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Stereochemical Surprises in the Lewis Acid-Mediated Allylation of Isatins

Devendra J. Vyas,[‡,†] Roland Fröhlich,[‡] and Martin Oestreich*[,‡]

[‡]*Organisch-Chemisches Institut, Westfälische Wilhelms-Universität Münster, Corrensstrasse 40, 48149 Münster, Germany, and* [†]*NRW Graduate School of Chemistry*

martin.oestreich@uni-muenster.de

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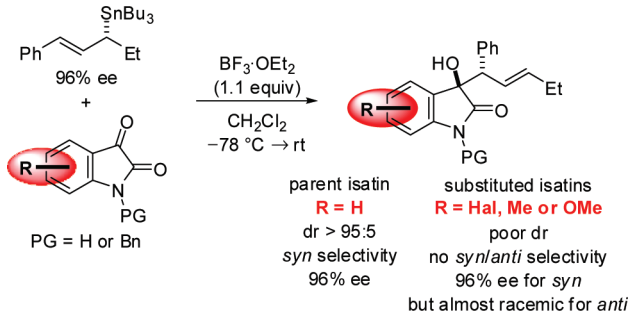

The $BF_3 \cdot OEt_2$-mediated allylation of isatin with an α-chiral allylic stannane is diastereo- and enantioselective. Conversely, allylation of any substituted isatin employing the identical protocol is not diastereoselective at all and only enantioselective for the major diastereomer having *syn* relative configuration. The *anti* isomer is, however, formed in almost racemic form. Both absolute and relative configurations are unambiguously secured by X-ray analysis of major isomers, and the stereochemical assignment of the other 3-substituted 3-hydroxy oxindoles is based on similar NMR spectroscopic characteristics. The remarkable observations are rationalized by an acyclic transition state model.

The oxindole ring is an ubiquitous substructure found in natural and synthetic alkaloids. Structural variation is introduced with substituents either at the benzene core (C-4−C-7 positions) or at the benzylic carbon atom (C-3 position). Substitution at that saturated carbon atom usually renders these molecules chiral, and the asymmetric syntheses of oxindoles with a tertiary or quaternary stereogenic C-3 position is currently garnering significant attention.[1,2] One way of forming chiral oxindoles is addition of nucleophiles to the electrophilic isatin carbonyl group, resulting in 3-substituted 3-hydroxy oxindoles.[2] Several unique transition metal-catalyzed[3−5] and organocatalyzed[6,7] methods are available for this, including arylation,[3] allylation,[4,5] aldol,[6] and Friedel−Crafts[5,7] reactions.

Our laboratory recently accomplished the enantiospecific preparation of a fragile α-chiral allylic stannane[8] by copper-catalyzed allylic substitution of an essentially enantiopure allylic precursor with $(Bu_3Sn)_2Zn$[9] [(*S*)-**1** → (*R*)-**2**, Scheme 1].[10] Subsequent $BF_3 \cdot OEt_2$-promoted allylation of aldehydes was *syn* diastereoselective and yielded homoallylic alcohols with excellent enantiomeric excesses and chirality transfers [(*R*)-**2** → *syn*-**3**, Scheme 1].[10] We reasoned that activated carbonyl compounds such as isatin would also participate in this highly stereocontrolled allylation. In anticipation of a rather systematic investigation employing a series of functionalized isatins, we were surprised to learn that the parent isatin behaves distinctly different from all substituted isatins tested.[12] In this Note, we share our unexpected observation that the levels of diastereo- as well as enantioselection in this reagent-controlled allylation are markedly dependent on any substitution of the isatin benzene core.

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(10) (a) Schmidtmann, E. S.; Oestreich, M. *Angew. Chem., Int. Ed.* **2009**, *48*, 4634–4638. (b) We were able to assign the relative (cf. the Supporting Information of ref 10a) but not the absolute configuration of the *syn* homoallylic alcohols obtained from the $BF_3 \cdot OEt_2$-mediated allylation of aldehydes (no chemical correlation possible and no X-ray analysis available). For the related thermal allylation, the absolute configuration of *anti* homoallylic alcohols was assigned based on a cyclic transition state model.

