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DECARBOXYLATIVE HALOGENATION OF INDOLECARBOXYLIC ACIDS USING HYPERVALENT IODINE(III) REAGENT AND ITS APPLICATION TO THE SYNTHESIS OF POLYBROMOINDOLES

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Abstract – Hypervalent iodine mediated decarboxylative halogenation of indoledicarboxylic acid derivatives was studied. The treatment of 1-methylindole-2,3-dicarboxylic acid with phenyliodine diacetate (PIDA) in the presence of lithium bromide gave 1-methyl-3,3-bromooxindole. However, the reaction of 1-(phenylsulfonyl)indole-2,3-dicarboxylic acid with PIDA in the presence of lithium bromide afforded 2,3-dibromo-1-(phenylsulfonyl)indole. In a similar manner, the 2,3-dichloro- and 2,3-diiodoindole derivatives could be obtained by the reaction of the indole-2,3-dicarboxylic acids with PIDA in the presence of lithium chloride and iodide. This method was optimized to the synthesis of polybromoindole alkaloids.

INTRODUCTION

The decarboxylative halogenation that can provide halogenated organic compounds from carboxylic acids by simple chemical transformation has become an increasingly important and attractive tool in organic synthesis.[1,2] The Hunsdiecker reaction, the reaction of dry silver (I) salts of aliphatic carboxylic acids with bromine to give organic bromide, is an example of classical decarboxylative halogenation reaction.[1] Because of the difficult preparation of anhydrous silver carboxylates, several Hunsdiecker-type reaction methods have thereafter been developed to simplify the procedure by using the various reagent conditions

such as thallium(I) or mercury(II) salts. To avoid the use of highly toxic reagents, Suárez introduced the decarboxylative iodination using hypervalent iodine reagent, phenyliodine diacetate (PIDA), and iodine under UV photolysis.[3-5] Although such metal salt free approaches constitute an important method in chemistry and several groups also report the devising methodology of hypervalent iodine mediated decarboxylative halogenations, their utility is limited for the reaction of aliphatic and α,β-unsaturated carboxylic acids in many cases.[6]

Halogenated indole derivatives are promising sources of new biologically active molecules.[7] Several halogenated indole derivatives have been isolated as the secondary metabolites of marine organisms tunicates (Figure 1).[8-11] Some of them are known to have a variety of actions including antibiotic and anticancer activities. Alternatively, halogenated indole derivatives could be attractive synthetic sources for conversion to other indole alkaloid derivatives.

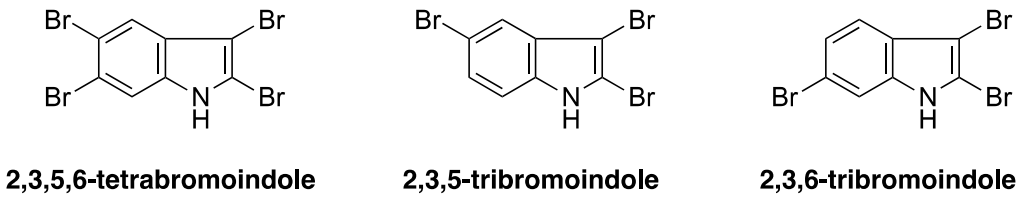


Figure 1. Halogenated indole derivatives isolated from marine organisms

In the course of our synthetic studies on indoles and related compounds, we have shown the utilities of indole-2,3-carboxylic acid derivatives and applied to the synthesis of indole alkaloids such as murrayaquinone-A, ellipticine, olivacine, caulersin and cryptosanguinolentine.[12-19] There is no approach to halogenated indole derivatives *via* decarboxylative halogenations except for the synthesis of the 2,3-diiodoindoles by the decarboxylative iodination of indole-2-carboxylic acids, but in the case of indole-2-carboxylic acids without having an electron-donating substituent, the yields of the 2,3-diiodoindoles are low.[20]

Previously, we reported the synthesis of the 2,3-dibromoindoles by the decarboxylative bromination of indole-2,3-dicarboxylic acids by using Oxone® and lithium bromide, but 2,3-dichloro- or 2,3-diiodoindoles were not obtained.[21] Very recently, we found the novel ability of hypervalent iodine (III)-LiX combination in decarboxylative halogenation.[22-24] In this paper, we provide a full account of our studies on the hypervalent iodine mediated decarboxylative halogenation of indolecarboxylic acid derivatives.[22] In addition, an effective utilization of this system for the synthesis of polybromoindole alkaloids was also described.

