Heteroatom Chemistry
Volume 25, Number 6, 2014

# Regioselective Nucleophilic Substitution of 5-Bromo-2-methoxytropone

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*Received 31 March 2014; revised 28 May 2014*

ABSTRACT: *The reaction of 5-bromo-2-methoxytropone with O- and N-nucleophiles, such as ethanol/potassium carbonate, sodium hydroxide, diethylamine, propylamine, p-chloroaniline/triethylamine, and p-phenylenediamine/triethylamine, gave corresponding 2-O- and 2-N-substituted troponoids. Alkyl diamines reacted with the substrate to produce bis(2-aminotropone)s. In the case of S-nucleophiles as 1-propanethiol, thiophenol, and 4-aminothiophenol with a base, the regioselective substitution at the 5-position occurred. Halogenation reagents, triphenyldibromophosphorane and its dichloro analogue, furnished 2,5-dibromo- and 2,5-dichlorotropones, respectively.* © 2014 Wiley Periodicals, Inc. Heteroatom Chem. 25:644–650, 2014; View this article online at wileyonlinelibrary.com. DOI 10.1002/hc.21201

## *INTRODUCTION*

Tropolone (**1a**) and its analogous troponoids have unique properties as formation of tropylium cations with acids and complexes with various metal ions [1]. Functional troponoids with their characteristics are the interesting class of compounds; however, their construction has not been much investigated. Liquid crystals [2], catalysts for polymerization [3], and light-emitting materials [4] having troponoid system were reported. For further development of this category, a wide variety of polysubstituted troponoids should be presented. It is known that 2-substituted troponoids could be prepared by the reaction of activated tropones (**1b-e**, Fig. 1) and their alkyl/aryl substituted analogues, which have a leaving group at their 2-position, with reagents having a nucleophilic oxygen atom or a nitrogen atom (*O*- or *N*-nucleophiles) [5]. However, substitution of activated troponoids with plural leaving groups has been rarely studied. As part of construction of polysubstituted troponoids, especially disubstituted ones, we focused on 5-bromo-2-methoxytropone (**2**) as shown in Fig. 1. Compound (**2**) has two different kinds of leaving groups, and its reactivity toward various nucleophiles is of interest. A few reaction of **2** with dimethyl- and diethylamines [6] and aryl cross-coupling one with palladium catalysts [7] were reported, whereas there is no systematic and comprehensive investigation. We report herein the reaction of **2** with some kinds of nucleophiles, resulting in the regioselective substitution on the basis of the nucleophilic atoms in the reagents.

## *RESULTS AND DISCUSSION*

It is known that activated troponoids (**1c**) and (**1e**) reacted with thiourea to generate 2-*S*-substituted compounds (**3**) as HX salts (X = OTs and Cl). A thermal intramolecular cyclization of **3** and successive dehydration gave iminium salts (**4a**), which were hydrolyzed to furnish 2*H*-cyclohepta[*d*]thiazol-2-one (**4b**) [8, 9]. Compound (**4b**) has a unique reactivity and could be transformed into a novel heptafulvene as shown in Scheme 1 [9].

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This paper is dedicated to Professor Renji Okazaki on the occasion of his 77th birthday.

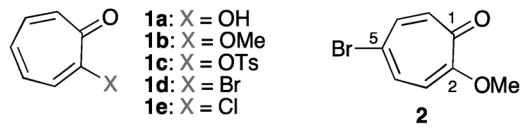



FIGURE 1 Tropolone and activated troponoids.

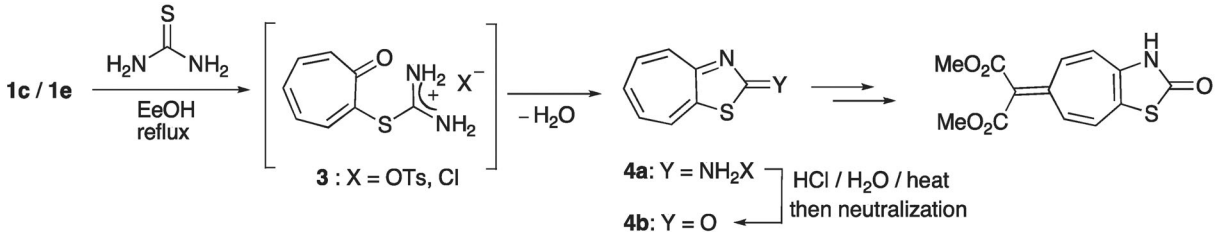
In expectation of conversion into a 5-bromo derivative (**5b**), we tried treatment of **2** with thiourea (Scheme 2). As a result, surprisingly, neither a 2-*S*-substitute (**6**) nor its cyclized imine (**5a**) was formed at all, and the product was a hydrobromide of 5-substituted compound (**7**) replacing a bromine atom of **2** with a sulfur atom of thiourea. This result indicates that compound (**2**) has an ability to be substituted at the 5-position. If the reactivity at the 2- and 5-positions could be controlled by reaction conditions, **2** would be a useful precursor for construction of various 2,5-disubstituted tropones. Therefore, we decided that the reaction of **2** with other kinds of nucleophiles is worth trying.

