(IR, NMR) were consistent with the assigned structures in all cases.

General Procedure for O-, N-, and S-Trimethylsilylation (Table I). Freshly distilled Me_3SiCN (1.1 g, 0.11 mol) was added dropwise directly to the substrate (0.10 mol) under a nitrogen atmosphere. An exothermic reaction occurred immediately as HCN formed was vented and trapped in a bottle containing an aqueous solution of sodium hydroxide. The reaction was then stirred at the indicated temperature. The progress of the reaction was monitored by TLC at regular intervals. Soon after the completion of the reaction, a stream of nitrogen was allowed to pass through the mixture for 5 min. The resulting clear oil, practically pure at this stage, was distilled to afford the desired compound. Physical constants (mp, bp) and spectral properties (IR, ^1H NMR) of all products were in agreement with the reported data.

General Procedure for the Preparation of Alkylsilyl Cyanide (Table II). *n*-Butyllithium (Aldrich, 1.6 M in hexane, 200 mL, 0.32 mol) was transferred under nitrogen pressure into a 1-1 round-bottomed flask containing 300 mL of dry toluene. The mixture was stirred and cooled to 0 °C as Me_3SiCN (36 g, 0.36 mol) was added dropwise over a period of 10 min. There was immediate precipitation of LiCN as a white solid. After the addition was complete, the reaction mixture was stirred for an additional 15 min. The chloroalkylsilane (0.30 equiv) was added to the LiCN slurry in one lot. The reaction mixture was heated to reflux overnight under nitrogen and then filtered by a course fritted disk under nitrogen pressure. The solid was washed with two small portions of cyclohexane. The filtrate was concentrated under reduced pressure to a small volume. Distillation yielded the desired alkylsilyl cyanide, of which the physical constants and spectral properties are the same as those of the known compounds.

General Procedure for O-Alkylsilylation (Table III). Alkylsilyl cyanide (0.1 equiv) was added to the hydroxylic compound (0.1 equiv) under a nitrogen atmosphere. The neat mixture was stirred at the indicated conditions. Soon after the completion of the reaction, the product was purified either by recrystallization from hexane or by distillation. spectral properties and combustion analyses of all new compounds were consistent with the assigned structure.

General Procedure for C-Trimethylsilylation (Table IV). Preparation of 1-Hexynyltrimethylsilane. *n*-Butyllithium in hexane (1.6 M, 62.5 mL, 0.1 mol) was added dropwise to a solution of 1-hexyne (8.2 g, 0.1 mol) in hexane (100 mL) at room temperature. An exothermic reaction was observed. Me_3SiCN (10 g, 0.1 mol) was then added to the reaction mixture. After being stirred for 5 min, the slurry mixture was filtered, and the solid was washed with a small portion of hexane. The filtrate was concentrated and distilled at amospheric pressure to yield 9.6 g (60%) of the title compound, bp 153–155 °C (lit.[31] bp 155 °C).

Reaction of Me_3SiCN with Naphthalene–Sodium. To a cold solution (0–5 °C) of naphthalene (12.8 g, 0.1 mol) in 100 mL of dry THF was added metallic sodium (2.5 g, 0.11 mol). The solution was stirred at 5 °C for 4 h as sodium was being consumed. Me_3SiCN (25 g, 0.25 mol) was then added to the dark green solution. There was immediate precipitation of sodium cyanide. Solvent was removed under reduced pressure, and the residue was taken up in cyclohexane, washed with water, dried over $MgSO_4$, and evaporated to a semisolid. This was distilled under reduced pressure [135–150 °C (0.1 mmHg)] to a semisolid which consisted of unreacted naphthalene, 1,2-bis(trimethylsilyl)-1,2-dihydronaphthalene and 1,4-bis(trimethylsilyl)-1,4-dihydronaphthalene. ^1H NMR spectrum ($CDCl_3$, Me_4Si) of the distilled mixture exhibits the following characteristic peaks: δ 7.0 (m), 6.2 (t), 5.8 (d), 5.7 (s), 3.1 (br s), 2.3 (s), 2.0 (d).

