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A NOVEL METHOD OF PREPARATION FOR ORTHOCARBOXYLATES FROM DITHIOCARBOXYLATES AND DIALKOXYDIBUTYLSTANNANES

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The reaction of methyl dithiocarboxylates with dialkoxydibutylstannanes at 60-95°C afforded the corresponding trialkyl orthocarboxylates in good yields.

The most generally applicable syntheses of orthocarboxylates involve alcoholysis of nitriles in strong acid medium and that of tri- or poly-haloalkane under basic conditions.[1,2] In recent years, dithiocarboxylates (1) became to be easily prepared directly from Grignard reagent, carbon disulfide, and an alkylating agent such as iodomethane.[3] And, we already established a novel method of preparation for orthocarbonates by the reaction of alkoxybutylstannanes with carbon disulfide.[4,5] Such situations encourage us to investigate a new type of preparation method for orthocarboxylates (3) by the reaction of 1 with dialkoxydibutylstannanes (2).

$$\underset{\underline{1}}{2\ R\text{-}\overset{\overset{S}{\|}}{C}\text{-}SMe} + \underset{\underline{2}}{3\ Bu_2Sn(OR')_2} \longrightarrow \underset{\underline{3}}{2\ RC(OR')_3} + \underset{\underline{4}}{2\ Bu_2SnS} + \underset{\underline{5}}{Bu_2Sn(SMe)_2} \qquad (1)$$

A typical procedure was as follows: methyl dithiocarboxylate (1; R=Ph, 1.35 g, 8 mmol) was mixed with an excess of 2 (R'=Me; 4.76 g, 16 mmol) under a dry nitrogen atmosphere and heated for 6 h at 60°C with stirring. The reaction mixture was distilled to afford 3 (R=Ph, R'=Me) in 70% yield (1.0 g); bp 93-95°C/12 mmHg (ref.[1] 114-115°C/25 mmHg); NMR (CCl_4) δ=3.04 (s, 9, CH_3), and 7.1-7.6 ppm (m, 5, Ph); IR ($HCCl_3$) 1060 cm^{-1} (ν_{C-O}). Dibutylstannyl sulfides 4 and 5 were not isolated separately, because they were co-oligomeric in the mixture.[6] The results of the reactions of various kinds of alkoxystannanes (2) with dithiocarboxylates (1) are summarized in Table 1.

Such type of the reaction (Eq. 1) is widely applicable to preparation of 3, because starting materials 1 and 2 are easily available and the reaction condition is mild due to weak basicity[7] and large reactivity of 2.

The mechanism of reaction (Eq.1) has not been established yet. But, it was found that 1 (R=Ph) was partially transesterified with 2 (R'=Me) under the reaction condition to form methyl thion-benzoate (characteristic methyl signal at δ=3.17 ppm was observed during the reaction), and the thion-benzoate reacted further with 2 to afford 3 (R=Ph, R'=Me). These results suggest that the reaction (Eq. 1) proceeds via thion-carboxylate (Eq. 2).

$$\underline{1} \overset{\cdot}{+} \underline{2} \xrightarrow[-\underline{5}]{} R\text{-}\overset{\overset{S}{\|}}{C}\text{-}OMe \xrightarrow[-\underline{4}]{+\underline{2}} \underline{3} \qquad (2)$$

Table 1. Yields of Orthocarboxylates (3) in the Reaction of Dithiocarboxylates (1) with Two Equivalents of Dialkoxydibutylstannanes (2)

R in 1	R' in 2	Reactn. Condn. Temp./°C	Time/h	Yeild of 3[a] %	Bp of 3 °C/mmHg
C_6H_5	Me	65	6	70	93-95/12
	Et	85	3	78	122-125/5
	n-Bu	95	18[b]	45	146-150/13
$2\text{-}CH_3C_6H_4$	Me*	95	13	60	103-104/15
	Et*	95	24	68	121-124/13
$4\text{-}CH_3C_6H_4$	Me	65	4	91	120-123/18
	Et*	95	6	98	132-134/12
$3\text{-}CH_3OC_6H_4$	Me*	65	6	82	122-124/12
	Et*	95	16	71	128-130/13
$4\text{-}CH_3OC_6H_4$	Me	65	8	76	133-135/13
	Et*	95	12	73	136-138/12
$4\text{-}ClC_6H_4$	Me	65	10	89	115-118/16
	Et*	95	36	82	129-132/13
Me	Et	60	1	52	45-47/12
Me_2CH	Me	60	4	85	130-135
	Et	60	4	62	49-51/12

a) Satisfactory analytical and IR or NMR spectroscopic data were obtained for all compounds prepared. b) The unreacted 1 was detected by NMR in the reaction mixture, contrary to the general cases where 1 was almost consumed.
* New compounds.

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