According to the anticipation, we first attempted the reaction with *O*-nucleophiles (Scheme 3, left). The treatment of **2** in boiling ethanol with potassium carbonate as a base furnished a single component of 5-bromo-2-ethoxytropone (**8**). The reaction with sodium hydroxide proceeded only at the 2-position to give a known product (**9**) [10]. Phenol did not react in spite of the presence of potassium carbonate or sodium hydride. In the case with *N*-nucleophiles, the same 2-selectivety was shown regardless of alkyl or aryl amines (Scheme 3, right). That is, diethylamine, propylamine, and *p*-chloroaniline/triethylamine reacted with **2** under boiling conditions to give 2-aminotropones (**10**) [6b], (**11**), and (**12**), respectively. From the products analysis, it is found that 5-substitution of **2** and further one of the products (**8–12**) with the *O*- and *N*-nucleophiles did not proceed in these conditions.

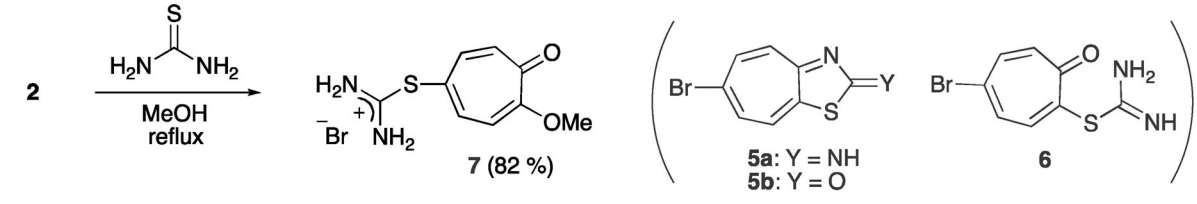
Next, we examined the reaction with *S*-nucleophiles in expectation of the 5-selective substitution (Scheme 4, left). The treatment of **2** with 1-propanethiol in the presence of potassium carbonate furnished the desired 5-substituted compound, 2-methoxy-5-propylthiotropone (**13**). Thiophenol with triethylamine gave a 5-substitute (**14**). Substitution with the thiolates at room temperature occurred only at the 5-position of **2**, and 2-substituted and/or 2,5-disubstituted products were not formed at all.

Triphenyldibromophosphorane and its dichloro analogue could convert ethers and esters into corresponding alkyl/aryl halides and acid halides, respectively [11]. We attempted the reaction of **2** with these reagents as halide nucleophiles (Scheme 4, right). The treatment with the former afforded 2,5-dibromotropone (**15**). In the case with 2 mol equiv of the latter reagent afforded only 2,5-dichlorotropone (**16**), whereas with 1 mol equiv of the latter reagent gave a trace amount of 5-chloro-2-methoxytropone together with **16** and recovery of **2**. These results suggest that the first attack of the nucleophile would occur at the 5-position of **2**.