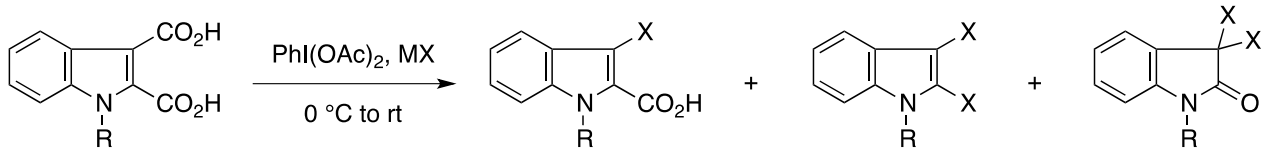
RESULTS AND DISCUSSION

As our initial approach, the decarboxylative halogenation of 1-(phenylsulfonyl)indole-2,3-dicarboxylic acid (**1**)[25] was studied. The reaction using 1-3 equivalents of $PhI(OAc)_2$[26] in the presence of the same equivalents of lithium bromide in THF gave a 3-bromoindole-2-carboxylic acid (**3a**) or a mixture of **3a** and 2,3-dibromoindole (**5a**),[27] but the treatment of **1** with $PhI(OAc)_2$ (4 equivalents) afforded **5a** in 86% yield (Table 1, entries 1-3). However, when the reaction of **1** with $PhI(OAc)_2$ was carried out using potassium bromide instead of lithium bromide, 5 equivalents of $PhI(OAc)_2$ or CH_2Cl_2 as the solvent, the yields of **5a** were relative low (33–72%, entries 4-6). The catalytic hypervalent iodine oxidation condition using *m*-CPBA (*m*-chloroperoxybenzoic acid)[28] was ineffective for this reaction (entry 7). To extend our procedure to the decarboxylative iodination and chlorination, the $PhI(OAc)_2$ mediated reaction was carried out using lithium chloride or iodide, and dichloro- or diiodoindoles **5**[29] was successfully obtained in good yield, where other reagents such as Oxone® and CAN (Cerium (IV) ammonium nitrate)[21] were ineffective for these reactions (entries 8-13).

Next, we examined the decarboxylative halogenation of 1-methylindole-2,3-dicarboxylic acid (**2**).[30] The reaction using 1 equivalent or 2 equivalents of $PhI(OAc)_2$ in the presence of the same equivalents of lithium bromide in THF gave 3-bromoindole-2-carboxylic acid (**4a**) in 57% or 74% yields, respectively (entries 14, 15). When the reaction of **2** with 3 equivalents of $PhI(OAc)_2$ was examined, the corresponding 2,3-dibromoindole (**6a**), the desired product, was not isolated and 3,3-dibromo-1-methyloxindole (**8a**)[31] was obtained as the sole product in 78% yield (entry 16). In addition, the reaction of **2** with 3 equivalents of $PhI(OAc)_2$ in CH_2Cl_2 instead of THF also afforded **8a** in slightly lower yield (73%, entry 17). As for the decarboxylative iodination and chlorination of **2**, the $PhI(OAc)_2$ mediated reaction in the presence of lithium chloride gave 3,3-dichloro-1-methyloxindole (**8b**)[32] in 77 % yield, and 2,3-diiodo-1-methylindole (**6c**)[33] was isolated in 87% yield in the presence of lithium iodide (entries 18, 21). In each case, other reagents such as Oxone® and CAN were ineffective for these reactions (entries 19, 20, 22, 23).

One possible explanation for the formation of 3,3-dihalo-1-methyloxindole (**8a** and **8b**) is envisaged as shown in Scheme 1. The halogenation of 2,3-dihalo-1-methylindole (**6**), which would obtained after the second Hunsdiecker-type decarboxylative halogenation of **4**, lead to intermediate **9**. Treatment of **9** with water by workup provides **8,** where **8c** was not obtained, probably due to steric hindrance. The absence of 3,3-dihalo-1-(phenylsulfonyl)oxindole on the reaction with **1**, possessing electronwithdrawing *N*-substituent may support this explanation. Although the detailed reaction mechanism is still not clear, the dibromooxindole derivatives could be also potentially attractive synthons in indole alkaloid syntheses.

