Reactions of Tetrasulfur Tetranitride with Tropolone and Its Several Halogeno Derivatives. Preparations of 4*H*-Cyclohepta[*c*][1,2,5]thiadiazol-4-ones, 6*H*-Cyclohepta[*c*][1,2,5]thiadiazol-6-one, and 7*H*-Cyclohepta-[1,2-*c*:3,4-*c'*]bis[1,2,5]thiadiazol-7-ones

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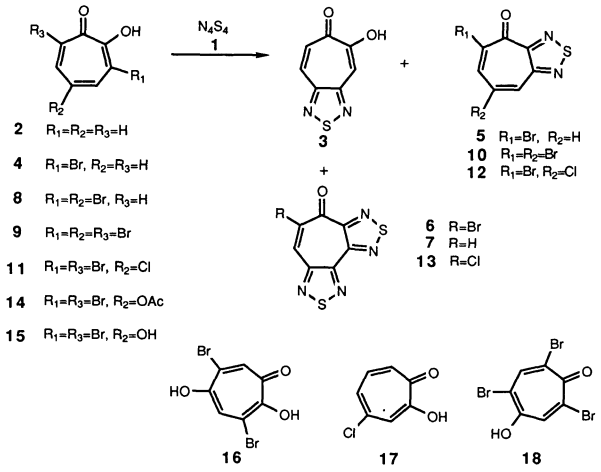
Synopsis. The reactions of tropolones with tetrasulfur tetranitride gave 4*H*-cyclohepta[*c*][1,2,5]thiadiazol-4-ones, 6*H*-cyclohepta[*c*][1,2,5]thiadiazol-6-one, and 7*H*-cyclohepta[1,2-*c*:3,4-*c'*]bis[1,2,5]thiadiazol-7-ones (9—56% yields) in one step. The yields of the products were not improved so much under high pressure and by the addition of a radical initiator.

Recently, we reported the reactions of tetrasulfur tetranitride (**1**) with alkyl- and alkylhalogeno phenols to give 2,1,3-benzothiadiazoles in a one-step procedure.[1] From the reactions of **1** with bromocatechols and bromoresorcinols, benzobis- and benzotris[1,2,5]thiadiazoles were prepared.[2] Dihydroxynaphthalene derivatives also gave the corresponding naphtho[1,2,5]thiadiazoles.[3] The 1,2,5-thiadiazole ring system was converted by reduction to 1,2-diamino-, 1,2,3,4-tetraamino-, and hexaaminobenzenes[2] and also used as a building unit for preparation of electron acceptors and electron donors.[4,5] In these regards, since the reaction of **1** was limited to benzenoids, we extended the reaction of **1** to troponoids to prepare new heterocyclic troponoids.

When a toluene solution of tropolone (**2**) and **1** was refluxed for 9 h, a single product (**3**) was obtained after silica-gel chromatography. The ^{1}H NMR spectrum of **3** showed three olefinic proton signals, a singlet at δ=7.76 and an *AB* quartet with a large magnitude of vicinal spin-spin coupling constant (J=12.5 Hz) at δ=7.29 and 8.10, confirming that the seven-membered ring is maintained. Therefore, the structure of **3** can be identified to be 5-hydroxy-6*H*-cyclohepta[*c*][1,2,5]-thiadiazol-6-one. Since we had previously experienced that the yields of thiadiazoles are frequently improved by the use of halogeno derivatives,[1] we then turned our attention to reactions with halogeno tropolones. In contrary to **2**, the reaction with 3-bromotropolone (**4**) was somewhat complicated and gave three products (**5**—**7**), of which **5** was a 1:1-condensation product and the others were 2:1-condensates. The NMR spectrum of **5** showed two doublet signals at δ=8.14 (J=9.5 Hz)



Scheme 1.

Table 1. Reaction Conditions and Product Yields of Tropolones with **1**

Substrate (Ratio)	Temp/°C	Press/bar	Time/h	Additive	Products/% 5	6	7	10
4 (1:1)	110	1	14	—	4	2	26	
4 (1:2)	110	1	10	—	8	7	25	
4 (1:2.6)	110	1	10	—	11	9	18	
4 (1:3)	110	1	14	V-40		15	28	
4 (1:3)	110	1	48	—		14	26	
4 (1:5)	110	1	21	V-40	10	6	16	
4 (1:5)	110	1	21	—	2	2	10	
4 (1:5)	110	1	48	—		16	31	
9 (1:2)	110	1	9	—		21		35
9 (1:3)	110	1	21	—		36		
9 (1:3)	100	3000	10	—		47		
9 (1:3)	110	1	12	V-40		36		12
9 (1:3)	100	3000	10	V-40		41		12
9 (1:3.5)	110	1	16	V-40		40		8
9 (1:3)	110	1	48	—		44		

