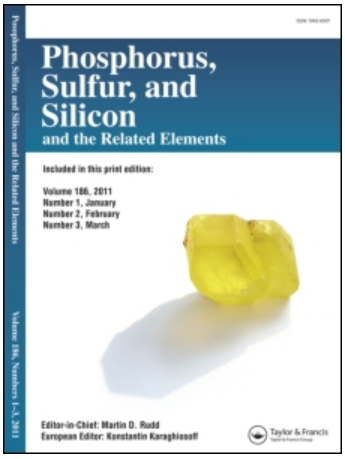

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Bonita C. Musial[a]; Michael E. Peach[a]
[a] Department of Chemistry, Acadia University, Wolfville, Nova Scotia, Canada

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NUCLEOPHILIC SUBSTITUTION OF HEXABROMOBENZENE WITH THIOLATE ANIONS†

BONITA C. MUSIAL and MICHAEL E. PEACH‡

Department of Chemistry, Acadia University, Wolfville, Nova Scotia, Canada B0P 1X0

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Reaction of hexabromobenzene with methane- and ethanethiolate gave substitution and protodebromination products.

In continuation of the study of the reactions of the thiolate anion with haloaromatic compounds,[1] the reactions of hexabromobenzene have been studied. The reactions observed are summarized below.

$C_6Br_6 + MeS^- \rightarrow C_6Br_5SMe$, $C_6Br_4(SMe)_2$, $C_6Br_2(SMe)_4$, C_6Br_5H, $C_6Br_2H(SMe)_3$, $C_6H_2Br_3(SMe)$

$C_6Br_6 + EtS^- \rightarrow C_6Br_4H(SEt)$, C_6Br_5H, $C_6Br_4H_2$

$C_6Br_6 + SH^- \rightarrow$ mainly C_6Br_6

Comparison with the analogous reactions of hexafluorobenzene and hexachlorobenzene, studied using the same solvent system (ethylene glycol-pyridine),[2] shows that in all cases, nucleophilic replacement of the halogen occurred but only in the case of hexabromobenzene was protodehalogenation observed. Initial protodebromination, and then nucleophilic substitution was observed when bromopentafluorobenzene was treated under the same conditions with the methanethiolate anion.[3] Protodebromination of hexabromobenzene on treatment with the methoxide anion occurred in methyl ethyl ketone or methanol, but only nucleophilic substitution occurred in pyridine forming pentabromoanisole and *m*-dimethoxytetrabromobenzene.[4]

Pentabromothiophenol has been prepared from the Grignard reagent, C_6Br_5MgBr, after suitable treatment with sulfur and acidification,[5] but it cannot be prepared from the fully halogenated benzene and the hydrogen sulfide anion, HS^-, as can pentafluoro- and pentachloro-thiophenols.[6,7] Difficulties have been experienced in our laboratories using the hydrogen sulfide anion as a nucleophile, because the thiol generated can further act as a nucleophile and polymeric products and tars form.

Compounds such as $C_6Br_4(SMe)_2$ and $C_6Br_2(SMe)_4$ containing only bromine and sulfur attached to the aromatic nucleus have not been reported previously, although their fluoro and chloro analogs are known.[2] The structures of $C_6Br_4(SMe)_2$ and $C_6Br_2(SMe)_4$ are not known; the analogous fluoro and chloro compounds have *para* methyl thio groups and *para* halogen atoms respectively.[2,8] In $C_6Br_2(SMe)_4$, the bromine atoms may be *para* to each other. The proton NMR spectrum is a singlet. If they were *meta* or *ortho* to each other, two different signals (ratio 2 : 2) or three different signals (ratio 1 : 2 : 1) might be expected, although the symmetrical structure may affect the spectrum. The structures of the other products cannot be deduced from their proton NMR spectra.