Table 1. The decarboxylative halogenation of indole-2,3-dicarboxylic acids



1 (R = SO_2Ph)
2 (R = Me)

3 (R = SO_2Ph)
4 (R = Me)

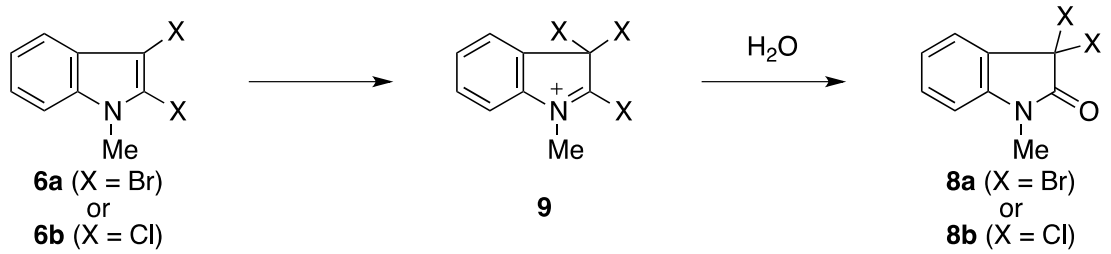
5 (R = SO_2Ph)
6 (R = Me)

7 (R = SO_2Ph)
8 (R = Me)

a : X = Br **b** : X = Cl **c** : X = I

Entry	R	Oxidant (equivalent)	MX (equivalent)	Solvent	Time (h)	Yield of **3** or **4** (%)[a]	Yield of **5** or **6** (%)[a]	Yield of **7** or **8** (%)[a]
1	SO_2Ph (**1**)	$PhI(OAc)_2$ (1)	Li**Br** (1)	THF	1	**3a** (80%)	-	-
2	SO_2Ph (**1**)	$PhI(OAc)_2$ (3)	Li**Br** (3)	THF	51	**3a** (35%)	**5a** (36%)	-
3	SO_2Ph (**1**)	$PhI(OAc)_2$ (4)	Li**Br** (4)	THF	2	-	**5a** (86%)	-
4	SO_2Ph (**1**)	$PhI(OAc)_2$ (4)	K**Br** (4)	THF	22	**3a** (6%)	**5a** (72%)	-
5	SO_2Ph (**1**)	$PhI(OAc)_2$ (5)	Li**Br** (5)	THF	3	-	**5a** (71%)	-
6	SO_2Ph (**1**)	$PhI(OAc)_2$ (5)	Li**Br** (5)	CH_2Cl_2	0.5	-	**5a** (33%)	-
7	SO_2Ph (**1**)	$PhI(OAc)_2$ (0.2), *m*-CPBA[b] (3.0)	Li**Br** (5)	THF	5	-	**5a** (35%)	-
8	SO_2Ph (**1**)	$PhI(OAc)_2$ (4)	Li**Cl** (4)	THF	2	-	**5b** (86%)	-
9[a]	SO_2Ph (**1**)	Oxone® (6)	Li**Cl** (6)	MeOH/H_2O	1	-	**5b** (21%)	
10	SO_2Ph (**1**)	CAN[c] (3)	Li**Cl** (3)	MeCN	1	-	-	-
11	SO_2Ph (**1**)	$PhI(OAc)_2$ (6)	Li**I** (6)	TFE/CH_2Cl_2	8	-	**5c** (89%)	-
12[d]	SO_2Ph (**1**)	Oxone® (6)	Li**I** (6)	MeOH/H_2O	24	-	-	-
13	SO_2Ph (**1**)	CAN[c] (3)	Li**I** (3)	MeCN	16	-	-	-
14	Me (**2**)	$PhI(OAc)_2$ (1)	Li**Br** (1)	THF	1	**4a** (57%)	-	-
15	Me (**2**)	$PhI(OAc)_2$ (2)	Li**Br** (2)	THF	2	**4a** (74%)	-	-
16	Me (**2**)	$PhI(OAc)_2$ (3)	Li**Br** (3)	THF	1	-	-	**8a** (78%)
17	Me (**2**)	$PhI(OAc)_2$ (3)	Li**Br** (3)	CH_2Cl_2	0.5	-	-	**8a** (73%)
18	Me (**2**)	$PhI(OAc)_2$ (4)	Li**Cl** (4)	THF	6	-	-	**8b** (77%)
19[d]	Me (**2**)	Oxone® (6)	Li**Cl** (6)	THF	24	-	-	-
20	Me (**2**)	CAN[c] (3)	Li**Cl** (3)	THF	24	-	-	-
21	Me (**2**)	$PhI(OAc)_2$ (4)	Li**I** (4)	THF	1.5	-	**6c** (87%)	-
22[d]	Me (**2**)	Oxone® (6)	Li**I** (6)	MeOH/H_2O	3	**4c** (88%)	-	-
23	Me (**2**)	CAN[c] (3)	Li**I** (3)	MeCN	24	-	-	-