Registry No. *n*-$C_4H_9OSiMe_3$, 1825-65-6; *n*-$C_8H_{17}OSiMe_3$, 14246-16-3; *sec*-$C_6H_{13}OSiMe_3$, 17888-63-0; $C_5H_{11}OSiMe_3$, 6689-16-3; $C_6H_5CH_2OSiMe_3$, 14642-79-6; $Me_3SiOCH_2CH_2OSiMe_3$, 7381-30-8; $C_6H_5OSiMe_3$, 1529-17-5; 2,6-$(C_6H_5)_2C_6H_3OSiMe_3$, 10416-72-5; $(C_2H_5)_2NSiMe_3$, 996-50-9; *n*-$C_4H_9SSiMe_3$, 3553-78-4; $C_6H_5CH_2SSiMe_3$, 14629-67-5; $C_6H_5SSiMe_3$, 4551-15-9; $CH_3CH_2COOSiMe_3$, 16844-98-7; $C_6H_5COOSiMe_3$, 2078-12-8; $C_6H_5CH(COOSiMe_3)_2$, 80372-12-9; *trans*-*p*-$AcOC_6H_4CH$=$CHCOOSiMe_2$-*t*-Bu, 103202-02-4; *p*-$O_2NC_6H_4COOSiMe_2$-*t*-Bu, 96185-30-7; *p*-$AcNHC_6H_4COOSiMe_2$-*t*-Bu, 103202-03-5; *p*-$AcNHC_6H_4OSiMe_2$-*t*-Bu, 103202-04-6; $C_6H_5CH_2OSiMe_2$-*t*-Bu, 53172-91-1; c-$C_6H_{11}OSiMe_2$-*t*-Bu, 67124-67-8; 1-adamantanecarboxylate $SiMe_2$-*t*-Bu, 103202-01-3; 1-naphthyl-$OCH_2CH(OH)CH_2OSiMe_2$-*t*-Bu, 103202-05-7; $C_6H_5CH(OH)CH_2OSiMe_2$-*t*-Bu, 71009-09-1; *p*-2-$PrC_6H_4OSi(OEt)_3$, 66967-06-4; c-$C_6H_{11}OSi(Et)_3$, 4419-18-5; $C_6H_5CH_2OSi(Et)_3$, 13959-92-7; $C_6H_5COOSi(Et)_3$, 1018-20-8; *t*-$C_4H_9COOSi(Et)_3$, 18002-65-8; *n*-$C_4H_9OSiMe_2Ph$, 18052-58-9; *m*-$AcOC_6H_4COOSiMe_2Ph$, 103202-06-8; $(C_6H_5CH_2O)_2SiMe_2$, 50870-64-9; $(C_6H_5O)_2SiMe_2$, 3440-02-6; *n*-$(C_4H_9O)_2SiPh_2$, 13320-38-2; *i*-$(C_3H_7O)_2SiPh_2$, 18056-95-6; HC≡$CSiMe_3$, 1066-54-2; *n*-BuC≡$CSiMe_3$, 3844-94-8; *t*-BuC≡$CSiMe_3$, 14630-42-3; PhC≡$CSiMe_3$, 2170-06-1; H_2C=$CHSiMe_3$, 754-05-2; (*E*)-*n*-BuCH=$CHSiMe_3$, 54731-58-7; $PhSiMe_3$, 768-32-1; *n*-$BuSiMe_3$, 1000-49-3; *t*-$BuSiMe_3$, 5037-65-0; *n*-BuC≡CCH_2SiMe_3, 84140-28-3; $(Me_3Si)_4C$, 1066-64-4; *n*-C_4H_9OH, 71-36-3; *n*-$C_8H_{17}OH$, 111-87-5; *sec*-$C_6H_{13}OH$, 626-93-7; $C_5H_{11}OH$, 75-84-3; $C_6H_5CH_2OH$, 100-51-6; $HOCH_2CH_2OH$, 107-21-1; C_6H_5OH, 108-95-2; 2,6-$(C_6H_5)_2C_6H_3OH$, 2432-11-3; $(C_2H_5)_2NH$, 109-89-7; *n*-C_4H_9SH, 109-79-5; $C_6H_5CH_2SH$, 100-53-8; C_6H_5SH, 108-98-5; CH_3CH_2COOH, 79-09-4; C_6H_5COOH, 65-85-0; $C_6H_5CH(CO_2H)_2$, 2613-89-0; Me_3SiCN, 