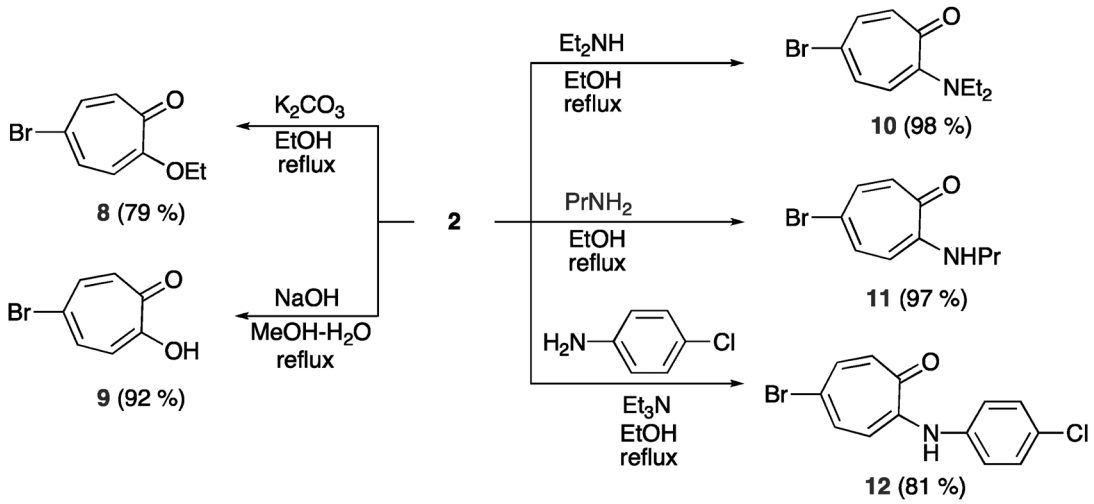
In this manner, the different reactivity at 2- and 5-positions of **2** was revealed according to the type of nucleophilic atoms in the reagents. The reason remains unknown; however, a tendency of the reactivity might be explained by using the Hard and Soft Acids and Bases (HSAB) concept [12]. That is, *S*-nucleophiles regarded as relatively soft bases would prefer to attack at the 5-position of **2**, whereas



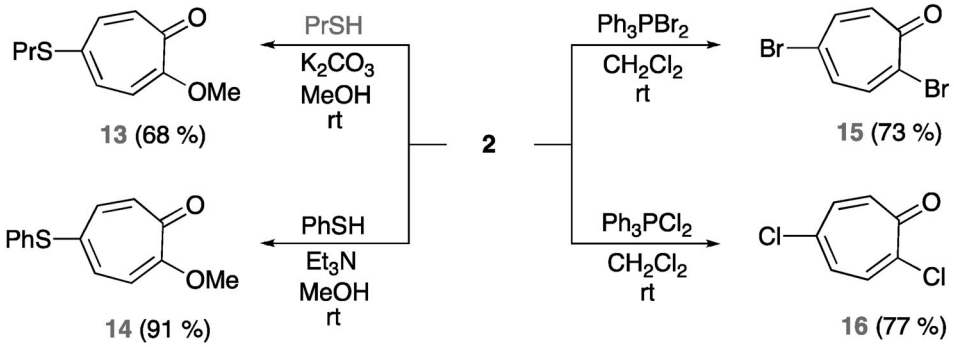

SCHEME 1




SCHEME 2




SCHEME 3

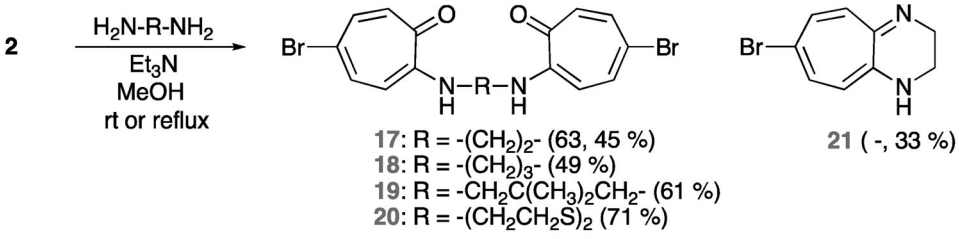



SCHEME 4

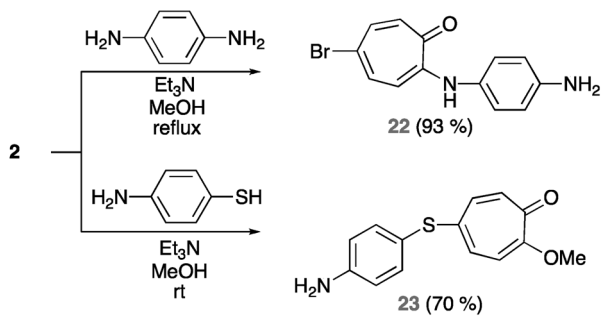
*O*- and *N*-nucleophiles regarded as relatively hard bases would prefer to attack at the 2-position.