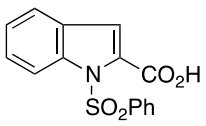
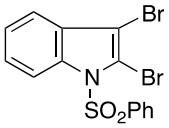
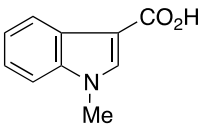
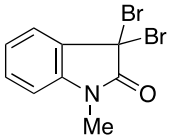
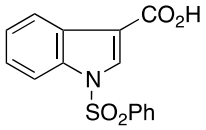
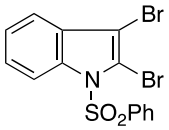
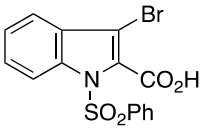
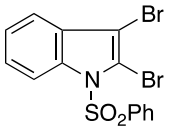
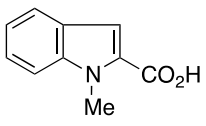
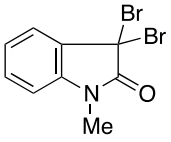
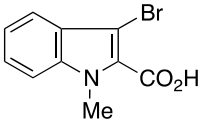
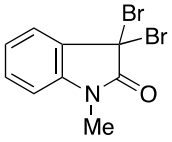
[a]Isolated Yield. [b]*m*-CPBA (*m*-chloroperoxybenzoic acid). [c]CAN (cerium (IV) ammonium nitrate). [d]Additive= Li_2CO_3 (1 eq).



Scheme 1. Plausible reaction mechanism leading to **8**

The reaction of 1-(phenylsulfonyl)indole-2-carboxylic acid (**10**) or 1-(phenylsulfonyl)indole-3-carboxylic acid (**11**) with 4 equivalents of $PhI(OAc)_2$ in the presence of 4 equivalents of lithium bromide in THF gave **5a** in 81-83% yields (Table 2, entries 1, 2), but from 1-methylindole-2-carboxylic acid (**12**) or 1-methylindole-3-carboxylic acid (**13**), **8a** was isolated in 80% yields (entries 3, 4). Thus, the same results were obtained with the reaction of indole-2,3-dicarboxylic acids (**1** and **2**) with $PhI(OAc)_2$ and lithium bromide. The reaction of **3a** with 2 equivalents of $PhI(OAc)_2$ in the presence of 2 equivalents of lithium bromide gave **5a** in 80% yield, while the reaction of **4a** with 2 equivalents of $PhI(OAc)_2$ in the presence of 2 equivalents of lithium bromide gave **8a** in 90% yield (entries 5, 6).

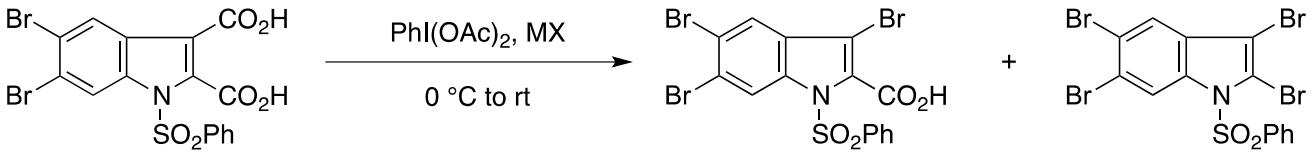
Table 2. The reaction indolecarboxylic acids with $PhI(OAc)_2$-LiBr

Entry	Substrates	Condi-tions[a]	Products	Yield (%)[b]	Entry	Substrates	Condi-tions[a]	Products	Yield (%)[b]
1[c]	 **10**	A	 **5a**	83	4	 **13**	A	 **8a**	80
2[d]	 **11**	A	 **5a**	81	5	 **3a**	B	 **5a**	80
3	 **12**	A	 **8a**	80	6	 **4a**	B	 **8a**	90

