tributyltin hydride were made up in benzene to the concentrations reported in Table I and treated as described above for 3-Cl. After the workup, ^1H NMR spectra in chloroform showed that the products were mixtures of 30-H and 31-H. The portion of each of the spectra between δ 3.5 and 4.5 was expanded, and ratios of 30-H to 31-H were determined by the cut and weigh method of integration. Data and results of computations of rate constant ratios are given in Table I.

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Registry No. 2-H, 13351-27-4; 3-Cl, 72182-74-2; 3-H, 79134-73-9; dechloro-3-H, 7322-46-5; 5-D, 79134-74-0; 5-H, 79134-75-1; dechloro-5-H, 61836-97-3; 7-OH, 72204-35-4; 7-OCS_2CH_3, 79134-76-2; 8-OH, 72182-84-4; 8-OMe, 79134-77-3; 8-OCS_2CH_3, 79199-35-2; 15-OH, 64600-13-1; 15-OCS_2CH_3, 79134-78-4; 23-Cl, 20852-67-9; 23-H, 68661-36-9; 24-Cl, 64600-09-5; 24-D, 79134-79-5; 24-H, 68661-37-0; 25-Cl, 64626-00-2; 25-D, 79199-36-3; 26-Cl, 20851-78-9; 30-Cl, 6476-45-5; 30-H, 5675-64-9; 30-OH, 1521-59-1; 30-OCS_2CH_3, 79134-80-8; 31-H, 951-20-2; *exo*-4-deuterio-2,3-benzobicyclo[3.2.1]octa-2,6-diene, 79134-81-9.

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Notes

Approach to the Synthesis of Symmetrically Substituted Thianthrenes

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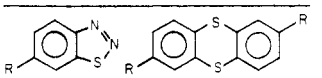
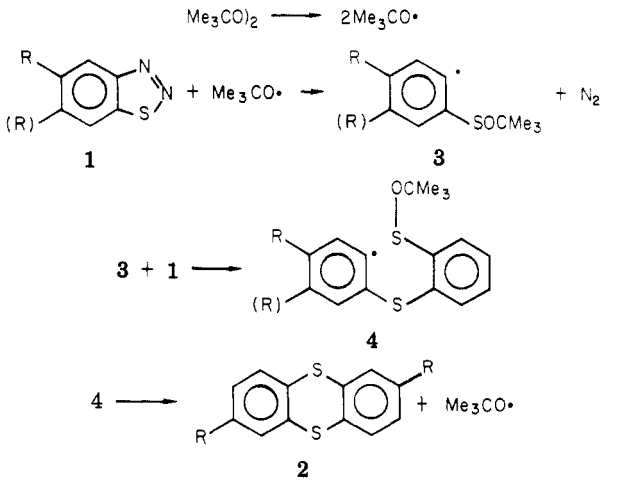
A number of thianthrene syntheses are available in the literature; thus, thianthrene can be obtained from reaction of benzene with sulfur monochloride,[1] from *o*-dichlorobenzene and H_2S at high temperature,[2] or by heating diphenyl disulfide in the presence of $AlCl_3$.[3] As for substituted thianthrenes, apart from electrophilic substitution of the thianthrene nucleus,[1b] applicable only in few cases, their syntheses are accomplished by reaction of the appropriate bis(*o*-iodophenyl) disulfide with copper,[4] by thermal cyclization of substituted 2-mercaptophenyl phenyl sulfide,[5] and by aprotic diazotization of substituted 2-(phenylthio)phenyl 2-aminophenyl sulfide.[6]

The advantage of these methods derives from the possibility of obtaining asymmetrically substituted thianthrenes, but they suffer from the unavailability of starting materials. One of the oldest and most versatile reactions for synthesis of symmetrically substituted thianthrenes is the thermal elimination of nitrogen from 1,2,3-benzothiadiazole[7] at 200–220 °C, but, as we have recently reported,[8] this reaction leads to a complex mixture, from which thianthrene has to be separated by column chromatography and can be isolated only in ca. 20% yield.

