nm (3.83); IR (KBr) 1631 cm^{-1} (C=N); ^1H NMR (100 MHz) δ=6.80 (1H, s, H-4), 6.72 (1H, s, H-1), 6.39 (1H, td, $J_{7,9}$=0.5 and $J_{7,8}$=11.7 Hz, H-7), 6.05 (2H, m, H-9, 10), 5.58 (1H, $J_{8,9}$=4.4 Hz, H-8), and 2.20 (3H, s, CH_3).

Found: M^+, 364.9059, 366.9056, and 368.9024 (1:2:1). Calcd for $C_{14}H_9NOBr_2$: M, 364.9051, 366.9032, and 368.9012.

*2,4-Dibromo-7-(2-methoxyanilino)tropone (**5c**).* A suspension of **1c** (80 mg) in ether was treated with an excess of ethereal diazomethane. After allowing it to stand for 1 d, the solvent was evaporated *in vacuo* and the residual solid was chromatographed in a short column of alumina with ether as an eluant, giving 80 mg (96%) of **5c**: yellow needless (from

methanol); mp 165—166°C; UV λ_{max} (MeOH) 264 (log ε, 4.18), 359 (3.95), and 438 nm (4.17); IR (KBr) 3250 (NH) and 1584 cm^{-1} (C=O); ^1H NMR (100 MHz, CD_3OD) δ=8.51 (1H, d, $J_{3,5}$=2.0 Hz, H-3), 7.57 (1H, dd, $J_{5,6}$=11.2 Hz, H-5), 7.1—7.4 (4H, m, H-3′, 4′, 5′, 6′), 6.91 (1H, d, H-6), and 3.88 (3H, s, CH_3).

Found: C, 43.70; H, 2.80; N, 3.64%; M^+, 387. Calcd for $C_{14}H_{11}NO_2Br_2$: C, 43.67; H, 2.88; N, 3.64%; M, 387.

*2-Bromo-7-(dimethylamino)tropone (**6a**).* A solution of 2-bromo-7-methoxytropone[11] (230 mg) and an excess of 40% aqueous dimethylamine in ethanol (5 ml) was heated at 70°C for 4 h. The solvent was evaporated *in vacuo* and the crude product was chromatographed in a column of silica gel with benzene–methanol (50:1) and recrystallized from methanol, giving 196 mg (80%) of **6a**, besides the recovered staring material (30 mg, 13%): yellow needles (from methanol); mp 93—94°C; UV λ_{max} (MeOH) 264 (log ε, 4.31), 358 (4.14), and 437 nm (4.05), (MeOH+3 M HCl) 255 (log ε, 4.27), 273 (4.10), 324 (3.80), 356 (4.01), and 437 nm (3.81); IR (KBr) 1580 cm^{-1} (C=O); ^1H NMR (270 MHz) δ= 7.93 (1H, d, $J_{3,4}$=9.5 Hz, H-3), 7.07 (1H, dd, $J_{5,6}$=10.2 and $J_{4,5}$=10.5 Hz, H-5), 6.52 (1H, d, H-6), 6.33 (1H, dd, H-4), and 3.14 (6H, s, $2CH_3$).

*2,4-Dibromo-7-(dimethylamino)tropone (**6c**).* Procedures similar to those for **6a** were followed. 2,4-Dibromo-7-methoxytropone (50 mg) afforded 35 mg (67%) of **6c** after purification by HPLC and recrystallization from methanol (10 mg of the starting material was recovered): yellow needles (from methanol); mp 96—97°C; UV λ_{max} (MeOH) 270 (log ε, 4.22), 356 (4.04), 369 (4.14), 443 (3.87), and 461 (3.86); IR (KBr) 1580 cm^{-1} (C=O); ^1H NMR (270 MHz) δ=8.16 (1 H, d, $J_{3,5}$=2.2 Hz, H-3), 7.33 (1H, dd, $J_{5,6}$=11.7 Hz, H-5), 6.24 (1H, d, H-6), and 3.13 (6H, s, $2CH_3$).