7677-24-9; LiCN, 2408-36-8; *trans*-*p*-AcC_6H_4CH=$CHCOOH$, 27542-85-4; *p*-$O_2NC_6H_4COOH$, 62-23-7; *p*-$AcHC_6H_4COOH$, 556-08-1; *p*-$AcNHC_6H_4OH$, 103-90-2; *o*-$HOC_6H_4CH_2OH$, 90-01-7; c-$C_6H_{11}OH$, 108-93-0; 1-naphthyl-$OCH_2CH(OH)CH_2OH$, 36112-95-5; $C_6H_5CH(OH)CH_2OH$, 93-56-1; *p*-2-PrC_6H_4OH, 99-89-8; *o*-HOC_6H_4COOH, 69-72-7; *t*-C_4H_9COOH, 75-98-9; *m*-$AcOC_6H_4COOH$, 6304-89-8; *i*-C_3H_7OH, 67-63-0; $HOCH_2C(CH_3)_2CH_2OH$, 126-30-7; *o*-HOC_6H_4OH, 120-80-9; $HOOCCH_2COOH$, 141-82-2; HC≡CNa, 1066-26-8; *t*-BuC≡CH, 917-92-0; PhC≡CH, 536-74-3; H_2C=$CHMgBr$, 1826-67-1; (*E*)-*n*-BuCH=CHLi, 62839-68-3; PhLi, 591-51-5; PhMgBr, 100-58-3; *n*-BuLi, 109-72-8; *n*-BuMgBr, 693-04-9; *t*-BuLi, 594-19-4; *t*-BuMgBr, 677-22-5; *n*-BuC≡CCH_2Li, 82511-26-0; $(Me_3Si)_3CLi$, 28830-22-0; methyl tetrakis(trimethylsilyl)-α-glucopyranoside, 2641-79-4; methyl tetrakis(trimethylsilyl)-α-mannopyranoside, 1769-06-8; *tert*-butyldimethylsilyl cyanide, 56522-24-8; triethylsilyl cyanide, 18301-88-7; dimethylphenylsilyl cyanide, 103201-99-6; dimethylsilyl dicyanide, 5158-09-8; diethylsilyl dicyanide, 103202-00-2; diphenylsilyl dicyanide, 4669-68-5; 2,2-diethyl-4*H*-1,3,2-benzodioxasilin, 103202-07-9; 2,2-diethyl-4-oxa-1,3,2-benzodioxasilin, 103202-08-0; 2,2-diethyl-4,4-dimethyl-1,3-dioxa-2-silacyclohexane, 18106-01-9; 2,2-diphenyl-1,3,2-benzodioxasilole, 14857-41-1; 4,6-dioxo-2,2-diphenyl-1,3-dioxa-2-silacyclohexane, 103202-09-1; 4-((1-naphthyloxy)methyl)-2,2-diphenyl-1,3-dioxa-2-silacyclopentane, 103202-10-4; methyl α-glucopyranoside, 97-30-3; methyl α-mannopyranoside, 617-04-9; *tert*-butylchlorodimethylsilane, 18162-48-6; chlorotriethylsilane, 994-30-9; chlorodimethylphenylsilane, 768-33-2; dichlorodimethylsilane, 75-78-5; dichlorodiethylsilane, 1719-53-5; dichlorodiphenylsilane, 80-10-4; 1-adamantanecarboxylic acid, 828-51-3; 3-((1-naphthyl)oxy)-1,2-propanediol, 36112-95-5; 1-hexyne, 693-02-7; naphthalene, 91-20-3; 1,2-bis(trimethylsilyl)-1,2-dihydronaphthalene, 1085-99-0; 1,4-bis(trimethylsilyl)-1,4-dihydronaphthalene, 1085-97-8.