[a]Condition A: $PhI(OAc)_2$ (4 equivalents), LiBr (4 equivalents), THF, rt, 1 h; Condition B: $PhI(OAc)_2$ (2 equivalents), LiBr (1 equivalent), THF, rt, 1 h. [b]Isolated Yield. [c]The reaction with 1 equivalent of $PhI(OAc)_2$ in the presence of 1 equivalent of LiBr gave **3a** in 80% yield. [d]The reaction with 1 equivalent of $PhI(OAc)_2$ in the presence of 1 equivalent of LiBr gave 3-bromo-1-(phenylsulfonyl)indole in 45% yield (recovery of **11**:53%).

The attractive results obtained in the hypervalent iodine mediated decarboxylative halogenation of indole-2,3-dicarboxylic acid derivatives prompted us to extent our procedure to the synthesis of polybromoindole alkaloids. When the reaction of 5,6-dibromo-1-(phenylsulfonyl)indole-2,3-dicarboxylic acid (**14**)[21] with 4 equivalents of $PhI(OAc)_2$ in the presence of 4 equivalents of lithium bromide (optimal condition in Table 1) was examined, 1-(phenylsulfonyl)-2,3,5,6-tetrabromoindole (**16**), the desired product, was obtained in low yield and 3,5,6-tribromo-1-(phenylsulfonyl)indole-2-carboxylic acid (**15**) was obtained as a major product (Table 3, entry 1). Further optimization of the reaction conditions revealed that the use of 5 equivalents of $PhI(OAc)_2$ in the presence of 5 equivalents of potassium bromide in THF-TFE (trifluoroethanol) afforded **16** in 83% yield (entries 2-7). The conversion of **16** to 2,3,5,6-tetrabromoindole[9] was achieved by treatment with tetrabutylammonium fluoride (TBAF) in THF in 92% yield (Scheme 2).

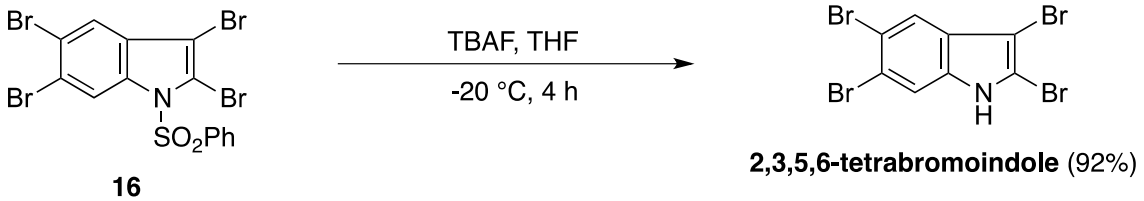
Table 3. The reaction 1-(phenylsulfonyl)lindole-2,3-dicarboxylic acid with $PhI(OAc)_2$-MX



14 **15** **16**

Entry	$PhI(OAc)_2$ (equiv)	MBr (equiv)	Solvent	Time (h)	Yield of **15** (%)[a]	Yield of **16** (%)[a]
1	4	LiBr (4)	THF	24	67	17
2	5	LiBr (5)	THF	24	50	31
3	5	NaBr (5)	THF	20	71	17
4	5	KBr (5)	THF	20	48	45
5	5	KBr (5)	MeCN	20	-	73
6	5	KBr (5)	TFE	2	(complex mixture)	
7	5	KBr (5)	THF-TFE[b]	3	-	83

