This article was downloaded by: [171.67.34.69] On: 12 March 2013, At: 04:37 Publisher: Taylor & Francis Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry

Publication details, including instructions for authors and subscription information: http://www.tandfonline.com/loi/lsyc20

Hypervalent lodine in Synthesis

Da Wei Chen ^a & Zhen Chu Chen ^a ^a Department of Chemistry, Hangzhou University, Hangzhou, 310028, P. R. China Version of record first published: 23 Sep 2006.

To cite this article: Da Wei Chen & Zhen Chu Chen (1995): Hypervalent lodine in Synthesis, Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry, 25:11, 1605-1616

To link to this article: <u>http://dx.doi.org/10.1080/00397919508015845</u>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <u>http://www.tandfonline.com/page/terms-and-conditions</u>

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing, systematic supply, or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae, and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand, or costs or damages

whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

HYPERVALENT IODINE IN SYNTHESIS: X V II. ACTION OF PHENYLIODINE(II) DICARBOXYLATES ON DIARYL DITELLURIDES: A NEW AND FACILE METHOD FOR THE PREPARATION OF ARENETELLURINIC MIXED ANHYDRIDES AND ARENETELLURINIC ANHYDRIDES

Da-Wei Chen and Zhen-Chu Chen*

Department of Chemistry, Hangzhou University Hangzhou, 310028, P.R. China

Abstract: A new and facile method for the preparation of arenetellurinic mixed anhydrides is described from diaryl ditellurides and phenyliodine (II) dicarboxylates. Hydrolysis of the arenetellurinic mixed anhydrides gives arenetellurinic anhydrides and a one — pot procedure involving the reaction of diaryl ditellurides with phenyliodine(II) dicarboxylates in a two—phase system of methylene chloride and aqueous solution of sodium hydroxide for the preparation of arenetellurinic anhydrides is provided. In recent years, a variety of organotellurium reagents have become available. The versatility of them in synthesis has been well recognized⁽¹⁾. One of family of organotellurium reagents, arenetellurinic mixed anhydrides (1) and arenetellurinic anhydrides (2), has received considerable interest because of their particular application in organic synthesis⁽²⁾, e. g., the acetoxytellurinylation⁽³⁾ and aminotellurinylation⁽⁴⁾ of olefins, intramolecular cyclofunctionalization of hydroxyolefins⁽³⁾, selective oxidation of thiols, hydroquinones, xanthates⁽⁵⁾, phosphines, thioamides, thioureas, thionoesters, and benzylic alcohols etc. ⁽⁶⁾.

$$\begin{array}{cccc}
O & O & O \\
Ar - Te & -OCOR & Ar - Te & -O-Te & -Ar \\
(1) & (2)
\end{array}$$

Although benzenetellurinyl acetate $(1 \text{ Ar}=\text{Ph}, \text{ R}=\text{CH}_3)$ was the first compound of arenetellurinic mixed anhydrides reported by Pant⁽⁷⁾, its synthetic details and properties were not provided. Ogura et al. treated the arenetellurinic anhydrides⁽²⁾ prepared from corresponding aryltellurium trihalides (3) with carboxylic acids or their anhydrides to form arenetellurinic mixed anhydrides⁽³⁾, (Scheme 1), which can be obtained in pure state or be used in further reaction after their in situ formation.

$$ArTeX_{3} \longrightarrow Ar - \begin{array}{c} O & O \\ \parallel & \parallel \\ Te & O \\ (3) \\ X = Cl, Br \end{array} Ar - \begin{array}{c} O & O \\ Te & O \\ RCOOH \text{ or } \\ (RCO)_{2}O \\ (1) \end{array} Ar - \begin{array}{c} O \\ Te \\ Te \\ (RCO)_{2}O \\ (1) \end{array}$$

(scheme 1)

Considering this preparation requirs two separated steps, it is still a need to develop a new, effective method for the preparation of arenetellurinic mixed anhydrides. Following our finding that phenyliodine (\mathbb{I}) dicarboxylates are efficient oxidizing agents for organotellurium (\mathbb{I}) species⁽⁸⁾, prompted us to examine the reaction of phenyliodine (\mathbb{I}) dicarboxylates with diaryl ditellurides. Such a reaction would provide a useful method for the preparation of arenetellurinic mixed anhydrides.

