JOC*Note*

Simplified Synthesis of 3-(1-Arylsulfonylalkyl) Indoles and Their Reaction with Reformatsky Reagents

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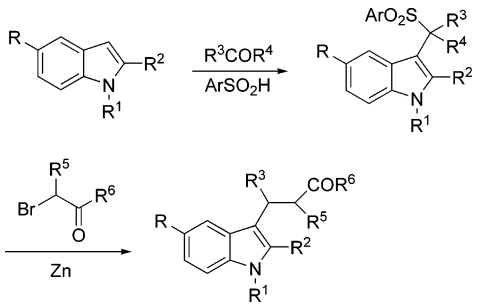
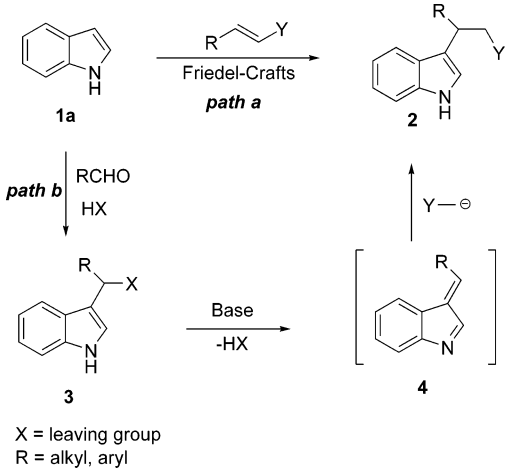


A simple procedure for the preparation of 3-(1-arylsulfonylalkyl) indoles by three-component condensation of indoles, carbonyls, and arenesulfinic acids is presented. The obtained products undergo a Reformatsky reaction leading to alkyl 3-(3-indolyl) alkanoates and (3-indolyl) ketones.

The electron-rich indole nucleus shows an enhanced reactivity toward carbon electrophiles that generally results in the formation of 3-substituted indole derivatives. The alkylation process occurs by way of a Friedel−Crafts (F−C) reaction exploiting electron-poor alkenes as electrophilic reagents (Scheme 1, path a).[1] Such substitution reactions are usually promoted by Lewis or Brønsted acids that can be nowadays employed even in a catalytic amount.[2] This feature makes the F−C reaction particularly suited for enantioselective processes using different catalytic systems.[3] The acidity level of the promoter needed for the F−C reaction is clearly affected by the electrophilic character of the olefin used.

SCHEME 1



Nitroalkenes usually require little activation to be introduced into the indole ring because of their intrinsic reactivity as electrophiles. Conversely, α,β-unsaturated esters, especially when substituted at the β-position, must be activated using strong Lewis acids to efficiently produce the corresponding adduct, unless an intramolecular process is realized.[4] A complementary indirect approach to obtain adducts **2** consists of the reaction of indole **1** with an aldehyde in the presence of a suitable reagent HX in which anion X^- is able to intercept the intermediate benzylic carbocation leading to 3-substituted indole **3** (Scheme 1, path b). Reaction of indolyl derivative **3** with a base would produce an elimination of HX, providing that X^- is a good leaving group, leading to vinylogous imino derivative **4**. Nucleophilic addition of carbanionic reagents to imine **4** affords the same compound **2** obtained by the direct method.[5] Elimination of amino groups from derivatives **3** ($X = NR_2$) obtained from Mannich-type reactions on indoles has long constituted the only available entry to imino intermediates **4** to be used in subsequent nucleophilic additions.[6]

Recently, we have demonstrated that reaction of various indoles **1** with α-amidoalkylphenyl sulfones **5**, in the presence of montmorillonite K-10 as an acid promoter, gives 3-(1-arylsulfonylalkyl) indoles **6** instead of the expected 3-(1-aminoethoxycarbonylalkyl) indoles **7** (Scheme 2).[7]

Sulfonyl derivatives of type **5** are known to undergo elimination of the arenesulfinic group under both acidic and basic conditions leading to reactive *N*-acilimino species that can be profitably employed in the reaction with different nucleophilic systems.[8] In our process, the amido derivative **7** which is initially

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(5) For a related strategy using vinylogous nitrone derivatives, see: Nicolaou, K. C.; Estrada, A. A.; Lee, S. H.; Freestone, G. C. *Angew. Chem., Int. Ed.* **2006**, *45*, 5364−5368.