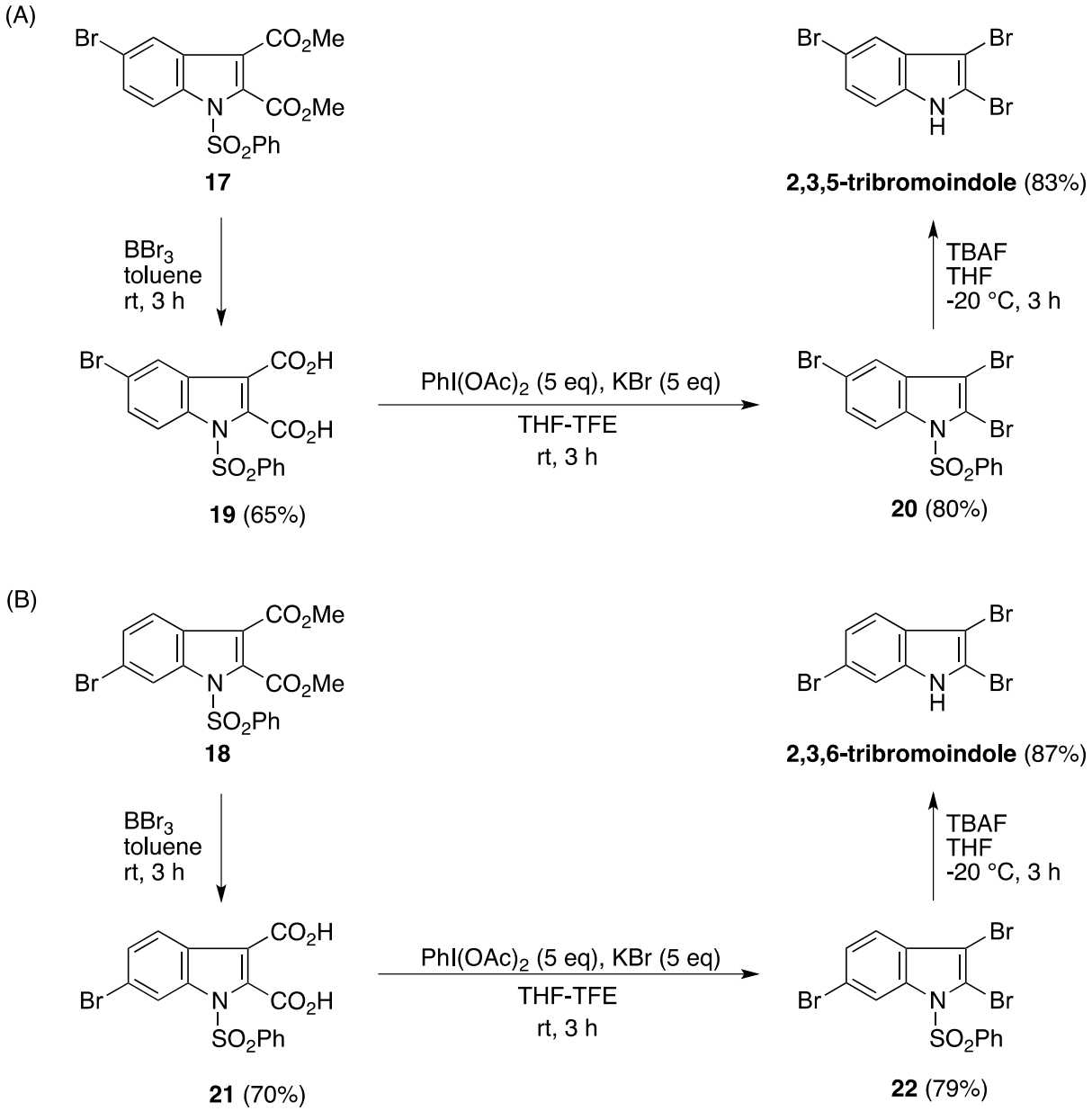
[a]Isolated Yield. [b]THF (0.5 h) then TFE (2.5 h).



16 **2,3,5,6-tetrabromoindole** (92%)

Scheme 2. Synthesis of 2,3,5,6-tetrabromoindole

The encouraging results obtained in Table 3 and Scheme 2 prompted us to extend our procedure to several polybromoindole alkaloid syntheses. Dimethyl bromoindole-2,3-dicarboxylates (**17** and **18**) were prepared according to the reported method.[34] The treatment of **17** boron tribromide gave the corresponding dicarboxylic acids (**19**) in 65% yield (Scheme 3A). The $PhI(OAc)_2$ mediated decarboxylative bromination of **19** afforded tribromo-1-(phenylsulfonyl)indole (**20**) in 80% yield. **20** could be converted to 2,3,5-tribromoindole[8] by treatment with tetrabutylammonium fluoride in 83%. In a similar manner, the synthesis of 2,3,6-tribromoindole[8] from **18** was also successfully completed *via* $PhI(OAc)_2$ mediated decarboxylative bromination (Scheme 3B).



