Electrophilic Addition of Bromodimethylsulfonium Bromide to Olefins

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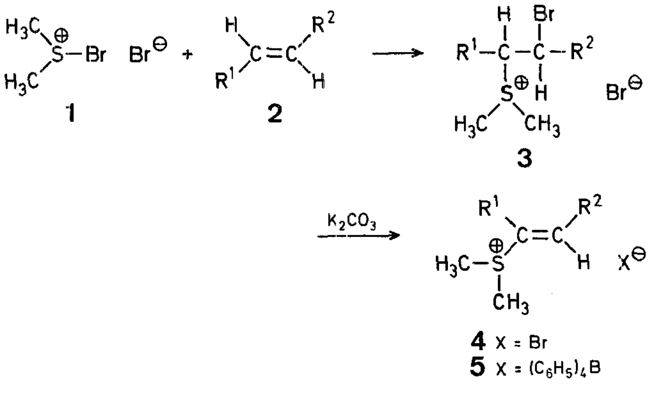
Bromine and dialkyl sulfides react to give stable yellow crystalline bromodialkylsulfonium bromides[1,2], the structures of which have been shown to possess a sulfur-bromine bond[3]. The simplest member, bromodimethylsulfonium bromide (**1**) is easily prepared by mixing the ingredients in aprotic solvents. Renewed interest in these reagents (or analogues)[4] in recent years has been demonstrated by nucleophilic displacement reactions at the sulfur cationic[4,8], α-carbon[2,9], or bromine site[6]. Compound **1** may be considered as a convenient storage method for the bromonium ion, by analogy with hypobromite[10], *N*-bromosuccinimide[11], or bromoazide[12]. We now report on its reaction with simple olefins **2** and demonstrate the versatility of this reagent.

The reagent **1**, prepared in dichloromethane or acetonitrile at −40 °C, was treated *in situ* with an olefin **2** under nitrogen at 0 °C. The reaction proceeded rapidly to deposit a white solid, with or without addition of cold pentane or ether, except in the case of stilbene (**2b**) where the mixture was heated to 40 °C for the reaction to occur. The white solid was shown to be the 1-bromo-2-sulfonium bromide **3** and the filtrate contained the 1,2-dibromides; the two types of compounds accounts for a quantitative yield. This is in good contrast to the previous workers who have found no sulfonium bromide formation in a similar reaction[3]. The compounds **2** in aqueous solution were readily dehydrobrominated with potassium carbonate to afford vinylsulfonium salts[13] **4** or **5** quantitatively, some of which were isolated as tetraphenylborates (**5c–f**) or pictrates (**4b**) (Table 1). Vinylsulfonium ions **4** were easily identified *in situ* (D_2O solution) by the presence of the ^1H-N.M.R. signals at about $\delta = 7$ ppm for the β-olefinic protons (Table 3). The sulfonium bromides **3** were washed thoroughly with ether and gave clean N.M.R. spectra which provided structural information (Table 2).



The treatment of 1,2-dibromophenylethane with dimethyl sulfide did not give a sulfonium salt of the type **3**. Bromotetrahydrothiophenium bromide also gave similar results. Reactive olefins, such as norbornene (**2g**) and styrene (**2e**), reacted

Table 1. Addition of Bromodimethylsulfonium Bromide (**1**) to Olefins **2** and Subsequent Dehydrobromination