*5-Bromo-2-(dimethylamino)tropone (**6d**).* 5-Bromo-2-methoxytropone[8] (270 mg) was similarly treated with an excess of 40% dimethylamine, giving 270 mg (94%) of **6d** after purification by chromatography in a column of silica gel with 50:1 benzene–MeOH: yellow oil; UV λ_{max} (MeOH) 257 (log ε, 4.23), 361 (4.18), and 430 nm (3.88), (MeOH+3 M HCl) 252 (log ε, 4.24), 364 (3.93), and 388 nm (3.92); IR (neat) 1590 cm^{-1} (C=O); ^1H NMR (270 MHz) δ=7.30 (1H, dd, $J_{3,4}$=11.2 and $J_{4,6}$=2.2 Hz, H-4), 7.26 (1H, dd, $J_{6,7}$=12.7 Hz, H-6), 6.70 (1H, d, H-7), 6.21 (1 H, d, H-3), and 3.09 (6 H, s, $2CH_3$).

*2-Bromo-7-(methylamino)tropone (**7b**).* A mixture of 7-bromo-2-methoxytropone (144 mg, 0.67 mmol), methylamine hydrochloride (184 mg, 2.72 mmol), and sodium hydride (48 mg, 2.0 mmol) in ethanol (3 ml) was heated at 80°C for 20 h. After cooling, the precipitates were filtered off and recrystallized from ethanol (removing NaCl by filtration), giving 133 mg (93%) of **7b**: yellow plates; mp 169—170°C; UV λ_{max} (MeOH) 250 (log ε, 4.27), 258 (4.36), 277 (3.81), 332 (3.95), 342 (4.06), 398 (3.89), and 420 nm (4.12); IR (KBr) 3280 (NH) and 1585 cm^{-1} (C=O); ^1H NMR (270 MHz) δ=8.14 (1H, dd, $J_{3,4}$=10.1 and $J_{3,5}$=1.0 Hz, H-3), 7.64 (1H, bs, NH), 7.33 (1H, td, $J_{4,5}$=$J_{5,6}$=10.1 Hz, H-5), 6.58 (1H, dd, $J_{4,6}$=1.0 Hz, H-6), 6.52 (1H, td, H-4), and 3.09 (3H, s, CH_3).

*Reaction of 2-Bromo-7-(2-hydroxyanilino)tropone (**1a**) Catalyzed by concd Hydrochloric Acid.* A similar treatment of **1a** (100 mg, 0.34 mmol) with acetic acid (5 ml) containing a trace amount of concd hydrochloric acid at 120°C for 4 h under nitrogen gave **2g** (see below, 20 mg, 25%), **2a** (27 mg, 29%), **2b** (4 mg, 6%), and **2c** (6 mg, 5%), besides the recovered **1a** (30 mg, 30%).

*6-Chlorocyclohepta[b][1,4]benzoxazine (**2g**)*: Brown needles (from benzene); mp 96—97°C; UV λ_{max} (MeOH) 224 (log ε, 4.21), 260 (4.29), 267 (4.26), 296 (3.77), and 413 nm (3.98), (MeOH+3 M HCl) 228 (log ε, 4.25), 264 (4.23), 270 (4.23), 324 (3.83), 425 (3.87), and 458 nm (3.81); IR (KBr) 1625 cm^{-1} (C=N); ^1H NMR (270 MHz) δ=6.87 (1H, m, $J_{2,3}$=$J_{3,4}$=7.8 and $J_{1,3}$=1.5 Hz, H-3), 6.86 (1H, m, $J_{1,2}$=7.8 Hz, H-1), 6.82 (1H, m, H-2), 6.59 (1H, dd, H-4), 6.18 (1H, d, $J_{7,8}$=11.8 Hz, H-7), 6.14 (1 H, d, $J_{9,10}$=12.8 Hz, H-10), 6.08 (1H, dd, $J_{8,9}$=7.5 Hz, H-9), and 5.69 (1 H, dd, H-8).

Found: M^+, 229.0301 and 231.0150 (3:1). Calcd for $C_{13}H_8NOCl$: M, 229.0294 and 231.0264.

*Reaction of 2-Bromo-7-(2-hydroxyanilino)tropone (**1a**) Catalyzed by Concd Hydrobromic Acid.* A similar treatment of **1a** (500 mg, 1.71 mmol) with acetic acid (10 ml) containing a trace amount of concd hydrobromic acid at 120°C for 4 h under nitrogen gave **2d** (220 mg, 47%), **2a** (15 mg, 3%), **2b** (28 mg, 8%), and **2c** (50 mg, 8%), besides the recovered **1a** (80 mg, 16%).

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