and 7.78 (J=11.7 Hz) and a doublet of doublets signal at 6.81. For the bromine-containing minor product, **6**, a singlet signal appeared at δ=8.84, while the bromine-free product, **7**, showed an AB quartet (J=13.0 Hz). The yields of **6** and **7** were improved to some extent when **1** was used in excess. The results are summarized in Table 1. Compounds **6** and **7** were also obtained from the reactions of 3,5-dibromotropolone (**8**) with **1** in 24 and 22% yields, respectively. From 3,5,7-tribromotropolone (**9**), another bromine-containing 1:1-condensate (**10**) was obtained in 21% yield together with **6** in 35% yield. Similarly, 3,7-dibromo-5-chlorotropolone (**11**) gave a dihalogeno 1:1-condensate (**12**) and an unseparable mixture of **6** and a chlorine-containing product (**13**). The results concerning the reaction of **9** with **1** under various conditions are tabulated in Table 1.

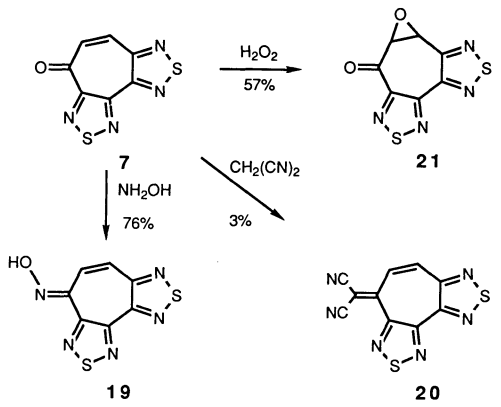
As shown in Table 1, the yields of products did not show much improvement, either under a high pressure of 3000 bar or by the addition of V-40, a radical initiator.

Furthermore, reactions with five halotroponoids (**14**—**18**) were carried out. No identified product has, however, been detected.

As an extention, the preparation of the tris[1,2,5]-thiadiazole derivative was investigated. No expected product was obtained from the reactions of **6** and **7** with **1** under similar conditions.

To check the reactivity of the carbonyl group of **7**, a couple of reactions with carbonyl reagents were attempted: Treatment with hydroxylamine hydrochloride and malononitrile afforded condensates (**19** and **20**) in 76 and 3% yields, respectively. The reaction of the carbonyl group in **7** with a bulky dicyanomethylene group was sterically unfavorable.

In order to introduce oxygen functions into the seven-membered conjugated system, the hydrogen peroxide-oxidation of **7** was carried out, and the epoxide (**21**) was obtained in 57% yield. However, an attempt to convert the epoxide to a hydroxy ketone, corresponding "tropolone", has so far been unsuccessful.



Scheme 2.

Although the yields of condensates between tropolones and tetrasulfur tetranitride were not high, the present method was valuable with respect to a one-step procedure for new heterocyclic troponoids.

Experimental

Reaction of Tropolone (2) with 1. A toluene solution (10 cm³) of **2** (174 mg) and **1** (287 mg) was stirred at room temperature for 1 h and refluxed for 9 h. The mixture was cooled and the solvent was evaporated. The residue was chromatographed on a silica-gel column to give 17.1 mg (9%) of **3** and 43.8 mg (25%) of **2**.

3: Brownish crystals (benzene), mp 146—148 °C (decomp); ^{1}H NMR[6] δ=7.29 (1H, d, J=12.5 Hz), 7.76 (1H, s), 8.10 (1H, d, J=12.5 Hz), and 8.10 (1H, s): ^{13}C NMR δ=108.2, 129.9, 132.7, 154.7, 155.0, 157.1, and 181.0; IR (KBr) 3290, 1632, 1592, 927, 883, 875, and 857 cm^{-1}; MS m/z (%) 180 (M^+, 41), 152 (base), 124 (40), 97 (17), 80 (21), 71 (15), and 52 (33).

Found: m/z 179.9992. Calcd for $C_7H_4N_2O_2S$: M, 179.9993.

Reaction of 3-Bromotropolone (4) with 1. a) A toluene solution (8 cm³) of **4** (150 mg) and **1** (166 mg) was refluxed for 14 h. The mixture was purified by silica-gel chromatography to give 7.8 mg (4%) of **5**, 4.3 mg (2%) of **6**, and 43.3 mg (26%) of **7**.

