Ring-opening and Ring-closing Reactions *via* Organometallic Compounds: New Preparative Methods for Spiro-orthocarbonates and Cyclic Iminocarbonates from Cyclic Dibutyltin Dialkoxides and Sulphides

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Summary Reactions of cyclic dibutyltin dialkoxides or sulphides with carbon disulphide or phenyl isothiocyanate provide a new and convenient synthetic route for spiro-orthocarbonates or cyclic iminocarbonates.

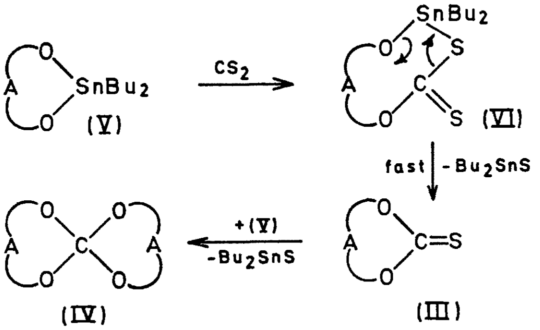
NOVEL synthetic methods for thionocarbonates (III) and spiro-orthocarbonates (IV) from the reactions between bis(tributyltin)alkylene glycolates and carbon disulphide at room temperature (Equation 1) have been reported.[1] The formation of the more stable Sn–S–Sn system and co-ordination of a sulphur atom to the non-bonded tin atom in the intermediate 1 : 1 adduct (II) were suggested as driving forces.

We report the reactions of carbon disulphide or phenyl isothiocyanate with cyclic dialkoxides (V) or sulphides (VIII) containing O–Sn–O or S–Sn–O systems.

The cyclic dialkoxides (Va—f) have been prepared by a variety of methods.[2,3]

Carbon disulphide (5 ml) and (V) (30 mmoles) were allowed to react in ethylene dichloride (40 ml) in a glass autoclave. The reaction conditions and the products are summarized in the Table.

Five- and six-membered-ring dialkoxides (Va—e) exist in stable dimeric forms,[3] and are much less reactive than monomeric compounds (I), which react exothermically with carbon disulphide at room temperature. Dimeric cyclic dialkoxides (V), except for (Vd), on reaction with carbon disulphide at 105—110° for 10 hr., give nearly quantitative yields of bis(alkylene) orthocarbonates and dibutyltin sulphide. These reactions proceed slowly below 80°. In contrast to the reactions of linear dialkoxides (I), thionocarbonates (III) could not be detected by i.r. spectrometry in reaction (2).

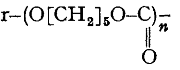


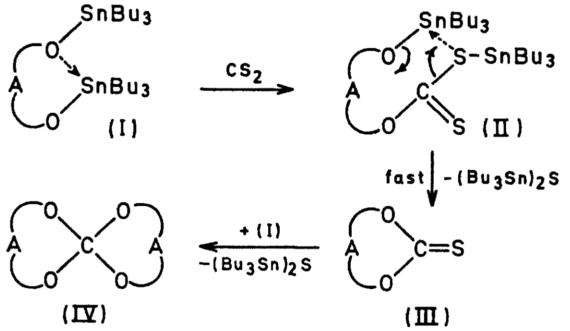
EQUATION 1

The seven-membered-ring dialkoxide (Vf) was reported

Reaction products from cyclic dibutyltin dialkoxides and CS_2 *in* $C_2H_4Cl_2$

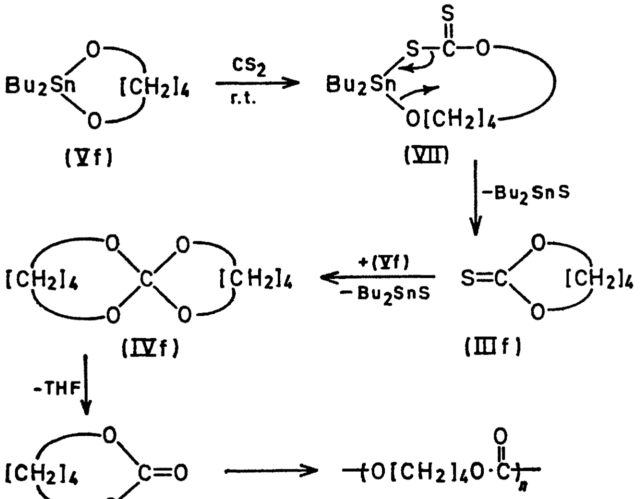
Cyclic alkoxide		Reaction conditions Temp.	Time (hr.)	Product and yield			M.p. and b.p.
(Va)	A = $[CH_2]_2$	105°	10	(IV)	A = $[CH_2]_2$	82%	b.p. 60—70°/0·5 mm[a] m.p. 143·0—143·5°
(Vb)	A = CHMe·CH_2	105°	10	(IV)	A = CHMe·CH_2	87%	b.p. 73°/2 mm
(Vc)	A = $[CHMe]_2$	110°	10	(IV)	A = $[CHMe]_2$	90%	b.p. 86°/3·5 mm
(Vd)	A = $[CMe_2]_2$	125°	20	4,4,5,5-Tetramethyl-2-oxo-1,3-dioxolan		trace	—
(Ve)	A = $[CH_2]_3$	105°	10	(IV)	A = $[CH_2]_3$	92%	b.p. 90°/0·06 mm m.p. 132—133°
(Vf)	A = $[CH_2]_4$	50°	4[b]	(IV)	A = $[CH_2]_4$	25%[c]	b.p. 110°/0·1 mm[a] m.p. 109·0—110·5°

