

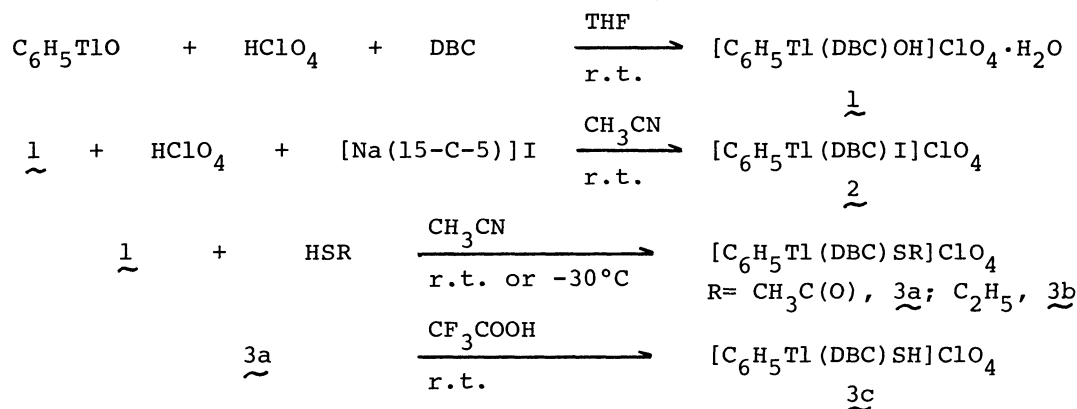
PREPARATION OF MONOPHENYLTHALLIUM(III)DIBENZO-18-CROWN-6 COMPLEXES  
WITH A SOFT LIGAND:  $[C_6H_5Tl(DBC)X]ClO_4$

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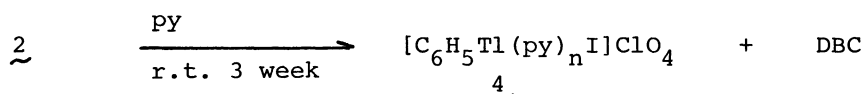
Monophenylthallium(III) complexes with a Tl-I or Tl-SR bond were prepared in the presence of dibenzo-18-crown-6. These complexes are stable in the air and to heat to their melting points. In the hydrogen sulfide complex,  $\nu(S-H)$  band was found at  $2570\text{ cm}^{-1}$  and  $\delta(Tl-SH)$  was observed at 1.15 ppm with  $^2J(Tl-SH) = 405\text{ Hz}$  in  $CH_2Cl_2$  solution.

Generally monophenylthallium(III) compounds are unstable in the presence of soft ligands such as  $I^-$  and decompose to thallium(I) ion.<sup>1)</sup> Therefore, monophenylthallium(III) compounds with Tl-I bond are very few.<sup>2,3)</sup> Monophenylthallium(III) compounds with Tl-S bond also are limited to the compounds with chelate ligands<sup>4-6)</sup> and the compounds with a thioalkyl or hydrogen sulfide group were not reported. One of reasons of unstability of the monophenylthallium(III) compounds is that two soft ligands can coordinate to the thallium atom at suitable positions simultaneously. It was reported that crown ethers form stable complexes with dimethylthallium(III) ion,<sup>7,8)</sup> in which a linear C-Tl-C moiety is perpendicularly fixed in the plane formed by six oxygen atoms. These complexes are inert to demetallation.<sup>7)</sup> In monophenylthallium(III)dibenzo-18-crown-6 complexes, therefore, only one soft ligand can coordinate to the thallium atom and isolation of the stable complexes with a Tl-I or Tl-SR bond may be expected.

Monophenylthallium(III)dibenzo-18-crown-6 complexes with a soft ligand were prepared by the procedures shown below.<sup>9)</sup> The complexes are soluble in  $CH_3CN$  or  $CH_2Cl_2$  and slightly soluble in  $CH_3OH$ . They are stable in the air and to heat to their melting points. The IR spectrum of  $\underline{3c}$  in  $CH_2Cl_2$  solution shows a strong and sharp band of S-H stretching frequency at  $2570\text{ cm}^{-1}$ . The S-H proton



resonance of  $\underline{3c}$  was observed at  $\delta = 1.15$  in the same solvent and was splitted by spin-spin coupling with the thallium nucleus ( $^2J(\text{Tl-SH}) = 405$  Hz). This signal was observed also in  $\text{CF}_3\text{COOH}$  ( $\delta = 0.76$ ,  $^2J(\text{Tl-SH}) = 396$  Hz), but disappeared in a mixed solvent of  $\text{CH}_2\text{Cl}_2$  and  $\text{CH}_3\text{OD}$ .  $\underline{3b}$  is stable at  $80^\circ\text{C}$  for 3 day in  $\text{CD}_3\text{CN}$  solution. It was also stable in the presence of excess amount of  $\text{C}_6\text{H}_5\text{CH}_2\text{SH}$  for a few day at room temperature in  $\text{CD}_3\text{CN}$  solution, but decomposition to  $\text{Tl}(\text{I})$  ion and a ligand substitution reaction giving  $[\text{C}_6\text{H}_5\text{Tl}(\text{DBC})\text{SCH}_2\text{C}_6\text{H}_5]\text{ClO}_4$  occurred simultaneously with a low rate. A demetallation reaction of  $\underline{2}$  occurred slowly in pyridine.



The presence of monophenyl(iodo)thallium(III) species,  $\underline{4}$ , in this solvent was deduced from the detection of the phenyl proton signals splitted by spin-spin coupling with the thallium nucleus.

#### References

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9. Elemental analyses of all complexes agree to the calculated values within 0.3%.  $\underline{1}$  % yield 90, mp  $132 - 140^\circ\text{C}$ .  $\underline{2}$  % yield 75, mp  $234 - 236^\circ\text{C}$ .  $\underline{3a}$  % yield 73, mp  $200 - 201^\circ\text{C}$ .  $\underline{3b}$  % yield 81, mp  $248 - 252^\circ\text{C}$ .  $\underline{3c}$  % yield 78, mp  $146 - 152^\circ\text{C}$ .

(Received April 23, 1982)