Table I

R				
				
1	2	mp, °C	yield, %	method
H	H	157	65, 85	A
6-Cl	Cl	185–186	70	A
5-CO_2Me	CO_2Me	185–186	80	B
5-OMe	OMe	134–135	35	A
5-OMe	OMe	134–135	75	B

Scheme I



We now report a new method of synthesis of symmetrically substituted thianthrenes from the appropriate 1,2,3-benzothiadiazole (1). In this case nitrogen elimination from 1 is induced by *tert*-butoxy radicals at a relatively low temperature (80–110 °C), in agreement with the general behavior exhibited by 1 toward radical species.[9] The reaction is carried out by refluxing a benzene solution of 1 and di-*tert*-butyl peroxide for ca. 18 h (method A) or by refluxing a solution of 1 in di-*tert*-butyl peroxide for ca. 10 h (method B); thianthrene (2) is obtained as the only identified product in good yield (see Table I) and with a

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(4) H. J. Berber and S. Smiles, *J. Chem. Soc.*, 1141 (1928).

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high degree of purity. Attempts to obtain 1,8-dimethylthianthrene (2, R = Me) from 7-methyl-1,2,3-benzothiadiazole (1, R = Me) failed; in fact, 1 (R = Me) did not react at lower temperature (method A), while at higher temperature (method B) the products were unidentifiable. As for the reaction pathway leading to thianthrene 2, a mechanism analogous to that previously reported for the reaction of 1 with methyl, phenyl, and arylthio radicals,[9] aryl nitrenes,[10] and diphenylcarbenes[11] can be invoked also in this case; attack of *tert*-butoxy radical on the sulfur atom of 1 would in fact lead to decomposition of the heterocyclic nucleus with nitrogen loss and formation of the radical intermediate 3 (Scheme I). Reaction of 3 with a further molecule of 1 would afford 4 and then 2 by intramolecular homolytic substitution at the sulfur atom.

Experimental Section

1,2,3-Benzothiadiazole[7b] and 6-chloro-[13] and 5-methoxy-1,2,3-benzothiadiazole[14] were prepared as described in the literature. Reaction products, thianthrene and 2,7-dichloro-,[6] 2,7-dimethoxy-,[8] and 2,7-bis(carbomethoxy)thianthrene,[12] were identified by mixture melting points with authentic specimens. Di-*tert*-butyl peroxide[15] is commercially available.

7-Methyl-1,2,3-benzothiadiazole. To a solution of the bis(2-methyl-6-nitrophenyl) disulfide[16] (10 g) in hot acetic acid (50 mL) were added in small portions powdered zinc (20 g) and concentrated hydrochloric acid (40–50 mL). The mixture was refluxed for 1 h and then cooled; addition of a solution of sodium acetate (30 g) in water (400 mL) led to formation of a precipitate, which was filtered, washed with water and EtOH (10 mL), and then dried. The obtained zinc salt of 2-methyl-6-aminothiophenol was then dissolved in boiling concentrated hydrochloric acid; when the resulting solution was cooled, the 2-mercapto-3-methylaniline hydrochloride (6.3 g, 60% yield; mp 196–197 °C) was isolated. This crude product was suspended in water (10 mL) containing 7 mL of hydrochloric acid and diazotized with 2.7 g of sodium nitrite at 5–10 °C. Extraction of the reaction mixture and purification of the crude product on a silica gel column gave the title compound: 75% yield; mp 33–34 °C; bp 157 °C (17 mm); mass spectrum, *m/e* 150 ($M^{+\cdot}$), 122, 78, 77. Anal. Calcd for $C_7H_6N_2S$: C, 55.9; H, 4.02; N, 18.67; S, 21.37. Found: C, 55.8; H, 3.91; N, 18.55; S, 21.04.