We found that the reaction of phenyliodine(\mathbb{I}) dicarboxylates (4) with diaryl ditellurides (5) readily occurred in a single step to afford the arenetellurinic mixed anhydrides (1). (Scheme 2).

PhI(OCOR)₂+ArTeTeAr
$$\xrightarrow{CH_2Cl_2}$$
Ar \xrightarrow{O} \parallel
(4) (5) (1) (1)

R	-	CH3
		CF_3

CH₂CI C₆H₅

	Ar=	R =
$Ar = C_6 H_5$	a: C ₆ H ₅	CF_3
$p-CH_3C_6H_4$	$b_{:} C_{6}H_{5}$	CH_3
p-CH ₃ OC ₆ H ₄	c: $p-CH_3C_6H_4$	CF_3
	d: $p-CH_3C_6H_4$	CH_3
	e: $p-CH_3OC_6H_4$	CF_3
	f: p-CH ₃ OC ₆ H ₄	CH_3
	$g: C_6H_5$	CH ₂ Cl
	$h_{1} p - CH_{3}C_{6}H_{4}$	$C_{6}H_{5}$

(Scheme 2)

To the stirred solution of the phenyliodine (II) dicarboxylate in methylene chloride was slowly added the appropriate diaryl ditelluride. Then, simple stirring of the mixture at room temperature for a period of time gave, aften workup and isolation, the desired arenetellurinic mixed anhydride in excellent yields, as shown in Table 1.

2 March 2013
04:37 1
.69] at (
1.67.34
by [17
loaded
Down

Table 1 Preparation of arenetellurinic mixed anhydrides (1)

	ו מחוב ד דובלמופ		ז מזבוובובווו	חווות חוווערת מוווול	IT onnin	
	•	¢	×70711.	mp,Lit mp(°C)	Analyses (с%, Н%
product(1)	Ar	۲ ۲	yield(%)	or Molecular formula	Calc.	Found
IJ	С,Н	CF ₃	92	182 - 184, $181 - 182^{(4)}$	28.62. 1.50.	29.22 , 1.68.
q	C, H,	CH ₃	95	148 - 150, $150 - 152^{(3)}$	34.34 . 2.88.	33.92 . 2.89.
ు	p-CH ₃ C ₆ H ₄	CF_3	93	166 - 169 C ₉ H ₇ F ₃ O ₃ Te	31.09 . 2.03.	31.20 , 2.11.
р	p-CH ₃ C ₆ H ₄	CH ₃	92	165 - 168 C ₉ H ₁₀ O ₃ Te	36.79, 3.42.	36.70, 2.92.
e	p-CH ₃ OC ₆ H ₄	CF_3	96	164 - 166 C ₉ H ₇ F ₃ O ₄ Te	29.71 . 1.94.	29.23, 1.78.
J	p-CH ₃ OC ₆ H ₄	CH3	06	154 - 156, $155 - 156^{(3)}$	34.89. 3.25.	33.92 , 3.06.
20	C,H,	CH ₈ CI	96	185–187 C ₈ H ₇ ClO ₃ Te	30.58, 2.24.	30.54 , 2.11.
h h	p−CH ₃ C ₆ H₄	C ₆ H ₅	93	249-251 $C_{14}H_{12}O_{3}Te$	47.25 , 3.40.	47.27 , 3.30.

