POLYANNULATED TROPYLIUM COMPOUNDS HAVING BENZOTHIAZINE AND RELATED HETEROCYCLIC RINGS. FORMATION OF o- AND p-BENZOQUINONOID PRODUCTS BY REARRANGEMENT[1]

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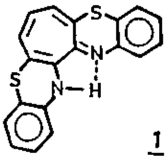
Abstract - Tropylium compounds having tri-annulated heterocycles (11 and 15) are obtained by the reaction of 2,4-dibromo-7-methoxy- and 3,5,7-tribromo-2-methoxytropone with o-aminophenol and o-aminobenzenethiol, via di-annulated compounds. Rearrangements to di- and tri-annulated o- and p-benzoquinonoid compounds (13, 16 and 20) take place during the attempted synthesis of some tri-annulated tropylium systems. Possible pathways for these reactions are discussed.

One of the authors (T.N.) and his coworkers obtained 14H-cyclohepta[1,2-b:4,3-b']-benzothiazine (1)[2] by the reaction of 3,7-dibromotropolone with o-aminobenzenethiol (3a). Later, present authors obtained[3] O-analogue 2 of 1 as one of the products of the reaction of 3-bromo-2-methoxytropone (4a) with o-aminophenol (3b). Compound 2 has later been obtained in a better yield by the condensation of 6-bromocyclohepta[b][1,4]benzoxazine (5a) with 3b in refluxing acetic acid followed



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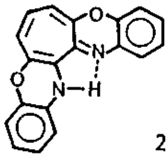

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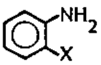
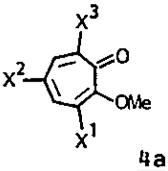
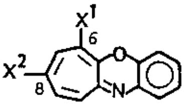


