Phenyl- and Tolylthallium(III) Bis(trichloroacetate)s; Preparation and Reactions

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Synopsis. Phenyl- and tolylthallium(III) bis(trichloroacetate)s [$ArTl(OCOCCl_3)_2$, **1** (Ar=phenyl or tolyl)] were prepared from thallium(III) oxide, trichloroacetic acid, benzene, and toluene. The replacement of the thallium moiety in **1** with iodo, chloro, cyano, selenocyanato, and nitro groups and the aromatic coupling of **1** proceeded smoothly to give the corresponding aromatic derivatives in good yields. In the presence of $PdCl_2$–NaOAc, **1** (Ar=phenyl) reacted with acrylonitrile and methacrylonitrile to afford cinnamonitriles(*trans* and *cis*) and a mixture of α-benzylacrylonitrile and β-phenylmethacrylonitriles(*Z* and *E*) respectively.

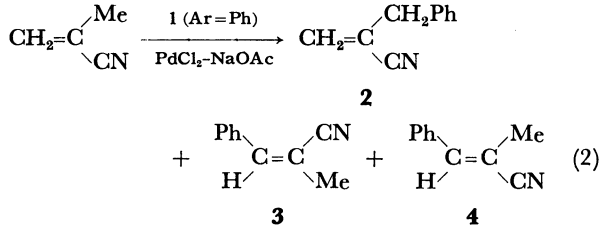
Direct aromatic thallation by thallium(III) acetate–$HClO_4$ in acetic acid[1] or thallium(III) trifluoroacetate in trifluoroacetic acid[2] is an effective method for the preparation of arylthallium(III) compounds, which are useful in organic syntheses. However, trifluoroacetic acid is an expensive and hazardous reagent, and the method using $HClO_4$ is dangerous in some cases because of the danger of explosion.[3] We have now found a simple method for direct aromatic thallation using trichloroacetic acid, useful for large-scale syntheses in the cases of benzene and toluene. We wish to report the preparation of phenyl- and tolylthallium(III) bis(trichloroacetate)s [$ArTl(OCOCCl_3)_2$, **1** (Ar=phenyl or tolyl)] and their use in organic syntheses.

A mixture of benzene or toluene, thallium(III) oxide, and trichloroacetic acid was stirred at 65—70 °C for 1—5 h to give a white solid of **1** (Scheme 1). The reaction conditions, the yields of **1**, the melting points,

$$2ArH + Tl_2O_3 + 4CCl_3CO_2H \longrightarrow \underset{\mathbf{1}}{2ArTl(OCOCCl_3)_2} \quad (1)$$

the isomer ratios, and the analytical and ^1H-NMR data are shown in Table 1. The scope of this aromatic thallation is, unfortunately, very limited; thus, **1** could not be obtained from anisole, thiophene, nitrobenzene, benzaldehyde, or methyl benzoate.[4] No aromatic thallation of benzene and toluene occurred when acetic, chloroacetic, or dichloroacetic acid was used under the conditions shown in Table 1.

The replacement of the thallium moiety in arylthallium(III) compounds with halogen,[5] pseudohalogen,[6] and a nitro group[7] and the aryl-coupling reaction[8] have been reported to give the corresponding aromatic derivatives. Although the yields of the products have depended on the kind of ligand on the thallium (*i.e.*, the yield of ArX is sometimes very low when the ligand is CN, Cl, OAc, or SCN), **1** where a ligand is CCl_3CO_2 was subjected quite successfully to all such reactions. Some typical results of the application of these reactions to **1** are summarized in Table 2. It has been known that arylthallium(III) compounds reacted with styrene and methyl acrylate in the presence of Li_2PdCl_4, the overall reaction being the replacement of an olefinic hydrogen by the aryl group.[9] When **1** (Ar=phenyl) was treated with styrene, ethyl acrylate, acrylonitrile, and methacrylonitrile in acetic acid or methanol in the presence of palladium(II) chloride or palladium metal and sodium acetate, *trans*-stilbene, ethyl cinnamate, cinnamonitriles(*trans*: *cis*=59: 41), and a mixture of α-benzylacrylonitrile (**2**) and (*Z*)- and (*E*)-β-phenylmethacrylonitriles (**3** and **4**) (**2**: **3**: **4**=55: 26: 19)