Complexes between *N*-Bromosuccinimide and Quaternary Ammonium Bromides and Their Role in the Addition of Bromine to Olefins

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N-Bromosuccinimide (SBr) is a reagent of remarkable versatility. It can participate in free radical chain reactions[1-4] as well as react by a variety of polar mecha-

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Table I. Complexes of *N*-Halosuccinimides and Quaternary Ammonium Halides

N-halosuccinimide SX	quaternary ammonium halide, R_4NX	ratio SX:R_4NX	mp, °C	yield, %	solv for crystallization	analyses							
						calcd				found			
						C	H	N	OE	C	H	N	OE
SBr	$[C_4H_9]_4NBr$	1:1	86–88 dec	86–90	CH_3CN–Et_2O or acetone–Et_2O	48.01	8.06	5.60	500	47.76	7.97	5.63	509
SBr	$[C_2H_5]_4NBr$	2:1	126–128	59	$CHCl_3$	33.94	4.99	7.42	283	34.45	5.32	7.34	284
SBr	$[C_2H_5]_4NBr$	1:1	103 dec	97	CH_3CN–Et_2O	37.13	6.23	7.22		36.98	6.04	7.25	
SBr	$C_6H_5CH_2N(C_2H_5)_3Br$	1:1	109–110	89	CH_3CN–Et_2O	45.35	5.82	6.22	450	45.42	5.74	6.37	

nisms.[5-13] Our recent work[14-18] has demonstrated that both SBr and *N*-chlorosuccinimide (SCl) can participate in rapid electron-transfer reactions with an appropriate nucleophile, e.g., the succinimide anion. With SBr the electron transfer probably occurs in a complex formed from SBr and a quaternary ammonium succinimide[15] and generates succinimidyl radicals which react to form maleimide, polymaleimide, and succinimide.[17]

Braude and Waight[9] have implicated complexes formed from SBr and quaternary ammonium bromides (R_4NBr) as intermediates in the addition of bromine to olefins by SBr. In the present work we will show that SBr–R_4NBr complexes are of some generality and that they can form with SBr to R_4NBr ratios of 1:1 and 2:1. The 1:1 SBr–tetrabutylammonium bromide complex has been studied in detail, and evidence will be presented to show that such complexes play a vital role in the mechanism by which quaternary ammonium bromides promote the reaction of SBr and olefins to give the dibromo compounds.

Results and Discussion

Braude and Waight[9] prepared 2:1 complexes from SBr and the two quaternary ammonium halides Et_4NBr and Et_4NI. We tried to repeat the preparation of the SBr–Et_4NBr complex and obtained a product having the reported 2:1 ratio and satisfactory analytical values for that composition, but our observed melting point (126–128 °C) was lower than the reported melting point of 144 °C. By starting with equivalent quantities of SBr and Et_4NBr and with a mixture of acetonitrile and ether as the solvent we were also able to prepare a 1:1 SBr–Et_4NBr complex.

Also prepared were the additional complexes shown in Table I. The designation "OE", the oxidation equivalent, in the analyses section of Table I refers to the values obtained by iodimetric titration of the SBr moiety of the complexes. For a 1:1 complex the value obtained is equivalent to the molecular weight, and for a 2:1 complex the value is equal to half the molecular weight.

It is not always possible to prepare both the 1:1 complex and the 2:1 complex from a single pair of reagents. In the reactions of SBr with Et_4NBr we did succeed in obtaining both complexes, but in the case of SBr and tetrabutylammonium bromide variations in both the initial reagent concentrations and the solvents used did not result in a successful preparation of the 2:1 complex.

The 1:1 SBr–Bu_4NBr complex was chosen for special study. It can be prepared in high yield and can be recrystallized easily from either acetonitrile–ether or acetone–ether. With the aid of infrared spectroscopy it can be demonstrated that the complex maintains its identity and is only partially dissociated in acetonitrile solution. A 0.0513 M SBr solution in acetonitrile shows a single absorption in the carbonyl region at 1730 cm^{-1}. As would be expected Bu_4NBr in acetonitrile (0.0498 M) shows no absorption in the carbonyl region of the spectrum. A 0.05 M solution of the complex in acetonitrile shows a new strong absorption in the carbonyl region at 1700 cm^{-1} and a much weaker absorption at 1730 cm^{-1}. The absorption at 1730 cm^{-1} is due to SBr and the new absorption at 1700 cm^{-1} is due to the complex. We estimate that the intensity of the absorption at 1700 cm^{-1} is at least double that of the absorption at 1730 cm^{-1}. In an acetonitrile solution that is 0.0525 M in the complex and 0.1016 M in added Bu_4NBr the strong absorption at 1700 cm^{-1} is still present, but the absorption at 1730 cm^{-1} is almost completely suppressed. Only a small shoulder is detectable. We conclude that the equilibrium (eq 1) is well to the right.