3a: X=SH
3b: X=OH
3c: X=NHMe

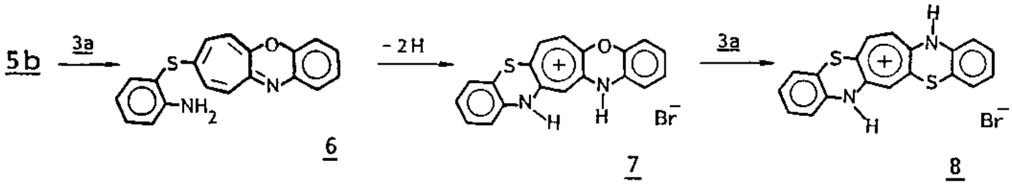


4a: X^1=Br, X^2=X^3=H
4b: X^1=X^2=X^3=Br
4c: X^1=X^3=H, X^2=Br



5a: X^1=Br, X^2=H
5b: X^1=H, X^2=Br
5c: X^1=X^2=Br

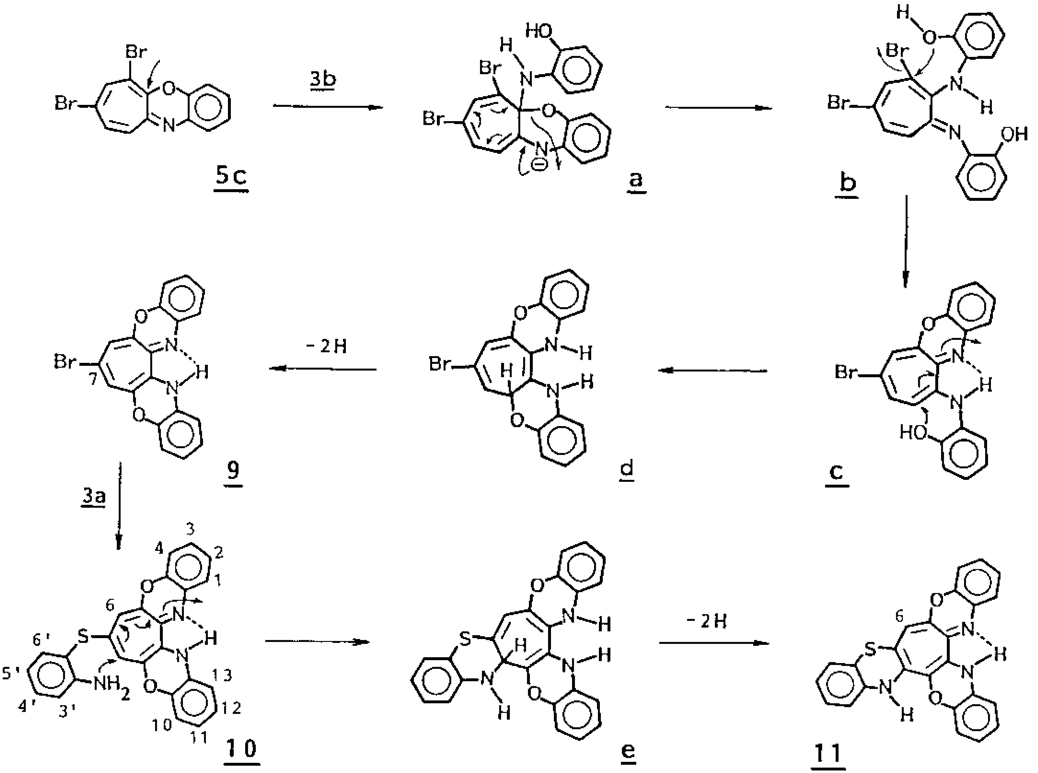
by autoxidation[4]. Very recently we have reported synthesis of the tropylium ion 7 from 8-bromo compound 5b and 3a in methanol at room temperature via S-substituted compound 6, and 7 has been led to the cation 8 having di-annulated benzothiazine rings by the intermolecular heterocycle-exchange reaction between 7 and 3a[5]. (Scheme 1)



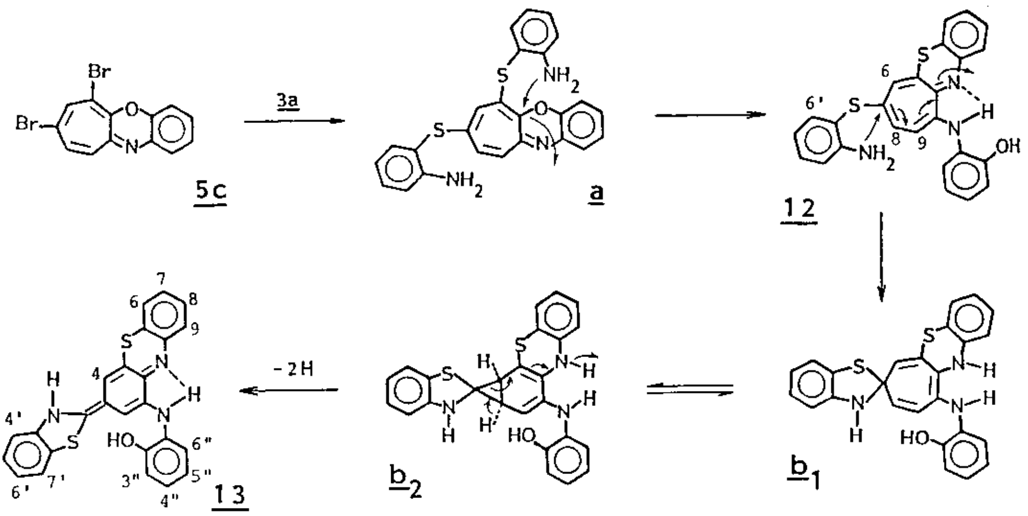
Scheme 1.

In this communication we wish to describe the synthesis of some tropylium compounds having tri-annulated heterocycles and interesting aspects of intramolecular transposition of heterocyclic ring on the seven-membered nucleus as well as some rearrangement reactions to o- and p-benzoquinonoid compounds during the attempted synthesis of these poly-annulated tropylium compounds.