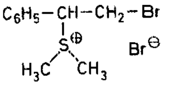
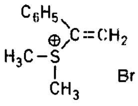
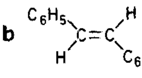
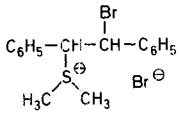
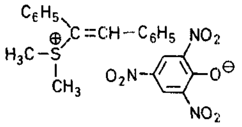
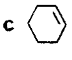
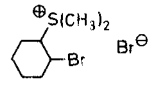
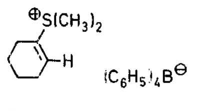
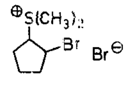
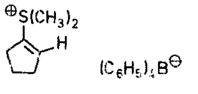
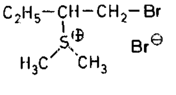
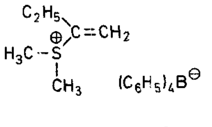
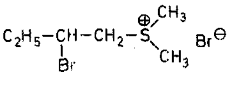
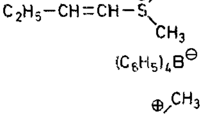
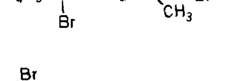
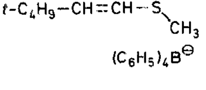
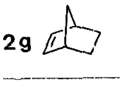
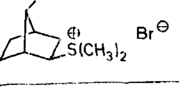
Olefin	Sulfonium Bromide	Yield [%]	Vinylsulfonium salt	Yield [%]
2a $C_6H_5-CH=CH_2$	**3a**  $C_6H_5-CH(\overset{\oplus}{S}(CH_3)_2)-CH_2-Br\ Br^{\ominus}$	86	**4a**  $C_6H_5(H_3C-\overset{\oplus}{S}(CH_3))C=CH_2\ Br^{\ominus}$	76
2b 	**3b**  $C_6H_5-CH(Br)-CH(\overset{\oplus}{S}(CH_3)_2)-C_6H_5\ Br^{\ominus}$	85	**4b** 	65
2c 	**3c** 	28	**5c** 	96
2d 	**3d** 	20	**5d** 	99
	3e  $C_2H_5-CH(\overset{\oplus}{S}(CH_3)_2)-CH_2-Br\ Br^{\ominus}$	9	**5e**  $C_2H_5(H_3C-\overset{\oplus}{S}(CH_3))C=CH_2\ (C_6H_5)_4B^{\ominus}$	100
2e $C_2H_5-CH=CH_2$	**3e'**  $C_2H_5-CH(Br)-CH_2-\overset{\oplus}{S}(CH_3)_2\ Br^{\ominus}$	9	**5e'**  $C_2H_5-CH=CH-\overset{\oplus}{S}(CH_3)_2\ (C_6H_5)_4B^{\ominus}$	—
2f $t-C_4H_9-CH=CH_2$	**3f**  $t-C_4H_9-CH(Br)-CH_2-\overset{\oplus}{S}(CH_3)_2\ Br^{\ominus}$	16	**5f**  $t-C_4H_9-CH=CH-\overset{\oplus}{S}(CH_3)_2\ (C_6H_5)_4B^{\ominus}$	92
2g 	**3g** 	46	—	—

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Table 2. Characterization of Compounds **3**, **4**, and **5**