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(7) Ballini, R.; Palmieri, A.; Petrini, M.; Torregiani, E. *Org. Lett.* **2006**, *8*, 4093−4096.

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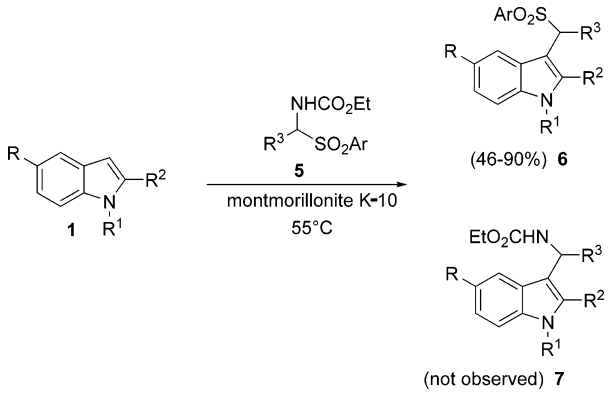
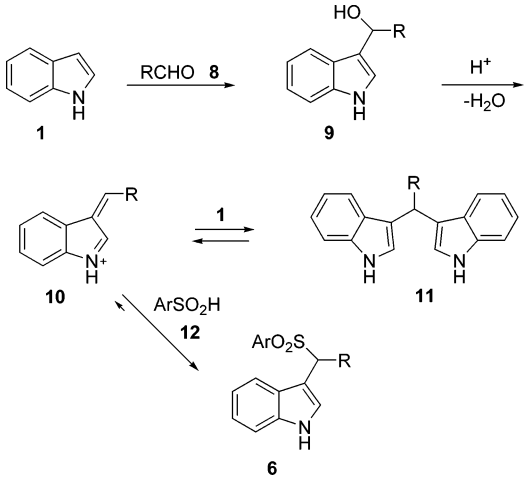
SCHEME 2



SCHEME 3



formed by reaction of **1** with **5** probably suffers an acid-promoted elimination of ethyl carbamate giving a vinylogous iminium ion that by reaction with arylsulfinic acid released from **5** produces the final compound **6**. Sulfonyl indoles **6** are effective precursors of imino derivatives of type **4**, and their utility has been demonstrated in the preparation of linear and branched 3-alkyl indoles by reductive desulfonylation or reaction with Grignard reagents.[7] While monitoring the formation of compounds **6** using the former procedure, the presence in the reaction mixture of bisindole derivatives that slowly disappear has always been observed along with the increasing formation of the final products **6**. It is known that aldehydes **8** react with indoles **1** under F−C conditions to afford bisindoles **11** as main products (Scheme 3).

Formation of bisindoles **11** is possible because the initially formed indolylalkanols **9** in acidic conditions suffer elimination of water giving a vinylogous iminium ion **10** that reacts with a second molecule of indole.[9] Therefore, we considered the possibility of accessing sulfonyl indoles **6** using a related procedure in which arylsulfinic acids **12** act as promoters and effective trapping nucleophiles of the intermediate iminium ions **10**. Upon mixing an indole **1** with an appropriate carbonyl derivative **8** and arylsulfinic acids **12** in the presence of *p*-toluenesulfonic acid (50% mol), it is possible to observe after

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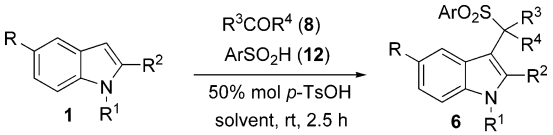
TABLE 1. Synthesis of 3-(1-Arylsulfonylalkyl) Indoles 6 by Condensation of Carbonyl Derivatives 8 in the Presence of Arylsulfinic Acids 12



