

From the potassium hydroxide extract was recovered 3.5 g. (54%) of *n*-octylnitramine. From the carbon tetrachloride solution was obtained 1.7 g. of liquid whose infrared spectrum showed nitrate ester absorption.

When dinitrogen pentoxide (0.065 mole) was added to a mixture of *n*-octylamine (17.0 g., 0.13 mole) and *n*-octylnitramine (11.5 g., 0.066 mole) in the above manner, there was obtained 6.5 g. of *n*-octylnitramine, 2.2 g. of the unidentified solid, and 7.0 g. of residue whose infrared spectrum indicated it was mainly *n*-octyl nitrate.

Dinitrogen pentoxide, triethylamine and diisopropylamine. A solution of 0.070 mole of dinitrogen pentoxide in 200 ml. of carbon tetrachloride was added to 20.2 g. (0.20 mole) of triethylamine in 150 ml. of carbon tetrachloride at -30° . The solution turned red. After complete addition of the dinitrogen pentoxide, 20.2 g. (0.20 mole) of diisopropylamine was added dropwise. The solution was allowed to warm to room temperature and then washed with water, 10% hydrochloric acid, and again with water. After drying over magnesium sulfate, the carbon tetrachloride was removed to leave only 0.2 g. of residue. Similar results were obtained when the dinitrogen pentoxide-triethylamine solution was allowed to warm to 20° before addition of the diisopropylamine, and when the dinitrogen pentoxide was added to a triethylamine-diisopropylamine mixture.

Dinitrogen pentoxide, pyridine and diisopropylamine. A solution of 3.3 ml. (0.041 mole) of pyridine in 50 ml. of methylene chloride was cooled to -20° and 0.037 mole of dinitrogen pentoxide in 30 ml. of methylene chloride was added dropwise. A white solid precipitated. The mixture was stirred 5 min. at -20° after addition of the dinitrogen pentoxide, and then 11.2 ml. (0.08 mole) of diisopropylamine was added dropwise. The reaction mixture slowly turned a deep red. When the reaction mixture had warmed to 0° , 10% hydrochloric acid was added and the organic layer was then separated and washed with water. Evaporation of the methylene chloride left 1.5 g. of a dark residue, the infrared spectrum of which indicated no secondary nitramine was present.

Dinitrogen pentoxide, 2-chloropyridine and diisopropylamine. When dinitrogen pentoxide (0.045 mole) in methylene chloride (30 ml.) was added to 2-chloropyridine (0.10 mole) in 60 ml. of methylene chloride at -20° there was a yellowing of the solution but no solid precipitated. Diisopropylamine (0.10 mole) was then added, and the reaction worked up as in the case of pyridine. There was no evidence for the formation of diisopropyl nitramine.

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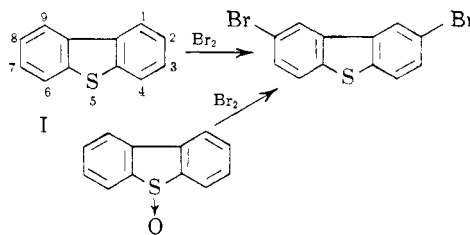
Bromination in the Thianthrene System

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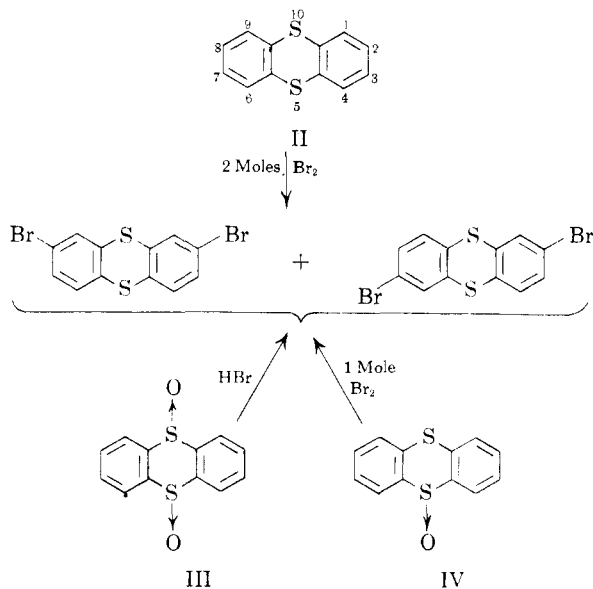
Received August 21, 1957