$$SBr + Bu_4NBr \rightleftharpoons \text{complex} \quad (1)$$

When the SBr–Bu_4NBr complex (as a 0.6 M solution in acetonitrile) was decomposed by refluxing for 2.5 h, three products resulted. These were succinimide (60% yield), polymaleimide (30.6% yield), and tetrabutylammonium tribromide (57.9% yield). The details on the determination of succinimide and the isolation of both the polymaleimide and the tribromide are given in the Experimental Section. This decomposition reaction will occur in the presence of 2,6-lutidine, and exploratory kinetic runs (UV, monitored at the 400 nm Br_3^- shoulder) on the SBr, Br^- reaction ($[SBr]_o$ = 1.5 mM, $[Br^-]_o$ = 9.1 mM) in the presence of 2,6-di-*tert*-butyl-4-methyl pyridine (16 mM) showed that the reaction has a half-life of ca. 20 h at 50 °C.

The tribromide is known, mp 72.5–74 °C,[19] and its reaction with crotonic acid in ethylene chloride to form 2,3-dibromobutyric acid has been studied.[19] We have

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prepared the tribromide in nearly quantitative yield by adding equivalent bromine to an acetonitrile solution of tetrabutylammonium bromide, and the product is easily purified by crystallization from methanol.

Tetrabutylammonium tribromide in acetonitrile is an effective reagent for adding bromine to a double bond. The solution of the tribromide in acetonitrile is dark red and turns lighter as the tribromide reacts, eventually turning colorless when all of the tribromide is consumed. In a 0.2 M acetonitrile solution of the tribromide bromine is added to 3,3-dimethyl-1-butene in 95% yield within 1 h and to cyclohexene in 90% yield immediately on mixing. Tetrabutylammonium tribromide is, thus, an effective reagent for adding bromine to a double bond, and this result is to be expected on the basis of the successful use of other tribromides to effect similar reactions.[20,21]

Decomposition of the complex in benzene gave results similar to those observed in acetonitrile. Refluxing a 0.40 M solution for 5 h led to three products: polymaleimide (31%), succinimide (68%), and tetrabutylammonium tribromide (59%). Both in this experiment and in the decomposition in acetonitrile there is no effective bromine acceptor, and the tribromide is a stable product. In the presence of a bromine acceptor, e.g., 3,3-dimethyl-1-butene, the tribromide is no longer a final product. When an acetonitrile solution that initially contained 0.02 mol of the complex and 0.039 mol of 3,3-dimethyl-1-butene was permitted to react either by letting it stand 48 h at room temperature or by refluxing for 3 h, no tribromide was obtained. Under the former conditions the products were polymaleimide (10%), succinimide (64%), and 3,4-dibromo-2,2-dimethylbutane (52%). After refluxing, the products were polymaleimide (13%), succinimide (60%), and 3,4-dibromo-2,2-dimethylbutane (45%).

An electron transfer from bromide ion to SBr, occurring within the SBr–Bu_4NBr complex, can account adequately for the formation of succinimide and the tribromide but fails to rationalize the ready formation of polymaleimide. In addition such a reaction is not energetically favorable. A more attractive rationalization involves an X-philic reaction. Such reactions have been reviewed for cases where the leaving group is a carbanion.[22] The formulation in eq 2 is suggested, and we would note that the well-known reaction of SBr and HBr to form SH and Br_2 is an acid catalyzed X-philic reaction.

$$SBr, Br^- \rightleftharpoons [>N^{\delta-}\cdots Br^{\delta+}\cdots Br^{\delta-}] \rightleftharpoons S^- + Br_2 \quad (2)$$