7-Bromo-14H-cyclohepta[1,2-b:4,3-b']bis[1,4]benzoxazine (9) was prepared from 6,8-dibromo compound 5c and 3b by an intramolecular hetero-ring transposition via a - c, followed by dehydrogenation as shown in Scheme 2[6]. When 9 and 3a were allowed

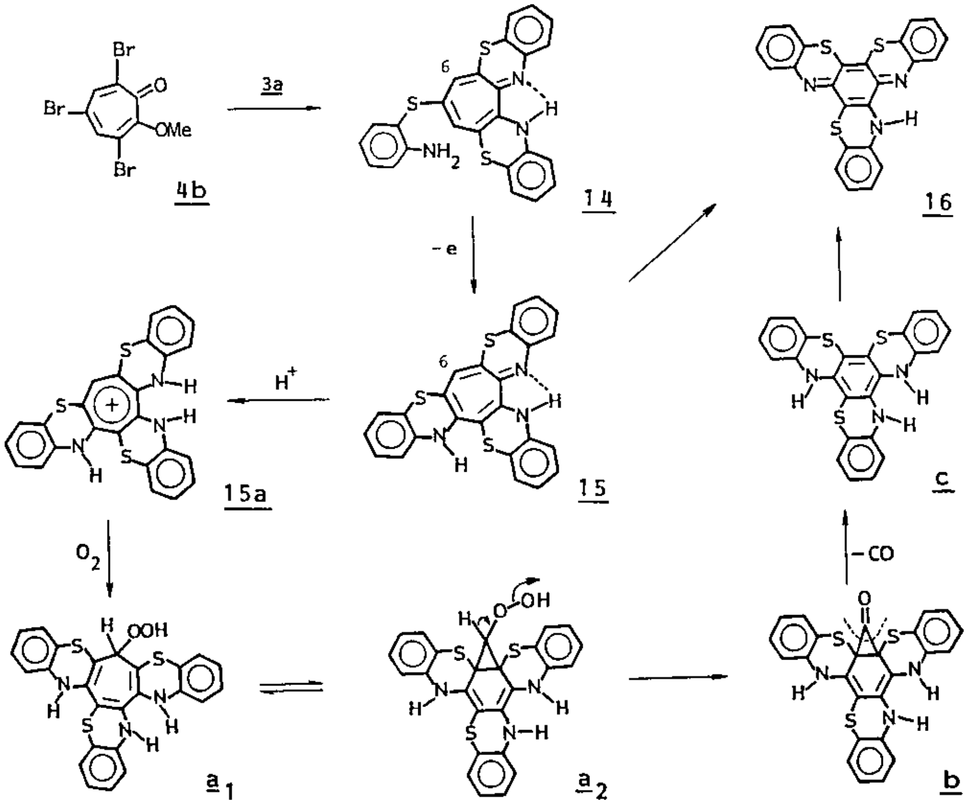


Scheme 2.



Scheme 3.

to stand at room temperature S-substituted compound 10[7] was obtained (85% yield). 10 was dehydrocyclized in acetic acid by anodic oxidation, giving 11[8].

