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SYNTHESIS OF THIOCYANATES BY OXYTHALLATION OF OLEFINS

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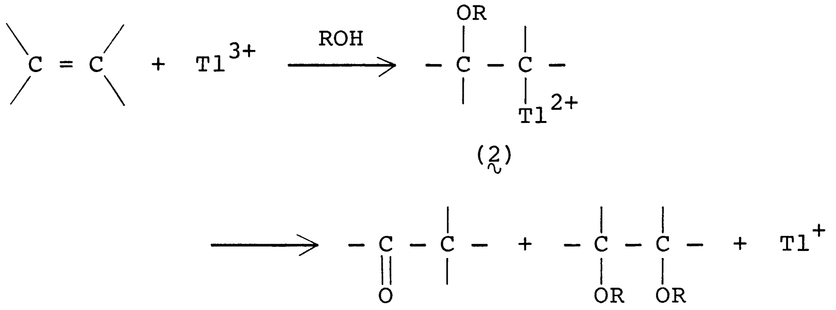
A convenient method to introduce a thiocyano group into an olefin with thallium triacetate is described. The reaction proceeds via oxythallation, replacement of an acetate ion with a thiocyanate ion, and dethallation, successively.

Rapidly increasing application of thallium compounds to organic synthesis has been reported in recent years.[1)] The latest paper by Taylor and co-workers demonstrates the utility of aromatic thallation to synthesize aryl thiocyanates (Eq. 1, X = SCN).[2)] As a part of the research project to develop the synthetic

$$\underset{(1)}{\mathrm{ArTl(OCOCF_3)_2}} \xrightarrow{X^-} \mathrm{ArTlX_2} \longrightarrow \mathrm{ArX} + \mathrm{TlX} \qquad (1)$$

method of thiocyanates using thallium, the present authors accomplished independently the similar photochemical synthesis of aryl thiocyanates via aromatic thallation.[3)] In this paper, another novel method to synthesize thiocyanates via oxythallation of olefins is described.

Oxidation of an olefin with Tl(III) is known to proceed via oxythallation reaction (Eq. 2):[4)]

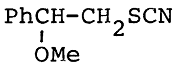
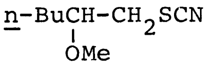
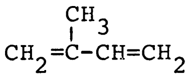
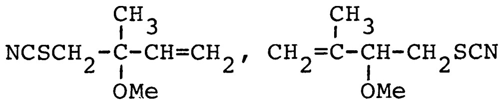
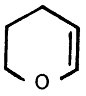
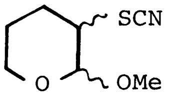
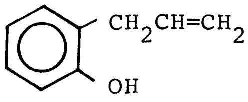
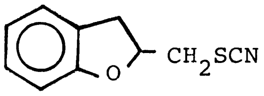
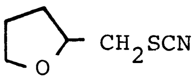
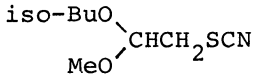
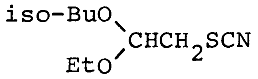
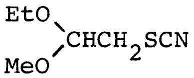
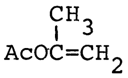
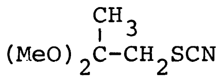


(2)

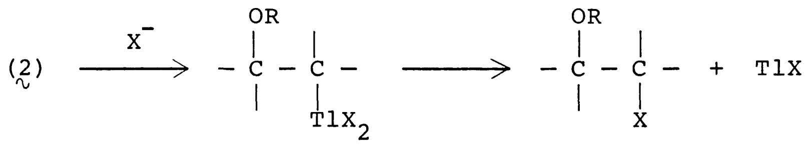
(R = CH_3 or CH_3CO)

The facts that, at least in some cases, oxythallation adducts (2) are stable enough to be isolated,[5)] and that the facile exchange of the anionic groups in arylthallium bis(trifluoroacetates) (1) is the key step in the synthesis of a variety of substituted aromatics using thallium (Eq. 1)[2,3,6)] suggest the possibility of a novel synthetic procedure via oxythallation of an olefin,

Table 1. Synthesis of Oxythiocyanates[a)]

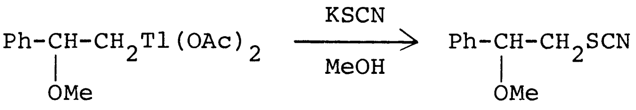
	Olefin	Solvent	Yield, %[b)]	Product[c)]
1	$PhCH=CH_2$	MeOH	46	 $PhCH(OMe)-CH_2SCN$
2	n-BuCH=CH_2	MeOH	59	 n-$BuCH(OMe)-CH_2SCN$
3	 $CH_2=C(CH_3)-CH=CH_2$	MeOH	15	 $NCSCH_2-C(CH_3)(OMe)-CH=CH_2$, $CH_2=C(CH_3)-CH(OMe)-CH_2SCN$ (51:49)
4		MeOH	7.6	
5		MeOH AcOH	38 47	
6	$CH_2=CH(CH_2)_3OH$	CH_3CN	54	
7	iso-BuOCH=CH_2	MeOH	40	$(MeO)_2CHCH_2SCN$,  $(iso\text{-}BuO)(MeO)CHCH_2SCN$ (54:46)
		EtOH	49	$(EtO)_2CHCH_2SCN$,  $(iso\text{-}BuO)(EtO)CHCH_2SCN$ (61:39)
8	$EtOCH=CH_2$	MeOH	41	$(MeO)_2CHCH_2SCN$,  $(EtO)(MeO)CHCH_2SCN$ (36:64)
		EtOH	38	$(EtO)_2CHCH_2SCN$
9	$AcCH=CH_2$	MeOH	25	$(MeO)_2CHCH_2SCN$
		EtOH	27	$(EtO)_2CHCH_2SCN$
10	 $AcOC(CH_3)=CH_2$	MeOH	60	 $(MeO)_2C(CH_3)-CH_2SCN$

replacement of anionic groups with other nucleophiles, and dethallation (Eq. 3):



$$(2)\ \xrightarrow{X^-}\ -\overset{OR}{\underset{|}{\overset{|}{C}}}-\underset{TlX_2}{\overset{|}{C}}-\ \longrightarrow\ -\overset{OR}{\underset{|}{\overset{|}{C}}}-\underset{X}{\overset{|}{C}}-\ +\ TlX \qquad (3)$$

