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NOTE

REACTION OF TRIORGANOSTIBINE SULFIDES WITH STABLE TIN–TIN BONDS

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Hexaalkylditins are slowly oxidized in air to bis(trialkyltin) oxides, and they react with sulfur to give bis(trialkyltin) sulfides[1]. On the other hand, the Sn–Sn bond in hexaarylditins cannot be cleaved by oxygen[2,3]. Since the Sb–S bond in trimethylstibine sulfide has been found to be quite reactive[4,5], we have allowed triorganostibine sulfides to react with the stable hexaorganoditins mentioned above.

In the reactions of trimethylstibine sulfide and triphenylstibine sulfide with hexaphenylditin and of trimethylstibine sulfide with hexabenzylditin in refluxing chloroform, sulfur insertion takes place to give bis(triorganotin)sulfides quantitatively [eqn. (1)].

$$R_3SbS + R'_3SnSnR'_3 \rightarrow R_3Sb + (R'_3Sn)_2S \qquad (1)$$

$$R = CH_3;\ R' = C_6H_5, C_6H_5CH_2 . \quad R = C_6H_5;\ R' = C_6H_5$$

However, no reaction occurred between triphenylstibine sulfide and hexabenzylditin, even upon prolonged heating in chloroform.

When these ditins were heated with elemental sulfur under similar reaction conditions, no reaction occurred. The enhanced reactivity of the triorganostibine sulfides may be attributed to the semi-polar Sb–S bond which undergoes facile reductive cleavage upon interaction with the tin atoms of the ditins[4,6].

Triorganostibine sulfides did not react with hexaphenyldigermane and hexaphenyldisilane. This is consistent with the proposed trend of the oxidative cleavage reactions of the Group IVb metal–metal bond, that is, there appears to be a major break between germanium and tin[7].

EXPERIMENTAL

The preparations of trimethylstibine sulfide and triphenylstibine sulfide have already been described[6,8]. Hexaphenylditin[9] and hexabenzylditin[3] and hexaphenyldigermane[10] and hexaphenyldisilane[11] were prepared according to directions in the literature. A new compound, bis(tribenzyltin) sulfide, was also prepared from tribenzyltin chloride and sodium sulfide (m.p. 85°) (Found: C, 62.07; H, 4.97; Sn, 29.00. $C_{42}H_{42}SSn_2$ calcd.: C, 61.79; H, 5.20; Sn, 28.96%.)

Reaction of triorganostibine sulfides with hexaorganoditins

All of the reactions were carried out by heating under reflux in chloroform solutions containing equimolar amounts of triorganostibine sulfide and hexaorganoditin. The results are summarized in Table 1.

Mixed melting points of the reaction products with authentic specimens of the respective compounds were not depressed.

TABLE 1

RESULTS OF THE REACTIONS OF TRIORGANOSTIBINE SULFIDES WITH HEXAORGANODITINS (EQN. 1)

Reactants		Reaction time (h)	Yield (%) of products	
R_3SbS	R'_6Sn_2		R_3Sb	$(R'_3Sn)_2S$
$R=CH_3$	$R'=C_6H_5$	1	75	94[a]
CH_3	$C_6H_5CH_2$	1	90	91[a]
C_6H_5	C_6H_5	1	98	76[b]
C_6H_5	$C_6H_5CH_2$	24	no reaction	

[a] Excess aqueous hydrogen peroxide was added to oxidize the trimethylstibine formed in the reaction mixture. From the chloroform layer was obtained bis(triorganotin) sulfide. The trimethylstibine oxide obtained by evaporating the aqueous layer was allowed to react with bromine in chloroform to give dibromotrimethylantimony. [b] To the reaction products obtained by removing chloroform was added 10 ml of n-hexane. The white precipitates insoluble in n-hexane were recrystallized from acetone to give bis(triphenyltin) sulfide. Triphenylstibine was obtained from the n-hexane layer.

Attempted reaction of hexaorganoditins with sulfur

Hexabenzylditin or hexaphenylditin and an excess of sulfur in chloroform were heated under reflux for 3 h. Evaporation of the chloroform gave unreacted ditins in quantitative yields.

Attempted reactions of triorganostibine sulfides with hexaphenyldigermane and hexaphenyldisilane

Equimolar amounts of trimethylstibine sulfide or triphenylstibine sulfide and hexaphenyldigermane or hexaphenyldisilane in chloroform were heated at reflux for 3 h. Removal of the solvent gave the starting materials quantitatively.

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REFERENCES

1 R. K. Ingham, S. D. Rosenberg and H. Gilman, *Chem. Rev.*, 60 (1960) 459.
2 H. Gilman and S. D. Rosenberg, *J. Org. Chem.*, 18 (1953) 1554.
3 K. K. Law, *J. Chem. Soc.*, (1926) 3243.
4 J. Otera and R. Okawara, *J. Organometal. Chem.*, 16 (1969) 335.
5 J. Otera and R. Okawara, *J. Organometal. Chem.*, 11 (1969) 353.
6 M. Shindo, Y. Matsumura and R. Okawara, *J. Organometal. Chem.*, 11 (1968) 299.
7 H. Gilman, W. H. Atwell and F. K. Cartledge, *Advan. Organometal. Chem.*, 4 (1966) 1.
8 L. Kaufmann, *Ber.*, 41 (1908) 2764.
9 E. Krause and R. Becker, *Ber.*, 53 (1920) 173.
10 G. T. Morgan and H. D. K. Drew, *J. Chem. Soc.*, 127 (1925) 1760.
11 W. Schlenk, J. Renning and G. Racky, *Ber.*, 44 (1911) 1178.