Reagents having two nucleophilic atoms would supply two-to-one substitutes, which have two tropone nuclei bridged by a nucleophile moiety. The reaction of **2** with 0.5 mol equiv of alkyl diamines, such as ethylenediamine, 1,3-propanediamine, 2,2-dimethyl-1,3-propanediamine, and cystamine, at room temperature afforded corresponding bis(2-aminotropone)s (**17**), (**18**), (**19**), and (**20**) as expected (Scheme 5). In the only case with ethylenediamine under boiling conditions, aminotroponimine (**21**) was produced together with **17**. Compound (**21**) would arise from a thermal intramolecular cyclization of a one-to-one substitute of **2** and ethylenediamine and successive dehydration. This is a rare case because of the difficulty of imination in troponoids under basic conditions.

On the other hand, aryl *N*,*N*- and *N*,*S*-nucleophiles such as *p*-phenylenediamine and 4-aminothiophenol produced one-to-one substitutes of **2** and the nucleophiles (Scheme 6). The same




SCHEME 5




SCHEME 6

regioselectivety mentioned above was shown, and the products were 2-*N*- and 5-*S*-substitutes (**22**) and (**23**), respectively. A 2-*N*-substitute with 4-aminothiophenol was not formed at all. Further substitution of **22** and **23** did not proceed even if using an excess amount of **2** or the nucleophiles.

In conclusion, we have found the regioselective nucleophilic substitution of 5-bromo-2-methoxytropone (**2**) according to the type of nucleophilic atoms in the reagents. Further work, aimed at elucidation of the regioselectivity using computational chemistry and in the construction of various troponoids with two different substituents at 2- and 5-positions, is in progress.

## *EXPERIMENTAL*

Melting points were determined with a laboratory devices MEL-TEMP apparatus and are uncorrected. $^1$H and $^{13}$C NMR spectra ($SiMe_4$ as the internal standard) were obtained with Bruker AV500, AV 400, AV300, and AC300 spectrometers. IR spectra were obtained with a Perkin–Elmer System 2000 FT instrument. MS spectra were obtained with JEOL JMS700AM and Bruker AutoflexIII spectrometers. Unless otherwise stated, the spectra were taken in the following solvents/media: IR, KBr; $^1$H and $^{13}$C NMR, $CDCl_3$, and DMSO-$d_6$; MS spectra were taken at FAB and MALDI-TOF methods. The progress of reactions was followed by thin-layer chromatography method using a Merck Silica gel $60F_{254}$.

### *The Reaction of 5-Bromo-2-methoxytropone (**2**) with Thiourea*

A solution of **2** (431 mg, 2.0 mmol) and thiourea (2.0 mmol) in absolute ethanol (10 mL) was boiled for 13 h under argon. The resulting precipitate was filtered and washed with ethanol to give **7** (479 mg, 82%); pale yellow solids; mp 220–221°C; $^1$H NMR (300 MHz, DMSO-$d_6$): $\delta$ 3.91 (s, 3H), 6.94 (d, $J$ = 10.3 Hz, 1H), 6.98 (d, $J$ = 12.7 Hz, 1H), 7.39 (dd, $J$ = 12.7, 1.8 Hz, 1H), 7.65 (dd, $J$ = 10.3, 1.8 Hz, 1H), 8.93–9.08 (br, 4H); IR (KBr): $\nu$ 3016, 1660, 1622, 1567; MS (FAB, NBA): $m/z$ 211 ([M – Br]$^+$). Anal. calcd for $C_9H_{11}BrN_2O_2S$: C, 37.13; H, 3.81; N, 9.62. Found: C, 37.43; H, 3.75; N, 9.49.

### *The Reaction of **2** with Ethanol/Potassium Carbonate*

An absolute ethanol (2.0 mL) solution of **2** (65 mg, 0.30 mmol) with potassium carbonate (0.30 mmol) was boiled for 24 h under argon. The solvent was removed in vacuo, and the residue was purified by silica gel column chromatography to give **8** (55 mg, 79%); yellow needles; mp 124–125°C; $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ 1.53 (t, $J$ = 7.0 Hz, 3H), 4.11 (q, $J$ = 7.0 Hz, 2H), 6.48 (d, $J$ = 10.9 Hz, 1H), 7.01 (d, $J$ = 13.2 Hz, 1H), 7.38 (dd, $J$ = 10.9, 2.0 Hz, 1H), 7.41 (dd, $J$ = 13.2, 2.0 Hz, 1H); IR (KBr): $\nu$ 1614, 1574; MS (FAB, NBA): $m/z$ 229 (MH$^+$), 231 ([MH + 2]$^+$). Anal. calcd for $C_9H_9BrO_2$: C, 47.19; H, 3.96. Found: C, 47.34; H, 3.84.