(2)

(Scheme 2) were produced respectively in good to excellent yields.[10] The product distributions in the latter two reactions were very close to those obtained in the reaction of phenylmercury(II) chloride under similar conditions, showing the presence of the same reactive species, probably the phenylpalladium(II) species. This is the first example of the arylation of α,β-unsaturated nitriles by the use of arylthallium(III) compounds and also of the arylation of olefins by arylthallium(III) compounds by the use of palladium metal as a catalyst. Some typical results are listed in Table 2.

Table 1. Preparation of **1** and their characterization

Aromatics (mol)		Tl_2O_3 (mol)	CCl_3CO_2H (mol)	Yield of **1** (%) Ar		Mp (dec) (°C)	Found (Calcd) (%) C	H	NMR (in CH_3OD) *o*-	*m*-	*p*-	J_{Tl-H}(Hz) *p*-CH_3
Toluene[a]	0.7	0.03	0.12	Tolyl[c]	64	182—184	21.62 (21.30	1.44 1.14)	974	358		58
Benzene[b]	0.8	0.03	0.12	Phenyl	66	220	19.74 (19.81	1.02 0.83)	915	345	115	

a) At 70 °C for 1 h. b) At 70 °C for 5 h. c) *o*: *m*: *p*=9: 5: 86, determined by analyzing the products obtained by nitrodethallation.[7]

TABLE 2. RESULTS OF THE REACTIONS OF **1** WITH VARIOUS REAGENTS

1 (2 mmol) Ar	Reagent (mmol)		Solvent (ml)		Temp (°C)	Time (h)	Product and yield(%)[a]
Ph	KI	10	$THF+H_2O$	10+10	65	0.5	Iodobenzene 71
Tolyl	KI	10	$THF+H_2O$	10+10	65	0.5	Iodotoluene 94[b]
Ph	$CuCl_2 2H_2O$	2	Dioxane	20	101	5	Chlorobenzene 69
Ph	CuCN	8	Pyridine	20	115	4	Benzonitrile 64
Ph[c]	$Cu(SeCN)_2$	279	Dioxane	200	101	0.5	Selenocyanatobenzene 71
Tolyl	$NaNO_2$	6	CF_3CO_2H	15	25	3	Nitrotoluene 90[b]
Ph	$PdCl_2$	2	AcOH	20	117	1	Biphenyl 100
	NaOAc	4					
Ph	$PdCl_2$	2	AcOH	20	117	1	*trans*-Stilbene 86
	NaOAc	4					
	Styrene	10					
Ph	$PdCl_2$	2	AcOH	20	117	1	Ethyl cinnamate 91
	NaOAc	4					
	Ethyl acrylate	10					
Ph	Pd[c]	2	MeOH	20	66	1	*trans*-Stilbene 100
	NaOAc	4					
	Styrene	10					
Ph	$PdCl_2$	2	AcOH	20	117	4	*trans*- and *cis*-Cinnamonitriles[e] 100
	NaOAc	4					
	Acrylonitrile	10					
Ph	$PdCl_2$	2	AcOH	20	117	4	**2**+**3**+**4**[f] 61
	NaOAc	4					
	Methacrylonitrile	10					

a) Determined by GLC. b) Isomer ratio not determined. c) Preparative scale experiment. **1** (Ar=Ph), 162 mmol. The yield is the isolated one (see Experimental). d) *o*: *m*: *p*=9: 5: 86. e) *trans*: *cis*=59: 41. Reaction with PhHgCl (for 1 h) afforded an 80% yield of a mixture of *trans*- and *cis*-cinnamonitriles (*t*: *c*=65: 35). f) **2**: **3**: **4**=55: 26: 19. Reaction with PhHgCl (for 1 h) gave a 57% yield of a mixture of **2**, **3**, and **4** (**2**: **3**: **4**=46: 31: 23).