1a R = R[1]= R[2]= H
1b R = R[1]= H, R[2]= Me
1c R = R[1]= H, R[2]= Ph
1d R = R[2]= H, R[1]= Me
1e R = MeO, R[1]= R[2]= H
1f R = R[1]= H, R[2]= CO_2Et

12a Ar = 4-MePh
12b Ar = Ph

8a R[3]= Et, R[4]= H
8b R[3]= *n*-C_5H_{11}, R[4]= H
8c R[3]= $PhCH_2CH_2$, R[4]= H
8d R[3]= *c*-C_6H_{11} , R[4]= H
8e R[3]= Ph, R[4]= H
8f R[3]= 4-NO_2Ph, R[4]= H
8g R[3]= R[4]= Me

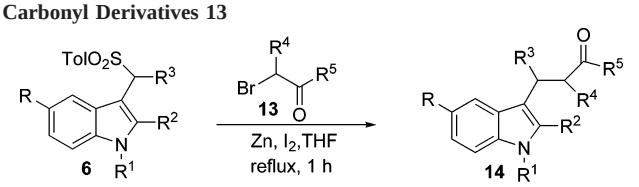
entry	indole **3**	carbonyl **8**	sulfinic acid **12**	product **6**	solvent	yield[a] (%)
1	**1a**	**8b**	**12a**	**6a**	EtOAc	80
2	**1a**	**8c**	**12a**	**6b**	EtOAc[b]	68
3	**1b**	**8b**	**12a**	**6c**	EtOAc[b]	75
4	**1b**	**8d**	**12b**	**6d**	EtOAc	82
5	**1b**	**8g**	**12a**	**6e**	CH_2Cl_2	70
6	**1b**	**8e**	**12a**	**6f**	EtOAc	95
7	**1c**	**8b**	**12a**	**6g**	EtOAc	67
8	**1c**	**8f**	**12a**	**6h**	EtOAc	81
9	**1d**	**8b**	**12a**	**6i**	EtOAc	80
10	**1e**	**8b**	**12a**	**6j**	CH_2Cl_2	79
11	**1f**	**8a**	**12a**	**6k**	CH_2Cl_2[b]	71
12	**1f**	**8c**	**12a**	**6l**	CH_2Cl_2[b]	75

[a] Yield of pure isolated products. [b] At reflux.

2.5 h formation of 3-(1-arylsulfonylalkyl) indoles **6** in good yield (Table 1). Ethyl acetate is generally the solvent of choice for most of the substrates tested; however, it has been observed that in some instances the yield may be improved by performing the reaction in dichloromethane. The acidity level provided by arylsulfinic acids is often unable to allow for an efficient decomposition of the intermediate bisindole **11**, so addition of *p*-toluenesulfonic acid is necessary to ensure better yields of products **6**. Indole as well as its substituted derivatives efficiently react with aliphatic and aromatic aldehydes thus avoiding the need for using α-amido sulfones as reagents for the preparation of compounds **6**. Furthermore, 2-substituted indoles such as 2-phenylindole **1c** which react sluggishly under the previous conditions can be readily transformed into sulfones **6g**,**h** in satisfactory yields (Table 1, entries 7 and 8). Interesting results are also obtained using acetone **8g** as a carbonyl derivative that reacts even at room temperature (Table 1, entry 5); however, the procedure would probably require optimization for other ketones that give rather disappointing outcomes in these conditions.

At this point, to further develop the chemistry of compounds **6**, we decided to test the reactivity of these sulfonyl derivatives toward stabilized carbanions with the aim to implement the functional array of the original molecular structure. Among various metal enolates, Reformatsky reagents are certainly those of more practical use being generated using α-halo carbonyl derivatives in the presence of zinc metal in various solvents.[10] Furthermore, imines as well as iminium ions have been demonstrated to react quite efficiently with these organozinc

TABLE 2. Synthesis of 3-Indolylpropanoates 14 by Reformatsky Reaction of 3-(1-Arylsulfonylalkyl) Indoles 6 with 2-Bromo Carbonyl Derivatives 13