Downloaded by [171.67.34.69] at 04:37 12 March 2013

IR spectrum, cm ⁻¹ (KBr)	3075,1690,1590,1485,1445,1340,1310,1205,1145,1060,1020,1000, 920,840,795,735,720,685,460.	3065, 3010, 2940, 2870, 1585, 1485, 1450, 1380, 1315, 1185, 1160, 1065, 1020, 1000, 925, 735, 685, 660, 460.	3070, 2940, 2880, 1690, 1660, 1600, 1500, 1435, 1400, 1315, 1200, 1145, 1065, 1015, 950, 840, 800, 720, 665, 480.	3080, 3050, 2985, 2940, 2890, 1645, 1605, 1500, 1400, 1375, 1310, 1215, 1190, 1120, 1075, 1015, 800, 660, 485.	3085, 3025, 2960, 2860, 1690, 1600, 1580, 1505, 1470, 1450, 1410, 1305, 1265, 1185, 1145, 1065, 1035, 825, 790, 720, 665, 520.	3080, 3025, 2950, 2850, 1600, 1580, 1505, 1470, 1450, 1410, 1375, 1300, 1260, 1185, 1105, 1065, 1025, 820, 790, 650, 590, 515.	3070, 3030, 2970, 1650, 1485, 1445, 1365, 1320, 1270, 1235, 1175, 1065, 1020, 1000, 925, 780, 735, 685, 625, 525, 480, 455, 435.	3070, 3050, 2930, 2880, 1705, 1650, 1635, 1615, 1585, 1500, 1405, 1400, 1325, 1305, 1195, 1180, 1120, 1075, 1025, 1015, 940, 840, 800, 710, 680, 625, 575, 550, 480, 420.
COMPOUND	la	1b	lc	1d	le	lf	50	lh

1a-h
spunod
of com
spectra
R
Table 2

HYPERVALENT IODINE IN SYNTHESIS. XVII

1609

Downloaded by [171.67.34.69] at 04:37 12 March 2013

compound	ð(ppm)
la	7. 3-7. 6(m, 3H, ArH), 7. 7-8. 1(m, 2H, ArH).
1b	2. 13(s, 3H, CH ₃), 7. 5-7. 7(m, 3H, ArH), 7. 8-8. 1(m, 2H, ArH).
lc	2. 35 (s, 3H, CH ₃), 7. 37 (d, J = 6Hz, 2H, ArH), 7. 87 (d, J = 6Hz, 2H, ArH). •
ld	1. 77(s, 3H, CH ₃), 2. $60(s, 3H, CH_3)$, 7. $20(d, J = 6Hz, 2H, ArH)$, 7. 78(d, $J = 6Hz, 2H, ArH)$.
le	3. 72 (s, 3H, CH ₃), 6. 98 (d, J = 9Hz, 2H, ArH), 7, 78 (d, J = 9Hz, 2H, ArH).
Jf	1. $85(s, 3H, CH_3)$, 3. $77(s, 3H, CH_3)$, 6. $83(d, J = 8Hz, 2H, ArH)$, 7. $80(d, J = 8Hz, 2H, ArH)$.
1g	4. 03(s, 2H, CH ₂), 7. 2-7. 6(m, 3H, ArH), 7. 7-8. 2(m, 2H, ArH).
1h	2. 42(s, 3H, CH ₃), 7. 3-8. 2(m, 9H, ArH). **

¹H-NMR spectra of compounds la-h **Table 3**

Determined in d_6-DMSO . * * Determined in CDCl₃

*

CHEN AND CHEN

The products 1 were characterized by elemental analyses, IR, and ¹HNMR spectra. The data of IR and ¹H-NMR spectra are summarized in Table (2,3). This reaction represents a new and facile method and superior procedure for the preparation of arenetellurinic mixed anhydrides.