The S^-, formed in eq 2, can then react with SBr as previously described[17] to give SH and polymaleimide as shown in eq 3. The bromide ion formed in eq 3 can

$$S^- + SBr \rightarrow SH + \text{polymer} + Br^- \quad (3)$$

provide the additional function of reacting with bromine formed in eq 2 to give the tribromide ion, thus shifting the equilibria in eq 2 to the right. If this reasoning is correct, it should be possible to prepare the complex by the reverse of reaction 2. When tetrabutylammonium succinimide in acetonitrile solution was treated with exactly 1 equiv of bromine the product isolated was the SBr–tetrabutylammonium bromide complex, obtained in 90.7% yield. This is the way SBr is generally prepared, except that the reaction is performed in water, in which SBr is difficulty soluble but the bromide salt is very soluble.

Experimental Section

Preparation of the Complexes. The procedure used to prepare the 2:1 SBr–Et_4NBr complex was that described by Braude and Waight.[9] The 1:1 SBr–Et_4NBr complex was prepared by dissolving Et_4NBr (2.10 g; 0.01 mol) in hot acetonitrile (50 mL) and adding SBr (1.78 g; 0.01 mol) and then ether (25 mL). The solution was refrigerated, and more ether (15 mL) was added after crystallization had started. The yield was 2.8 g (97%), mp 103 °C dec.

The procedure for preparing the 1:1 SBr–Bu_4NBr complex was also satisfactory for preparing the 1:1 SBr–benzyltriethylammonium bromide complex in Table I. SBr (3.56 g; 0.02 mol) and Bu_4NBr (6.45 g; 0.02 mol) were added to a mixture of ether (50 mL) and acetonitrile (25 mL). The mixture was stirred until a homogeneous solution resulted. This was filtered; ether (50 mL) was added. On refrigeration the product (8.6 g; 86% yield) crystallized, mp 85–86 °C dec. A sample recrystallized for analysis from ether–acetonitrile had mp 86–88 °C dec. In an alternate preparation the reagents, in the quantities indicated above, were dissolved with warming in a mixture of ether (50 mL) and acetone (50 mL). The solution was filtered, and ether (70 mL) was added gradually. On refrigeration the complex crystallized: yield, 9.0 g (90%); mp 85–87 °C dec.

Reactions of the SBr–Tetrabutylammonium Bromide Complex. 1. Decomposition in Acetonitrile. The SBr–Bu_4NBr complex (15 g; 0.03 mol) in acetonitrile (50 mL) was refluxed 2.5 h, and then refrigerated overnight. This gave 0.54 g of insoluble red polymer, mp above 300 °C, which was characterized as polymaleimide by the methods previously described.[17] The above filtrate was made up to a volume of 100 mL and analyzed for succinimide by VPC. The solution was found to be 0.18 M in succinimide. The acetonitrile solution was taken to dryness at the water pump. The residue was taken up in boiling methanol (150 mL), and the solution was cooled in the freezer. This yielded a first crop of 5.36 g of orange solid, mp 70–73 °C. A small portion (0.35 g) of this product did not redissolve in methanol and was shown to be polymaleimide. The remaining material was tetrabutylammonium tribromide, and recrystallization raised the mp to 71–74 °C, with no depression on mixed melting point with an authentic sample of the tribromide. Concentration of the original methanol solution provided a second crop (0.58 g) of the tribromide. To summarize, the observed product yields were 60% succinimide, 30.6% polymaleimide, and 57.9% tetrabutylammonium tribromide.

2. Decomposition in Benzene. The complex (10 g; 0.02 mol) in benzene (50 mL) was decomposed by refluxing for 5 h. The workup was essentially that described for the decomposition in acetonitrile. The products found were 31% polymaleimide, 68% succinimide, and 59% tetrabutylammonium tribromide.