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(12) Related but unexplained observations were made in organocatalyzed aldol reactions. In one case, the enantiomeric excess obtained with the parent isatin (84% ee) was substantially higher than those found for substituted isatins (e.g., 49% ee for 7-chloro-substitued isatin).[6g] In another case, the enantiomeric excess was excellent for 4,6-dibromo-substituted isatin (92% ee) but only racemic material was formed with isatin itself (2% ee).[6i]

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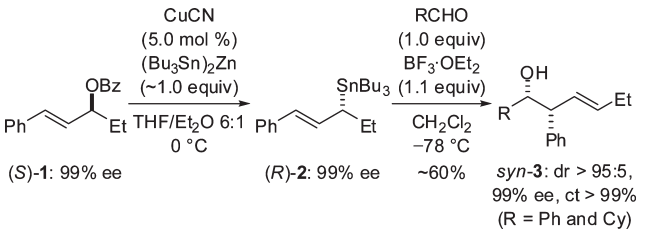
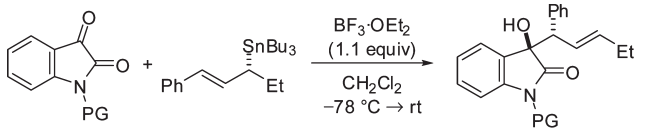
SCHEME 1. Stereoselective Allylation of Aldehydes with an α-Chiral Allylic Stannane[a,b]



[a]The absolute configuration of (*R*)-**2** is clearly determined by the stereochemical course of the substitution, therefore its enantiomeric excess is unchanged.[11] [b]The absolute configuration of *syn*-**3** is not assigned.[10b]

TABLE 1. Diastereo- and Enantioselective Allylation of Isatin[a]



entry	isatin	PG[b]	oxindole	yield (%)[c]	dr[d]	ee (%)[e]	ct (%)[f]
1	**4a**	H	**5a**	78	>95:5	96	99
2	**4b**	Me	**5b**	85	>95:5	92	96
3	**4c**	Bn	**5c**	84	>95:5	92	96
4	**4d**	Boc	**5d**	traces			

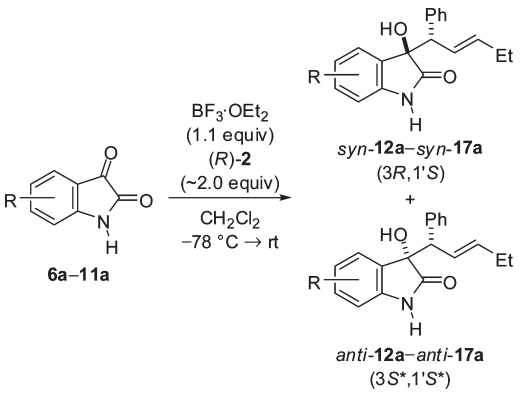
[a]All reactions were conducted with $BF_3 \cdot OEt_2$ (1.1 equiv) and (*R*)-**2** (~2.0 equiv) with a substrate concentration of 0.5 M in CH_2Cl_2 at −78 °C → rt. [b]PG = protective group with Bn = benzyl and Boc = *tert*-butoxycarbonyl. [c]Isolated yield of analytically pure material after flash chromatography. [d]*Syn*:*anti* ratio determined by ^{1}H NMR spectroscopy prior to purification by integration of the baseline-separated resonance signals of the diastereomers (cf. the Supporting Information). [e]Determined by HPLC analysis on chiral Daicel Chiralpak and Chiralcel columns. [f]Chirality transfer based on allylic stannane (*R*)-**2** (96% ee).

Our investigation commenced with the allylation of four isatins, either unprotected or protected at the nitrogen atom (**4a** and **4b**−**d**, Table 1). To our delight, allylic stannane (*R*)-**2** (96% ee) reacted cleanly with **4a**−**c** with superb stereocontrol (Table 1, entries 1−3). Oxindoles **5a**−**c** were formed as almost single stereoisomers with *syn* relative configuration[13] (vide infra). Only Boc protection was not compatible with the reaction conditions (Table 1, entry 4).