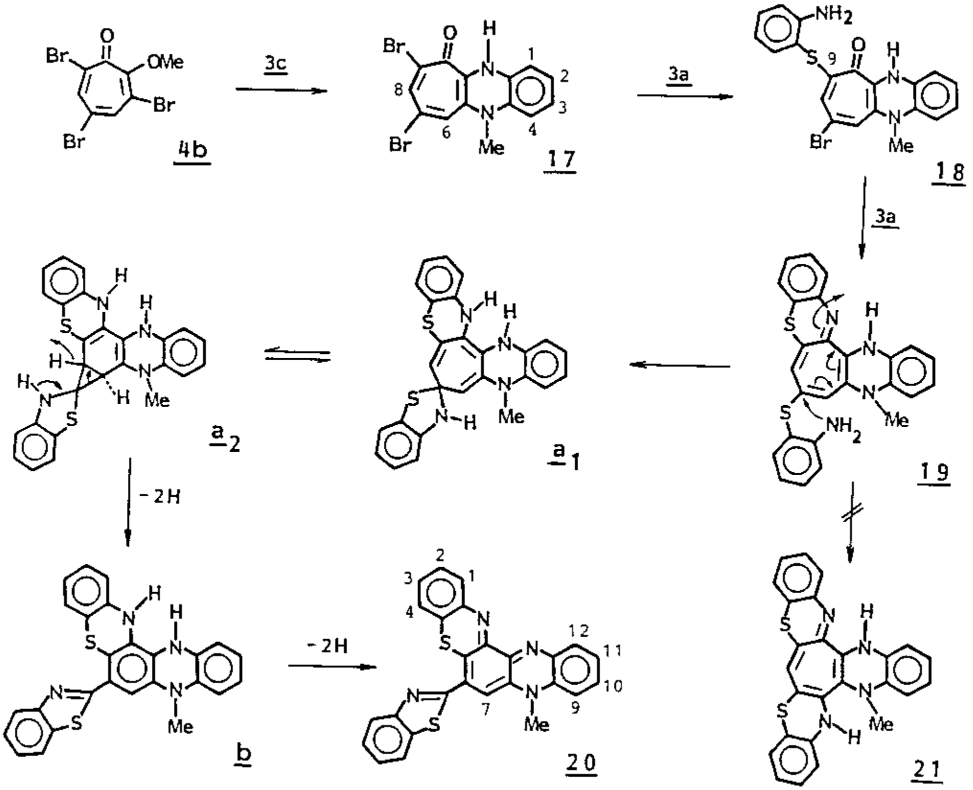


Scheme 4.

Reaction of 5c with an excess of 3a in methanol-chloroform at room temperature for 1 day gave, via intermediate a followed by the ring conversion, di-S-substituted compound 12[9], which afforded p-benzoquinonoid derivative 13[10] on attempted ring-closure by anodic oxidation. This rearrangement is considered to proceed via spiro intermediate b_1 and its norcaradiene form b_2, followed by the oxidative H-abstraction as shown in Scheme 3.

We next synthesized tropylium compound 15 having tri-annulated benzothiazine ring. Namely, treatment of 3,5,7-tribromo-2-methoxytropone (4b) with an excess of 3a at room temperature gave compounds 14[11] which by anodic oxidation gave the ring-closed compound 15[12]. The deep green-colored cation 15a was easily converted in air or with DDQ in acetic acid into the one-carbon-less p-benzoquinone-diimide derivative 16[13], presumably via hydroperoxide a_1 and its norcaradiene form a_2 and decarbonylation as shown in Scheme 4.

Treatment of 4b with N-methyl-o-phenylenediamine (3c) gave dibromo compound 17[14] (68%), which in turn condensed with 3a in chloroform to give the mono-S-substituted compound 18[15] (86%). When a mixture of 18 and 3a was heated at 100 °C in a sealed tube (or further kept standing at room temperature for a day), a rearranged product having o-benzoquinone-diimide structure 20[16] was obtained, instead of the expected tri-annulated tropylium compound 21. Compound 20 is presumed to be produced from 19 via spiro intermediate a_1 and its norcaradiene form a_2 and then b, followed by dehydrogenation (Scheme 5).



Scheme 5.

It should especially be noted that interesting p- and o-benzoquinonoid compounds 13, 16, and 20, which are otherwise very difficult to prepare, are produced very easily by the present reaction schemes.