Product	m.p. [°C]	Molecular Formula[a] or Lit. m.p. [°C]	I.R. (nujol) ν [cm^{-1}]	^{1}H-N.M.R. (D_2O/DSS$_{int.}$) δ [ppm]	^{13}C-N.M.R. (D_2O/DSS$_{int.}$) δ [ppm]
3a	145–148°	$C_{10}H_{14}Br_2S$ (326.1)	1470, 1420, 1228, 995, 715	2.69 (s, 3H); 2.98 (s, 3H); 4.24 (dd, 1H, J=8.5 Hz, 14.5 Hz); 4.26 (dd, 1H, J=6.5 Hz, 14.5 Hz); 5.21 (dd, 1H, J=8.5 Hz, 6.5 Hz); 7.6 (m, 5H)	23.6 (q); 25.6 (q); 29.6 (t); 62.0 (d); 130.1 (s); 130.7 (d); 131.0 (d); 132.4 (d)
3b	210–216°	$C_{16}H_{18}Br_2S$ (402.2)	3020, 1495, 1200, 1185, 1000, 700, 635, 615	2.54 (s, 6H); 5.23, 5.63 (AB-q, 2H, J=10 Hz); 7.0–7.4 (m, 10H)[b]	26.1 (q); 27.7 (q); 51.4 (d); 73.2 (d); 129.6; 130.3; 130.8; 131.1; 131.4; 131.7; 132.1; 132.9; 133.8; 134.0; 137.6[b]
3c	153–155°	$C_{32}H_{36}BBrS$[c] (543.4)	1435, 1210, 1010, 985, 695	1.3–2.5 (m, 8H); 2.68 (s, 3H); 2.78 (s, 3H); 3.70 (dt, 1H, J=4 Hz, 10 Hz); 4.10 (dt, 1H, J=4 Hz, 10 Hz)	19.1 (q); 23.3 (q); 24.1 (t); 25.3 (t); 25.6 (t); 37.9 (t); 49.4 (d); 60.1 (d)
3d	147–149°	—	1425, 1340, 1215, 1055, 1010, 940, 765	1.6–2.5 (m, 6H); 2.79 (s, 3H); 2.89 (s, 3H); 3.96 (m, 1H, J=5 Hz); 4.39 (dd, 1H, J=5 Hz, 5.5 Hz)	23.3 (t); 23.7 (q); 24.7 (q); 27.8 (t); 37.7 (t); 47.0 (d); 62.3 (d)
3e+**3e′**	—	—	1435, 1420, 1265, 1240, 1020	1.14 (t, 3H, J=7 Hz); 1.18 (t, 3H, J=7 Hz); 2.02 (m, 4H); 2.99 (s, 6H); 3.00 (s, 3H); 3.04 (s, 3H); 3.95 (m, 5H); 4.4 (m, 1H)[d]	9.8 (q); 11.1 (q); 21.0 (t); 22.5 (q); 22.9 (q); 25.0 (q); 26.2 (q); 28.9 (t); 31.1 (t); 49.2 (d); 51.7 (t); 57.8 (d)[d]
3f	173–174°	—	1430, 1250, 1170, 1015, 900	1.12 (s, 9H); 2.98 (s, 3H); 3.04 (s, 3H); 3.94 (m, 2H); 4.37 (dd, 1H, J=6 Hz, 7.5 Hz)	24.2 (q); 26.3 (q); 35.9 (s); 49.7 (t); 59.8 (d)
3g	198–201°	$C_9H_{16}Br_2S$ (316.1)	1430, 1415, 1305, 1255, 990, 780, 740	1.48 (m, 5-H_{endo}, 6-H_{exo}); 1.78 (m, 5-H_{exo}, $J_{4\text{-}H, 5\text{-}H}$=4 Hz); 1.89 (m, 6-$H_{exo}$, $J_{1\text{-}H, 6\text{-}H}$=5 Hz); 2.22 (dd, 3-$H_{endo}$, J=8.5 Hz, 15 Hz); 2.39 (m, 3-H_{exo}, J=5.6 Hz, 15 Hz); 2.62 (m, 4-H, $J_{4\text{-}H, 5\text{-}H}$=4 Hz); 2.90 (s, 3H); 2.93 (d, 1-H, $J_{1\text{-}H, 6\text{-}H}$=5 Hz); 3.00 (s, 3H); 3.59 (dd, 2-H_{endo}, J=8.5 Hz, 5.6 Hz); 4.26 (m, 7-H_{anti}, $J_{7\text{-}H, 3\text{-}H}$=1.2 Hz)[e]	24.5 (q); 24.7 (q); 25.3 (q); 27.4 (t); 32.5 (t); 43.3 (d); 45.0 (d); 54.8 (d); 58.3 (d)
4a	179–181° (dec)	—	—	3.04 (s, 6H); 6.38 (s, 2H); 7.55 (m, 5H)[f,g]	—
4b	159–162° (dec)	161° (dec)[14]	—	3.08 (s, 6H); 6.8–7.7 (m, 11H); 8.70 (s, 2H)[h]	—
5c	196–198°	$C_{32}H_{35}BS$ (462.5)	—	1.76 (m, 4H); 2.33 (m, 4H); 2.92 (s, 6H); 6.92 (m, 1H)[f]	—
5d	207–210°	$C_{31}H_{33}BS$ (448.5)	—	1.4–3.0 (m, 6H); 2.99 (s, 6H); 6.97 (m, 1H)[f]	—
5e+**5e′**	180–230°	$C_{30}H_{33}BS$ (436.5)	—	2.94 (s); 2.99 (s); 6.13 (AB-q, $\Delta\delta$=4 Hz, J=1.8 Hz); 6.24 (dt, J=16 Hz, 1 Hz); 7.00 (dt, J=16 Hz, 6 Hz)[f]	—
5f	175–177°	$C_{32}H_{37}BS$ (464.5)	—	1.12 (s, 9H); 2.94 (s, 6H); 6.20, 6.96 (AB-q, 2H, J=15 Hz)[f]	—