Encouraged by these results, we continued testing functionalized, unprotected isatins applying the identical protocol (**6a**−**11a**, Table 2). Any donor or acceptor substituent in the C-5 position was detrimental to diastereoselectivity, and substantial amounts of the *anti* isomer were formed (Table 2, entries 1−4). Aside from that deterioration, the enantiomeric purity of the individual diastereomers held another surprise. The transfer of chirality was immaculate for *syn* isomers but close to none for *anti* isomers. We were able to verify this intriguing finding for the 5-Me-substituted isatin (**6a** → *syn*-**12a** and *anti*-**12a**, Table 2, entry 1). Changing the position of

(13) All oxindoles are depicted in the usual (yet improper) way, and the *syn* and *anti* descriptors cannot be assigned based on these drawings. If the longest carbon chain including the carboxyl group is extended in a zigzag conformation, the 3*R*,1′*S* absolute configuration corresponds to *syn* relative configuration.

TABLE 2. Allylation of Unprotected Substituted Isatins[a]



entry	isatin	R	oxindole	yield (%)[b]	dr[c]	ee (%)[d,e]	ct (%)[f]
1	**6a**	5-Me	**12a**	79	87:13	94 (5)	98
2	**7a**	5-OMe	**13a**	75	89:11	96 (−)	99
3	**8a**	5-F	**14a**	89	80:20	95 (−)	99
4	**9a**	5-Br	**15a**	80	75:25	n.d.	
5	**10a**	4-Br	**16a**	57[g]	n.d.	99[h]	99
6	**11a**	7-Cl	**17a**	77	70:30	88 (−)	89

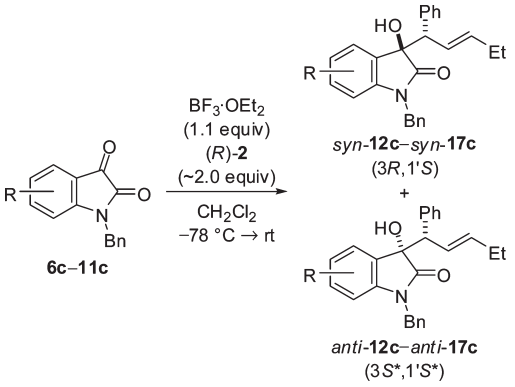
[a]All reactions were conducted with $BF_3 \cdot OEt_2$ (1.1 equiv) and (*R*)-**2** (~2.0 equiv) with a substrate concentration of 0.5 M in CH_2Cl_2 at −78 °C → rt. [b]Isolated yield of analytically pure material after flash chromatography. [c]*Syn*:*anti* ratio determined by ^{1}H NMR spectroscopy prior to purification by integration of the baseline-separated resonance signals of the diastereomers (cf. the Supporting Information). [d]Determined by HPLC analysis on chiral Daicel Chiralpak and Chiralcel columns. [e]Enantiomeric excess of minor diastereomer (*anti*) in parentheses. [f]Chirality transfer based on allylic stannane (*R*)-**2** (96% ee). [g]Not full conversion, and only isolated yield of major diastereomer (*syn*). [h]Enantiopure allylic stannane (*R*)-**2** (99% ee) used. n.d. = not determined.

the substituent even worsened the situation. Allylation of a 4-substituted isatin was sluggish (Table 2, entry 5), and a substituent in the C-7 position resulted in poor diastereocontrol and chirality transfer (Table 2, entry 6).

The same but more pronounced trends were seen with isatins benzylated at the nitrogen atom (**6c**−**11c**, Table 3). We were able to confirm the partial loss of stereochemical information in the minor *anti* isomer. The reaction of the 7-substituted benzylated isatin was particularly remarkable because the diastereoselectivity was reversed, now favoring *anti* rather than *syn* relative configuration (Table 3, entry 6). The chirality transfer was again poor but enantiomeric excesses were moderate for both diastereomers.