Successful bromination of heterocycles is of significance in synthetic organic chemistry since the bromo derivatives can be converted to the corresponding carboxylic acids, boronic acids, silanes, amines, and phenols through a halogen-metal interconversion reaction followed by treatment with carbon dioxide, tri-*n*-butyl borate, chlorotriphenylsilane, methoxylamine, and oxygen, respectively. Dibenzothiophene (I) brominates in the 2,8-posi-

tions.¹ The 2,8-dibromodibenzothiophene is also obtained by the action of bromine on dibenzothiophene-5-oxide,² a reaction in which the sulfoxide undergoes bromination accompanied by reduction.



Thianthrene (II) reacts³ with a molar equivalent of bromine to give a fair yield of 2-bromothianthrene, and with two molar equivalents of bromine to give a high yield of a mixture of 2,7- and 2,8-dibromothianthrene. The isomeric mixture was also obtained in high yields by the action of hydrobromic acid on thianthrene-5,10-dioxide (III) and of bromine on thianthrene-5-oxide (IV).³ The product could not be separated into the two isomers probably due to the very similar physical properties of the two dibromothianthrenes. Oxidation of the mixture with hydrogen peroxide yielded another product which also melted over a wide range after several recrystallizations but gave an analysis corresponding to a dibromothianthrene-5,5,10,10-tetroxide.³



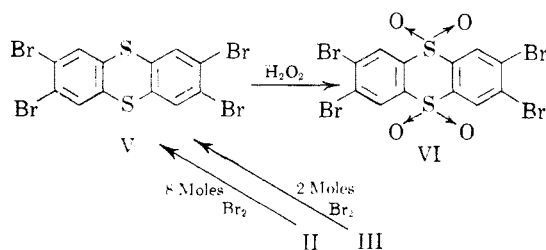
In the present investigation we found additional support for considering the dibromothianthrene as a mixture of 2,7- and 2,8-dibromothianthrene. The thianthrene molecule has the 2-, 3-, 7-, and 8-posi-

(1) C. R. Neumoyer and E. D. Amstutz, *J. Am. Chem. Soc.*, **69**, 1920 (1947).

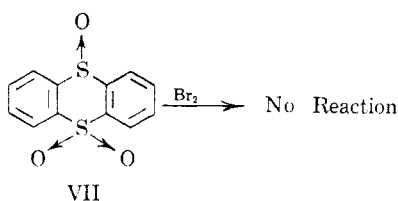
(2) H. Gilman and R. K. Ingham, *J. Am. Chem. Soc.*, **73**, 4982 (1951).

(3) H. Gilman and D. R. Swayampati, *J. Am. Chem. Soc.*, **77**, 5944 (1955).

tions *para* to one or the other of the two sulfur atoms. Considering that the bromination should occur at one or more of the *para* positions,^{1,3,4} it is seen that the treatment of II with bromine should give one monobromo-, two dibromo-, one tribromo- and one tetrabromothianthrene. Hence, in the formation of a tri- or tetrabromothianthrene the difficulty of obtaining a sharp-melting product would not be encountered. We found that II and an excess of bromine gave a 41% yield of 2,3,7,8-tetrabromothianthrene (V), melting at 291–292°. The same product was also obtained in 28% yield by the action of two molar equivalents of bromine on III. Oxidation of V with hydrogen peroxide gave an excellent yield of 2,3,7,8-tetrabromothianthrene-5,5,10,10-tetroxide (VI), melting at 357–358° with decomposition.



Thianthrene-5-oxide,³ like other sulfoxides such as dibenzothiophene-5-oxide² and 10-ethylphenothiazine-5-oxide,⁴ is reduced during the process of bromination. Thianthrene-5,5-dioxide, a sulfone, does not react with bromine.³ It was considered interesting to study the action of bromine on thianthrene-5,5,10-trioxide (VII), which has both the sulfoxide and the sulfone groups. Bromine was found to have no action on VII when a mixture of the two was refluxed for a period of 16 hours.