### *The Reaction of **2** with Sodium Hydroxide*

To an absolute methanol (1.5 mL) solution of **2** (65 mg, 0.30 mmol), 0.60 M sodium hydroxide (0.60 mmol) was added under argon and boiled for 13 h. The reaction mixture was quenched with 1.0 M hydrochloric acid, and the aqueous layer was extracted with diethyl ether. The organic layer was dried over magnesium sulfate, and the solvent was removed under reduced pressure. The residue was purified by silica gel column chromatography to give **9** [10] (56 mg, 92%); yellow solids; mp 150–151°C; $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ 7.11 (d, $J$ = 11.8 Hz, 2H), 7.67 (d, $J$ = 11.8 Hz, 1H); IR (KBr): $\nu$ 3114, 1605, 1566; MS (FAB, NBA): $m/z$ 201 (MH$^+$), 203 ([MH + 2]$^+$). Anal calcd for $C_7H_5BrO_2$: C, 41.82; H, 2.51. Found: C, 41.57; H, 2.70.

### *The Reaction of **2** with Alkyl Amines*

A solution of **2** with alkyl amines (diethylamine and propylamine; 4.0 mol equiv) in absolute ethanol (0.15 mM) was boiled for 24 h under argon. After removal of the solvent in vacuo, the residue was purified by silica gel column chromatography to give **10** [6b] (98%) and **11** (97%), respectively.

*5-Bromo-2-(diethylamino)tropone (**10**).* Yellowish brown crystals; mp 183–185°C; $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ 1.22 (t, $J$ = 7.0 Hz, 6H), 3.53 (q, $J$ = 7.0 Hz, 4H), 6.22 (d, $J$ = 11.4 Hz, 1H), 6.62 (d, $J$ = 12.5 Hz, 1H), 7.21 (dd, $J$ = 11.4, 2.4 Hz, 1H), 7.27

(dd, $J$ = 12.5, 2.4 Hz, 1H); IR (KBr): $\nu$ 1614, 1563; MS (FAB, NBA): *m/z* 256 ($MH^+$), 258 ($[MH + 2]^+$). Anal. calcd for $C_{11}H_{14}BrNO$: C, 51.58; H, 5.51; N, 5.47. Found: C, 51.66; H, 5.41; N, 5.39.

*5-Bromo-2-(propylamino)tropone (***11***).* Yellowish brown plates; mp 85–86°C; $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ 1.05 (t, $J$ = 7.3 Hz, 3H), 1.70–1.82 (m, 2H), 3.26 (q like, $J$ = 7.3 Hz, 2H), 6.29 (d, $J$ = 11.4 Hz, 1H), 6.92 (d, $J$ = 12.5 Hz, 1H), 7.29 (br, 1H), 7.44–7.50 (m, 2H); IR (KBr): $\nu$ 3249, 1585, 1512; MS (FAB, NBA): *m/z* 242 ($MH^+$), 244 ($[MH + 2]^+$). Anal. calcd for $C_{10}H_{12}BrNO$: C, 49.61; H, 5.00; N, 5.79. Found: C, 49.64; H, 4.91; N, 5.51.

### *The Reaction of* **2** *with p-Chloroaniline/ Triethylamine*

A solution of **2** (65 mg, 0.30 mmol) with *p*-chloroaniline (0.93 mmol) and triethylamine (0.93 mmol) in absolute ethanol (1.5 mL) was boiled for 24 h under argon. After removal of the solvent in vacuo, the residue was purified by silica gel column chromatography to give **12** (76 mg, 81%); yellow crystals; mp 175–177°C; $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ 6.85 (d, $J$ = 11.2 Hz, 1H), 7.06 (d, $J$ = 12.5 Hz, 1H), 7.22 (d, $J$ = 8.6 Hz, 2H), 7.41 (d, $J$ = 8.6 Hz, 2H), 7.43 (dd, $J$ = 11.2, 2.2 Hz, 1H), 7.57 (dd, $J$ = 12.5, 2.2 Hz, 1H), 8.65 (br, 1H); IR (KBr): $\nu$ 3208, 1589, 1548; MS (FAB, NBA): *m/z* 310 ($MH^+$), 312 ($[MH + 2]^+$), 314 ($[MH + 4]^+$). Anal. calcd for $C_{13}H_9BrClNO$: C, 50.27; H, 2.92; N, 4.51. Found: C, 50.36; H, 2.85; N, 4.50.