The absolute and relative configurations were assigned by X-ray analysis of (3*R*,1′*S*)-**13c**, (3*R*,1′*S*)-**14c**, and (3*S**,1′*S**)-**17c**. Separation of the diastereomeric oxindoles by flash chromatography on silica gel was possible in the benzyl-protected series, and the pure major isomers were highly crystalline. The molecular structure of enantiopure (3*R*,1′*S*)-**13c** is depicted in Figure 1 (for the molecular structures of (3*R*,1′*S*)-**14c** and (3*S**,1′*S**)-**17c**, see the Supporting Information). The *syn* and *anti* relationships of all oxindoles were deduced from diagnostic ^{1}H and ^{13}C NMR characteristics: The chemical shifts of the hydrogen atom at C-1′ and its ^3J coupling constant as well as those of the stereogenic carbon atoms (C-3 and C-1′) were clearly assignable to the diastereomers (for a tabulated list of chemical shifts and coupling constants, see the Supporting Information).

TABLE 3. Allylation of Benzyl-Protected Substituted Isatins[a]



entry	isatin	R	oxindole	yield (%)[b]	dr[c]	ee (%)[d,e,f]	ct (%)[g]
1	**6c**	5-Me	**12c**	90	81:19	98 (36)	99
2	**7c**	5-OMe	**13c**[h]	91	67:33	98 (21)	99
3	**8c**	5-F	**14c**[h]	85	62:38	96 (−)	97
4	**9c**	5-Br	**15c**	79	60:40	94 (−)	95
5	**10c**	4-Br	**16c**	38[i]	n.d.	97	98
6	**11c**	7-Cl	**17c**[h]	86	43:57	79 (81)	80

[a]All reactions were conducted with $BF_3 \cdot OEt_2$ (1.1 equiv) and (*R*)-**2** (~2.0 equiv) with a substrate concentration of 0.5 M in CH_2Cl_2 at −78 °C → rt. [b]Isolated yield of analytically pure material after flash chromatography. [c]*Syn*:*anti* ratio determined by ^1H NMR spectroscopy prior to purification by integration of the baseline-separated resonance signals of the diastereomers (cf. the Supporting Information). [d]Determined by HPLC analysis on chiral Daicel Chiralpak and Chiralcel columns. [e]Enantiomeric excess of minor diastereomer (*anti*) in parentheses. [f]Enantiopure allylic stannane (*R*)-**2** (99% ee) used. [g]Chirality transfer based on allylic stannane (*R*)-**2** (96% ee). [h]X-ray analysis of the major diastereomer. [i]Not full conversion, and only isolated yield of major diastereomer (*syn*). n.d. = not determined.

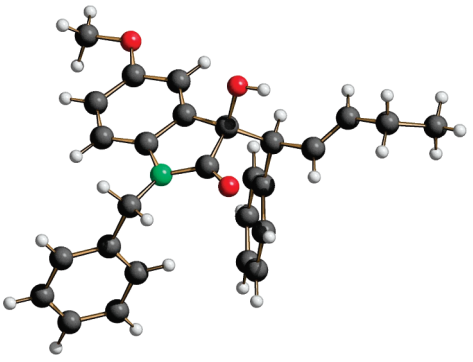


FIGURE 1. Molecular structure of (3*R*,1′*S*)-**13c**.

The relative and absolute configuration is secured for the major oxindole diastereomer, and the configuration of the allylic stannane is also known.[10,11] Moreover, there is no ambiguity in the facial selectivity (C=O of isatin and C=C of allyl fragment) because of the excellent enantiomeric excesses of the *syn* isomer. We therefore propose an antiperiplanar acyclic transition state to rationalize the *R* configuration at C-3 and *S* configuration at C-1′ of the *syn* oxindoles (**TS**, Figure 2). We cannot predict transition states for the *anti* oxindoles as these are formed in almost racemic form. With no information about the facial selectivity in that diastereomeric pathway, we might only hypothesize that the relative energies of the stereoisomeric transition states yielding enantiomeric, that is racemic, *anti* oxindoles must be similar.