EXPERIMENTAL⁵

Thianthrene (II) and bromine. To 6.48 g. (0.03 mole) of II⁶ was added 38.4 g. (0.24 mole) of bromine. The reaction commenced immediately with the evolution of hydrogen bromide. To the dark solid was added 20 ml. of glacial acetic acid and the resulting red suspension was refluxed for 16 hr. The mixture was treated with a dilute solution of sodium thiosulfate to remove the excess bromine. The white product was filtered, washed with water, and dried to give 15.32 g. of crude 2,3,7,8-tetrabromothianthrene (V) melting over the range 247–264°. Two recrystallizations from xylene (Norit-A) yielded 6.56 g. (41%) of nearly pure V melting

(4) H. Gilman and J. Eisch, *J. Am. Chem. Soc.*, **77**, 3862 (1955).

(5) All melting points reported herein are uncorrected.

(6) K. Fleischer and J. Stemmer, *Ann.*, **422**, 265 (1921).

at 288–290°. The analytical sample, obtained by an additional recrystallization from xylene, melted at 291–292°.

Anal. Calcd. for $\text{C}_{12}\text{H}_4\text{Br}_4\text{S}_2$: Br, 60.08; S, 12.03. Found: Br, 59.72, 59.53; S, 12.02.

Thianthrene-5,10-dioxide (III) and bromine. To 1.5 g. (0.006 mole) of the α -form⁷ of III⁸ was added 2 ml. of bromine. To the resulting dark solid was added 5 ml. of glacial acetic acid and the solution was refluxed for 5 hr. A crystalline product began to crystallize out soon after the solvent began to reflux. At the end of the reaction period the mixture was cooled and treated with a dilute solution of sodium thiosulfate to remove the unused bromine. The white product was filtered, washed with water, and dried to give 3.35 g. of the crude V. Successive recrystallizations from chloroform and xylene yielded 0.9 g. (28%) of pure V melting at 291–292°. A mixture of this product with that obtained from II and bromine melted undepressed.

2,3,7,8-Tetrabromothianthrene-5,5,10,10-tetroxide (VI). To a hot suspension of 2.13 g. (0.004 mole) of V in 50 ml. of glacial acetic acid was added a solution of 5 ml. of 30% hydrogen peroxide in 20 ml. of glacial acetic acid and the suspension was refluxed for 4 hr. The mixture was cooled and the white product was filtered and dried to give 2.25 g. (95%) of VI melting at 357–358° with decomposition.

Anal. Calcd. for $\text{C}_{12}\text{H}_4\text{Br}_4\text{O}_4\text{S}_2$: Br, 53.63; S, 10.73. Found: Br, 52.99, 52.91; S, 10.63, 10.61.

Thianthrene-5,5,10-trioxide (VII) and bromine. A mixture of 2.64 g. (0.01 mole) of VII,³ 2 ml. of bromine, and 2 ml. of glacial acetic acid was refluxed for 16 hr. The excess bromine was destroyed with a dilute solution of sodium thiosulfate. The white product was filtered, washed with water, and dried to yield 2.52 g. (95%) of crude VII melting over the range 210–221°. Recrystallization from glacial acetic acid yielded 2.14 g. (81%) of pure VII melting at 221.5–222.5°. A mixture of the product with authentic VII³ melted undepressed.

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(7) E. Bergmann and M. Tschudnowsky, *Ber.*, **65**, 457 (1932).

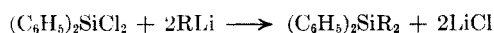
(8) K. Fries and W. Vogt, *Ber.*, **44**, 756 (1911).

Tetrasubstituted Higher Aliphatic and Phenyl Silanes

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Received Aug. 23, 1957

We wish to report the synthesis and physical properties of a number of new tetra-substituted silanes prepared in connection with a study in this laboratory of the higher aliphatic silanes. These compounds, Table I, were prepared by treatment of a slight excess of a chlorosilane with an organolithium compound according to the usual procedure.



The intermediate organolithium compounds were obtained directly by the action of lithium on *n*-octyl-, 2-octyl-, 2-ethylhexyl- and 2-cyclohexylethylbromides in yields of 87, 76, 64 and 88%, respectively.