[a] With sublimation. [b] Without solvent. [c] Accompanied by the formation of polymer– $-(O[CH_2]_5O-\underset{\underset{O}{\|}}{C})_n-$



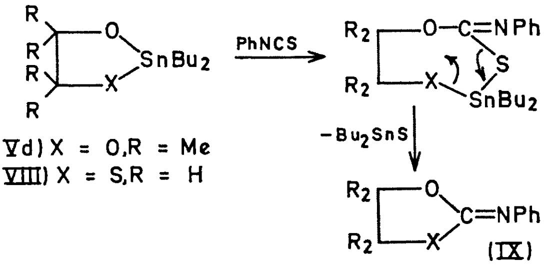
EQUATION 2

to be monomeric at room temperature,[3] and might be more reactive than dimeric five- and six-membered-ring compounds. The reaction mixture of carbon disulphide and (Vf) showed an i.r. band at 1175 cm^{-1}, which may be assigned as a $\nu_{C=S}$ band of the inserted product (VII) in Equation (3). Subsequent heating of (VII) at 50° for 4 hr. gave a 25% yield of bis-(1,4-butylene) orthocarbonate, 77% of poly-(1,4-butylene carbonate) (m.p. 141—153°), dibutyltin sulphide, and tetrahydrofuran. The formation of tetrahydrofuran and the polycarbonate is due to the decomposition of (Vf) (Equation 3).



EQUATION 3

The cyclic compound (Vd) hardly reacted at all with carbon disulphide during 20 hr. at 125°, and was recovered from the reaction mixture in 92% yield, accompanied by a trace amount of cyclic carbonate which was detected by an i.r. absorption band at 1790 cm^{-1}, and is probably a decomposition product of the corresponding spiro-orthocarbonate as was suggested in our previous papers.[1,4] However, reaction of (Vd) with phenyl isothiocyanate at 87°.for 40 hr., gave (quantitatively) 2,3-dimethyl-2,3-butylene phenyliminocarbonate (IX; R = Me, X = O) b.p. 120—125°/0·4 mm; m.p. 79—81°. The reaction between (Va) and phenyl isothiocyanate occurred more readily (55°; 2 hr.) and ethylene iminocarbonate (b.p. 148—150°/1.5 mm; m.p. 70—71°) was obtained in 98% yield.



EQUATION 4

2,2-Dibutyl-1,3,2-oxathiastannacyclopentane (VIII), on reaction with phenyl isothiocyanate at 55° for 5 hr. afforded a 95% yield of ethylene thioliminocarbonate (IX; X = S, R = H), m.p. 65·0—65·5°, and 98% of dibutyltin sulphide. On the other hand, the reaction of (VIII) with carbon disulphide at 120° for 15 hr., gave ethylene thiolcarbonate (b.p. 98—100°/6 mm), which would be one of the decomposition products of 1,6-dioxa-4,9-dithiaspiro[4,4]nonane. Compound (VIII) was less reactive than the corresponding dioxolan (Va), requiring severe reaction conditions.

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[1] S. Sakai, Y. Kiyohara, K. Itoh, and Y. Ishii, *J. Org. Chem.*, submitted for publication.

[2] H. E. Remsden and C. K. Banks, U.S.P., 1957, 2,789,994 [*Chem. Abs.*, 1957, **51**, 14,786]; J. Bornstein, B. R. La Liberter, T. M. Andrews, and J. C. Montermoso, *J. Org. Chem.*, 1959, **24**, 886; W. J. Considine, *J. Organometallic Chem.*, 1966, **5**, 263; R. C. Mehrotra and V. D. Gupta, *ibid.*, 1965, **4**, 145.

[3] J. Pommier and J. Valade, *J. Organometallic Chem.*, 1968, **12**, 433.

[4] S. Sakai, Y. Asai, Y. Kiyohara, K. Itoh, and Y. Ishii, submitted for publication in *Organometallics in Chem. Synthesis.*