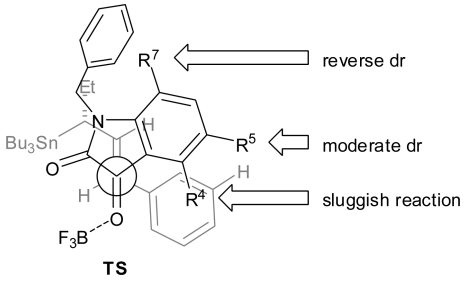


FIGURE 2. Suggested acyclic transition state for the *syn* selective allylation, and the role of substituents at the isatin benzene core.

The transition state **TS** might provide a few clues as to why substituents at the isatin benzene core erode the diastereoselectivity. A substituent in the C-4 position dramatically diminishes reactivity, not even reaching full conversion. Steric interaction between R^4 at C-4 and the phenyl group of **2** might account for that. Along the same lines, R^5 at C-5 is not effecting reactivity but diastereoselectivity. The influence of R^7 at C-7 is particularly difficult to explain because it even reverses the diastereoselectivity. We think that a substituent in the C-7 position gears the spatial orientation of the benzyl group, thereby bringing about steric conflict with the tin moiety in **2**. This effect is less pronounced if the nitrogen atom is unprotected.

The reagent-controlled allylation of isatin using our enantioenriched allylic stannane produced the 3-substituted 3-hydroxy oxindole with high diastereoselectivity (dr > 95:5) and superb chirality transfer (99%). However, these excellent levels of stereoselection were only obtained for the parent isatin, none of the functionalized isatins afforded comparable selectivities. The configurational assignment allowed for the development of a simple model, helping to understand these unexpected findings. We hope to show here that seemingly minor changes in a reactant might well result in dramatic changes in the reaction outcome. For isatin allylation, it is certainly advisable to include more examples than that of the parent compound.[12]

Experimental Section

General Procedure for $BF_3 \cdot OEt_2$-Promoted Allylation of Isatins. The indicated isatin (0.20 mmol) is dissolved under inert atmosphere in dry CH_2Cl_2 (3.0 mL) at −78 °C. $BF_3 \cdot OEt_2$ (0.22 mmol, 1.1 equiv, 1.0 M in CH_2Cl_2) is added to this solution, and the solution is briefly brought to rt. Cooling to −78 °C is followed by the addition of a solution of freshly prepared enantioenriched allylic stannane (*R*)-**2** (~0.40 mmol, ~2.0 equiv, 96% ee or 99% ee) in dry CH_2Cl_2 (1.0 mL). The reaction mixture is then allowed to warm to rt. At full conversion (TLC monitoring), Me_3Al (0.50 mmol, 2.5 equiv, 2 M in toluene) is added at 0 °C,[14] and the reaction mixture is maintained at rt for an additional 2 h. H_2O is added (dilute aqueous HCl must not be used to quench the reaction as epimerization of the oxindole is observed), and the aqueous phase is extracted with CH_2Cl_2 (3 × 5.0 mL). The combined organic layers are back-extracted with H_2O (3 × 5.0 mL), washed with brine, and dried over Na_2SO_4. Evaporation of the solvents under reduced pressure affords the crude oxindoles as a mixture of diastereomers, followed by purification by flash chromatography on

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silica gel with cyclohexane (150 mL) to remove tin impurities and then cyclohexane/*tert*-butyl methyl ether mixtures.