### *The Reaction of* **2** *with 1-Propanethiol/ Potassium Carbonate*

An absolute methanol (1.5 mL) solution of **2** (65 mg, 0.30 mmol) and 1-propanethiol (0.30 mmol) with potassium carbonate (0.30 mmol) was stirred for 12 h at room temperature under argon. The solvent was removed in vacuo, and the residue was purified by silica gel column chromatography to give **13** (43 mg, 68%); yellow needles; mp 54–55°C; $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ 1.50 (t, $J$ = 7.2 Hz, 3H), 1.70 (sext, $J$ = 7.2 Hz, 2H), 2.89 (t, $J$ = 7.2 Hz, 2H), 3.92 (s, 3H), 6.66 (d, $J$ = 10.5 Hz, 1H), 7.01 (dd, $J$ = 10.5, 1.8 Hz, 1H), 7.11 (d, $J$ = 12.5 Hz, 1H), 7.24 (dd, $J$ = 12.5, 1.8 Hz, 1H); IR (KBr): $\nu$ 1614, 1557; MS (FAB, NBA): *m/z* 211 ($MH^+$). Anal. calcd for $C_{11}H_{14}O_2S$: C, 62.83; H, 6.71. Found: C, 63.00; H, 6.54.

### *The Reaction of* **2** *with Thiophenol/ Triethylamine*

A solution of **2** (65 mg, 0.30 mmol) with thiophenol (0.60 mmol) and triethylamine (2.4 mmol) in absolute methanol (1.5 mL) was stirred for 24 h at room temperature under argon. After removal of the solvent in vacuo, the residue was purified by silica gel column chromatography to give **14** (67 mg, 91%); pale yellow needles; mp 198–199°C; $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ 3.92 (s, 3H), 6.63 (d, $J$ = 10.7 Hz, 1H), 7.06 (d, $J$ = 12.5 Hz, 1H), 7.07 (dd, $J$ = 10.7, 2.0 Hz, 1H), 7.19 (dd, $J$ = 12.5, 2.0 Hz, 1H), 7.35–7.42 (m, 5H); IR (KBr): $\nu$ 1618, 1580; MS (FAB, NBA): *m/z* 245 ($MH^+$). Anal. calcd for $C_{14}H_{12}O_2S$: C, 68.83; H, 4.95. Found: C, 68.82; H, 4.87.

### *The Reaction of* **2** *with Halogenation Reagents*

A solution of **2** with halogenation reagents (triphenyldibromophosphorane: 1.0 mol equiv; triphenyldichlorophosphorane: 2.0 mol equiv) in dry dichloromethane (0.15 mM) was stirred for 24 h at room temperature under argon. After removal of the solvent in vacuo, the residue was purified by silica gel column chromatography to give **15** (73%) and **16** (77%), respectively.

*2,5-Dibromotropone (***15***).* Pale yellow needles; mp 84–85°C; $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ 6.96 (d, $J$ = 12.9 Hz, 1H), 7.21 (dd, $J$ = 10.4, 2.2 Hz, 1H), 7.38 (dd, $J$ = 12.9, 2.2 Hz, 1H), 7.80 (d, $J$ = 10.4 Hz, 1H); IR (KBr): $\nu$ 1609, 1583; MS (FAB, NBA): *m/z* 263 ($MH^+$), 265 ($[MH + 2]^+$), 267 ($[MH + 4]^+$). Anal. calcd for $C_7H_4Br_2O$: C, 31.86; H, 1.53. Found: C, 32.16; H, 1.82.

*2,5-Dichlorotropone (***16***).* Pale yellow needles; mp 87–88°C; $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ 7.09 (dd, $J$ = 10.3, 2.2 Hz, 1H), 7.12 (d, $J$ = 12.9 Hz, 1H), 7.28 (dd, $J$ = 12.9, 2.2 Hz, 1H), 7.63 (d, $J$ = 10.3 Hz, 1H); IR (KBr): $\nu$ 1621, 1580; MS (FAB, NBA): *m/z* 175 ($MH^+$), 177 ($[MH + 2]^+$), 179 ($[MH + 4]^+$). Anal. calcd for $C_7H_4Cl_2O$: C, 48.04; H, 2.30. Found: C, 48.36; H, 2.61.

