REACTION OF ESTERS OF THIO ACIDS OF TRIVALENT ARSENIC WITH ORGANOMAGNESIUM COMPOUNDS

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It is known that tribenzylarsine and other products are formed when tributyl arsenite is reacted with benzylmagnesium chloride [1]. The bahavior of the esters of the thio acids of trivalent arsenic in Grignard reactions is not reported in the literature.

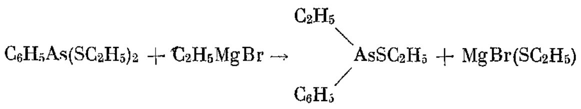
We established that the esters of the thio acids of trivalent arsenic react with organomagnesium compounds with the evolution of heat and either the complete or partial cleavage of the As–S bonds. The corresponding tertiary arsines (a) and mercaptans (b) are formed when the reactants are taken in the ratios indicated in the general scheme given below

$$R_nAs(SR')_{3-n} + (3-n)\,R''MgBr \rightarrow R_nR''_{3-n}As + (3-n)HSR' \quad R = C_6H_5,\ C_2H_5$$
$$C_3H_5;\ R' = n\text{-}C_4H_9,\ C_6H_5CH_2;\ R'' = C_2H_5,\ C_6H_5;\ n = 0,\ 1,\ 2$$

The transition of one thio ester to another can be accomplished by alkylating the esters of the thio acids of trivalent arsenic with organomagnesium compounds. Thus, for example, triethyl trithioarsenite is alkylated with a molar amount of ethylmagnesium bromide to S,S-diethyl ethyl dithioarsonite

$$(C_2H_5S)_3As + C_2H_5MgBr \rightarrow C_2H_5As(SC_2H_5)_2 + MgBr(SC_2H_5)$$

while S,S-diethyl phenyl dithioarsonite is alkylated by ethylmagnesium bromide to S-ethyl ethyl phenyl thioarsinite



$$C_6H_5As(SC_2H_5)_2 + C_2H_5MgBr \rightarrow (C_2H_5)(C_6H_5)AsSC_2H_5 + MgBr(SC_2H_5)$$

In Table 1 are given the starting compounds and their ratios, and also the isolated products, as well as their yields and analytical data.

EXPERIMENTAL

Reaction of Tribenzyl Trithioarsenite with Ethylmagnesium Bromide (Molar ratio 1:3). To the ethylmagnesium bromide obtained from 9 g of magnesium and 35.6 g of ethyl bromide in 150 ml of ether, with stirring, was added a solution of 48 g of tribenzyl trithioarsenite in 50 ml of absolute ether at such a rate that the ether boiled steadily. The reaction mixture was refluxed for 3 h and then it was decomposed under cooling with ice water, and then with dilute HCl solution (1:4). The ether layer was separated, dried over $MgSO_4$, and from the liquid, remaining after distilling off the ether, were isolated two main fractions (see Table 1, Expt. 1): I) bp 46-48° (25 mm); n_D^{20} 1.4796; 10.5 g = triethylarsine (from [5]: bp 140°); II) bp 71.5-73° (10 mm); n_D^{20} 1.5760; 30 g = benzyl mercaptan (from [6]: bp 87° (18 mm); n_D^{25} 1.5729).

The reactions of S,S-dibutyl phenyl dithioarsonite and S-butyl ethyl phenyl thioarsinite with phenylmagnesium bromide were run under analogous conditions (see Table 1, Expts. 2 and 3).

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TABLE 1

	Starting compound	Isolated reaction products and their constant	Yield %	Empirical formula	Found/Calculated, %
1	$(C_6H_5CH_2S)_3As+3\ C_2H_5MgBr$	a) $(C_2H_5)_3As$ T. Bp. 46-48° (25 mm) n_D^{20} 1.4796	56.5	$C_6H_{15}As$	As $\frac{43.14}{43.52}$
		b) $C_6H_5CH_2SH$ T. Bp. 71.5-73° (10 mm) n_D^{20} 1.5760	74.6	C_7H_8S	
2	$C_6H_5As(SC_4H_9\text{-}n)_2+2C_6H_5MgBr$	a) $(C_6H_5)_3As$* T. mp. 56-57° (ethanol)	41.0	$C_{18}H_{15}As$	As $\frac{24.29}{24.46}$
		b) $n\text{-}C_4H_9SH$ T. Bp. 96-98°	31.8	$C_4H_{10}S$	
3	$\genfrac{}{}{0pt}{}{C_2H_5}{C_6H_5}{>}AsSC_4H_9\text{-}n+C_6H_5MgBr$	a) $C_2H_5As\ (C_6H_5)_2$† T. Bp. 101.5-103° (0.008 mm) n_D^{20} 1.6151 d_4^{20} 1.2387	31.3	$C_{14}H_{15}As$	As $\frac{28.44}{29.00}$
		b) $n\text{-}C_4H_9SH$ T. Bp. 95-96°	32.0	$C_4H_{10}S$	
4	$(C_2H_5S)_3As+C_2H_5MgBr$	$C_2H_5As(SC_2H_5)_2$ T. Bp. 58-59° (0.1 mm) n_D^{20} 1.5760 D_4^{20} 1.2572	73.1	$C_6H_{15}As_2S_6$	As $\frac{33.05}{33.11}$ S $\frac{28.81}{28.35}$
5	$C_6H_5As(SC_2H_5)_2+C_2H_5MgBr$	$C_2H_5(C_6H_5)AsSC_2H_5$‡ T. Bp. 136-138° (10 mm) n_D^{20} 1.5970 d_4^{20} 1.2615	33.0	$C_{10}H_{15}AsS$	As $\frac{30.72}{30.93}$ S $\frac{13.47}{13.22}$

*From [2]: mp 56°.
†From [3]: bp 162-163° (10mm).
‡From [4]: bp 143-144° (10 mm); n_D^{20} 1.5980; d_4^{20} 1.2613.

Reaction of Triethyl Trithioarsenite with Ethylmagnesium Bromide (Molar ratio 1 : 1). To a solution of triethyl trithioarsenite in 50 ml of absolute ether, with stirring and cooling to −5°C, was added in drops a solution of ethylmagnesium bromide, obtained from 1.2 g of Mg and 5.6 g of ethyl bromide in 100 ml of absolute ether. The reaction mixture was refluxed for 2 h, the obtined white precipitate was filtered, and the filtrate was fractionally distilled in vacuo. We isolated 8 g of S,S-diethyl ethyl dithioarsonite with bp 58-59° (0.1 mm); n_D^{20} 1.5760; d_4^{20} 1.2572 (see Table 1, Expt. 4). From [7]: bp 80-82° (2 mm); n_D^{20} 1.5750; d_4^{20} 1.2555.

The reaction of S,S-diethyl phenyl dithioarsonite with ethylmagnesium bromide was run in a similar manner (Expt. 5).

CONCLUSIONS

Depending on the molar ratios, the esters of the thio acids of trivalent aresnic are alkylated by organomagnesium compounds to give the corresponding tertiary arsines or the esters of the thio acids of trivalent arsenic.

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