[a] Satisfactory microanalyses obtained: C ±0.26, H ±0.40.
[b] Trifluoroacetic acid solution with TMS as external standard.
[c] Analysis of tetraphenylborate; m.p. 186–188 °C (dec.).
[d] Spectra of 1 : 1 mixture.
[e] 400 MHz spectrum; all other spectra recorded at 60 or 100 MHz.
[f] Spectra obtained from solutions of the corresponding bromide **3** in D_2O containing potassium carbonate; DSS (2,2-dimethyl-2-silapentane-5-sulfonate) as internal standard.
[g] The tetraphenylborate in DMSO-d_6 shows an AB-quartet δ=6.30, 6.48 ppm (J=3.5 Hz).
[h] $CDCl_3$ solution of picrate.

even at −40 °C but others reacted reasonably rapidly only at near 0 °C. Slow reactions at a low temperature seem to give better yields of sulfonium salts **3**. However, even for low yield cases, the separation of **3** from dibromo adducts is clean and simple so that the process is preparatively useful.

The addition to *trans*-stilbene (**2b**), cyclohexene (**2c**), and cyclopentene (**2d**) occurs stereospecifically to give single sulfonium ions **3**; the stereochemical course of addition is *trans* as shown by the clean *trans*-configuration of **3c**. Together with the typical non-classical carbonium ion-rearrangement in the addition to norbornene (**2g**) to give **3g**, the reaction patterns indicate brominium ion-initiated electrophilic addition to olefins[15]. It is surprising to observe partial and complete changes in regiospecificity in the addition to 1-butene (**2e**) and 3,3-dimethyl-1-butene (**2f**). In the former case, since neither the reaction in the dark nor under oxygen alters the product pattern, intrusion of a radical mechanism is rather unlikely. The regiospecificity of the formation of **3e′** and **5e′** could be explained by steric control in directing the entry of a dimethyl sulfide group in the polar addition process. This requires that the initially formed bridged bromonium ion must be fairly tight and the ring does not open until the sulfide approaches the reaction site substantially.

1-Bromo-2-sulfonium Bromides 3; General Procedure:
To a solution of dimethyl sulfide (10 ml, 130 mmol) in acetonitrile (50–70 ml), kept at −10 °C under nitrogen, a solution of bromine (5.98 g, 37.4 mmol) in carbon tetrachloride (10 ml) is added to give an orange solution with a yellow precipitate. To the stirred mixture of **1** an olefin **2** (50–100 mmol) is injected. Within several minutes of stirring at 0 °C, white precipitates are formed. The mixture is warmed up to room temperature and ether (100 ml) is added. The white precipitates are filtered and washed with ether or pentane to give the sulfonium bromides **3**.

Vinylsulfonium Salts 4 or 5; General Procedure:
To a solution of a sulfonium bromide **3** (7 mmol) in water (50 ml), solid sodium carbonate (2.0 g) is added and the mixture is stirred for a few minutes at 25–60 °C. A solution of sodium tetraphenylborate (7.8 mmol) in water (50 ml) is added to the solution of the vinylsulfonium bromide **4** to give white precipitates (5–6 mmol) of **5** which are isolated by suction. A solution of a bromide **3** and sodium carbonate in D_2O exhibited a clean ^{1}H-N.M.R. spectra for the vinylsulfonium ion.

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