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7. 10: Reddish violet needles, mp 263-264 °C; Uv (MeOH) 277, 300(sh), 360, 518, 600(sh), and 690(sh) nm, (MeOH + HCl) 279, 332, 405, and 550 nm; ^{1}H nmr (270 MHz in $CDCl_3$) δ=4.31 (2H, br, NH_2), 5.56 (2H, s, H-6,8), 6.44 (2H, dd, J=8.0 and 2.0 Hz, H-4,10), 6.63 (2H, dd, J=8.0 and 2.0 Hz, H-1,13), 6.66 (2H, td, J=8.0 and 2.0 Hz, H-3,11), 6.72 (2H, td, dd, J=8.0 and 2.0 Hz, H-2,12), 6.77 (1H, td, J=8.0 and 2.0 Hz, H-4'), 6.80 (1H, dd, J=8.0 and 2.0 Hz, H-6'), 7.15 (1H, br, NH), 7.26 (1H, m, H-5'), and 7.37 (1H, dd, J=8.0 and 2.0 Hz, H-3'); ms m/z 423 (M^+).
8. 11: Dark violet needles, mp >300 °C; Uv (MeOH) 264, 315(sh), 480, and 610(sh) nm, (MeOH + HCl) 280(sh), 350, 555, 595(sh), and 700 nm; ^{1}H nmr (270 MHz in $CDCl_3$) δ=6.54 (1H, s, H-6), 6.84-7.66 (12H, m, other H); ^{13}C nmr (67.2 MHz in $CDCl_3$) δ=112.6, 114.6, 114.8, 117.3, 122.7, 124.2, 124.4, 124.6, 127.2, 128.3, 129.3, 129.8, 129.9, 130.5, 130.9, 131.8, 133.6, 133.7, 136.8, 140.3, 146.4, 146.6, 147.4, 147.6, and 148.4; ms m/z 437 (M^+).
9. 12: Red oil; Uv (MeOH) 286 and 480 nm, (MeOH + HCl) 280, 358, and 510 nm; ^{1}H nmr (270 MHz in C_6D_6) δ=3.64 (2H, br, NH_2), 6.04 (1H, dd, J=11.7 and 1.8 Hz, H-8), 6.22 (1H, d, J=11.7 Hz, H-9), 6.58 (1H, d, J=1.8 Hz, H-6), 6.50-6.70 (7H, m, other H), 7.04-7.44 (4H, m, other H), and 7.52 (1H, dd, J=7.7 and 1.5 Hz, H-6'); ms m/z 441 (M^+).
10. 13: Yellow crystal, mp >300 °C; Uv (MeOH) 262, 302, and 400 nm; ^{1}H nmr (270 MHz in DMSO-d_6) δ=6.76-7.06 (8H, m, H-6,7,8,9,4',5',6',7'), 7.20 (1H, d, J=1.5 Hz, H-4), 7.30 (1H, d, J=1.5 Hz, H-2), 7.37 (1H, td, J=8 and 1.5 Hz, H-4" or 5"), 7.47 (1H, td, J=8 and 1.5 Hz, H-5" or 4"), 7.92 (1H, dd, J=8 and 1.5 Hz, H-3" or 6"), 8.04 (1H, dd, J=8 and 1.5 Hz, H-6" or 3"), 8.24 (1H, s, NH), 8.33 (1H, s, NH), and 9.65 (1H, s, OH); ms m/z 439 (M^+).

11. 14: Reddish violet needles (from benzene), mp 171 $^{\circ}$C; Uv (MeOH) 248, 296, and 508 nm (log ε 4.45, 4.42, and 3.94); ^{1}H nmr (270 MHz in $CDCl_3$) δ =4.26 (2H, br, NH_2), 5.99 (2H, s, H-6,8), 6.76 (1H, td, J=8 and 2 Hz, H-5'), 6.75-6.86 (5H, m, H-1,4,10,13,3'), 6.89 (2H, td, J=8 and 2 Hz, H-3,11 or 2,12), 7.00 (2H, td, J=8 and 2 Hz, H-2,12 or 3,11), 7.23 (1H, td, J=8 and 2 Hz, H-4'), 7.34 (1H, dd, J=8 and 2 Hz, H-6'), 8.88 (1H, br, NH); ^{13}C nmr (67.8 MHz, in $CDCl_3$) δ =76.5, 77.0, 77.5, 113.8, 115.5, 118.9, 121.2, 122.5, 125.4, 125.5, 127.6, 127.7, 128.3, 131.6, 136.3, 136.9, 140.9, 143.2, and 148.6; ms m/z 455 (20), 348 (19), 320 (37), 287 (27), 255 (12), and 125 (100). Found: m/z 455.0591. Calcd for $C_{25}H_{17}N_3S_3$: M, 455.0597.

12. 15: Red needles, mp 215 $^{\circ}$C; Uv (MeOH) 270, 312, 355, and 480 nm, (MeOH + HCl) 265, 310, 395, and 572 nm; ^{1}H nmr (270 MHz in $CDCl_3$) δ =7.04 (1H, s, H-6) and 7.20-7.68 (12H, m, other H); ^{13}C nmr (67.8 MHz in $CDCl_3$) δ =96.2, 117.2 124.2, 124.3, 124.7, 124.9, 125.7, 126.2, 127.1, 127.2, 127.5, 128.3, 128.5, 128.6, 129.4, 130.1, 130.2, 131.0, 131.1, 140.2, 141.7, 141.9, 150.3, 150.6, and 153.1. Found: m/z 453.0422. Calcd for $C_{25}H_{15}N_3S_3$: M, 453.0431.