3. Reaction with 3,3-Dimethyl-1-butene. 3,3-Dimethyl-1-butene (5.0 mL; 3.27 g; 0.039 mol) was added to the SBr–Bu_4NBr complex (10 g; 0.02 mol) dissolved in acetonitrile (30 mL). The solution was refluxed 3 h, cooled to room temperature, and made up to a volume of 100 mL with acetonitrile. By VPC analysis the solution was found to be 0.09 M in 3,4-dibromo-2,2-dimethylbutane and 0.12 M in succinimide, thus indicating yields of 45% and 60%, respectively, for the two products. A portion of the above solution (75 mL) was taken to dryness at the water pump, and the residue was taken up in methanol (25 mL). On refrigeration polymaleimide (0.2 g) precipitated. This represents a yield of 13.4% for the total 100 mL of solution.

Tetrabutylammonium Tribromide. Bromine (16 g; 0.1 mol) was added dropwise, with stirring, to a solution of Bu_4NBr (32.2 g; 0.1 mol) in acetonitrile (150 mL). The solution was taken to dryness at the water pump, and the residue was crystallized from methanol (200 mL), yield, 46.6 g (96%). Recrystallization from methanol yielded 37 g (77%) of the tribromide, mp 72–74 °C.

Reaction of Tetrabutylammonium Tribromide with 3,3-Dimethyl-1-butene. The tribromide (4.82 g; 0.01 mol) and 3,3-dimethyl-1-butene (3.0 mL; 1.96 g; 0.023 mol) were made up to a volume of 50 mL with acetonitrile. Within 1 h the red bromine color had disappeared, and the solution had gone colorless. Analysis by VPC indicated that 1,2-dibromo-3,3-dimethylbutane was formed in 95% yield.

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Reaction of Tetrabutylammonium Tribromide with Cyclohexene. Tetrabutylammonium tribromide (4.82 g; 0.01 mol) and cyclohexene (3.0 mL; 2.43 g; 0.0296 mol) were made up to a volume of 50 mL with acetonitrile. The bromine color disappeared as soon as the solution was mixed. Analysis by VPC indicated that cyclohexane dibromide had formed in 90% yield.

Reaction of Tetrabutylammonium Succinimide with Bromine in Acetonitrile. Bromine (3.76 g; 0.0235 mol) in purified acetonitrile (6 mL) was added portionwise with shaking and cooling to a 0.942 M solution of tetrabutylammonium succinimide in acetonitrile (25 mL; 0.0236 mol). Ether (100 mL) was added, and the solution was seeded and stored in the freezer. After crystallization had advanced, more ether (200 mL) was added. The product was the SBr–Bu_4NBr complex; 10.67 g (90.7% yield); mp 83–85 °C dec. The infrared spectrum of this product was identical with that of an authentic sample of the complex.

Registry No. SBr, 128-08-5; $(C_4H_9)_4NBr$, 1643-19-2; $(C_2H_5)_4NBr$, 71-91-0; $C_6H_5CH_2N(C_2H_5)_3Br$, 5197-95-5; $SBr\cdot(C_4H_9)_4NBr$, 103191-58-8; $2SBr\cdot(C_2H_5)_4NBr$, 103191-59-9; $SBr\cdot(C_2H_5)_4NBr$, 103191-60-2; $SBr\cdot C_6H_5CH_2N(C_2H_5)_3Br$, 103191-61-3; $(C_4H_9)_4N^+Br_3^-$, 38932-80-8; $H_2C{=}CHC(CH_3)_3$, 558-37-2; $(H_3C)_3CCHBrCH_2Br$, 640-21-1; $S\cdot(C_4H_9)_4N^+$, 74830-30-1; cyclohexene, 110-83-8; cyclohexane dibromide, 5401-62-7.

Chemistry of 1,1-Dioxothiopyrans. 2. Synthesis, Structure, and Properties of 4-Diazo-2,6-diphenyl-4*H*-thiopyran 1,1-Dioxide

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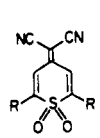
The discovery of dicyanomethylene derivatives of thiopyran 1,1-dioxides **1** (DCTD) as electron-transporting species in electrophotography[1] has stimulated much interest in the design and synthesis of many other structurally related compounds. The best method of preparing **1** is to condense malononitrile with the corresponding ketone, such as **2**, in the presence of piperidine in alcohol.[2] This procedure, however, did not work well with active methylene compounds less acidic than malononitrile. In attempts to activate the carbonyl group of 2,6-diphenyl-4*H*-thiopyran 1,1-dioxide (**2**), we synthesized a remarkably stable diazo derivative of **2**, 4-diazo-2,6-diphenyl-4*H*-thiopyran 1,1-dioxide (**3**) (DATD), whose synthesis, X-ray single-crystal structure, and chemical properties are described here.