Scheme 3. Synthesis of tribromoindoles

In conclusion, we have demonstrated the decarboxylative halogenation of indolecarboxylic acid derivatives using the Hunsdiecker-type reaction. The exciting result obtained with the reaction of the indole-2,3-dicarboxylic acids (**1**) with $PhI(OAc)_2$-MX system prompted us to extend our procedure to the synthesis of polybromoindole alkaloids such as 2,3,5,6-tetrabromoindole, 2,3,5-tribromoindole, and 2,3,6-tribromoindole. Further studies along this line are now in progress.

EXPERIMENTAL

All melting points were determined on a Yanagimoto micromelting point apparatus and are uncorrected. ^{1}H NMR spectra were recorded at 300 MHz. Infrared (IR) absorption spectra (cm^{-1}) were recorded using a JASCO FT/IR-7000 spectrophotometer. The high MS were recorded by a JEOL-HX100 spectrometer. Column chromatography was performed on Silica gel 60 N (Kanto Chemical Co., Inc.). Compounds **10**-**13** were commercially available. Compounds **1**,[25] **2**,[30] **14**,[21] **17**,[34] and **18**[34] were prepared by known methods.

Compounds **3a**, **4a**, **5a**, **8a**, **16**, and 2,3,5,6-Tetrabromoindole have been previously reported by us and the spectral data were in full agreement with those reported.[21]

Typical Procedure for the decarboxylative halogenation of indole-2,3-dicarboxylic acid with $PhI(OAc)_2$ in the presence of lithium halide: To a mixture of $PhI(OAc)_2$ and lithium halide in THF (10 mL) was added indole-2,3-dicarboxylic acids (1 mmol) at 0 °C and then the reaction mixture was stirred at room temperature. Water was added to the reaction mixture and the mixture was extracted with CH_2Cl_2. The combined extracts were washed with 2-3% sodium thiosulfate solution, then water, and dried over Na_2SO_4. The extracts were concentrated under reduced pressure to give a solid, which was purified by column chromatography on silica gel to afford the halogenoindole derivatives.

2,3-Dichloro-1-(phenylsulfonyl)indole (5b). Mp 122 °C; ^{1}H NMR ($CDCl_3$) δ: 7.30-7.63 (6H, m), 7.84-7.92 (2H, m), 8.28 (1H, br d, *J* = 8.0 Hz, H-7 or H-4); ^{13}C NMR (DMSO-d_6) δ: 168.80, 140.58, 131.85, 129.16, 125.13, 124.70, 124.14, 109.08, 26.98; HRMS (EI) *m/z*: Calcd for $C_{14}H_9NO_2Cl_2S$: 324.9677. Found: 324.9737; CAS Registry Number [1260070-91-4].

2,3-Diiodo-1-(phenylsulfonyl)indole (5c).[29] Mp 165-167 °C (lit.,[29] mp 166-167 °C); ^{1}H NMR ($CDCl_3$) δ: 7.25-7.60 (6H, m), 7.90 (2H, br d, *J* = 8.0 Hz), 8.28 (1H, br d, *J* = 8.0 Hz, H-7); CAS registry number [80360-26-5].

3,3-Dichloro-1-methyloxindole (8b).[32] Mp 144-147 °C (lit.,[32] 143 °C); IR (*Nujol*) □: 1740 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ: 3.25 (3H, s, CH_3), 6.85 (1H, d, *J* = 8.0 Hz, H-4 or H-7), 7.17 (1H, t, *J* = 8.0 Hz, H-5 or H-6), 7.39 (1H, t, *J* = 8.0, 1.5 Hz, H-6 or H-5), 7.61 (1H, d, *J* = 8 Hz, H-7 or H-4); ^{13}C NMR (DMSO-d_6) δ: 168.80, 140.58, 131.85, 129.16, 125.13, 124.70, 124.14, 109.08, 26.98; CAS registry number [114380-33-5].

2,3-Diiodo-1-methylindole (6c).[33] Mp 76-77 °C (lit.,[33] 76-78 °C); ^{1}H NMR ($CDCl_3$) δ: 3.89 (3H, s, CH_3), 7.1-7.42 (2H, m); ^{13}C NMR (DMSO-d_6) δ: 138.11, 131.15, 122.71, 120.80, 120.50, 111.06, 99.78, 71.72, 36.09; HRMS (EI) *m/z*: Calcd for $C_9H_7NI_2$: 382.8668. Found: 382.8671; CAS registry number [180623-97-6].