(3*R*)-3-Hydroxy-3-[(1*S*,2*E*)-1-phenylpent-2-enyl]indolin-2-one (*syn*-5a, Table 1, entry 1). *syn*-**5a** was prepared from isatin (**4a**, 30 mg, 0.20 mmol) according to the general procedure. Purification by flash column chromatography on silica gel (cyclohexane and cyclohexane/*tert*-butyl methyl ether = 60/40) afforded the analytically pure title compound as a mixture of diastereomers [47 mg, 78%, dr > 95:5, 96% ee for (3*R*,1′*S*)-**5a**] as a white solid: $[\alpha]^{20}_{D}$ +62.9 (*c* 1.05, $CHCl_3$); mp 150 °C; the enantiomeric excess was determined by HPLC analysis with a Chiralcel OD-H column (90/10 *n*-heptane:*i*-PrOH; flow rate 0.8 mL/min; λ = 210 nm; t_{major} = 23.8 min, t_{minor} = 12.8 min); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.00 (t, *J* = 7.5 Hz, 3H), 2.04−2.17 (m, 2H), 3.29 (s, 1H), 3.81 (d, *J* = 9.6 Hz, 1H), 5.86 (dt, *J* = 15.2, 5.9 Hz, 1H), 5.98 (dd, *J* = 15.2, 9.7 Hz, 1H), 6.64 (d, *J* = 7.5 Hz, 1H), 6.98−7.05 (m, 1H), 7.07−7.20 (m, 7H), 7.77 (br s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.7, 25.9, 57.5, 78.5, 109.9, 110.1, 122.7, 123.9, 125.0, 127.2, 128.0, 129.2, 129.7, 137.6, 139.4, 140.7, 179.4; IR (ATR) ν 3458, 3191, 2960, 2360, 2337, 1695, 1622, 1469, 1347, 1298, 1267, 1221, 1153, 974 cm^{-1}; HRMS (ESI) calcd for $C_{19}H_{19}NO_2Na$ $[M + Na]^+$ 316.1308, found 316.1306. Anal. Calcd for $C_{19}H_{19}NO_2$ (293.36): C, 77.79; H, 6.53; N, 4.77. Found: C, 77.45; H, 6.46; N, 4.61.

(3*R*)-1-Benzyl-3-hydroxy-3-[(1*S*,2*E*)-1-phenylpent-2-enyl]indolin-2-one (*syn*-5c, Table 1, entry 3). *syn*-**5c** was prepared from 1-benzylindoline-2,3-dione (**4c**, 47 mg, 0.20 mmol) according to the general procedure. Purification by flash column chromatography on silica gel (cyclohexane and cyclohexane/*tert*-butyl methyl ether = 70/30) afforded the analytically pure title compound as a mixture of diastereomers [65 mg, 84%, dr > 95:5, 92% ee for (3*R*,1′*S*)-**5c**] as a white solid: $[\alpha]^{20}_{D}$ +25.8 (*c* 3.90, $CHCl_3$); mp 156 °C; the enantiomeric excess was determined by HPLC analysis with a Chiralcel OD-H column (90/10 *n*-heptane:*i*-PrOH; flow rate 0.8 mL/min; λ = 210 nm; t_{major} = 11.4 min, t_{minor} = 9.7 min); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.02 (t, *J* = 7.5 Hz, 3H), 2.10−2.19 (m, 2H), 3.25 (s, 1H), 3.90 (d, *J* = 10.2 Hz, 1H), 4.53 (d, *J* = 15.9 Hz, 1H), 4.88 (d, *J* = 15.9 Hz, 1H), 5.93 (dt, *J* = 15.2, 6.2 Hz, 1H), 6.13 (dd, *J* = 15.2, 10.3 Hz, 1H), 6.42 (d, *J* = 7.7 Hz, 1H), 6.90−6.98 (m, 2H), 6.99−7.24 (m, 11H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.7, 25.9, 43.9, 57.5, 78.0, 109.4, 122.8, 124.1, 124.5, 127.1, 127.1, 127.5, 128.1, 128.7, 128.8, 129.2, 129.7, 135.3, 137.7, 139.8, 143.2, 177.4; IR (ATR) ν 3347, 2967, 2362, 1697, 1613, 1493, 1469, 1383, 1352, 1176, 976 cm^{-1}; HRMS (ESI) calcd for $C_{26}H_{25}NO_2Na$ $[M + Na]^+$ 406.1778, found 406.1779.

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Supporting Information Available: List of diagnostic chemical shifts and coupling constants, molecular structures, experimental procedures, and characterization data, as well as ^{1}H and ^{13}C NMR spectra for all compounds. This material is available free of charge via the Internet at http://pubs.acs.org.