Experimental

All the organic materials were commercial products and were distilled before use. Commercial inorganic materials were used without further purification. The organic product mixtures were analyzed by GLC by the use of a Shimadzu 4BMPF apparatus on EGSS-X-(15%)–Chromosorb-W (1 or 3 m) and Apiezon-L (1 m) columns (carrier gas, N_2). The NMR spectra were recorded on a Varian EM-360 spectrometer in CH_3OD, $CDCl_3$, or CCl_4, using tetramethylsilane as the internal standard.

Preparation of **1** *(Ar=phenyl).* A brown heterogeneous mixture of thallium(III) oxide (Tl_2O_3, 13.7 g, 30 mmol), trichloroacetic acid (19.6 g, 120 mmol), and benzene (70 ml) was stirred at 70 °C for 5 h to give a white, heterogeneous mixture. After the mixture had been cooled down to room temperature, the solid was filtered off, washed with benzene, and dried *in vacuo* over silica gel. Almost pure **1** (Ar=phenyl) was thus obtained; 24.0 g (39.6 mmol, 66% yield based on Scheme 1). This is soluble in alcohols, tetrahydrofuran, dimethyl sulfoxide, *N*,*N*-dimethylformamide, and pyridine and insoluble in chloroform, carbon tetrachloride, diethyl ether, and hexane.

The reaction of toluene was similarly carried out to give pure **1** (Ar=tolyl, *o*: *m*: *p*=9: 5: 86) in a 64% yield.

Preparation of Phenyl Selenocyanate from **1** *(Ar=phenyl).* The following is a typical example of the reactions of **1** with various reagents on a preparative scale. A black suspension of **1** (Ar=phenyl) (98.4 g, 162 mmol) and $Cu(SeCN)_2$ (76.2 g, 279 mmol) in dioxane (200 ml) was stirred at reflux for 0.5 h. After the mixture had then been cooled to room temperature, the precipitated dark grey solid was filtered off and washed with ether (*ca.* 50 ml). Water (200 ml) was added to the combined solution of the filtrate and the ether washing, and then it was extracted with ether (200 ml×3). The ether extract was washed with aqueous NaCl and dried over $MgSO_4$. Distillation afforded 21 g (115 mmol, 71% yield) of almost pure phenyl selenocyanate; bp 110—120 °C/4 mmHg (lit,[11] bp 134 °C/10 mmHg).

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4) From ethylbenzene at 70 °C for 24 h, a pure **1** (Ar=ethylphenyl) could not be obtained, the nitrodethallation of the crude product showing the formation of at least a 9% yield of **1** (*o*: *m*: *p*=10: 8: 82). In this case, 1-phenylethyl trichloroacetate was also formed: isolated yield, 14%; bp 110 °C/5 mmHg; NMR (δ, $CDCl_3$), 1.65 (d, 3H), 5.92 (q, 1H), 7.27 (s, 5H). From chlorobenzene at 65—70 °C for 20 h, **1** (Ar=chlorophenyl) was obtained in an 18% yield; mp 205 °C (dec) (*o*: *m*: *p*=24: ≈0: 76).

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10) A mixture of **2**, **3**, and **4** was isolated by distillation; bp 120—125 °C/20 mmHg; Found: C, 83.95; H, 6.25; N, 9.46%. Calcd for $C_{10}H_9N$: C, 83.88; H, 6.34; N, 9.78%. NMR (δ, CCl_4) for **2**, 3.58 ($PhC\underline{H}_2$), 5.72 and 5.96 ($=CH_2$).

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