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Hypervalent Iodine in Synthesis: 13: Action of Phenyliodine(III) Dicarboxylates on Diaryltellurides: A Facile and General Method for the Preparation of Diaryltellurium Dicarboxylates

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ABSTRACT

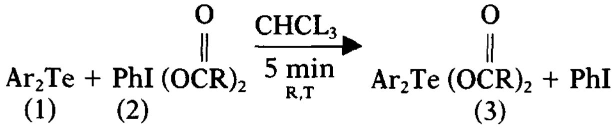
A facile and general method for the preparation of diaryltellurium dicarboxylates is described. The method involves simply the stirring of phenyliodine(III) dicarboxylates with diaryltellurides in chloroform at room temperature.

INTRODUCTION

In recent years, there has been considerable interest in hypervalent iodine(III) compounds as reagents for organic synthesis. Among the most important reagents are phenyliodine(III) dicarboxylates. They have been used effectively in acyloxylations at sp, sp^2, or sp^3 carbon atoms to give the corresponding acyloxy-derivatives [1]. However, thus far, the acyloxylations of phenyliodine(III) dicarboxylates at heteroatoms have seldom been reported [2]. As part of our general interest in synthetic applications of phenyliodine(III) dicarboxylates, we investigated the possibility of extending this acyloxylation to heteroatoms. We first studied the reaction of phenyliodine(III) dicarboxylates with diaryltellurides. Such a reaction could provide a useful route to diaryltellurium dicarboxylates. Herein are described the results of these experiments.

RESULTS AND DISCUSSION

The acyloxylation of diaryltellurides (**1**) with phenyliodine(III) dicarboxylates (**2**) was found to occur readily in a single step. This affords the diaryltellurium dicarboxylates (**3**) (Equation 1). Simple stirring of the appropriate diaryltellurides (**1**) with the appropriate phenyliodine (III) dicarboxylates (**2**) in chloroform at room temperature for 5 minutes gave, after workup and isolation, the desired diaryltellurium dicarboxylates (**3**) in excellent yields, as shown in Table 1.



$$\underset{(1)}{Ar_2Te} + \underset{(2)}{PhI\,(O\overset{\overset{O}{\|}}{C}R)_2} \xrightarrow[5\ \text{min}\ \text{R.T}]{CHCL_3} \underset{(3)}{Ar_2Te\,(O\overset{\overset{O}{\|}}{C}R)_2} + PhI \qquad (1)$$

Ar =	R =
p-$CH_3C_6H_4$	CH_3
p-ClC_6H_4	CF_3
p-$CH_3OC_6H_4$	Ph

Ar	R
a:p-$CH_3C_6H_4$	CH_3
b:p-$CH_3C_6H_4$	CF_3
c:p-$CH_3C_6H_4$	Ph
d:p-ClC_6H_4	CH_3
e:p-ClC_6H_4	CF_3
f:p-ClC_6H_4	Ph
g:p-$CH_3OC_6H_4$	CH_3
h:p-$CH_3OC_6H_4$	CF_3
i:p-$CH_3OC_6H_4$	Ph

Dedicated to Prof. Yao-Zeng Huang on the occasion of his eightieth birthday.

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TABLE 1 Product Yields and Physical Properties of Diaryltellurium Dicarboxylates (**3**)