The oxythallation adduct (3) from styrene with thallium triacetate in methanol was prepared according to Kabbe.[4b)] Addition of potassium thiocyanate to the methanol solution of 3 at room temperature caused the immediate precipitation of a yellow solid, which turned white after several minutes. Work-up as usual gave the expected oxythiocyanate (4) in a 65% yield. As a synthetic



$$\underset{OMe}{Ph\text{-}CH}\text{-}CH_2Tl(OAc)_2\ \xrightarrow[MeOH]{KSCN}\ \underset{OMe}{Ph\text{-}CH}\text{-}CH_2SCN \qquad (4)$$

(3) (4)

procedure, potassium thiocyanate was added to the reaction mixture of styrene and thallium triacetate in methanol at room temperature. The product 4 was isolated in a 46% yield based on the styrene used. In the same manner, several other olefins were converted to the corresponding oxythiocyanates in reasonable yields. The reactivities of these olefins were compared by carrying out the reaction under the constant conditions. The results are summarized in Table 1. Indene, cyclohexene, 2-methyl-2-butene, and N-vinyl-2-pyrrolidone did not react under these conditions.

The yield change with time followed by vpc in the case of 1-hexene in methanol showed that the maximum yield up to 97% was obtained for the reaction time of 4-10 hr, and the yield decreased gradually at the longer reaction time. In the case of isobutyl vinyl ether in methanol, the sharp maximum of a 80% yield was observed at the reaction time of 4 hr, then the yield decreased steeply. Apparently, the main factors determining the reaction yield are the reactivity of the starting olefin and the stability of the oxythallation adduct.

The exchange of an alkoxy group observed in vinyl ethers indicates the presence of an equilibrium between an olefin and an oxythallation adduct. This is verified by following the reaction of isobutyl vinyl ether in methanol and by determining the relative yield change of the normal and the exchanged acetal

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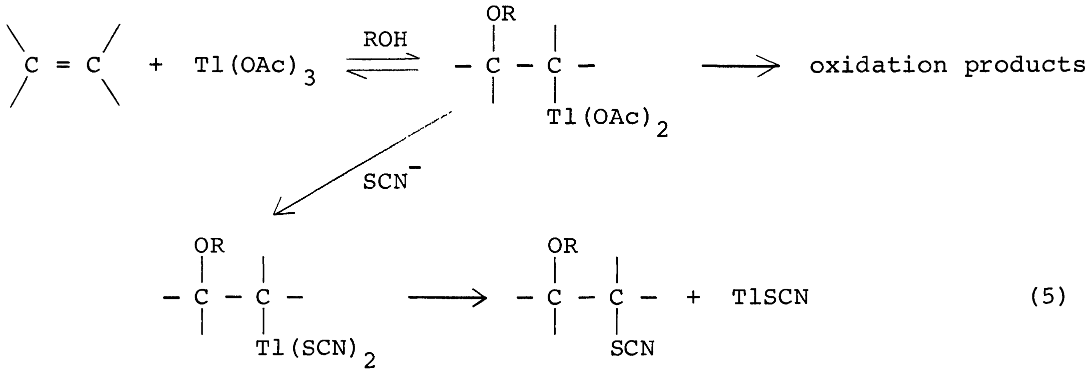
a) An olefin (0.05 mol) and thallium triacetate (0.079 mol) were stirred in 150 ml of an solvent for 30 min at room temperature. Then 22.5 g (0.23 mol) of potassium thiocyanate was added into the solution, and products were isolated as usual.

b) The yields recorded are apparently not the optimum yields for these reactions.

c) Satisfactory elemental analyses and spectroscopic data were obtained for all these compounds.

with reaction time. The control experiment showed the absence of the exchange of an alkoxy group in the products under the reaction conditions.

The appearance of the yellow solid on addition of potassium thiocyanate into the oxythallation mixture and fading of the color after several minutes may indicate the transient precipitation of the intermediate thallium compound **5**. These results suggest the possible mechanism of the reaction as follows:



(**5**)

(5)

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1. For a review, see E. C. Taylor and A. McKillop, *Accounts Chem. Res.*, **3**, 338 (1970).
2. E. C. Taylor, F. Kienzle, and A. McKillop, *Synthesis*, **1972**, 38.
3. H. Mitani, T. Ando, and Y. Yukawa, unpublished. Our synthetic method is almost same as that reported by Taylor *et al.*,$^{2)}$ except that dimethylsulfoxide was used as a solvent instead of water to keep the reaction solution homogeneous. Benzene, toluene, anisol, and *t*-butyl-, chloro-, and fluorobenzene were used as aromatic substrates, and very similar results as theirs were obtained.
4. (a) R. R. Grinstead, *J. Org. Chem.*, **26**, 238 (1961).
   (b) H.-J. Kabbe, *Ann.*, **656**, 204 (1962).
5. R. Criegee, *Angew. Chem.*, **70**, 173 (1958).
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   (b) A. McKillop, J. D. Hunt, M. J. Zelesko, J. S. Fowler, E. C. Taylor, G. McGillivray, and F. Kienzle, *ibid.*, **93**, 4841 (1971).

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