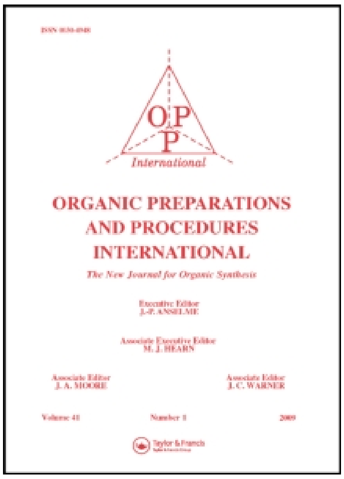

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LEWIS ACID CATALYZED PREPARATION OF TETRAMETHYLHEXATHIOADAMANTANE

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LEWIS ACID CATALYZED PREPARATION OF TETRAMETHYLHEXATHIOADAMANTANE

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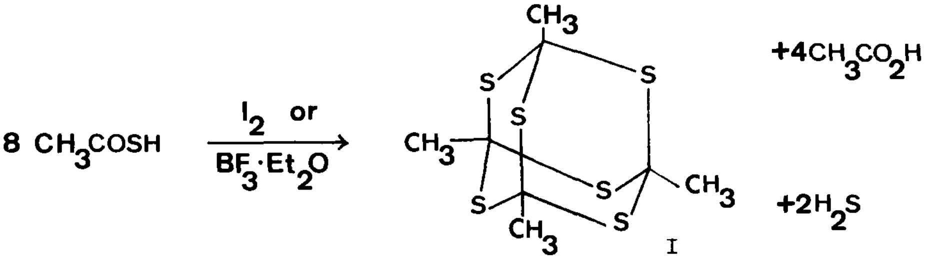
We have utilized two new and convenient processes for the synthesis of tetramethylhexathioadamantane (I)[1,2] from thiolacetic acid. The compound is useful both as a lubricant additive,[3] and as a thermal stabilizer in poly(methylmethacrylate)[4] where it promotes antiseize properties and confers oxidative



I

stability. The two synthetic procedures reported herein involve the use of boron trifluoride etherate or iodine as the catalyst.

These procedures are less hazardous and require less time for the isolation of products than the hydrogen sulfide/Lewis acid treatment of acetic acid used previously.[5]

EXPERIMENTAL

<u>Procedure 1</u> <u>(Boron Trifluoride)</u>.- Thiolacetic acid (9 ml, 127.1 mmoles) was stirred with boron trifluoride etherate (7.0 ml, 55.5 mmoles) for approximately one week under a $CaCl_2$ drying tube. The white precipitate which was formed was collected and washed with 150 ml of a 5% sodium bicarbonate solution. The residual white powder was dried thoroughly under vacuum to yield 2.61 g (55%) of crude I, mp. 214-216°, which was then recrystallized from chloroform (1.5 <u>M</u> solution) giving 2.10 g (44%) of white crystals, mp. 224-225° (corr.), lit.[1] mp. 224-225°.

<u>Procedure 2</u> <u>(Iodine)</u>.- Thiolacetic acid (1.0 ml, 11.0 mmoles) was allowed to react with 608 mg (2.39 mmoles) of iodine in a round bottom flask under a $CaCl_2$ drying tube at room temperature for one day. The contents of the flask were dissolved in 30 ml of chloroform and washed with two 30 ml portions of a 5% sodium bicarbonate solution. The chloroform layer was dried over magnesium sulfate, filtered and concentrated to about 20 ml. The resulting solution was then chromatographed over a basic alumina column (20 x 3.3 cm) and eluted with chloroform, yielding 0.31 g of crude product. Upon recrystallization from chloroform (1.5 <u>M</u> solution), 0.22 g (52%) of I was obtained, mp.

224-225°.

IR (KBr): 2960 cm^{-1} (m), 2908 cm^{-1} (w), 1433 cm^{-1} (m), 1362 cm^{-1} (s), 1352 cm^{-1} (s), 1086 cm^{-1} (s), 1022 cm^{-1} (s), 715 cm^{-1} (vs).

^1H NMR ($CDCl_3$): 2.09 ppm (s, CH_3).

^{13}C NMR ($CDCl_3$); 58.4 ppm (s, quaternary carbon); 29.14 ppm (quartet, CH_3).

Anal. Calcd for $C_8H_{12}S_6$: C, 31.96; H, 4.02.

Found: C, 32.04; H, 3.88

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