Preparation of bromo-1-(phenylsulfonyl)indole-2,3-dicarboxylic acids: To a solution of dimethyl bromo-1-(phenylsulfonyl)indole-2,3-dicarboxylate derivative (1 mmol) in toluene (10 mL) was added 1M boron tribromide in a CH_2Cl_2 solution (3 mL). The mixture was then stirred at room temperature overnight. Water was added to reaction mixture and the precipitate was collected by filtration and washed with water, then with *n*-hexane. The bromo-1-(phenylsulfonyl)indole-2,3-dicarboxylic acid was used without further purification.

5-Bromo-1-(phenylsulfonyl)indole-2,3-dicarboxylic acid (19). ^{1}H NMR ($CDCl_3$) δ: 7.45-7.62 (5H, m, arom), 7.86 (1H, s, H-6), 7.87 (1H, d, *J* = 8.0 Hz, H-4), 8.17 (1H, d, *J* = 9.2 Hz, H-7).

6-Bromo-1-(phenylsulfonyl)indole-2,3-dicarboxylic acid (21). ^{1}H NMR ($CDCl_3$) δ: 7.30-7.64 (5H, m, arom), 7.86 (1H, s, H-6), 7.91 (2H, d, *J* = 7.6 Hz, H-4, 5), 8.50 (1H, s, H-7).

Typical Procedure for the decarboxylative bromination of bromoindole-2,3-dicarboxylic acid with PhI(OAc)$_2$ in the presence of potassium bromide: To a mixture of $PhI(OAc)_2$ and potassium bromide in THF (10 mL) was added bromoindole-2,3-dicarboxylic acids (1 mmol) at 0 °C. After 0.5 h of stirring, the solvent was exchanged to TFE (10 mL) and the reaction mixture was stirred for 2.5 h at room temperature. Water was added to the reaction mixture and the mixture was extracted with CH_2Cl_2. The combined extracts were washed with 2-3% sodium thiosulfate solution, then water, and dried over Na_2SO_4. The extracts were concentrated under reduced pressure to give a solid, which was purified by column chromatography on silica gel to afford the bromoindole derivatives.

2,3,5-Tribromo-1-(phenylsulfonyl)indole. ^{1}H NMR ($CDCl_3$) δ: 7.45-7.62 (5H, m, arom), 7.86 (1H, s, H-6), 7.87 (1H, d, *J* = 8.0 Hz, H-4), 8.17 (1H, d, *J* = 9.2 Hz, H-7).

2,3,6-Tribromo-1-(phenylsulfonyl)indole: ^{1}H NMR ($CDCl_3$) δ: 7.30-7.64 (5H, m, arom), 7.86 (1H, s, H-6), 7.91 (2H, d, *J* = 7.6 Hz, H-4, 5), 8.50 (1H, s, H-7).

Syntheses of polybromoindoles: A 1M solution of tetrabutylammonium fluoride in THF (0.04 mL) was added to a mixture of polybromo-1-(phenylsulfonyl)indole in THF (1 mL) at -20 °C under argon and the reaction mixture was stirred for 1 h at the same temperature. Hydrochloric acid (2 %) was added to the mixture and then extracted with $CHCl_3$. The extracts were washed with water, dried over Na_2SO_4, then concentrated under reduced pressure to afford a residue, which was purified by column chromatography (*n*-hexane : AcOEt = 3:1) to give the polybromoindole.

2,3,5-Tribromoindole.[8] Mp 150-151 °C from EtOAc/hexane (lit.,[8] mp 150-151 °C); IR(KBr) ν: 2918, 2850, 1635, 1456, 1434 cm^{-1} ; ^{1}H NMR ($CDCl_3$) δ: 7.13 (1H, d, *J* = 8.8 Hz, H-7), 7.29 (1H, dd, *J* = 8.8,

1.8, H-6), 7.61 (1H, d, J = 1.1 Hz, H-4), 8.34 (1H, br s, N-H); CAS Registry Number [918529-97-2].

2,3,6-Tribromoindole.[8] Mp 74-75 °C from EtOAc/hexane (lit.,[8] mp 74-75 °C); IR(KBr) ν: 2918, 2850, 1635, 1456, 1434 cm^{-1}; ^1H NMR ($CDCl_3$) δ: 7.61 (1H, s, H-4 or H-7), 7.76 (1H, s, H-7 or H-4), 8.38 (1H, br s, NH); CAS Registry Number [918530-08-2].

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