13. 16: Blue violet needles ($CHCl_3$), mp >300 $^{\circ}$C; Uv (MeOH) 250, 322, 530(sh), and 570 nm, (MeOH + HCl) 258, 324, 424, 572(sh), 643, and 700(sh) nm; ^{1}H nmr (270 MHz in $CDCl_3$) δ =6.49 (1H, d, J=7.7 Hz), 6.74 (1H, t, J=7.3 Hz), 6.87 (1H, d, J=7.3 Hz), 6.88 (1H, t, J=7.7 Hz), 7.1-7.4 (6H, m), 7.55 (1H, d, J=8 Hz), 7.59 (1H, s, NH), and 7.70 (1H, d, J=8 Hz). Found: m/z 439.0257. Calcd. for $C_{24}H_{13}N_3S_3$: M, 439.0274.

14. 17: Violet crystal (MeOH), mp >300 $^{\circ}$C; Uv (MeOH) 254, 290, 484, and 583 nm; ^{1}H nmr (270 MHz in $CDCl_3$) δ =2.94 (3H, s, N-CH_3), 6.24 (1H, dd, J=8.0 and 1.5 Hz, H-4), 6.37 (1H, dd, J=8.0 and 1.5 Hz, H-1), 6.49 (1H, d, J=1.8 Hz, H-6), 6.62 (1H, td, J=8.0 and 1.5 Hz, H-2), 6.74 (1H, td, J=8.0 and 1.5 Hz, H-3), 7.35 (1H, br, NH), and 7.69 (1H, d, J=1.8 Hz, H-8); ms m/z 382 (M^+).

15. 18: Reddish violet solid; Uv (MeOH) 238, 288, 362, 489, and 544(sh) nm; ^{1}H nmr (270 MHz in $CDCl_3$) δ =2.95 (3H, s, Me), 4.28 (2H, br, NH_2), 6.24 (1H, dd, J=7.5 and 1.3 Hz, H-4), 6.33 (1H, d, J=1.5 Hz, H-8), 6.34 (1H, dd, J=5.6 and 1.3 Hz, H-1), 6.42 (1H, d, J=1.5 Hz, H-6), 6.62 (1H, td, J=6.9 and 1.3 Hz, H-2), 6.69 (1H, td, J=6.9 and 1.3 Hz, H-3) 6.80 (1H, td, J=6.9 and 1.3 Hz, H-5'), 6.83 (1H, dd, J=6.9 and 1.3 Hz, H-3'), 7.29 (1H, td, J=6.9 and 1.3 Hz, H-4'), 7.38 (1H, dd, J=6.9 and 1.3 Hz, H-6'), and 8.14 (1H, br, NH). Found: m/z 425.0216. Calcd for $C_{20}H_{16}ON_3SBr$: M, 425.0199.

16. 20: Blue violet crystal ($CHCl_3$-MeOH), mp 195-200 $^{\circ}$C; Uv (MeOH) 273, 323(sh), 357, 447, and 544 nm; ^{1}H nmr (270 MHz in $CDCl_3$) δ =3.43 (3H, s, CH_3), 6.11 (1H, s, H-7), 7.04 (1H, dd, J=8 and 1.5 Hz, H-9), 7.09 (1H, td, J=8 and 1.5 Hz), 7.11 (1H, dd, J=7 and 1.5 Hz), 7.18-7.30 (4H, m), 7.33-7.42 (3H, m), 7.70 (1H, dd, J=8 and 1.5 Hz), and 7.73 (1H, dd, J=8 and 1.5 Hz); ms m/z 448 (100), 434 (60), 433 (60), 402 (30), 401 (28), and 124 (20). Found: m/z 448.0817. Calcd for $C_{26}H_{16}N_4S_2$: M, 448.0817.

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