13a R^4= H, R^5= OMe
13b R^4= H, R^5= OEt
13c R^4= H, R^5= O*t*-Bu
13d R^4= Me, R^5= OMe
13e R^4= H, R^5= Ph

entry	sulfonyl indole **6**	2-bromo carbonyl **13**	product **14**	yield[a] (%)
1	**6a**	**13a**	**14a**	80
2	**6b**	**13d**	**14b**	75[b]
3	**6c**	**13a**	**14c**	90
4	**6c**	**13c**	**14d**	89
5	**6c**	**13e**	**14e**	88[c]
6	**6f**	**13b**	**14f**	66
7	**6j**	**13b**	**14g**	67

[a] Yield of pure isolated products. [b] Diastereomeric mixture (3:2). [c] At reflux, 2.5 h.

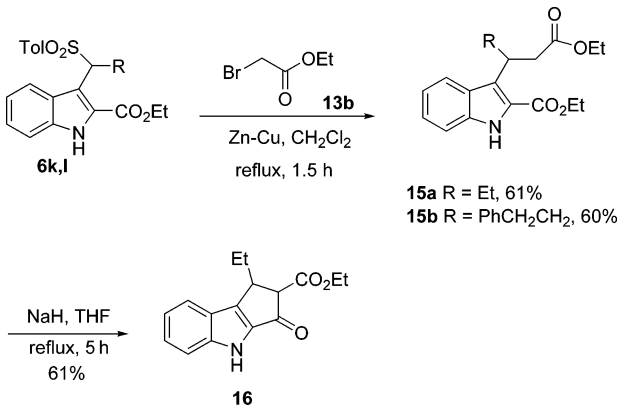
derivatives.[11] Refluxing a THF solution of sulfonyl indoles **6** with 2-bromo carbonyl compounds **13** in the presence of zinc metal and a catalytic amount of iodine for 1 h ensures a complete conversion of the indole **6** to the corresponding 3-indolylpropanoates **14** and 3-indolylpropanone **14e** (Table 2).

An excess of the Reformatsky reagent is obviously needed to promote the elimination of the arenesulfinic acid giving the imino derivative **4** which acts as an effective electrophile in the reaction with the organozinc reagent. Different 2-bromoacetates have been tested for this procedure with satisfactory results; reaction using methyl 2-bromopropanoate **13d** leads to the corresponding 3-indolylpropanoate **14b** with good yield but poor diastereoselectivity (3:2) (Table 2, entry 2). 2-Bromoacetophenone **13e** can also be employed in this procedure, although 2.5 h at reflux is needed to observe a complete conversion of sulfonyl indole **6c** into 3-indolyl ketone **14e** (Table 2, entry 5).

3-Sulfonyl indoles **6k**,**l** obtained from ethyl 2-indolecarboxylate **1f** have been proven to be poorly reactive in the above-cited conditions for the Reformatsky reaction; a different form of activated zinc, namely, the zinc copper couple in dichloromethane at reflux, is needed to obtain the desired diesters **15** (Scheme 4).[12]

These 1,6-difunctionalized derivatives **15** are ideal substrates for a Dieckmann condensation that can be carried out using sodium hydride in THF at reflux leading to β-keto ester **16**.

SCHEME 4



Tricyclic β-keto esters of type **16** are pivotal intermediates for the synthesis of tetracyclic lactam compounds that are of potential interest as neurotransmitters.[13]

In summary, a new procedure for the preparation of 3-(1-arylsulfonylalkyl) indoles by a three-component coupling of simple and commercially available reagents has been devised. The synthetic significance of these sulfonyl derivatives is demonstrated for their reaction with Reformatsky reagents that efficiently produces 3-indolylpropanoate esters which are amenable of other synthetic manipulations. Because in principle many other nucleophilic systems can be made to react with these reactive sulfonyl indoles, further studies are currently underway in our laboratory.