A plausible mechanism for the above process is given in scheme 3.

$$\operatorname{ArTe-TeAr}^{(4)}(\operatorname{ArTeOCOR})\xrightarrow{(4)}\left[\operatorname{Ar}-\operatorname{Te-OCOR}^{(4)}\right]\xrightarrow{O}\operatorname{Ar}-\operatorname{Te}^{(4)}\operatorname{Te}O\operatorname{COR}^{(4)}\right]\xrightarrow{O}\operatorname{Ar}-\operatorname{Te}O\operatorname{COR}^{(4)}$$

$$(5)$$

$$(6)$$

$$(7)$$

$$(1)$$

(scheme 3)

Initially diaryl ditelluride reacts with phenyliodine(\mathbb{I}) dicarboxylate to produce aryltellurinyl carboxylate (6), which is similar to the formation of benzeneselenenyl trifluoroacetate from the reaction of diphenyl diselenide with phenyliodine(\mathbb{I}) bis(trifluoroacetate)⁽⁹⁾. Then (6) is further oxidized by second molecular of phenyliodine (\mathbb{I}) dicarboxylate to give arenetellurium tricarboxylate (7) which can subsequently transform to the arenetellurinic mixed anhydride (1).

Arenetellurinic anhydrides are mild oxidizing reagents. The current method for the preparation of them is essentially based upon the hydrolysis of the corresponding aryltellurium trihalides⁽⁵⁾. We found that arenetellurinic mixed anhydrides are easily hydrolyzed to the arenetellurinic anhydrides. For example, simple stirring of compound (la) in 10% aqueous NaOH for several minutes gave, after acidification, the phenyltellurinic anhydride in nearly quantitative yield. Considering the diaryl ditellurides did not react with sodium hydroxide, we investigated a one — pot procedure for the preparation of arenetellurinic anhydrides (2) from the reaction of phenylio-

dine(II) dicarboxylates (4) with diaryl ditellurides (5) in a twophase system of methylene chloride and 10% aqueous NaOH. (scheme 4).

PhI(OCOR)₂+ ArTeTeAr
$$\xrightarrow{CH_2Cl_2-aq. NaOH} Ar - \stackrel{O}{\overset{\parallel}{T}} e -O - \stackrel{\parallel}{T} e -Ar$$
(4) (5) (2)

(scheme 4)

The results are shown in Table 4,5. This reaction represents an alternative for the preparation of arenetellurinic anhydrides.

All melting points are uncorrected. 'H-NMR spectra were determined for solutions in CDCl₃ or d₆-DMSO with TMS as internal standard at 60 MHz on a varian EM-360 spectrometer. IR spectra were recorded on a PE - 683 spectrometer. Elemental analyses were measured on a carlo Erta 1106 instrument.

Arenetellurinic mixed anhydrides 1; General procedure:

A solution of diaryl ditelluride (0. 5mmol) in methylene chloride (5mL) was added to a stirred solution of phenyliodine(II) dicarboxylate (1. 5mmol) in same solvent (15mL) at room temperature. The colour of diaryl ditelluride faded quickly. After stirring about 15 min. the solvent was removed in vacuo and petroleum ether (bp. $30-60^{\circ}$ C, 15mL) was added to the residue. The solid was collected and recrystallized from methylene chloride—petroleum ether or benzene—petroleum ether to give the pure arenetellurinic mixed anhydride. All relevant data are summarized in the Table 1, 2,3.

Benzenetellurinic anhydride (2a):

Benzenetellurinyl trifluoroacetate (1a) (0. 34 g. 1. 0mmol) was added to a stirred aqueous solution of 10% sodium hydroxide (10mL). The solid of benzenetellurinyl trifluoroacetate was disap-

	C%, H%	Found	31. 06, 2. 24.	34. 59, 2. 77.	32. 64, 2. 50.	43.01, 2.31
	Analyses (Calc.	31. 50, 2. 20.	34. 61 , 2. 88.	32.47 . 2.71.	43.05 . 2.51.
c anhydrides (2)	mp(°C), Lit. mp(°C)	or Molecular formula	$220-222 m C_{12}H_{10}O_{3}Te_{2}$	242—246 C ₁₄ H ₁₄ O ₃ Te ₂	208 - 210, $205 - 210^{65}$	228—232 C ₂₀ H ₁₄ O3Te2
enetellurinio		yleid (20)	06	91	92	06
reparation of are	Reaction time	(min)	20	30	30	20
Table 4 F	Reagent(4)	Я	CF3	СН	СН,	CF3
	product(2)	Ar	C,H,	p-CH ₃ C ₆ H ₄	p-CH ₃ OC ₆ H ₄	