5: Pale yellow crystals (methanol), mp 160—161 °C (decomp); ^{1}H NMR δ=6.81 (1H, dd, J=11.7, 9.5 Hz), 7.78 (1H, d, J=11.7 Hz), and 8.14 (1H, d, J=9.5 Hz); ^{13}C NMR δ=126.5, 128.8, 135.9, 138.8, 155.7, 157.5, and 172.3; IR (KBr) 1637, 1615, 880, 845 and 815 cm^{-1}; UV (MeOH) 222 (ε 11900, sh), 231.6 (12800), 266.8 (11000), 301 (2200, sh), and 370.8 nm (6300); MS m/z (%) 244 (M^++2, 89), 242 (M^+, 87), 216 (61), 214 (57), 163 (23), 135 (base), 108 (24), 76 (24), and 50 (19).

Found: C, 34.82; H, 1.33; N, 11.68%. Calcd for $C_7H_3N_2OSBr$: C, 34.59; H, 1.24; N, 11.52%.

6: Yellow crystals (chloroform–hexane), mp 236—238 °C (decomp); ^{1}H NMR δ=8.84 (1H, s); ^{13}C NMR δ=131.9, 133.6, 149.9, 150.0, 153.0, 153.6, and 172.1; IR (KBr) 1645, 1390, 1265, 1105, 895, 880, and 860 cm^{-1}; UV (MeOH) 207 (ε 19200, sh), 220 (18500, sh), 231.6 (19400), 266.4 (16000), 300 (4000, sh), and 369.6 nm (9000); MS m/z (%) 302 (M^++2, base), 300 (M^+, 92), 274 (63), 272 (59), 221 (30), 193 (71), 161 (20), 83 (48), and 64 (39).

Found: C, 28.02; H, 0.40; N, 18.55%. Calcd for $C_7H_4N_4OS_2Br$: C, 27.92; H, 0.33; N, 18.61%.

7: Yellow crystals (chloroform–hexane), mp 168—170 °C (decomp); ^{1}H NMR δ=7.10 (1H, d, J=13.0 Hz) and 7.96 (1H, d, J=13.0 Hz); ^{13}C NMR δ=131.2, 132.6, 150.8, 151.1, 154.4, 155.9, and 178.1; IR (KBr) 1635, 1420, 1095, 875, 870, and 855 cm^{-1}; UV (MeOH) 205.6 (ε 18500), 243.2 (9700), 254 (8100, sh), 286.4 (15500), and 314.0 nm (15400); MS m/z (%) 222 (M^+, 8), 194 (53), 142 (33). 116 (26), 84 (49), 58 (73), 52 (80), and 46 (base).

Found: C, 37.63; H, 0.71; N, 25.01%. Calcd for $C_7H_2N_4OS_2$: C, 37.83; H, 0.91; N, 25.21%.

b) A toluene solution (150 cm³) of **4** (1.04 g) and **1** (4.76 g) was refluxed for 48 h. Silica-gel chromatography gave 248 mg (16%) of **6** and 356 mg (31%) of **7**.

Reaction of 3,5-Dibromotropolone (8) with 1. A toluene solution (15 cm³) of **8** (68.8 mg) and **1** (136 mg) was refluxed for 12 h to give 18.2 mg (24%) of **6** and 12 mg (22%) of **7**.

Reaction of 3,5,7-Tribromotropolone (9) with 1. a) A toluene solution (7 cm³) of **9** (193 mg) and **1** (219 mg) was refluxed for 7.5 h. Silica-gel chromatography gave 37.2 mg (21%) of **10** and 57.9 mg (35%) of **6**.

10: Yellow crystals (benzene), mp 194—196 °C (decomp); ^{1}H NMR δ=8.20 (1H, d, J=1.8 Hz) and 8.37 (1H, d, J=1.8 Hz); ^{13}C NMR δ=122.6, 130.3, 134.7, 142.5, 144.0, 156.0, and 171.5; IR (KBr) 1639, 920, 880, and 850 cm^{-1}; UV (MeOH) 212.0 (ε 15100), 232.4 (17000), 268.0 (16000), 308 (2500, sh), and 375.2 nm (7500); MS m/z (%) 324 (M^++4, 53), 322 (M^++2, base), 320 (M^+, 50), 296 (32), 294 (63), 292 (31), 215 (45), 213 (44), 150 (58), 134 (34), 76 (26), 57 (30), and 50 (25).

Found: C, 26.39; H, 0.72; N, 8.51%. Calcd for $C_7H_2N_2OSBr_2$: C, 26.11; H, 0.63; N, 8.70%.

b) A toluene solution (8 cm³) of **9** (50.1 mg) and **1** (79 mg) was heated at 100 °C for 10 h under 3000 bar. Silica-gel chromatography gave 20 mg (47%) of **6**.