Experimental Section

General Procedure for the Preparation of Sulfonyl Indoles 6. To a stirred solution of indole **1** (3.2 mmol), arylsulfinic acid **12** (3.6 mmol), and *p*-toluenesulfonic acid monohydrate (1.5 mmol) in EtOAc or CH_2Cl_2 (10 mL) (see Table 1) was added the carbonyl compound **8** (3 mmol). The resulting reaction mixture was stirred at rt or at reflux for 2.5 h (see Table 1) and was then treated with saturated $NaHCO_3$ (7 mL). The aqueous layer was extracted with CH_2Cl_2 (3 × 20 mL), and the combined organic extracts were dried over Na_2SO_4 and treated with activated charcoal. The crude product **6** obtained after filtration through a short celite pad and removal of the solvent at reduced pressure was purified by flash chromatography (hexanes/ethyl acetate 80:20).

1-Methyl-1-(2-methyl-1*H*-3-indolyl)ethyl (4-Methylphenyl) Sulfone (6e). Yield: 70%. White solid, mp 165−167 °C. IR (cm^{-1}, nujol): 3331, 1115. ^1H NMR ($CDCl_3$, 400 MHz) δ: 2.00 (s, 6H), 2.15 (s, 3H), 2.33 (s, 3H), 6.92−6.98 (m, 1H), 7.02−7.09 (m, 3H), 7.21 (d, 1H, J = 7.7 Hz), 7.30 (d, 2H, J = 8.1 Hz), 7.61 (d, 1H, J = 8.1 Hz), 8.01 (bs, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 16.0, 21.7, 25.0, 65.9, 108.1, 110.4, 119.9, 121.3, 122.2, 128.7, 128.9, 130.4, 132.8, 134.7, 135.3, 144.2. GC-MS (70 eV): *m*/*z* 171 (100), 156, 129, 77. Anal. Calcd for $C_{19}H_{21}NO_2S$ (327.44): C, 69.69; H, 6.46; N, 4.28. Found: C, 69.74; H, 6.49; N, 4.25.

General Procedure for the Preparation of Esters 14. To a stirred solution of 2-bromo derivative **13** (2.1 mmol), Zn dust (5 mmol), and I_2 (0.2 mmol) in dry THF (12 mL) was added the appropriate sulfonyl indole **6** (1 mmol). The resulting suspension was stirred at reflux for 1 h and then treated with 2 N HCl (5 mL). The aqueous layer was extracted with CH_2Cl_2 (3 × 20 mL), and the combined organic extracts were dried over Na_2SO_4. The crude

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product **14** obtained after removal of the solvent at reduced pressure was purified by flash chromatography (hexanes/ethyl acetate 90:10).

***tert*-Butyl 3-(2-Methyl-1*H*-3-indolyl)octanoate (14d).** Yield: 89%. Waxy solid. IR (cm^{-1}, nujol): 3360, 1712, 1150. ^1H NMR ($CDCl_3$, 400 MHz) δ: 0.78−0.85 (m, 3H), 1.10−1.28 (m, 6H), 1.24 (s, 9H), 1.65−1.77 (m, 1H), 1.81−1.93 (m, 1H), 2.38 (s, 3H), 2.70 (d, 2H, J = 7.6 Hz), 3.26−3.35 (m, 1H), 7.00−7.11 (m, 2H), 7.25 (d, 1H, J = 7.7 Hz), 7.58 (d, 1H, J = 7.3 Hz), 7.75 (bs, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 12.4, 14.3, 22.8, 27.9, 28.1, 32.0, 34.2, 35.1, 42.1, 80.0, 110.4, 113.6, 119.0, 119.5, 120.7, 127.7, 131.4, 135.7, 172.9. GC-MS (70 eV) *m*/*z*: 329, 273, 258, 214 (100), 202, 157, 144, 130, 57. Anal. Calcd for $C_{21}H_{31}NO_2$ (329.48): C, 76.55; H, 9.48; N, 4.25. Found: C, 76.60; H, 9.51; N, 4.27.

General Procedure for the Preparation of Compounds 15. To a stirred solution of ethyl 2-bromo acetate **13b** (2.1 mmol) and Zn−Cu couple (200 mg) in dry CH_2Cl_2 (8 mL) was added the appropriate sulfonyl indole **6** (1 mmol). The resulting suspension was stirred at reflux for 1.5 h and then treated with 2 N HCl (5 mL). The aqueous layer was extracted with CH_2Cl_2 (3 × 20 mL), and the combined organic extracts were dried over Na_2SO_4. The crude product **15** obtained after removal of the solvent at reduced pressure was purified by flash chromatography (hexanes/ethyl acetate 90:10).