### *The Reaction of* **2** *with Alkyl Diamines*

A solution of **2** with alkyl diamines (ethylenediamine, 1,3-propanediamine, 2,2-dimethyl-1,3-propanediamine, and cystamine dihydrochloride; 0.5 mol equiv) and triethylamine (1.1 mol equiv; only in the case of cystamine dihydrochloride: 2.6 mol equiv) in absolute methanol (0.10 mM) was stirred for 24 h at room temperature under argon. After removal of the solvent in vacuo, the residue was purified by aluminum oxide (active V) column chromatography to give **17** (63%), **18** (49%), **19** (61%), and **20** (71%), respectively. Ethylenediamine (0.5 mol equiv) in the presence of triethylamine (1.1 mol equiv) reacted with **2** in absolute methanol

(0.10 mM) under boiling conditions for 24 h to give **21** (33%) together with **17** (45%).

*Bis(2-aminotropone) (**17**).* Ocher solids; mp 280°C (dec.); $^1$H NMR (500 MHz, $CDCl_3$): $\delta$ 3.68 (m, 4H), 6.31 (d, $J$ = 11.0 Hz, 2H), 6.94 (d, $J$ = 13.0 Hz, 2H), 7.50–7.53 (m, 6H); $^{13}$C NMR (100 MHz, DMSO-$d_6$): $\delta$ 40.9 (2C), 108.2 (2C), 114.2 (2C), 127.5 (2C), 138.6 (2C), 139.6 (2C), 155.6 (2C), 175.8 (2C); IR (KBr): $\nu$ 3308, 1594; MS (MALDI-TOF, dithranol): *m/z* 425 ($MH^+$), 427 ([MH + 2]$^+$), 429 ([MH + 4]$^+$). Anal. calcd for $C_{16}H_{14}Br_2N_2O_2$: C, 45.10; H, 3.31; N, 6.57. Found: C, 44.80; H, 3.30; N, 6.41.

*Bis(2-aminotropone) (**18**).* Ocher plates; mp 167–168°C; $^1$H NMR (500 MHz, $CDCl_3$): $\delta$ 2.19 (quint, $J$ = 6.5 Hz, 2H), 3.45 (q like, $J$ = 6.5 Hz, 4H), 6.27 (d, $J$ = 11.0 Hz, 2H), 6.95 (d, $J$ = 12.0 Hz, 2H), 7.22 (br, 2H), 7.49 (dd, $J$ = 11.0, 2.0 Hz, 2H), 7.52 (dd, $J$ = 12.0, 2.0 Hz, 2H); IR (KBr): $\nu$ 3254, 1591; MS (MALDI-TOF, dithranol): *m/z* 439 ($MH^+$), 441 ([MH + 2]$^+$), 443 ([MH + 4]$^+$). Anal. calcd for $C_{17}H_{16}Br_2N_2O_2$: C, 46.39; H, 3.66; N, 6.36. Found: C, 46.14; H, 3.60; N, 6.12.

*Bis(2-aminotropone) (**19**).* Ocher powder; mp 154–155°C; $^1$H NMR (500 MHz, $CDCl_3$): $\delta$ 1.21 (s, 6H), 3.21 (d like, $J$ = 6.5 Hz, 4H), 6.24 (d, $J$ = 11.0 Hz, 2H), 6.94 (d, $J$ = 12.5 Hz, 2H), 7.36 (dd, $J$ = 11.0, 2.5 Hz, 2H), 7.39 (br, 2H), 7.50 (dd, $J$ = 12.5, 2.5 Hz, 2H); $^{13}$C NMR (125 MHz, $CDCl_3$): $\delta$ 24.1 (2C), 36.7, 50.1 (2C), 108.0 (2C), 116.3 (2C), 127.8 (2C), 138.3 (2C), 140.4 (2C), 154.9 (2C), 175.9 (2C); IR (KBr): $\nu$ 3260, 1594; MS (MALDI-TOF, dithranol): *m/z* 467 ($MH^+$), 469 ([MH + 2]$^+$), 471 ([MH + 4]$^+$). Anal. calcd for $C_{19}H_{20}Br_2N_2O_2$: C, 48.74; H, 4.31; N, 5.98. Found: C, 48.42; H, 4.17; N, 5.75.