Compound	*Yield (%)*	*MP (°C)*	*IR (KBr) cm^{-1}*	*^{1}H NMR*		*Elemental Analysis*	
						Found	*Calculated*
3a	89	180–183	1645	1.95 (s, 6H), 2.40 (s, 6H) 7.26 (d, 4H), 7.70 (d, 4H)		lit. mp	178–180°C [10]
3b	95	215.9	1700	2.45 (s, 6H), 7.27–7.83 (m, 8H)	C H	40.08 2.48	40.34 2.63
3c	96	236.8	1650	2.40 (s, 6H) 7.20–7.51 (m, 10H) 7.67–8.10 (m, 8H)		lit. mp	230°C [7]
3d	92	175.9	1640	1.97 (s, 6H) 7.28–7.95 (m, 8H)	C H	40.79 2.95	40.99 3.01
3e	96	142.9	1737	7.40–7.95 (m, 8H)	C H	33.30 1.34	33.32 1.39
3f	90	195.5	1650	7.30–8.1 (m, 18H)	C H	52.55 3.02	52.67 3.06
3g	97	139.1	1640	1.98 (s, 6H), 3.83 (s, 6H) 7.00 (d, 4H), 7.84 (d, 4H)		lit. mp	135–137°C [10]
3h	98	149.2	1700	3.83 (s, 6H), 7.05 (d, 4H) 7.70 (d, 4H)		lit. mp	152°C [3]
3i	94	209.9	1645	3.81 (s, 6H), 6.98 (d, 4H) 7.27–7.52 (m, 6H) 7.82–8.10 (m, 8H)		lit. mp	210°C [7]

The diaryltellurium dicarboxylates obtained were characterized by elemental analyses (for unknown compounds) and by IR and ^{1}H NMR spectra. The data are summarized in Table 1.

Diaryltellurium dicarboxylates (**3**) have attracted considerable interest because of their biocidal activities [3] and applications in organic synthesis [4] and in industry [5]. Existing methods for the preparation of (**3**) are essentially based upon the reaction of diaryltellurium dichlorides with silver carboxylates [6], the reaction of the dichlorides with a carboxylate anionic exchange resin [7], the reaction of diaryltellurium dichlorides with carboxylic acids in the presence of silver oxide [7,8], or the reaction of diaryltelluroxides with carboxylic acids or anhydrides [9]. In view of the high cost of silver salts and because the preparation of diaryltellurium dichlorides or diaryltelluroxides utilizes diaryltellurides, these methods seem to be less attractive than the one described herein that uses diaryltellurides directly. Although Pant [10] reported that diaryltellurides were directly converted to diaryltellurium diacetates by use of lead tetraacetate, this method is only suitable for the preparation of diacetate derivatives. In the method herein described, the procedure is simple and convenient because diaryltellurides are directly used and a variety of phenyliodine(III) dicarboxylates are easily obtained.

In summary, we have demonstrated that the reaction of phenyliodine(III) dicarboxylates with diaryltellurides can be utilized for the synthesis of diaryltellurium dicarboxylates. This method has some advantages, such as the ease of obtaining starting materials, mild reaction conditions, simplicity of the procedure, and excellent yields. The range of useful applications of phenyliodine(III) dicarboxylates as an acyloxylating reagent at heteroatoms has been extended.

EXPERIMENTAL

Proton nuclear magnetic resonance (^{1}H NMR) spectra were recorded at 60 MHz on a Varian EM-360 spectrometer in $CDCl_3$ solution with Me_4Si as an internal standard and are reported in δ units. Infrared spectra were recorded on a PE-683 infrared spectrophotometer and are reported in cm^{-1} units. Elemental analyses were performed on a Carlo Erba 1106 instrument. All melting points were taken on a Delta Series DSC7 instrument.

Materials

Diaryltellurides [11], phenyliodine(III) diacetate [12], phenyliodine(III)bis(trifluoroacetate) [13], and phenyliodine(III) dibenzoate [14] were prepared according to methods given in the literature.

*General Procedure for the Preparation of Diaryltellurium Dicarboxylates (**3**)*

A mixture containing 1 mmol of diaryltelluride and an equimolar amount of phenyliodine(III) dicarboxylate was placed in a flask and stirred in chloroform (~20 mL) at room temperature for 5 minutes. After evaporation of the solvent, fifteen milliliters of petroleum ether (70–90°C) was added to the residue, and the mixture was allowed to stand in the refrigerator overnight. The crystals that had formed were collected by suction filtration and purified by recrystallization from methylene chloride/hexane.

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