Reaction of 3,7-Dibromo-5-chlorotropolone (11) with 1. A toluene solution (10 cm³) of **11** (203 mg) and **1** (264 mg) was refluxed for 9 h. Silica-gel chromatography of the mixture gave 41.8 mg (23%) of **12** and 46.2 mg of a mixture of **6** (21%) and **13** (9%).

12: Brown needles (benzene), mp 134—136 °C (decomp); ^{1}H NMR δ=7.97 (1H, d, J=1.8 Hz) and 8.23 (1H, d, J=1.8 Hz); IR (KBr) 1640, 1600, 1360, 930, 880, and 855 cm^{-1}; MS m/z (%) 280 (M^++4, 28), 278 (M^++2, base), 276 (M^+, 72), 252 (19), 250 (61), 248 (46), 234 (11), 232 (15), 171 (23), 169 (63), and 50 (21).

Found: m/z 275.8781 (M^+), 277.8772 (M^++2), and 279.8710 (M^++4). Calcd for $C_7H_2N_2OClBr$: 275.8760 (M), 277.8740 (M+2), and 279.8710 (M+4).

Attempted Reactions of Halotroponoids (14+18) with 1. A toluene solution of a halotroponoid and **1** was refluxed for 9 h. No expected product was detected.

Reaction of 6 with 1. A toluene solution (4 cm³) of **6** (10 mg) and **1** (9.2 mg) was refluxed for 11 h. Compound **6** (10 mg) was recovered unchanged.

Reaction of 7 with 1. A toluene solution (8 cm³) of **7** (13.6 mg) and **1** (13.5 mg) was refluxed for 13 h. Compound **7** (13.4 mg) was recovered unchanged.

Reaction of 7 with Hydroxylamine Hydrochloride. To an ethanol solution (3 cm³) of **7** (20.2 mg) was added an aqueous solution (3 cm³) of hydroxylamine hydrochloride (6.9 mg) in the presence of AcONa (12.7 mg) and the mixture was refluxed for 5.5 h. The solvent was evaporated and the residue was washed with water to give 16.4 mg (76%) of **19**.

19: Yellow crystals (diethyl ether), mp 194-197 °C (decomp); IR (KBr) 3342, 3246, 1627, 1032, and 953 cm^{-1}; MS m/z (%) 237 (M^+, base) and 207 (61).

Found: m/z 236.9782. Calcd for $C_7H_3N_5OS_2$: M, 236.9779.

Reaction of 7 with Malononitrile. To an anhydrous dichloromethane solution (7 cm³) of **7** (78.3 mg) and malononitrile (34.9 mg) were added $TiCl_4$ (0.2 cm³) and then anhydrous pyridine (0.3 cm³) at 0 °C. The mixture was stirred at room temperature for 5 h. The mixture was diluted with a 10% aqueous HCl solution and extracted with AcOEt. After evaporating the solvent, the residue was purified by silica-gel chromatography to give 2.6 mg (3%) of **20**.

20: Yellow crystals (benzene), mp 188—190 °C (decomp); ^{1}H NMR δ=7.51 (1H, d, J=12.8 Hz) and 7.70 (1H, d, J=12.8 Hz); IR (KBr) 2216, 1615, and 1526 cm^{-1}; UV (MeOH) 208.8 (ε13400), 265 (6200, sh), 271.2 (6700), 308.0 (9400), 351 (8400, sh), 366 (9300, sh), and 387.2 nm (10300); MS m/z (%) 270 (M^+, base), 244 (12), 218 (9), 85 (11), 83 (24), and 63 (10).

Found: m/z 269.9786. Calcd for $C_{10}H_2N_6S_2$: M, 269.9782.

Epoxidation of 7. To an anhydrous DMSO solution (5 cm³) of **7** (50.6 mg) were added 35% H_2O_2 (2 cm³) and $(n\text{-Bu})_4NF$ (115 mg) and the mixture was stirred at room temperature for 13 h. The mixture was poured into water and extracted with AcOEt. Silica-gel chromatography of the residue gave 30.9 mg (57%) of **21**.

21: Colorless crystals (chloroform-hexane), mp 177—178 °C; ^{1}H NMR δ=4.44 (1H, d, J=4.4 Hz) and 5.02 (1H, d, J=4.4 Hz); ^{13}C NMR δ=55.2, 64.5, 149.1, 150.5, 154.7, 155.0, and 188.7; IR (KBr) 1703, 1030, 885, 842, and 819 cm^{-1}; MS m/z (%) 238 (M^+, 11), 210 (10), 138 (10), 86 (34), 71 (30), 58 (47), and 46 (base).

Found: C, 35.28; H, 0.76; N, 23.46%. Calcd for $C_7H_2N_4O_2S_2$: C, 35.29; H, 0.85; N, 23.52%.

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