In the reactions using the ethanethiolate anion, protodebromination and subsequent nucleophilic substitution of the product occurred. The reaction conditions were the same as those used with the methanethiolate anion, and indicate that the methanethiolate anion is a better nucleophile under these conditions towards hexabromobenzene than the ethanethiolate anion. The presence of the hydrogen, after the protodebromination (or the methyl/ethyl thio group, as in C_6Br_5X) probably activates the haloaromatic towards nucleophilic substitution. Protodebromination occurred twice, forming $C_6Br_4H_2$ in the ethanethiolate reaction, the main product having *para* hydrogen atoms, with smaller amounts of another isomer or of a mixture of the other isomers which could not be separated by column chromatography and was identified from its mass spectrum.

† Part VI in the series "The thiolate anion as a nucleophile". For Part V, see Ref. 1.

‡ To whom all correspondence should be addressed.

TABLE I
Reaction stoichiometry and products

Molar ratio RS^-: C_6Br_6	Products	Yields (%)[a]	Purfication[b]
4(MeS^-)	$C_6Br_2(SMe)_4$	16	1($CHCl_3$)
	p-$H_2C_6Br_4$	3	3
	$C_6Br_2H(SMe)_3$	15	3,2
1(MeS^-)	$C_6Br_4(SMe)_2$	13	3,1(Me_2CO)
	C_6Br_5H	21	3
	C_6Br_5SMe	14	3,1(Me_2CO)
	$C_6Br_3H_2SMe$	8	3
	C_6Br_6	33	3
4(EtS^-)	$C_6Br_4H_2$	28	1(Me_2CO),2
	$C_6Br_4H(SEt)$	30	3
	$C_6Br_4H_2$	12	3
1(EtS^-)	C_6Br_5H	15	2
	C_6Br_6	72	3
1(HS^-)	C_6Br_6	63	1($CHCl_3$)

[a] Based on C_6Br_6.
[b] 1-recrystallization; 2-sublimation; 3-column chromatography.

with hexane or hexane-benzene gradient elution. The reactions were performed using 10 moles of C_6Br_6. The solvent mixture was refluxed for 15 minutes and then kept at room temperature for 45 minutes before quenching. In some cases, extreme difficulty was experienced in the purification of the products; small amounts of products were characterized from their mass spectra. Known compounds were identified by their mps and chemical analysis. Details of the new compounds are shown in Table II.

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TABLE II
Physical properties and analyses of new compounds

Compound	mp (°C)	Found (%) C	Found (%) H	Found (%) S	Calculated (%) C	Calculated (%) H	Calculated (%) S	H NMR[a] (ppm)
C_6Br_5SMe	119-121	16.2	0.6	6.3	16.2	0.6	6.2	2.59 S
$C_6Br_4(SMe)_2$	157.5-158.5	19.9	1.4	12.8	19.8	1.2	13.2	2.71 S
$C_6Br_2(SMe)_4$	195-197	28.5	2.9	30.5	28.6	2.9	30.5	2.52 S
$C_6Br_3H_2SMe$	149-150	23.3 66.2 (Br)	1.6	8.8	23.3 66.4 (Br)	1.4	8.9	2.42 S (Me) 7.74 S (ArH)
$C_6Br_2H(SMe)_3$	98-100	28.9	2.5	25.8	28.9	2.7	25.7	2.45 T (Me, $J \simeq 0.3$ Hz) 2.46 S (Me) 2.49 S (Me) 7.29 D (ArH, $J = 1.3$ Hz)
$C_6Br_4H(SEt)$	94-95	21.5	1.3	7.1	21.2	1.3	7.1	1.42 T (Me) 3.15 Q (CH_2) 8.00 D (ArH, $J = 0.06$ Hz)

[a] in $CDCl_3$ solution, TMS internal standard; S = singlet, D = doublet, T = triplet, Q = quartet.

EXPERIMENTAL

The experimental techniques used have been described previously.[2] Reagents were all available commercially. NMR spectra were recorded on a Varian HA 100, infrared spectra on a Perkin-Elmer 457 and mass spectra on a DuPont 21-491 mass spectrometer. Microanalyses were performed by Mikroanalytisches Laboratorium Beller, Göttingen, W. Germany and Organic Microanalyses (Dr. C. Daessle), Montreal, Canada.

Details of the reaction conditions, products isolated, and methods of purification are shown in Table I. Column chromatography was effected on a silica gel, 100-200 mesh,

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