5-(Carbomethoxy)-1,2,3-benzothiadiazole. A solution of 2-nitro-4-(carbomethoxy)chlorobenzene[17] (18.3 g) in EtOH (45 mL) was treated with a solution of sodium disulfide, obtained by dissolving 1.6 g of sulfur in a water solution of $Na_2S{\cdot}9H_2O$ (12 g). The mixture was refluxed for 3 h and then poured into water; filtration of the reaction mixture gave crude bis[2-nitro-4-(carbomethoxy)phenyl] disulfide: 17.6 g; mp 205–206 °C. This product was dissolved in methylene chloride (150 mL) and reduced by catalytic hydrogenation with 10% Pd/C as the catalyst. Filtration of the catalyst and evaporation of the solvent gave crude bis[2-amino-4-(carbomethoxy)phenyl] disulfide (13.6 g), which was suspended in 25 mL of water containing 19 mL of concentrated hydrochloric acid and diazotized with 5.7 g of sodium nitrite at 5–10 °C. Extraction of the reaction mixture and purification of the crude residue on a silica gel column gave the title product: 10 g (70% yield); mp 112–113 °C (lit.[18] mp 102–106 °C); mass spectrum, *m/e* 194 ($M^{+\cdot}$), 166, 135; IR 1725 (γ_{max}), 1290 cm^{-1}.

Synthesis of Thianthrenes. Method A. A solution of the appropriate benzothiadiazole (0.05 mol) and di-*tert*-butyl peroxide (10 mL) in benzene (20 mL) was refluxed for ca. 18 h. The thianthrene, which crystallized on cooling of the reaction mixture was collected and washed with *n*-pentane. With 6-methoxy-1,2,3-benzothiadiazole the reaction is very slow; chromatography of reaction mixture on a silica gel column with *n*-pentane/ether (90:10) as eluant gave 2,7-dimethoxythianthrene (35%) together with starting materials (60%). With the 5-(carbomethoxy) and 7-methyl derivatives the reaction failed; evaporation of the solvent gave unchanged starting product.

Method B. A solution of the appropriate benzothiadiazole (0.05 mol) in di-*tert*-butyl peroxide (25 mL) was refluxed for ca. 10 h. The thianthrene crystallized by cooling of the reaction mixture was filtered and washed with *n*-pentane. The reaction failed with the 7-methyl derivative; in this case a tarry, unidentified product was formed in 100% yield.

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Registry No. 1 (R = H), 273-77-8; 1 (R = Cl-6), 23644-01-1; 1 (R = CO_2Me-5), 23616-15-1; 1 (R = OMe-5), 31860-05-6; 2 (R = H), 92-85-3; 2 (R = Cl), 60420-80-6; 2 (R = CO_2Me), 65178-26-9; 2 (R = OMe), 54815-69-9; 7-methyl-1,2,3-benzothiadiazole, 78805-01-3; bis(2-methyl-6-nitrophenyl)disulfide, 56202-21-2; 2-methyl-6-aminothiophenol Zn, 78804-25-8; 2-mercapto-3-methylaniline hydrochloride, 78805-02-4; 2-nitro-4-(carbomethoxy)chlorobenzene, 14719-83-6; bis[2-nitro-4-(carbomethoxy)phenyl]disulfide, 35350-37-9; bis[2-amino-4-(carbomethoxy)phenyl]disulfide, 78822-61-4; di-*tert*-butyl peroxide, 110-05-4.

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(15) Di-*tert*-butyl peroxide is relatively safe to handle since it decomposes very slowly at ordinary temperatures and can be distilled or refluxed at atmospheric pressure without hazard. However, it is advisable to work only in small scale and to use a protective screen during refluxing.
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Synthesis of Isoquinolines from Indenes

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The report by Miller and Frincke[1] of their synthesis of isoquinolines from indenes by ozonolysis followed by treatment of the intermediates with ammonia prompts us to report the results of a related investigation. Our rationale for seeking a route to isoquinolines via indenes was very similar to Miller and Frincke's. We chose to use osmium tetraoxide and sodium metaperiodate for the oxidation step, a procedure that also has precedent, having been used in a synthesis of illudine by Woodward and Hoye.[2] However, the latter authors met with limited success when they used the procedure with a catalytic amount of osmium tetraoxide[3] and found it necessary to use a stoichiometric quantity of this reagent. At the outset we had been aware that only catalytic amounts of osmium tetraoxide should be used if the method were to be of general utility. It had been our hope that we could find conditions under which the synthesis could be carried out in one operation by having all of the reactants, the indene, sodium metaperiodate, a catalytic amount of osmium tetraoxide, and ammonia, present together in solution. We did, indeed, succeed in converting indene to isoquinoline in 67% yield by this procedure, but the reaction proceeded very slowly, and several days were required for the con-

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