HYPERVALENT IODINE IN SYNTHESIS. XVII

Downloaded by [171.67.34.69] at 04:37 12 March 2013

1613

Downloaded by [171.67.34.69] at 04:37 12 March 2013

compound 2	IR spectrum, cm ⁻¹ (KBr)
$[C_6H_5Te(O)]_2O$	3070, 3000, 1585, 1485, 1440, 1315, 1205, 1185, 1135, 1060, 1020,1000,735,685,665,610,455.
$[P-CH_3C_6H_4Te(O)]_2O$	3080, 3040, 2940, 2880, 1605, 1500, 1455, 1400, 1315, 1215, 1190,1120,1065,1020,800,700,665,610,580,485.
$[p-CH_3OC_6H_4Te(O)]_2O$	3080, 3010, 2960, 2850, 1600, 1580, 1500, 1470, 1455, 1405, 1300, 1260, 1180, 1105, 1065, 1025, 825, 785, 705, 670, 560, 510.
Te(0)]2O	3070, 1635, 1600, 1520, 1515, 1465, 1440, 1390, 1375, 1345, 1265, 1205, 1140, 1025, 850, 795, 765, 725, 645, 610, 510, 410.

Table 5 IR spectra of compounds 2

peared at once. After stirring 10min. the solution was acidified with acetic acid to afford white precipitate. The precipitate was filtered, washed with water and dried in vacuo to give benzenetellurinic anhydride as a crystalline powder (0. 22g, 96%), mp. 220 -222°C; (Found: C, 31. 06; H, 2. 24. C₁₂H₁₀O₃Te₂ requires C, 31. 50; H, 2. 20%).

Arenetellurinic anhydride 2; General procedure:

Phenyliodine(II) dicarboxylate (1.5mmol) was added to a solution of diaryl ditelluride (0.5mmol) in methylene chloride (10mL) and 10% aqueous solution of sodium hydroxide (10mL). The twophase system was stirred vigorously at room temperature for 20-30min. After the reaction was complete the organic layer was separated and the water layer was treated as above to give arenetellurinic anhydride. All relevant data are summarized in the Table 4,5.

Acknowledgment: This research was supported by the NSF of Zhejiang, P.R. China.

Reference:

- (1) Petragnani, N.; Comasseto, J.V. Synthesis 1991,793,898.
- (2) Hu, N. X.; Aso, Y.; Otsubo, T; Ogura, F. Phosphorus sulfur 1988, 38, 177, Otsubo, T; Hu, N. X.; Aso, Y.; Ogura, F. Kenkyu Hokoku Asahi Garasu Zaidan 1990, 56, 89. (Chem. Abstract 1991, 115, 91320).
- (3) Hu, N. X.; Aso, Y.; Otsubo, T; Ogura, F. J. Org. Chem. 1989,54,4391.
- (4) Hu, N. X.; Aso, Y.; Otsubo, T.; Ogura, F. J. Org. Chem. 1989,54,4398.
- (5) Barton, D. H. R.; Finet, J. P.; Thomas, M. Tetrahedron 1986,42,2319.
- (6) Hu, N. X.; Aso, Y.; Otsubo, T.; Ogura, F. Tetrahedron Lett. 1986,27,6099.

- (7) Pant, B. C. Tetrahedron Lett. 1972, 4779.
- (8) Liu, Z. D.; Chen, Z. C. Heteroatom Chemistry 1992, 3,559.
- (9) Unpublished result from our laboratory.

(Received in the UK 21 June 1994)