*Bis(2-aminotropone) (**20**).* Yellow solids; mp 200°C (dec.); $^1$H NMR (500 MHz, $CDCl_3$): $\delta$ 2.97 (t, $J$ = 6.5 Hz, 4H), 3.65 (q like, $J$ = 6.5 Hz, 4H), 6.31 (d, $J$ = 11.0 Hz, 2H), 6.94 (d, $J$ = 13.0 Hz, 2H), 7.42 (br, 2H), 7.47–7.52 (m, 4H); $^{13}$C NMR (125 MHz, $CDCl_3$): $\delta$ 35.4 (2C), 41.2 (2C), 107.7 (2C), 113.9 (2C), 127.1 (2C), 138.2 (2C), 139.2 (2C), 154.7 (2C), 175.1 (2C); IR (KBr): $\nu$ 3245, 1589; MS (MALDI-TOF, dithranol): *m/z* 517 ($MH^+$), 519 ([MH + 2]$^+$), 521 ([MH + 4]$^+$). Anal. calcd for $C_{18}H_{18}Br_2N_2O_2S_2$: C, 41.71; H, 3.50; N, 5.41. Found: C, 41.42; H, 3.34; N, 5.21.

*Aminotroponimine (**21**).* Orange powder; mp 140°C (dec.); $^1$H NMR (500 MHz, $CDCl_3$): $\delta$ 3.56 (s, 4H), 6.20 (d, $J$ = 11.3 Hz, 2H), 6.87 (d, $J$ = 11.3 Hz, 2H); IR (KBr): $\nu$ 3220; MS (MALDI-TOF, dithranol): *m/z* 225 ($MH^+$), 227 ([MH + 2]$^+$). Anal. calcd for $C_9H_9BrN_2$: C, 48.02; H, 4.03; N, 12.45. Found: C, 48.30; H, 3.88; N, 12.18.

### *The Reaction of **2** with p-Phenylenediamine/ Triethylamine*

A solution of **2** (50 mg, 0.23 mmol) with *p*-phenylenediamine (0.35 mmol) and triethylamine (0.72 mmol) in absolute methanol (1.2 mL) was boiled for 24 h under argon. After removal of the solvent in vacuo, the residue was purified by silica gel column chromatography to give **22** (63 mg, 93%); red plates; mp 188–189°C; $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ 3.78 (br, 2H), 6.71 (d, $J$ = 11.2 Hz, 1H), 6.74 (d, $J$ = 8.5 Hz, 2H), 7.01 (d, $J$ = 12.3 Hz, 1H), 7.04 (d, $J$ = 8.5 Hz, 2H), 7.39 (dd, $J$ = 11.2, 2.2 Hz, 1H), 7.53 (dd, $J$ = 12.3, 2.2 Hz, 1H), 8.59 (br, 1H); IR (KBr): $\nu$ 3335, 3244, 3208, 1589; MS (FAB, NBA): *m/z* 291 ($MH^+$), 293 ([MH + 2]$^+$). Anal. calcd for $C_{13}H_{11}BrN_2O$: C, 53.63; H, 3.81; N, 9.62. Found: C, 53.57; H, 3.57; N, 9.56.

### *The Reaction of **2** with 4-Aminothiophenol/ Triethylamine*

A solution of **2** (101 mg, 0.47 mmol) with 4-aminothiophenol (0.71 mmol) and triethylamine (1.86 mmol) in absolute methanol (4.0 mL) was stirred for 20 h at room temperature under argon. After removal of the solvent in vacuo, the residue was purified by silica gel column chromatography to give **23** (85 mg, 70%); yellow powder; mp 164–165°C; $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ 3.95 (s, 3H), 4.09 (br, 2H), 6.57 (d, $J$ = 10.8 Hz, 1H), 6.71 (d, $J$ = 8.8 Hz, 2H), 6.74 (dd, $J$ = 10.8, 1.8 Hz, 1H), 7.07 (d, $J$ = 12.4 Hz, 1H), 7.12 (dd, $J$ = 12.4, 1.8 Hz, 1H), 7.29 (d, $J$ = 8.8 Hz, 2H); IR (KBr): $\nu$ 3339, 3222, 1633, 1556; MS (FAB, NBA): *m/z* 260 ($MH^+$). Anal. calcd for $C_{14}H_{13}NO_2S$: C, 64.84; H, 5.05; N, 5.40. Found: C, 65.05; H, 4.90; N, 5.24.

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