Ethyl 3-(3-Ethoxy-1-ethyl-3-oxopropyl)-1*H*-2-indolecarboxylate (15a). Yield: 61%. Oil. IR (cm^{-1}, neat): 3400, 1722. ^1H NMR ($CDCl_3$, 400 MHz) δ: 0.49 (t, 0.3H, J = 7.3 Hz), 0.81 (t, 2.7H, J = 7.3 Hz), 1.09 (t, 3H, J = 7.3 Hz), 1.44 (t, 2.7H, J = 7.3 Hz), 1.53 (t, 0.3H, J = 7.3 Hz), 1.81−2.07 (m, 2H), 2.91 (d, 2H, J = 7.7 Hz), 4.00 (q, 2H, J = 7.3 Hz), 4.11−4.27 (m, 1H), 4.37−4.48 (m, 2H), 7.07−7.17 (m, 1H), 7.25−7.33 (m, 1H), 7.37 (d, 0.9H, J = 8.1 Hz), 7.44 (d, 0.1H, J = 8.5 Hz), 7.79 (d, 0.9H, J = 8.5 Hz), 8.16 (d, 0.1H, J = 8.1 Hz), 8.96 (bs, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 12.7, 14.2, 14.5, 27.9, 35.1, 40.3, 60.3, 61.1, 112.1, 119.6, 120.0, 122.2, 123.3, 123.8, 125.4, 125.7, 136.2, 162.5, 172.9. GC-MS (70 eV) *m*/*z*: 317, 244, 242, 230, 184, 170, 156 (100), 140, 128, 115, 29. Anal. Calcd for $C_{18}H_{23}NO_4$ (317.38): C, 68.12; H, 7.30; N, 4.41. Found: C, 68.17; H, 7.34; N, 4.43.

Ethyl 1-Ethyl-3-oxo-1,2,3,4-tetrahydrocyclopenta[*b*]indole-2-carboxylate 16. To a stirred suspension of NaH (0.06 g, 2.5 mmol) in dry THF (6 mL) was added diester **15a** (0.32 g, 1 mmol) at room temperature. The resulting mixture was stirred at reflux for 5 h and after cooling was treated with 2 N HCl (3 mL). The aqueous layer was extracted with CH_2Cl_2 (3 × 20 mL), and the combined organic extracts were dried over Na_2SO_4. The crude product obtained after removal of the solvent at reduced pressure was purified by flash chromatography (hexanes/ethyl acetate 90:10) giving 0.17 g of ketoester **16** as an oil (yield 61%). IR (cm^{-1}, nujol): 3350, 1374, 1136. ^1H NMR ($CDCl_3$, 400 MHz) δ: 1.06 (t, 3H, J = 7.7 Hz), 1.30 (t, 3H, J = 7.3 Hz), 1.71−1.86 (m, 1H), 2.06−2.20 (m, 1H), 3.67 (d, 1H, J = 2.1 Hz), 3.75−3.81 (m, 1H), 4.25 (q, 2H, J = 7.3 Hz), 7.16 (t, 1H, J = 7.3 Hz), 7.38 (d, 1H, J = 7.3 Hz), 7.50 (d, 1H, J = 8.5 Hz), 7.71 (d, 1H, J = 8.1 Hz), 9.86 (bs, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 11.9, 14.4, 27.7, 41.1, 61.7, 64.3, 114.1, 121.0, 122.2, 123.1, 127.9, 137.0, 144.7, 150.0, 170.1, 187.9. GC-MS (70 eV) *m*/*z*: 199, 170 (100), 140, 115. Anal. Calcd for $C_{16}H_{17}NO_3$ (271.31): C, 70.83; H, 6.32; N, 5.16. Found: C, 70.88; H, 6.34; N, 5.13.

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Supporting Information Available: Spectral and physical data for compounds not included in the Experimental Section and copies of ^1H and ^{13}C NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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