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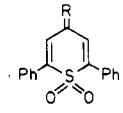
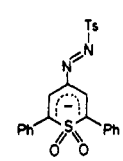


2 (R=O)
3 (R=N_2)
4 (R=N–NHTs)
5 (R=N–NH_2)
6 (R=N–N=PPh_3)
7 [R=N–NH–P(O)(OMe)$_2$]



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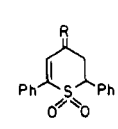
Results and Discussion

Synthesis. Most organic diazo compounds are unstable unless they are stabilized by conjugation with strong electron-withdrawing groups such as carbonyls and cyclopentadienes.[3] The only previously known diazo derivative of a heterocyclic sulfone is diazothioxanthen 1,1-dioxide, which was prepared from the corresponding 9,9-dihydro derivative and tosyl azide in the presence of EtOK in EtOH.[4] This method is not applicable to thiopyran sulfones because of the difficulty of synthesizing the corresponding 4,4-dihydro-2,6-diphenylthiopyran 1,1-dioxide.[2]

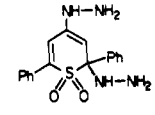
Heating **2** with 1 equiv of *p*-toluenesulfonohydrazide in ethanol produced a mixture of products. The major component isolated was not the expected tosyl hydrazone **4**, but a compound (orange needles) that was free of the tosyl group. Its IR spectrum has a strong band at 2100 cm^{-1} characteristic of diazo stretching. Mass and ^1H NMR spectra and combustion analyses are consistent with the diazo thiopyran structure of **3**. Presumably, the tosylhydrazone **4** formed in situ has an unusually acidic proton on nitrogen because of the highly stabilized anion shown in structure **8**.

Deprotonation under the reaction conditions in the presence of the weakly basic *p*-toluenesulfonohydrazide followed by α elimination of toluenesulfinate led to the formation of **3**. Indeed, the reaction was much cleaner when **2** was refluxed with 2 equiv of *p*-toluenesulfonohydrazide in ethanol, and the diazo compound **3** crystallized directly out of the reaction mixture on cooling. The yield of **3**, after purification was 48%.

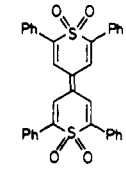
Further support of this rationale was provided by experiments in which the dihydro derivative **9** under the same reaction conditions produced only the tosylhydrazone **10**. The latter, which cannot delocalize the incipient anion



9 (R=O)
10 (R=N–NHTs)
11 (R=N_2)



12



13

as can **8**, cannot readily be deprotonated and α-eliminate the toluenesulfinate to give the diazo compound **11** under the reaction conditions.

Likewise, reaction of **2** with 1 equiv of hydrazine produced only the hydrazone **5**. However, the same reaction run in the presence of 2 equiv of hydrazine gave the 2:1 adduct, which was assigned the structure **12** on the basis of elemental and ^1H NMR analyses. The diadduct presumably was formed from **5** by Michael addition of hydrazine at C2 followed by 1,3-prototropic shift. In Me_2SO-d_6, **12** easily reverted to **5** on addition of D_2O.

Chemical Properties. DATD (**3**) is a remarkably stable compound, mp 131 °C dec, which can be stored indefinitely in the solid state at ambient conditions. Structurally, diazothiopyran **3** can be considered as a sulfone analogue of *p*-diazobenzeneoxide.[5] However, **3** is far more stable than *p*-diazobenzeneoxide photochemically. For instance, when an argon-degassed 0.02 M solution of **3** in acetonitrile was irradiated with a 200-W Hg–Xe lamp for 48 h, a TLC assay showed that about 30% of **3** survived without decomposition. Thermally, DATD decomposed under toluene reflux (2 h) to at least five products, from which only a small amount of the dimer **13**[2] was detected. In cyclic voltammetry, DATD displayed a single, irreversible reduction wave at −0.92 V (Pt vs. SCE).

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